The Handbook of Environmental Chemistry 101

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Jill Crossman
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Contaminants of the Great Lakes

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The Handbook of Environmental Chemistry

Volume 101

Founding Editor: Otto Hutzinger

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Contaminants of the Great Lakes

Volume Editors: Jill Crossman · Chris Weisener

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Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last four decades, as reflected in the more than 150 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Series Editors

Preface

The Great Lakes are a globally important freshwater resource, containing more than 20% of the earth's surface freshwater. This resource is currently threatened by contaminants, which impair water quality and impact the ecological and economic health of the lakes. The effectiveness of contaminant management strategies has to date proven highly variable, due to a range of factors from insufficient and poor understanding of biological, chemical and physical interactions, to those of evolving climate change. This book addresses our current knowledge gaps and highlights a road towards a sustainable solution, for scientists, policymakers, water resource managers and the general public.

Following an introductory overview, this book begins with three chapters focusing on current knowledge and recent advances in the understanding of the source, transport and fate of a series of key contaminants. These range from legacy additions of polybromides, polychlorides and heavy metals, to developing concerns surrounding microplastics. The possibility of interactions between both existing and emerging contaminants is also addressed here.

In addition to chemical contaminants, biological pollution such as harmful algal blooms and invasive species are a persistent issue within the Great Lakes. The next three chapters focus on these biological stressors and their associated ecological impacts, including their effects upon resident fish populations. Uniquely, the ability of invasive species to propagate legacy contaminant effects is highlighted.

The vast watershed areas and huge volumes of water making up the Great Lakes have historically made it difficult to conduct studies at the spatial and temporal resolution required for developing fully validated process-based models, and knowledge gaps in contaminant issues within these lakes have been attributed, at least in part, to a lack of available data. The penultimate two chapters therefore highlight recent technological advances in identifying, monitoring and modelling contaminant source, transport and fate within the Great Lakes. These chapters reveal ways forward in providing scientists with the data they require to bridge these gaps in process understanding.

Under increasing pressure from population growth and climate change, both societies and ecosystems dependent upon the Great Lakes will require continued enhancements in the rate of resource restoration. The final two chapters focus on management difficulties and opportunities, considering the additional challenges brought about by changes in landuse and climate and ultimately by the transboundary nature of these issues. It is clear that lake and habitat restoration will only be possible with advances in science, policy and governance, without which the health of the Great Lakes will continue to decline.

It is our hope that this book will raise awareness of these environmental issues and associated gaps in research infrastructure and knowledge and encourage scientists, policymakers and others to engage with the potential technological and management solutions. We would like to thank each of the authors and publishers for their contributions to this volume.

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Contaminants in the Great Lakes: An Introduction

J. Crossman and C. Weisener

Contents

Abstract The Great Lakes represents a combined watershed containing one fifth of the world's freshwater supply and supporting one of the largest ecosystems on the planet. Contaminants, emitted to the lake through both past and present anthropogenic activity, have stressed this important aquatic ecosystem, e.g. through toxic algal blooms, bioaccumulation of heavy metals and hydrocarbons, and invasion of non-naïve species. This introductory chapter provides the broader context for the following ten chapters, which explore this broad range of both established and emerging contaminants. We examine contaminant sources, transport pathways and fate, and address one of the most difficult challenges in the Great Lakes, of engaging effective solutions. Lastly, we discuss the knowledge gaps and future research directions required to protect this valuable freshwater resource.

Keywords Algal blooms, Biomagnification, Ecosystem, Microplastics, Plasticizers, Volatilization

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1 The World's Largest Freshwater Lakes Under Stress

The Laurentian Great Lakes provide one fifth of the world and over 80% of North America with their supply of surface freshwater. They support an annual fisheries economy of over $7 billion, in addition to being a critical aquatic ecosystem [1]. The Great Lakes have been subject to significant and large-scale anthropogenic stress [2], including contamination and climate and land use change. Together, these multiple stressors have been associated with ecosystem deterioration, with the shallowest of the lakes, Lake Erie, being described as "literally dying" in the 1960s [3]. Contamination of this resource has been pervasive, persistent, and cumulative, and combined with issues of interactions between both historic and emerging contaminants, it is considered one of the greatest potential threats to global public health [4].

In the USA, the Safe Drinking Water Act defines contamination as any "physical, chemical, biological or radiological substance or matter in water" [5] or in other words anything present in water apart from H_2O molecules. However the presence of a contaminant does not inherently indicate that a water supply is of poor quality. Instead thresholds of toxicological concern (TTC) have been established for individual chemicals and biological agents as guidelines for water quality standards, based upon acceptable daily exposure levels for particular organisms within aquatic ecosystems and for humans in drinking water [6]. Within the Great Lakes, a notable range of chemical and biological contaminants are of particular concern (Fig. 1) and are addressed within this volume, including legacy chemicals which were released several decades ago but which are persistent in the environment and chemical contaminants which are still actively discharged, including nutrients such as nitrate and phosphorus. Biological contaminants are also considered here, including harmful algal blooms (HABs) and a range of invasive species. Finally, a series of "emerging contaminants," or contaminants of emerging concern, such as microplastics, are also examined. These contaminants are typically defined as those whose individual or combined impact is not yet fully understood [7] and for which, as acceptable exposure levels cannot yet be defined, TTCs cannot be established, and further study is required to determine to what extent they are of concern.

The effectiveness of management strategies in addressing contamination of Great Lakes water resources has so far proven highly variable, due to factors ranging from restricted data availability; limited understanding of biological, chemical, and physical process interactions; and changing climate and land use. In addition, current and historical exposure to contaminants has differed between individual Great Lakes, which, coupled with varying water volumes and retention times [8], affects both the rate at which they can be removed and their current concentrations within each water body (Fig. 1). Ultimately however the Great Lakes as a system continues to be at risk. This volume exposes some of the current knowledge gaps and highlights a research road toward a sustainable solution. Specifically, the following chapters consider technological advances in identifying, monitoring, and predicting contaminant sources, transport, and fate within the Great Lakes and characterize interactions

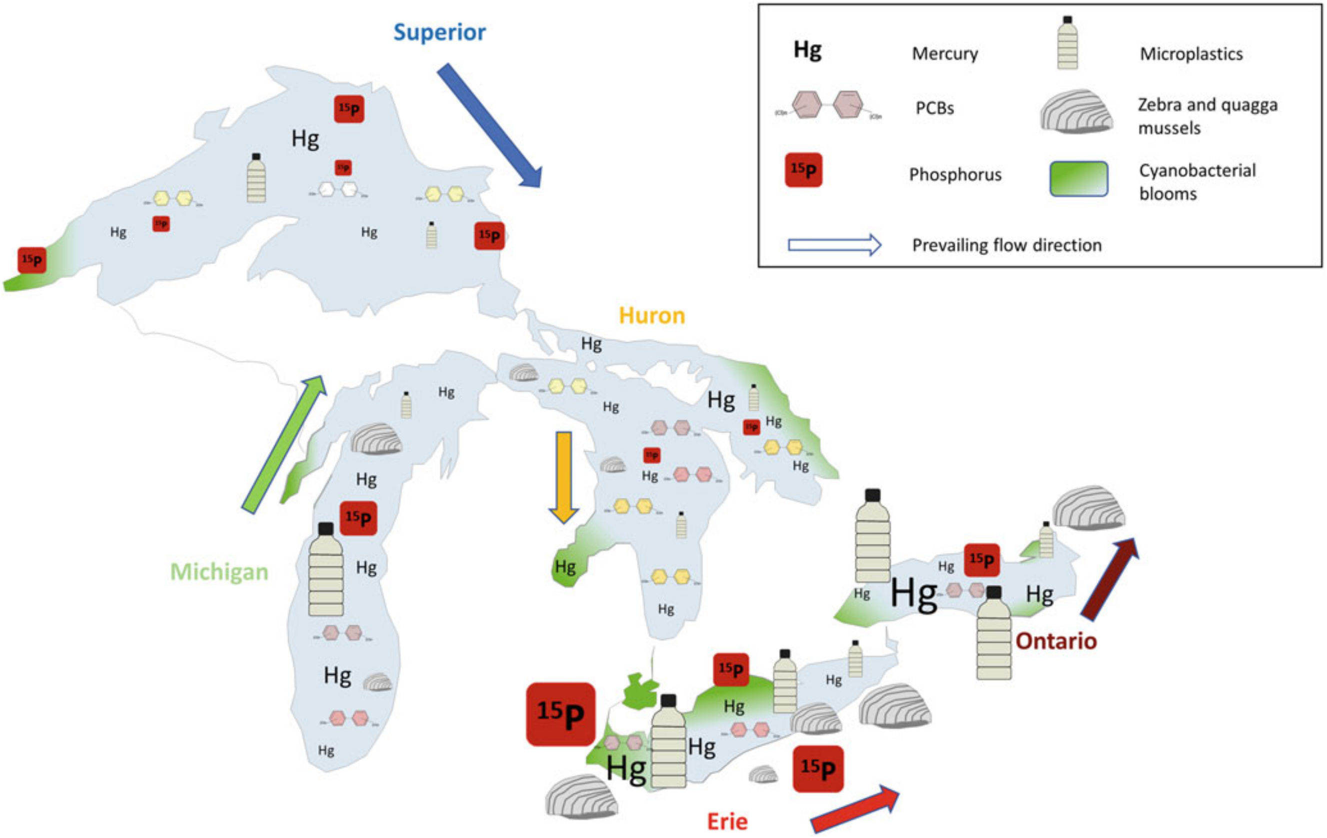

Fig. 1 Current contamination levels within the Laurentian Great Lakes, illustrating mercury [9] and PCB sediment concentrations [10]; phosphorus [11] and microplastic concentrations in the water column [12]; zebra and quagga mussel numbers [10], and presence/absence of cyanobacterial blooms [13]. Relative concentration or numbers of contaminants are illustrated by increasing icon size, with the exception of PCBs where relative concentrations are indicated by color, from white (low) through yellow (medium) to red (high)

between existing and emerging contaminants. Importantly, in considering the transboundary nature of contaminants issues, this volume contains contributions from a combination of US and Canadian academic and government scientists.

2 Source, Transport, and Impacts of Existing and Emerging Contaminants

The ability to assess and restore Great Lakes ecosystems, along with their goods and services, remains a challenge for science and society. Currently, areas which have experienced significant environmental degradation are categorized as areas of concern (AOCs), which are identified according to 14 indicators of change in chemical, physical, and biological integrity known as "beneficial use impairments" (BUIs). Once a site is identified as an AOC, all associated BUIs must be resolved before it can be considered restored and de-listed [14]. The BUIs include degradation of aesthetics, loss of fish and wildlife habitat, degradation of phytoplankton populations, eutrophication, taste or odor problems, and restrictions on fish consumption. Resolution of BUIs and restoration of AOCs are therefore inherently linked to the requirement for an improved understanding of sources, transport, and fate of the contaminants addressed in this volume.

2.1 *Persistent/Legacy Chemicals*

Eradicating sources of contaminants in the Great Lakes can take decades, for example, polychlorinated biphenyls (PCBs) and other organochlorine contaminants first began to accumulate in Great Lakes' sediments during the 1920s, associated with the simultaneous boom of the manufacturing industry [15]. Organochlorines were added to oil and used in transformers, as plasticizers, and as a lubricant. As such they were associated with a range of different industries including packing plants, paper mills, and machine shops. These thrived in the Great Lakes region from the 1920s to the 1970s, associated with the simultaneous boom of ore mining and metal processing [15]. As the automobile industry rose to become the largest in America, energy requirements increased, coal burning and mercury emissions elevated, and there was a rise in demand for leaded gasoline, aluminum, and iron (Chap. 4) [16].

Following the discovery of their adverse health effects, bioaccumulation and biomagnification, the manufacture of PCBs was banned in the 1970s. However due to their persistence in the environment, they are still found in high concentrations in some sediments throughout the Great Lakes Basin today. Indeed, most land sites which were contaminated with PCBs in the 1920s to 1970s through direct use and disposal continue to be a source of PCBs [15]. PCBs are highly mobile and can travel from their disposal site via air (volatilization and deposition) or water (direct tributary transport). Temporary storage of PCBs may occur where they settle on the lake bottom and are buried by sediment. When that sediment is re-suspended however, those PCBs become bioavailable again, and upon filter feeding by phytoplankton and mussels, and subsequent trophic bioaccumulation, contamination of the Great Lakes ecosystem continues.

In Chap. 3, Drouillard et al. [17] have examined data on heavy metal and organic contaminants within river and lake sediments collected throughout the Huron-Erie Corridor between 1999 and 2014. They find that although concentrations of some contaminants have declined compared to levels in the 1980s, there is little evidence for improvements during the 2000s, indicating a need for additional sediment cleanup efforts in the region. Similarly in Chap. 4, Szalińksa [16] finds that in lake sediments, elevated concentrations of heavy metals such as mercury are linked to historic industrial discharges. Contemporary use of heavy metals continues to be a significant source however, with over 477 t per year of mercury released globally from coal-based thermal power plants [18] and transported to water bodies through atmospheric deposition.

Over $580 million has been spent on sediment remediation strategies between 1986 and 1999 to reduce concentrations of persistent contaminants [19], the majority of which involve dredging and disposing of the top layer of contaminated sediment. The success of dredging approaches can be highly variable and must be evaluated periodically for effectiveness [20]. The work of Drouillard et al. [17] within the Huron-Erie Corridor provides support for the continued sediment remediation strategies applied within the Great Lakes.

2.2 Nutrients

Other sources of chemical contaminants can be more directly and immediately controlled; the nutrients nitrogen (N) and phosphorus (P) are a prime example of this. While occurring naturally in the environment, N and P exports began increasing due to anthropogenic activities as early as 200 years ago, when European immigrants significantly deforested the watersheds to establish agricultural industry and settle along the shorelines [21]. Deforestation led to elevated soil erosion and reduced biomass storage, and in combination with growing populations and associated increasing generation of human waste, nutrient exports to the lakes increased significantly. In Chap. 8, Beaton et al. [22] describe how, during the 1970s, atmospheric nitrogen deposition from fossil fuel combustion, and nutrients applied to land as inorganic fertilizer, increased the export levels of some nutrients still further.

Nutrient concentrations in the Great Lakes first became a concern when cyanobacteria, a species which can release toxins, began growing in dense blooms during the 1950s and 1960s [23]. It was discovered that P is a primary controlling factor in the development of these HABs, and as a result, policies were introduced in the USA and Canada through the Great Lakes Water Quality Agreement to reduce P inputs to the lakes. These policies initially led to a rapid decline in phosphorus loadings through the 1970s and 1980s [23] due to targeting of end-of-pipe or "point" sources including improving wastewater treatment methods to chemically remove P, separating stormwater and sewer drains, and through removal of P from laundry detergents. During this period, and associated with these P reductions, a decline in HABs was achieved [23].

More difficult to control however are diffuse nutrient sources [24], including atmospheric deposition, runoff from agricultural lands treated with fertilizer, and those released from wetlands under specific conditions. As control of nutrient inputs from point sources in the 1970s was much more effective, the remaining diffuse sources became the primary pathway of P transport to the Great Lakes by the 1980s [25]. Coupled with persistent diffuse P loadings, long-term storage and direct release mechanisms to lakes have slowed the response time of HABs to management efforts. For instance, P which has been absorbed onto bed sediment and stored for decades can be released in pulses, in a process known as "internal loading," making it difficult to distinguish between current and historical impacts of land management practices and which has been directly linked to individual HAB events in the Great Lakes [26]. Internal loading has been associated with anoxia of hypolimnetic waters and microbial processes in bed sediments [27, 28]. Microbial influences on contaminant fluxes across the sediment-water compartment throughout the Great Lakes remain to a large extent a "black box," although current molecular genetic technology stimulated by advances in rapid throughput DNA sequencing now enables characterization not only of the microbial composition but also of its function [29, 30].

In Chap. 10, Eimers [31] describes how, although total P concentrations have declined in the Great Lakes, nitrate levels have been increasing and suggests that shifts in watershed land use may be a contributing factor; and in Chap. 8, Beaton et al. [22] discuss the critical lack of information about the current state and predicted trends for future NO_3 pollution in the Great Lakes. Furthermore, despite the early success in HABs control, McKindles et al. [32] demonstrate how bloom frequency and toxicity have recently increased in all lakes with the exception of Lake Superior (Chap. 5). The reasons for this resurgence are largely unresolved, but it has been suggested that limiting factors other than P may also be contributing, including N, CO_2, light, and temperature [22, 32].

2.3 Biological and Emerging Contaminants

Contamination of the Great Lakes is not limited to chemical agents but includes living organisms, specifically the invasion of non-indigenous species first introduced by commercial shipping during the twentieth century. Perhaps the best known invasive species of the Great Lakes is the zebra mussel, a species of dreissenid mussel, which has had a striking impact on P concentrations. Dreissenids are filter feeders which remove particulate matter from suspension and which favor attachments to hard substrates in shallow waters; as such they have predominantly flourished in nearshore areas. Dreissenids remove particulates but excrete bioavailable P, and thus while increasing the clarity of the water and light penetration depth, zebra mussels also increase the bioavailable P fraction in nearshore areas, conditions favorable for increasing algal growth [33].

Dreissenids are a primary prey item for another invasive species, the round goby, which in turn is now a major food source of native fish species. In Chap. 6, De Roy and MacIsaac [34] describe how the impacts of this original biological contaminant have spread far beyond the direct impacts of dreissenids on nutrient concentrations. Instead, the impacts of biological contamination have spread throughout the trophic levels of the Great Lakes, ultimately linking both biological and chemical contamination issues, through dreissenid mobilization of organochlorines from sediments and subsequent ingestion by native and non-native predators, and lengthening of food chains leading to enhanced bioaccumulation of heavy metals such as mercury [34]. Critically, De Roy and MacIsaac highlight how the trophic effects of invasive species on native predators and on toxic metal bioaccumulation and biomagnification are poorly understood [34].

Possibly the least understood of the contaminants, however, are those of “emerging concern” (CEC). The definition of an emerging contaminant varies widely but typically includes danger to ecology or humans, consisting of either a perceived or real threat, combined with a lack of published standards [35]. Categories of CECs typically include hormones, pharmaceuticals (e.g., antidepressants and opioids), fragrances, pesticides [1], and most recently micro- and nanoplastics [36]. Microplastic sources include pellets from industry, fibers from textiles, and litter and debris left at beaches. They can end up in water bodies through direct dumping, but the more dominant pathway is through riverine transport originating from terrestrial sources and discharge from wastewater treatment plants.

CECs tend to be found in very low concentrations but are generally ubiquitous [37]. For example, in Chap. 2, Helm [36] examines microplastic abundance throughout the Great Lakes and finds reports of their presence in fish throughout Lakes Ontario, Superior, and Huron. Schoenfuss [1] explores existing evidence for the effects of CECs in laboratory and field studies in Chap. 7 and highlights obstacles and potential solutions to resource management efforts. While laboratory studies have demonstrated that CECs do impact health, e.g., microplastics impact zooplankton function [38] and hormones impact fish reproductive fitness [1], the direct interpretation of similar findings within the field has been hindered by uncertain organism exposure history and complicating environmental variables [1]. Critically, because CECs are found in such low concentrations, analysis can be costly and time-consuming, and due to the inherently “new” nature of CECs, standardized field sampling or analytical practices are often absent [36]. As a result, sampling for many CECs is not widely integrated into long-term monitoring programs, meaning data availability is limited and can be incomparable between dates and locations. This further restricts progress in this field, particularly with respect to potential interactive effects between co-occurring contaminants.

3 Progress in Critical Science and Future of Management Considerations

With emerging concerns, persistent toxic blooms, and invasive species added to the legacy of pollution from the industrial revolution, binational management solutions are imperative to the protection of this critical water resource and can only be supported by simultaneous advances in science. Historically, multi-year monitoring approaches and comprehensive modelling studies have been required to determine the source, transport, and pathways of contaminants within these complex Great Lake systems. Such modelling is inherently a data-intensive task, and the lack of available data has been a recurrent restriction on contaminant studies and management programs [39], predominantly associated with cost. Traditional water quality monitoring practices, such as discrete sampling and laboratory analyses, are expensive and labor intensive; therefore measurements are often taken at a monthly or bi-monthly resolution [40]. Due to potentially high rates of environmental flux, this is not only inadequate for causative determination but also results in significant uncertainty in estimates [41]. The speed at which some contaminants alter following removal from the natural environment (e.g., en route to the laboratory) provides an additional obstacle, for example, with some bioavailable fractions of P requiring near instantaneous analysis in order to obtain meaningful values [39].

Emerging "smart sensor" networks have begun to address some of these technical hurdles, by enabling on-site analysis of contaminants at sub-hourly frequencies and removing the costs associated with repeat field sampling and laboratory analysis. For example, discrete, solar-powered portable units can transmit sub-hourly data to in-office computers via telemetry [42], and through the recent development of low-power digestion techniques, new "WIZprobes" can for the first time analyze total phosphorus (TP) fractions in remote locations [43]. Such probes will revolutionize the accuracy of P load estimates from source to sink and enable monitoring of biochemical variables at a resolution which better captures process interactions. Furthermore, in Chap. 8, Beaton et al. [22] explore how multiple indicator approaches can achieve important insights with smaller "snapshots" of data, by combining measurements of elemental concentrations with stable isotope analysis. They describe how advances in compositional and isotopic geochemical approaches can in particular improve our understanding of nutrient transport and HAB response, by verifying relationships between the fundamental processes regulating terrestrial and aquatic nutrient sources and the metabolic responses promoting cyanobacterial growth. Such advances in our understanding may ultimately lead to an ability to develop early predictors of bloom events. In Chap. 9, Binding et al. [44] highlight how such early detection and monitoring are fundamental to the effective management of contamination. They explore how, combined with the advances in direct measurement technologies and improvements in data availability, the use of satellite remote sensing and development of novel algorithms provide the ability to track contaminants within the water column with unprecedented spatial coverage. Through these methods, alerts for events such as harmful algal blooms can be generated in near real-time.

4 Conclusion: Knowledge Gaps and Future Directions

The Great Lakes is a constantly evolving system, and our understanding of contaminant sources and pathways and methods of monitoring and analysis must keep pace with the rapidly changing land use and climate. Chapter 10 [31], for example, highlights the close connection between urban development, intensification of agricultural practices, and impacts on water resources. In addition, the relationship between rising air temperatures and heavier precipitation events in the Great Lakes region is described in both Chaps. 4 and 10 [16, 31], along with the projected likelihood that these trends will continue. In general, the potential impact of climate change on contaminant uptake and toxic metal accumulation is largely unknown and continues to be a critical research gap in the Great Lakes [34]. Research has shown however that increased rainfall and runoff are likely to enhance P loads to the Great Lakes from diffuse sources and that precipitation is one of the primary pathways for atmospheric mercury entering large water bodies [45, 46]. From this it can be concluded that reducing mercury concentrations in the atmosphere is essential in order to continue effective management of heavy metal loadings to the Great Lakes. In a promising step forward in 2012, key legislation was introduced by the EPA which required all power plants to install mercury-removing technologies. Following a change in administration, however, and despite infrastructure investments by the coal industry of $9.6 billion per year, the EPA later withdrew the legal justifications for this legislation. It is clear that while science and technology are crucial for informing policy, effective governance is equally essential in achieving policy goals, a topic explored in Chap. 11 by Creed and Friedman [47]. In examining the US and Canadian binational water quality agreements, they unfortunately find little evidence of integration beyond voluntary information sharing or soliciting advice [47]. It appears that despite making pledges to achieve joint goals by 2025 [48], federal, state, and provincial parties are predominantly implementing their action plans in isolation. Under increasing pressure from population growth and climate change, both societies and ecosystems dependent upon the Great Lakes will require continued enhancements in the rate of resource restoration. This will only be possible with advances in science, policy, and governance, without which the health of the Great Lakes will continue to decline [49].

While a myriad of historic, current, and emerging stressors facing the great lakes are considered in this volume, the assessment is by no means comprehensive. In particular, microbial and viral research is notable by its absence, although each could warrant the focus of an entire book. This volume does however aim to describe the most recent advancements in contaminant science and highlights critical gaps in areas which urgently require both research and policy attention.

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Part I
Source, Transport and Fate

Occurrence, Sources, Transport, and Fate of Microplastics in the Great Lakes–St. Lawrence River Basin

Paul A. Helm

Contents

Abstract Microplastics, plastic particles less than five millimeters in size, are found in each of the five Laurentian Great Lakes, their tributary streams and rivers, and the St. Lawrence River carrying Great Lakes water to the Atlantic Ocean. Although standardized methodologies and reporting criteria are needed as varying size groupings, particle character categories, and reporting units have been used in Great Lakes studies, a picture of microplastic pollution across the lakes is emerging. Greater abundances of microplastics are found near urban centers where rivers and

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municipal wastewater deliver plastics to the lakes, with fragments of plastic and fibers/lines generally the dominant particle types found, depending on locations sampled. Microplastic morphologies, the shape and character of plastic particles, provide source-specific information and indicate contributions of microplastics to beaches, lake and river waters, and sediment from industries (pellets, deflashing material, etc.), microbeads from personal care products, fragments and film from litter and debris (single-use plastics, bags, and food wrappers), and foam (insulation board, consumer packaging, and take-out containers). The relative roles of stormwater run-off (directly and through streams) compared to wastewater effluents in delivering microplastics to the Great Lakes are not known, but both are expected to be major pathways. Sediments are a major repository of microplastics, and high abundances were found in the Great Lakes region near major urban centers, especially where there are greater numbers of plastic sector businesses in adjacent watersheds. Few studies have examined the occurrence and uptake of plastics in biota from the Great Lakes, and further research is needed to determine the levels of exposure and potential for harm in both aquatic and terrestrial organisms, given the levels and types of microplastics present in the Great Lakes environment.

Keywords Beaches, Lake Ontario, Lake Superior, Sediment, Water

1 Introduction

Samuel de Champlain explored the inland waters of North America in the early 1600s, referring to the waters of what is now Georgian Bay in Lake Huron as “La Mer Douce,” the “Sweet Water Sea” on maps dated 1616 and 1632 [1]. It is fitting that this region, now known as the Laurentian Great Lakes, which has undergone immense cultural change since the 1600s, has also become a region that encapsulates one of the defining marks of humanity, plastic pollution. Whether incorporated into rock on beaches of Hawaii [2] or the sedimentary record of the Laurentian Great Lakes [3], plastic is now an indicator of the Anthropocene in the geological record [4].

Plastic pollution has been recognized as a marine issue, termed “marine debris,” “anthropogenic litter,” or “marine anthropogenic litter,” since reports of entanglement and ingestion of plastics in the 1960s, and plastic pellets in the early 1970s [5]. Despite controls to reduce dumping of waste at sea and initiatives to control pellet losses by industry, plastic debris and anthropogenic litter continued to accumulate on ocean beaches [5, 6]. The visibility of marine debris along beaches helped to spur ocean shoreline cleaning operations and voluntary shoreline/beach cleanup efforts, and soon extended to beaches in the Great Lakes region, highlighting that anthropogenic litter is not only an ocean issue. For example, the Adopt-a-Beach program organized by the Alliance for the Great Lakes in the USA and the Great

Canadian Shoreline Cleanup in Canada began in the early 1990s [7]. Since 2006, the National Oceanic and Atmospheric Administration (NOAA) has operated the Marine Debris Program, including in the Great Lakes, to address litter, debris, and derelict vessels and fishing gear.

Over the last 15 years, microplastics have come to the forefront as a form of plastic pollution. Microplastics are defined as any particles of plastic less than 5 mm in size [8]. Two main types of microplastics can also be defined: primary microplastics that are intentionally produced (e.g., pre-production pellets, microbeads in personal care products, and abrasives), and secondary microplastics that are produced in the environment (e.g., breakdown of larger plastic debris/litter and abrasion from in-use materials) [8]. As with marine anthropogenic litter, until recently knowledge on microplastics has been limited to ocean waters and shorelines.

Observations of pre-production pellets washing up along shorelines of Lake Huron in 2007 [9] and a release of pellets from a train derailment in Lake Superior in 2008 [10] were among the first reports of microplastics in the Great Lakes. The first peer-reviewed study published from the Great Lakes region that included microplastics examined plastic debris, including pre-production pellets, accumulated on beaches of Lake Huron [11]. In 2012, media reports emerged about findings of microplastics in Great Lakes water, including high amounts in Lake Erie (e.g., [12]). This study became the first peer-reviewed published report of microplastics, including microbeads from personal care products, collected from Great Lakes waters [13], and helped to advance legislative initiatives in the USA and Canada to ban the use of microbeads in such products.

Potential impacts of microplastics and plastic debris occurring in aquatic environments have been the subject of several review articles, particularly for the oceans (e.g., [14–16]), but also in freshwater environments [17, 18]. Concerns are driven by the propensity of organisms to ingest plastics either inadvertently (e.g., filter feeders) or intentionally, mistaking the debris and microplastics as food items. Observed effects due to ingestion tend to result from poor nutrition due to blockages or plastic replacing food items, alterations in feeding behavior, poorer health, reduced growth, and impacts on survival, with most impacts observed for organisms lower in the foodweb [15]. Effects occur across a range of plastic particle size, from nano- to micro- to macroplastics, and at various levels of biological organization, from the organism level down to macromolecules (e.g., lipid profiles) [19]. A detailed analysis of impacts of microplastics on fish and aquatic invertebrates suggests that prey species such as zooplankton may be more susceptible, and that effects may be more subtle than most standard regulatory endpoints capture (feeding, growth, reproduction, and survival) [20]. Microplastic particles may also serve as a vector for transport of chemical constituents (either plastic additives or compounds accumulated from the environment) and microbes including pathogens and invasive species [15]. The current review will not address effects of microplastics on organisms in the Great Lakes since, to date, no published reports have assessed toxic effects of microplastics to organisms from the basin.

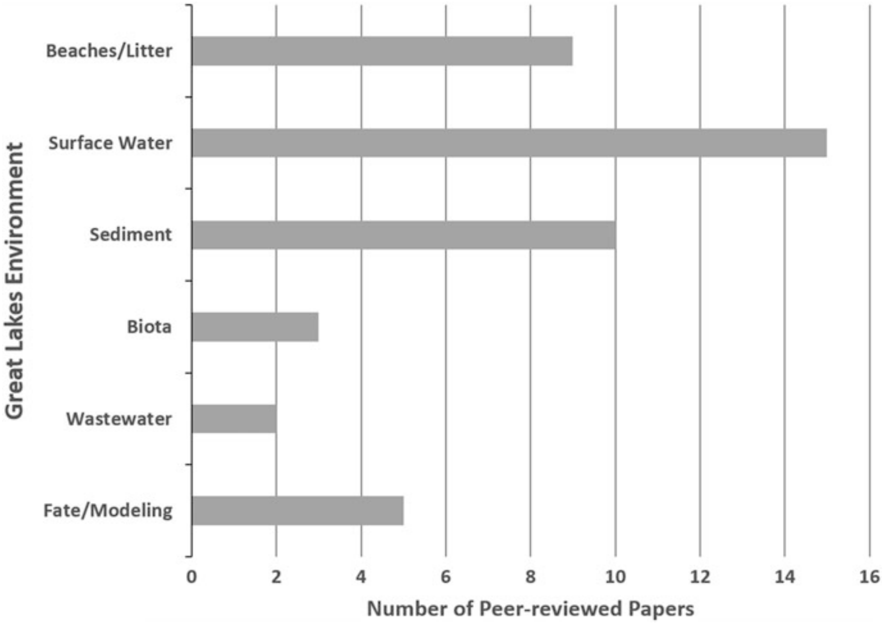

Fig. 1 Number of published peer-reviewed studies providing data, information on fate processes, and modeled distributions of microplastics in the Great Lakes–St. Lawrence River Basin

This review highlights the current state of knowledge of sources, occurrence, fate, and transport of microplastics in the Great Lakes–St. Lawrence River Basin, building on the first published review of plastic debris in the lakes by Driedger et al. [7] in 2015. At the time, there were just four peer-reviewed studies available on plastic as anthropogenic litter and microplastics in the Great Lakes region. This current review draws upon 31 peer-reviewed studies addressing microplastics and plastic debris in the basin (Fig. 1), as well as published thesis documents and preliminary results in conference proceedings. The occurrence of microplastics in the region, their sources, the pathways they take to the lakes, and the processes acting upon them within the lakes are summarized, and some of the challenges and knowledge gaps are identified to close the review.

2 Microplastics Sampling and Analysis in the Great Lakes

Microplastics differ substantially in character from other pollutants found in the Great Lakes (e.g., nutrients, persistent organic pollutants, and heavy metals), requiring sampling and analysis approaches to be adapted to undertake research and monitoring activities. The approaches used to collect, process, and quantify microplastic Great Lakes studies are briefly summarized in this section, highlighting limitations and their influences on data comparisons in this review, rather than providing a detailed methodology review as has been done previously [18, 21, 22].

Sampling for microplastics generally relies on techniques established for contaminant and biological assessments, with some modifications. Neuston nets used for plankton and zooplankton assessments, and versions of the manta nets modified for sampling organisms and debris at the water surface [23], have been the primary water sampling tools for in situ filtration of bulk water in both lake [13, 24–28] and river [29–32] studies in the Great Lakes region. Effluents of wastewater treatment plants (WWTPs) in the region were sampled using filtration with 355 μm sieves [33]. Bulk water samples have been collected via grabs of varying volumes for lake [34] and riverine waters within the basin [32, 35–37]. However, different net sizes have been used, ranging from 100 μm [25, 32] to 333 μm mesh [13, 24, 26–31]. The units for reporting data also differ with particle counts per unit area ($\# \text{ km}^{-2}$) typical of manta trawls [13, 24–27], and numbers per unit volume ($\# \text{ m}^{-3}$ or $\# \text{ L}^{-1}$) typical of grabs [32, 34–37] and neuston nets [27, 29–31]. Such variety in microplastics sampling and reporting makes direct comparisons across the basin more challenging.

Standard sampling techniques are sufficient for microplastics studies of bulk environmental matrices such as sediment and biota. For sediments in the Great Lakes region, petite ponar [27, 37–42], steel spoon [27], Ekman dredge [32], Shipek sampler [39, 41], gravity corer [39, 41], and box corer [3] have all been used for microplastics. Again, reporting units vary and have included number of particles per volume of sediment ($\# \text{ L}^{-1}$) [40], per mass dry weight of sediment ($\# \text{ kg}^{-1}$) [3, 27, 37, 39, 41, 42], and per area ($\# \text{ m}^{-2}$) [38]. Biota samples have been collected as part of other monitoring efforts, including bird nest/colony sample collections [43, 44] and using seine nets [35, 45], gill nets [46, 47], and electrofishing [45] for fish. Beach surveys for microplastics within the basin have used bulk collections to selected depths in grids and transects [3, 11, 39, 41, 48].

Prior to analysis, microplastics require separation from the sample matrix, which includes natural debris such as plant/animal matter/tissues, woody material, zooplankton and invertebrates, organic carbon, and sand. Great Lakes manta and neuston samples have been passed through sieves into size fractions, with macrodebris removed with the >4.75–5 mm fraction. Separation of microplastics can be achieved via picking from natural matter under a dissecting microscope [13] or, more commonly, by digesting the natural organic matter in a wet peroxidation (WPO) treatment using hydrogen peroxide (H_2O_2, 30–35%) with an iron catalyst ($Fe(II)SO_4$) [24–33, 49]. Microplastics in lake and river sediments have been isolated via direct picking [38], WPO [27, 32, 40], or using density separations with or without WPO. Density separation solutions consisting of sodium polytungstate (1.5 g cm^{-3}) [3, 39, 41, 42], saturated sodium chloride (1.2 g cm^{-3}) [32, 40], or zinc chloride (1.6 g cm^{-3}) [27] are mixed with samples to suspend materials then left to settle to separate lighter plastics from materials like sand. After settling, the bottom fraction with dense materials is released from funnels or the floating plastics are decanted from flasks. However, depending on the solution, plastics like polyvinyl chloride (PVC) and polyester may remain with denser materials [21], and it is not clear if the dense fractions are inspected in most studies.

Biological tissues have been treated using both WPO [35, 45, 46] and basic potassium hydroxide (KOH) [44–46] to dissolve gastrointestinal tracts.

Microplastics have been quantified in the Great Lakes via visual sorting, counting, and categorizing under a dissecting microscope (typically 10–80x magnification), with confirmatory analysis usually performed on a subset of suspected microplastics. Categorization, based on appearances and morphologies, usually includes pellets, fragments, foam, film or sheets, fibers, and lines (e.g., [13, 24, 29, 31, 48]). However, there are inconsistencies in the categories used and the specific morphologies assigned to them, making source apportionment challenging [50]. Microplastics from the basin have been verified by scanning electron microscopy (SEM)-electron dispersive X-ray spectroscopy (EDS) [13, 24, 25, 28], Fourier transform infrared (FTIR) spectroscopy [3, 24, 28, 44, 48], Raman spectroscopy [34, 39, 41, 44–46], and pyrolysis-gas chromatography (GC)-mass spectrometry [26, 27, 30, 40]. Raman and FTIR spectroscopy use vibrational bond energies within organic molecules to identify the microplastic polymers. Pyrolysis-GC analysis generates a pyrogram of products generally unique to individual polymers for identification, and can be quantitative, determining the mass of polymer in samples [51]. Analysis via EDS provides elemental compositions and is effective for differentiating inorganic from organic materials, although it may be less specific for carbon-based polymers unless unique elements are present.

A commonality among the isolation and analysis methods is their time-consuming and labor-intensive nature. Other screening techniques have been explored that aim to differentiate plastics from natural debris, such as selective staining of either the natural material (e.g., with Rose Bengal) [52] or the plastics with Nile Red [53]. Rose Bengal was used in a drinking water survey and testing of beers brewed with Great Lakes waters [52]. Although this approach may help distinguish natural particles, validation for accuracy of enumerating microplastics is still required. Research groups are working to automate instrumental analyses that can count and identify microplastics simultaneously via FTIR [54] and Raman [55] spectroscopy, but they have yet to be applied to Great Lakes studies. Quantitative analyses using pyrolysis-GC [51] may provide methodologies similar to those used for trace organic contaminants typical of regional monitoring programs. Together, these techniques may provide more efficient options for microplastics analysis.

Beyond efficiency gains, improvements are needed in quality assurance and quality control measures and in reporting practices (e.g., units, size fractions, and categories) that are applied to microplastics studies, as has been called for in several articles (e.g., [22, 56, 57]). While Great Lakes studies to date have included some measure of blank contamination during laboratory processing, necessary improvements include sampling blanks and positive controls (also called matrix spikes) with known amounts of microplastic particles [57]. Recently, interlaboratory comparisons have been initiated that assess comparability across methods and accuracy in overall performance [58]. This first report found underestimation by 20% and uncertainty due to misidentification of microplastics. Additional interlaboratory exercises will help standardize methods and reporting for monitoring and assessment of microplastics in the Great Lakes and elsewhere.

3 Microplastics Occurrence in the Great Lakes–St. Lawrence River Basin

Research and monitoring efforts over the last 8 years have documented widespread occurrence of microplastics on beaches, in water and sediments, and in biota across the Great Lakes region. Despite differences in methodologies and reporting conventions, compiling and comparing data from across the basin provides insights as to where information gaps exist, what types of microplastics are prevalent, and where efforts to address the issue are needed most.

3.1 Beaches

Beach and shoreline cleanups provided some of the earliest accounts of anthropogenic litter in the Great Lakes, contributing to the understanding of which activities are responsible for litter accumulation [7]. Recording the types, numbers, and/or weight of debris items by volunteers provides informative citizen science data. Although microplastics were not specifically included in the US Adopt-a-Beach cleanups, collection data provides strong evidence of the contributions of plastic [59] and sources (e.g., food-related and smoking-related) [60, 61]. The Great Canadian Shoreline Cleanup's "dirty dozen" list of the most commonly found litter items from 2018 shows cigarette butts as the most numerous items found, followed by "tiny plastic and foam" [62]. Of the remaining ten categories, seven are plastics-related items. Two cleanup sites in 2018 had high numbers of tiny plastic pieces, one in north central Lake Superior (mostly "nurdles"; pre-production pellets) and another in Lake Ontario [62].

Systematic beach surveys that included smaller plastic particles were conducted at sites around Lakes Huron, St. Clair, and Erie [48], and one site in Lake Ontario [3]. The number of plastic fragments found per square meter sampled generally increased moving from Lake Huron downstream into Lakes Erie and Ontario (Table 1). High densities of pre-production pellets were found at Sarnia Beach in Lake Huron (33 m^{-2}) [48] and Humber Bay Park in Toronto in Lake Ontario (8.8–21 m^{-2}) [3]. Greater densities of pellets were found along the US beaches in Lake Erie than the Canadian beaches [48]. Analyses of pellets by FTIR found a polyethylene (PE)/polypropylene (PP) ratio of 60/38, which reflects production patterns of these polymers. Similarly, pellets from Humber Bay Park in Toronto, Ontario were 73.5% PE and the remainder were PP [3].

Recent surveys of Canadian beaches in Lakes Erie and Ontario, sampling to 30 cm depth, reported microplastics on a particle per kilogram (kg) basis. Abundances ranged 20–470 microplastics kg^{-1} across five Lake Ontario beaches, with the greatest abundance on Sunnyside Beach in Humber Bay, Toronto [39]. In Lake Erie, abundances ranged from 50 to 146 microplastics kg^{-1} across six beaches [41]. Fragments tended to dominate over fibers at the Lake Ontario beaches, while the opposite

Table 1 Comparison of pre-production pellets, fragments, and foam collected using similar methods at beach sites around the Great Lakes [3, 48]

Lake	Pellets (# m^{-2})	Fragments (# m^{-2})	Foam (# m^{-2})
Huron (CA); 5 sites	0–33	0–0.8	0–0.8
Huron (US); 2 sites	0	0	0
St. Clair (CA); 4 sites	0–0.5	0.1–0.7	0–0.6
St. Clair (US); 5 sites	0–0.9	0.1–0.9	<0.1–4.7
Erie (CA); 6 sites	0–0.4	0.4–1.4	0–0.2
Erie (US); 4 sites	0.6–2.0	0.8–1.7	0–0.1
Ontario (Humber Bay Park)[a]	8.8–21	3.6–4.5	NR[b]

[a] One location, sampled on three different dates
[b] Polystyrene recorded by mass only at this location

was true at most of the Lake Erie beaches [39, 41]. In both cases, bead (industrial pellets, microbeads) counts were low compared to fibers and fragments. Preliminary results of a basin-wide, 67-beach survey for pre-production pellets show densities up to a very high abundance of 7,400 m^{-2} [63].

3.2 Surface Waters

Fifteen published studies have reported on microplastic pollution in surface waters of the Great Lakes–St. Lawrence River basin, with five sampling lake waters, seven focused in watersheds, and three including both watershed and lake sampling. This section summarizes the amounts, character, and distribution patterns observed for microplastics found in lake and river waters across the basin.

3.2.1 Lake Water

Microplastic abundances have been measured in surface waters of all five Great Lakes. Comparing data from five studies that used similar-sized mesh manta nets [13, 24, 27, 28, 64] shows that similar abundances were observed in the upper Great Lakes (Lakes Superior, Michigan, and Huron), while considerably greater abundances were found in the lower lakes, Lakes Erie, and Ontario (Fig. 2). A survey of Lakes Superior, Huron, and Erie found greater amounts in Lake Erie (466,000 microplastics km^{-2}; maximum) than in Lakes Superior (12,600 km^{-2} max.) and Huron (6,540 km^{-2} max.) [13] (Table 2). Abundances of up to 100,000 particles km^{-2} were observed in Lake Michigan [24] at sites reflecting more open lake conditions, similar to sites sampled by Eriksen et al. [13]. Sampling using smaller-sized mesh in manta nets (100 μm) in Lakes Superior, Huron, and Erie, Cable et al. [25] also found greater amounts of microplastics in Lake Erie than in Lakes Superior and Huron. However, capturing smaller-sized particles resulted in generally greater abundances than observed by Eriksen et al. [13] (Table 2). Cable et al. [25] also

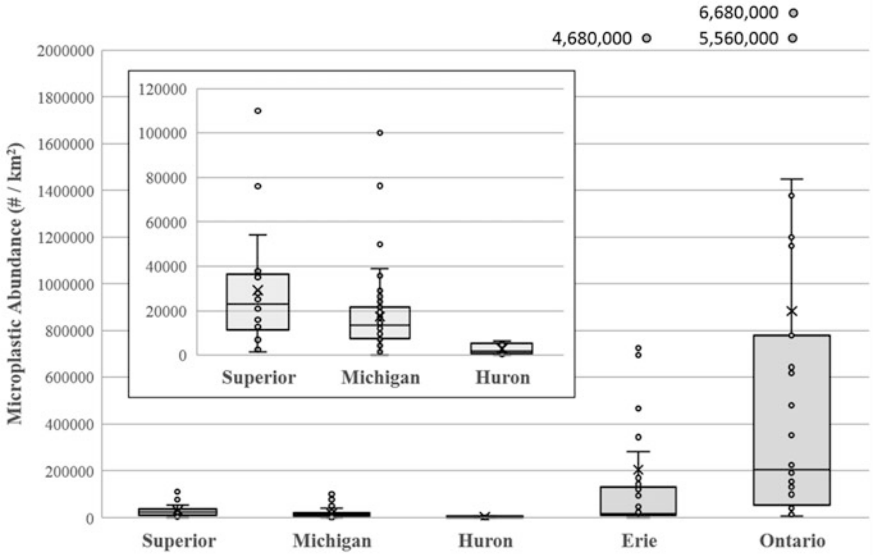

Fig. 2 Microplastic abundances in surface waters of the five Great Lakes as measured using 333 mm mesh manta trawls for Lakes Superior and Huron [13], Michigan [24], Erie [13, 28, 64], and Ontario [28, 64]. Circles represent individual data points. The line represents the median, “x” represents the mean, bottom and top of the box represent the 25th and 75th percentiles, respectively, whiskers represent the minimum and maximum, and circles outside of whiskers are outliers exceeding 1.5 times the interquartile range above the 75th percentile

collected samples in closer proximity to urban centers, river plumes, and WWTPs, finding generally higher abundances at these locations than in open lake samples. Lake Ontario contained higher microplastic abundances, averaging 230,000 km^{-2} (1,380,000 km^{-2} max.) for locations across the lake [28]. Samples collected in Lake Ontario at nearshore locations influenced by inputs from urbanized watersheds and wastewater resulted in considerably higher amounts (up to 6,680,000 km^{-2}) than at a lake background site [64] (Fig. 2; Table 2). Abundances in western Lake Superior reached a maximum of 110,000 km^{-2} near the Duluth WWTP [26] and were significantly greater across western Lake Superior sites [26] compared to those from the less-populated eastern part of the lake [13]. In a pan-Lake Superior survey, the greatest microplastic abundance was near Thunder Bay, Ontario (330,000 km^{-2}), the largest city adjacent to Lake Superior, and nearshore sites around the lake were significantly greater than offshore sites [65]. Good spatial coverage of abundance data has been reported for surface waters of Lakes Superior [13, 25, 26, 65], Michigan [24], Erie [13, 25, 28, 64], and Ontario [28, 64]. However, there is currently limited abundance information for parts of Lake Huron, especially Georgian Bay which has considerable recreational activity through the summer. Sampling at depths below the surface has only been undertaken has only near Milwaukee in Lake Michigan [27].

Table 2 Summary of microplastic abundances and particle morphologies of Great Lakes surface water studies

Lake/size class (mm)	Sampler	Microplastic counts (Range; # km^{-2})	Major morphology (%)	Ref.
Lake Superior				
<4.75–0.333	Manta	1,280–12,600	NR[a]	[13]
<4.75–1	Manta	1,160–8,900	39 fragments, 29 paint, 14 films	[25]
<1–0.106	Manta	240,000 ($n = 1$)	77 fragments, 23 fibers	[25]
<4.0–0.333	Manta	<dl[b]; 14,000–110,000	39 fibers/lines, 34 fragments, 21 films	[26]
<4.75–0.500	Neuston	6,620–333,000	65 fibers/lines 23 fragments, 8 films	[65]
Lake Michigan				
<4.75–0.333	Manta	0[b]; 1,410–100,000	81 fragments, 12 fiber/line, 4 pellets[c]	[24]
<4.75–0.333	Neuston	0.42–0.55 (# m^{-3})[d]	77 fibers/lines, 13 fragments, 8 foams	[27]
Lake Huron				
<4.75–0.333	Manta	0[b]; 456–6,540	NR[a]	[12]
<4.75–1	Manta	0–16,200	54 fibers, 21 fragments, 11 paint	[25]
<1–0.106	Manta	127,000–810,000	66 fragments, 34 fibers	[25]
Lake Erie				
<4.75–0.333	Manta	4,690–466,000	[a]49 pellets[c], 42 fragments, 8 foams	[12]
<4.75–1	Manta	0–604,000	59 fragments, 13 foam, 12 nurdles	[25]
<1–0.106	Manta	119,000–1,230,000	93 fragments, 7 fibers	[25]
<4.75–0.333	Manta	1,420–143,000	47 fragments, 33 pellets, 9 foams	[28]
<4.75–0.335	Manta	92,800–4,680,000	NR[e]	[64]
Lake Ontario				
<4.75–0.333	Manta	6,100–1,380,000	77 fragments, 12 pellets, 4 foams	[28]
<4.75–0.335	Manta	225,000–6,680,000	[e]50 fragments, 20 microbeads, 18 fibers	[64]
>0.125	Grab	0–2.4	34 fragments, 28 fibers, 27 films	[34]

[a] Average % morphology across all sites in L. Superior, L. Huron, and L. Erie, with 90% of particles found in L. Erie; NR – not reported separately by lake

[b] 1 sample with no plastic found or below detection limit (<dl)

[c] Pellets in these studies include spherical microbeads (consumer products) and industrial pellets

[d] Reported as mean number of particles per cubic meter across five depths

[e] Average % morphology across all sites in L. Erie and Ontario; most particles found in L. Ontario

The microplastic morphologies that dominated samples varied by study, lake, and size category (Table 2). Fragments were the most or second most abundant category across Lakes Superior, Huron, and Michigan, usually alternating with fibers. For example, two Lake Superior studies found fibers/lines were most abundant followed by fragments (39% and 34% [26], 65% and 23% [65]), while another found fragments were dominant in both size fractions sampled [25]. In Lake Michigan, fragments dominated (81%) followed by fibers/lines (12%) [24], but samples collected close to Milwaukee in Lake Michigan were opposite in relative abundances, with 77% fibers and 13% fragments [27]. Fragments and pellets/microbeads tended to be the most dominant categories in Lakes Erie and Ontario. Pellets contributed 49% and fragments 42% of all particles collected by Eriksen et al., mostly in Lake Erie [13]. Mason et al. found fragments were dominant in both Lake Erie and Ontario (47% and 77%, respectively) followed by pellets (33% and 12%) [28]. In both studies, spherical microbeads predominantly comprised the "pellets" category. Microbeads, consisting of spherical and irregular-shaped beads from personal care products, contributed 20% on average to Lake Ontario and Lake Erie nearshore samples [64].

Other microplastic categories contributed to varying degrees in lake waters. Films were the third most abundant microplastic found in Lake Superior, contributing 8–21% of total particles [25, 26, 65], and 27% in low volume Lake Ontario samples [34]. Paint chips contributed 29% and 11% in the <4.75–1 mm size fraction in Lakes Superior and Huron samples, respectively [25]. Pellets (microbeads) contributed 4% in Lake Michigan lake-wide samples, while foam particles were the third most abundant category (8%) near Milwaukee [27]. Foams also contributed 8% [13], 9% [28], and 13% [25] of microplastics in Lake Erie samples, and 4% in Lake Ontario [28]. Nurdles (pre-production pellets) contributed 12% of particles in the <4.75–1 mm size category from Lake Erie [25]. Fibers were also important, especially in smaller size fractions, for example, the <1–0.106 mm fraction in Lake Erie samples (7%) [25] and the >0.125 fraction in Lake Ontario grab samples (28%) [34]. More detailed and standardized categorization could facilitate better comparisons of types and source inputs of microplastics in future studies.

3.2.2 River Water

River banks in the Great Lakes–St. Lawrence River basin, as with lake and ocean shorelines, have been the subject of volunteer cleanups [62] and research documenting the types and abundance of debris, and factors influencing observations [59, 66]. Local metrics of human activity, such as beach parking, had a greater influence on observed anthropogenic litter abundance than broader urban land-use in several Chicago area rivers [66]. Across the five rivers sampled, plastic litter accounted for 48–65% of the items collected, compared to 21–46% of the items in the river beds [66], reflecting the influence of the buoyancy of the plastic materials. Along reaches of the Chicago River, a significantly greater abundance of anthropogenic litter was found by density (count/area) and mass than at Lake Michigan beaches, with the litter comprised of 18–54% plastic [59].

Several studies have measured microplastics in river water, with most conducted in Lake Michigan watersheds. Surface waters sampled with neuston nets in Chicago's North Shore Channel had average microplastic abundances of 730,000 m^{-2} (1.9 m^{-3}) upstream and 6,700,000 m^{-2} (18 m^{-3}) downstream [29] of a WWTP. Fibers followed by fragments were dominant in both upstream and downstream locations, but all particle types (fibers, fragments, foam, and pellets) were present in greater amounts downstream [29]. When expanded to include upstream and downstream locations of WWTPs in nine rivers in the metropolitan Chicago area, average microplastic concentrations ranged 0.5–5.9 m^{-3} upstream (mean 2.4 m^{-3}) and 0.8–11.2 m^{-3} downstream (mean 5.7 m^{-3}) [30]. Fibers, followed by pellets (round shape) and fragments, were generally the dominant morphologies at downstream sites, but varied across locations. In the Milwaukee River system, total microplastic concentrations collected with neuston nets ranged from 1.0 to 5.7 m^{-3} [27]. Additional patterns were revealed by sampling at varying depths. Greater abundances of most categories of plastics typically less dense than water occurred at the surface (e.g., fragments, pellet/bead, film, and foam). Fibers, consisting of polymers usually denser than water, were similarly abundant throughout the water column [27].

A survey of 29 watersheds across the Great Lakes basin was conducted using neuston nets to determine microplastic abundances and to assess the roles of watershed characteristics and hydrology on observed concentrations [31]. Microplastics were found in all low-flow and wet weather samples, ranging from 0.05 to 32 particle m^{-3} (median, 1.9 m^{-3}; mean 4.2 m^{-3}) across all samples. Fibers were the most abundant particle type (average, 71%) followed by fragments (17%) and foams (8%). Several watershed characteristics correlated with microplastic abundances; total particle abundances were significantly positively correlated ($p < 0.05$) with percent urban area, percent impervious surfaces, and population density, with fragments having the strongest positive correlations ($r = 0.40$–0.45). In contrast, percent agricultural lands and percent crop lands were negatively correlated, with lower microplastic concentrations when agricultural land accounted for higher proportions of watersheds [31]. There were no significant relationships to percentage WWTP effluent contributions to total flow for any microplastic type, and fibers did not correlate with any watershed characteristics included in the analysis.

Grab sampling has been conducted for microplastics in several river systems within the basin. Samples (2 L) taken from the St. Joseph, Milwaukee, and Muskegon Rivers averaged 4–90 microplastic particles L^{-1}, filtered to 0.45 μm [35]. Fibers (97–100%) were the dominant form of microplastics found, with fragments at 1.5–3%, and foam was only detected in 1 river (0.4%). Differences in water concentrations among the rivers were observed despite limited sampling, with watershed land-use likely playing a role: St. Joseph (agricultural) > Milwaukee (urban/agricultural) > Muskegon (forested), and the St. Joseph watershed had a considerably higher number of WWTP and non-WWTP dischargers

[35]. Microfibers sampled in the Salt Creek watershed (southern Lake Michigan area) had similar concentrations upstream and downstream of WWTPs, with means ranging from 2 to 3.2 fibers L^{-1} (500 mL samples; filtered to 0.45 μm) [36]. However, these values were in the range of field blanks. In urban Toronto, Ontario, and nearby agricultural streams to western Lake Ontario, concentrations ranged 2.3–29 L^{-1} and 0–4.0 L^{-1}, respectively (4 L grabs; >125 μm) [34]. In the Ottawa River, upstream of the St. Lawrence River near Ottawa, Canada, concentrations ranged from 0.05 to 0.24 particles L^{-1} (100 L samples, filtered to 100 μm) of which >95% were fibers [32]. Higher concentrations were found in the urban Rideau Canal and downstream of the Ottawa WWTP. Water samples (100 L; >100 μm) analyzed from ten locations in the St. Lawrence River had relatively consistent mean concentrations of 0.12 L^{-1} upstream and 0.16 L^{-1} downstream of WWTPs between Montreal and Quebec City, Quebec [37]. Given the variation in sampling and processing methods used for river sampling, a basin-wide comparison is not currently feasible.

3.3 Sediments

The occurrence of plastic in sediment of the Great Lakes–St. Lawrence River basin was first mentioned as being among the carbonaceous components collected from Lake Ontario in 1993 [67]. Ten peer-reviewed studies have since been reported on microplastics in basin sediments. Observed abundances are summarized in Table 3, although differences in units, the particle types isolated, and the methods used limit basin-wide comparisons.

The occurrence of spherical microbeads found in riverine sediments of the St. Lawrence River comprised the first published reports of microplastics in the basin [38]. Eight of ten locations between Cornwall, Ontario, and Quebec City, Quebec had microbeads present, with mean abundances ($n = 3$ or 4 per site) ranging 7–140,000 m^{-2}, with a median of 52 m^{-2}. Melting point analyses indicated the microbeads were PE, and the authors suggested the beads were likely from personal care products based on colors observed [38]. A subsequent study in the St. Lawrence River found microplastic concentrations in sediment ranged from 65 to 7,560 kg^{-1} dry weight, with microbeads dominating, followed by fragments and fibers [37]. Microplastics collected from sediment along a gradient downstream of the City of Ottawa WWTP in the Ottawa River ranged 0.1–0.45 g^{-1} dry weight, with fibers as the dominant particle type (>95%) [32]. Bed sediments sampled throughout the Thames River system in southern Ontario, which enters Lake St. Clair, had microplastic concentrations ranging from 6 to 2,440 kg^{-1} [42]. Concentrations did not differ significantly between urban and rural sites, and fragments were the dominant category. Sediments collected in a gradient downstream of a WWTP in the North Shore Channel in Chicago had abundances ranging 36–1,610 L^{-1}, with fibers followed by pellets (spheres) as the dominant morphologies at most sites [40]. In the Milwaukee and Menomonee Rivers, concentrations of up to 6,230 kg^{-1}

Table 3 Summary of microplastic abundance measured in sediment of the Great Lakes and St. Lawrence River Basin

Locations/Sample type	Abundances	Reference
St. Lawrence River, Quebec (grabs)	0–140,000 m^{-2}	[38]
St. Lawrence River, Quebec (grabs)	65–7,560 kg^{-1}	[37]
Ottawa River, Ontario (grabs)	100–450 kg^{-1}	[32]
North Shore Channel, Chicago (grabs)	36–1,610 L^{-1}	[40]
Milwaukee River, Wisconsin (grabs)	33–6,230 kg^{-1}	[27]
Thames River, Ontario (grabs)	6–2,440 kg^{-1}	[42]
Lake Ontario and St. Lawrence R.		
St. Lawrence River (grabs)	40–80 kg^{-1}	[39]
Tributaries (grabs)	40–1,740 kg^{-1}; 27,800 kg^{-1a}	[39]
Nearshore (grabs)	50–3,210 kg^{-1}	[39]
Nearshore (traps)	260–2,210 kg^{-1}	[39]
Toronto nearshore (cores)	670–4,270 kg^{-1}	[39]
Lake center (core, top 8 cm)	616 kg^{-1}	[3]
Niagara bar (core, top 8 cm)	87 kg^{-1}	[3]
Lake Erie		
Detroit river (grab)	27 kg^{-1}	[41]
Tributaries (grabs)	10–462 kg^{-1}	[41]
Nearshore (grabs)	0–391 kg^{-1}	[41]

[a] High sample from Etobicoke Creek

were found, with black sponge-like particles dominating, categorized as “foam” but which was identified as tire rubber by pyrolysis-GC [27].

Nearshore lake sediments have been surveyed for microplastics across the Canadian side of both Lakes Erie [41] and Ontario into the St. Lawrence River [39], and near Milwaukee in Lake Michigan [27] (Table 3). Lake Erie sediment concentrations ranged 0–391 kg^{-1}, with greater amounts observed near outlets of populated watersheds downstream of the Detroit River and near the Grand River mouth [41]. Tributary and Detroit River sites tended to have low abundances, except for the Welland Canal site (462 particles kg^{-1}). Fragments and fibers were the dominant microplastics found, with generally similar contributions at all but two sites [41]. Sediment microplastic abundances were an order of magnitude higher adjacent to the Greater Toronto Area than other areas of Lake Ontario [39] (Fig. 3) and Lake Erie (Table 3). Elevated lake sediment concentrations (up to 4,270 microplastics kg^{-1}) were found in Humber Bay and Toronto Harbor, which were strongly influenced by urban run-off through rivers and WWTP effluents. However, concentrations were much lower in the relatively enclosed Hamilton Harbor despite also receiving WWTP effluents and urban run-off [39]. Concentrations of approximately 200–300 kg^{-1} were measured in Milwaukee inner and outer harbor sediments, and nearshore lake sediment in the area contained 39 kg^{-1}, with fibers dominating followed by fragments in each case [27].

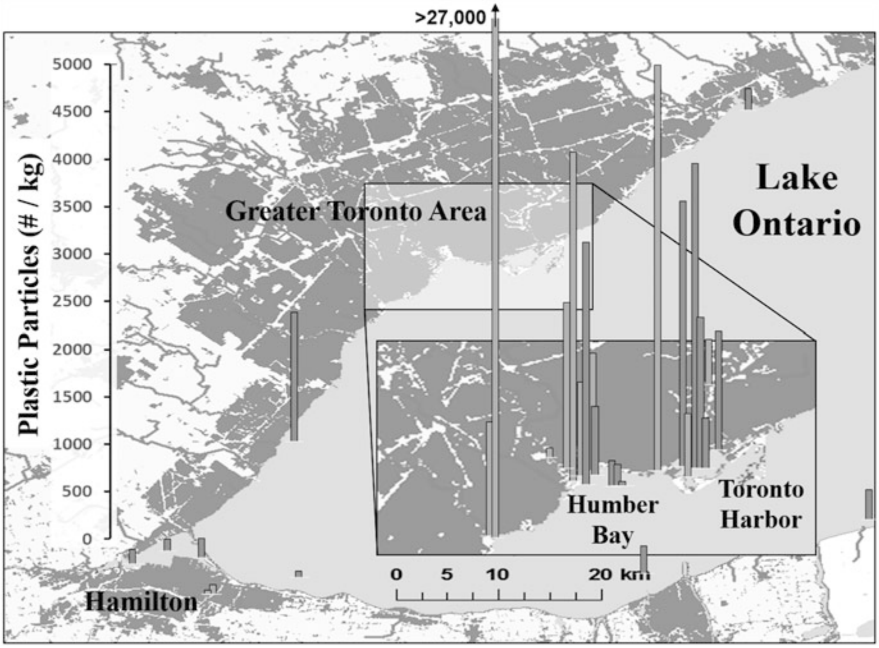

Fig. 3 Elevated microplastic concentrations in sediments collected from western Lake Ontario [39]

In both Lakes Erie and Ontario, polymer types identified by Raman spectroscopy were more diverse than has been observed in Great Lakes waters. In Lake Erie, the majority were PE, with some PP, and other plastics included polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), and polyurethane (PU) [41]. In Lake Ontario sediment, 14 different polymer types were identified, with PE the most abundant, followed by PS, PU, PP, PVC, and polystyrene sulfonate [39].

Dated lake sediment cores record depositional trends of persistent organic pollutants (POPs) in the Great Lakes region, tracking inputs and declines after regulation [68–70]. Sediment cores collected from Lake Ontario contained microplastic in the top 8 cm [3] (Table 3), which represents deposition over the past approximately 40 years in central Lake Ontario. The most recent slices had the most plastics consistent with increasing plastics production trends. All particles isolated in the study were fragments, with PE being the dominant polymer followed by PP [3]. The increasing trend is consistent with temporal observations elsewhere in beach sediments [71], and sediment cores in Asia and Africa [72], off coastal California [73], and in a small urban lake in the United Kingdom [74]. This demonstrates that sediment cores from the Great Lakes are useful to track microplastic trends overtime to evaluate reduction efforts, as has been done for POPs.

Other sediment-based sampling has found microfibers in the Salt Creek watershed (southern Lake Michigan) ranging 32–68 kg^{-1} dry weight sediment, with the greatest amount downstream of a WWTP [36]. In Georgian Bay (Lake Huron), offshore sediments had higher average microplastic abundances compared to near-shore Georgian Bay locations [75]. As is the case for water, standardizing size fractions, categorization schemes, and reporting units for microplastics in sediments will better facilitate base-wide monitoring and assessments.

3.4 Organisms

Despite considerable knowledge of interactions by marine organisms with plastic debris and microplastics (e.g., [14, 15]) and growing knowledge in freshwater environments [17, 18], only three published studies have reported the occurrence of microplastics in Great Lakes organisms to date. However, recent conference presentations indicate that additional data will become available to assess occurrence and exposure of Great Lakes biota to microplastics.

3.4.1 Fish

One published study to date documents microplastic contamination in fish in the Great Lakes region, having analyzed 11 species of fish from three tributaries (Milwaukee River, Muskegon River, and St. Joseph River) of Lake Michigan [35]. Round gobies (*Neogobius melanostomus*) had the greatest amounts in gut tracts, averaging 19 particles per fish, and fibers accounted for 97–100% of microplastics found across all species. No correlations were found between the amounts of microplastic in fish and water at the three sites. Feeding behavior did matter as zoobenthivores had significantly greater amounts of microplastics compared to detritivores at all sites, and greater than omnivores at one site [35]. Among round gobies, a significant correlation was observed between the number of microplastic particles present in the gut and fish length.

Several preliminary reports on microplastics in fish from Lakes Ontario, Superior, and Huron suggest widespread occurrence in fish across the basin, and that more information will soon be available on ingestion and uptake into Great Lakes biota. Forage fish [76] and predator chinook (*Oncorhynchus tshawytscha*) and coho (*Oncorhynchus kisutch*) salmon [77] from Lake Ontario had high detection frequencies of microplastics in gastrointestinal (GI) tracts (99% of forage fish; 89% in chinook, 100% in coho salmon). Forage fish averaged 3.7–7.1 fibers per fish and <0.1–1.0 fragments per fish [76], while salmon averaged 2 and 3.6 plastic particles in chinook and coho, respectively, leading the authors to suggest that salmon retained less plastic than their prey species [77]. Sportfish species from Lake Ontario near Toronto and Hamilton, Ontario, had microplastic abundances in GI tracts that were much higher, with benthic feeding fish containing up to several hundred microplastics [45]. Compared to fish from Lake Superior, Lake Ontario fish had greater abundances of microplastics in their GI tracts [46]. Fibers were dominant but more varied particle types were observed in Lake Ontario fish. Fish from two trophic levels in Lake Huron and Lake Ontario are also being examined [47].

3.4.2 Birds

Ingestion of plastics by seabirds in Canada has recently been reviewed [78]. In the Great Lakes, plastic debris was observed in the diets of herring gulls (*Larus argentatus*) in regurgitated pellets from the late 1970s as part of the "garbage" portion of their diet [43]. Garbage items were in 23–60% of pellets from Hamilton Harbor and 1–12% of pellets from other Lake Ontario locations. The plastic materials observed included bags, polystyrene, small plastic spheres and chips, and nylon lines (6–20 mm). The authors suggested the latter may have originated in fish stomachs [43]. Colonies near population centers had the highest frequency of garbage items.

Pre-fledgling double-breasted cormorant (*Phalacrocorax auritus*) chicks collected from three lower Great Lakes colonies (two near the urban/industrial Hamilton Harbour, western Lake Ontario; one on Mohawk Island, eastern Lake Erie north shore) had anthropogenic debris in >86% of samples [44]. Particles averaged 2.6–4.2 mm in length and abundances averaged 5.1–6.3 (max. 7–15) across the three sites, with no significant differences between sites. Fibers were dominant followed by fragments and film; pellets and spheres were occasionally found. The authors suggested that the prominence of fibers may indicate they originated from fish (e.g., trophic transfer) rather than from debris/fibers around the nests [44], consistent with the suggestion origins of fishing lines in gulls [43]. The stomachs of waterfowl gathered from across Canada contained plastic and other debris, but sampling in the Great Lakes region was limited [79]. Twenty-nine of 44 ring-billed gulls (*Larus delawarensis*) sampled from the St. Lawrence River near Montreal, Quebec, Canada had plastics in their GI tracts [80].

Clearly, microplastics are ingested by aquatic biota in the Great Lakes region. However, additional information is needed to assess whether impacts are occurring in the region, particularly in areas where plastic pollution has been found to be greatest.

4 Sources and Pathways of Microplastics to the Great Lakes

The sources of plastic debris and microplastics to the marine and freshwater environment have been the subject of previous reviews (e.g., [81, 82]). This review highlights knowledge of specific sources of microplastics in the Great Lakes and the pathways by which they are delivered to the lakes. Understanding the sources and where interventions can be applied along the path to the lakes will help to effectively reduce microplastic pollution. Large lakes like the Laurentian Great Lakes are expected to receive plastics from the terrestrial environment from pathways like those for oceans [15], including direct litter to beaches/shores, windblown litter and debris, streams and rivers, wastewater effluent discharges, and deposition from air.

4.1 Sources

Sources of plastics found in the Great Lakes were summarized by Driedger et al. [7] based on reports available at the time, and included microbeads from personal care products, pellets from industry, fibers from textiles, and litter and debris left at beaches. Beach and shoreline cleanup data from the Great Lakes, summarized for 2012, showed that 77–90% (lake-wide averages) of the litter and debris items collected were plastic [7].

Organization of collected litter and debris into categories based on common character (e.g., use and shape) or morphology provides source-specific information. The Great Canadian Shoreline Cleanup provides a list of the top 12 most commonly found litter items, or "Dirty Dozen" (Table 4), of which ten contain plastics. Several categories are specific to the type of litter, its use and source. Cigarette butts, containing cellulose acetate fibers, topped the list. Food wrappers, bottle caps, plastic bags, plastic bottles, straws, and coffee cups are all examples of specific single-use or recyclable consumer plastics that are likely to have been littered. Other categories such as tiny plastic and foam, other packaging, and foam are more general. They include production pellets from industry, and foams from various sources, such as broken up insulation board (e.g., construction sites), consumer goods (e.g., electronics), and take-out food containers. Such specific information helps guide policy development to address the litter, such as legislation and bylaws under development or implemented in many jurisdictions restricting single-use plastics (e.g., [83–85]).

Table 4 Top 12 "Dirty Dozen" debris items collected during Great Canadian Shoreline Cleanup activities in 2018 [62]

Rank	Litter items	# Collected (1,000's)
1	Cigarette butts[a]	560
2	Tiny plastic and foam	354
3	Food wrappers	56.1
4	Bottle caps	49.6
5	Paper materials	44.1
6	Plastic bags	26.5
7	Beverage cans	23.5
8	Plastic bottles	21.3
9	Straws	21.1
10	Other packaging	18.8
11	Foam	18.7
12	Coffee cups	14.3

[a] Included focused efforts by some groups to collect cigarette butts

The morphology of microplastic particles is also informative for source allocation in the Great Lakes. For example, Eriksen et al. noted that microspheres of varying colors collected from Great Lakes surface waters resembled those found in consumer products [13]. Similarly, pre-production pellets, found in beach surveys around Lake Huron, are clearly from industrial sources [11]. However, the categories typically used to group microplastics found in environmental samples are based on general morphologies (fragment, foam, fiber/line, film, and pellets), and not particular to a specific source [50]. As for beach/shoreline materials, developing more source-specific categories may allow a more direct assessment of microplastic source contributions to the Great Lakes, especially for size ranges captured by neuston/manta nets (333 μm to 5 mm) that better accommodate visual characterization. For example, separation of "irregular microbeads" contained in personal care products and plastic debris from commercial cutting and grinding processes from the broad "fragment" category demonstrated that commercial activities are major contributors to overall microplastic abundances a sample collected adjacent to Toronto in Lake Ontario [50]. Such a finding alters the general view that fragments are predominantly from the breakup of litter/debris associated with single-use plastics. While there is some subjectivity in assigning microplastics to specific categories, the development of detailed visual character keys based on many source and process-based samples should help to reduce subjectivity, as purpose-built spectral libraries improve identification by Raman and Fourier transform infrared spectroscopy [86].

Together with microplastic morphologies, the locations where specific plastic types are abundant, adjacent land-uses, and the presence of local discharges are all important for understanding microplastic pollution sources. In addition to the microspheres in lake water [13], pellets (referring to spherical beads in personal care products) were found at greater abundances in river waters downstream of WWTP discharge points, indicating their use in wash-off products as the primary source [29, 30]. Although spherical microbeads found in sediments along the St. Lawrence River were suggested to be from personal care products [38], the depicted beads were gray, black, and amber in color and the location with the greatest abundance was the effluent channel from a nuclear reactor facility. Given these considerations, additional uses and sources of microbeads likely contributed to their presence.

Microplastic character in Great Lakes sediments, combined with land-use in the adjacent watersheds, provided a strong indication of industrial source contributions to plastics in Lake Ontario by Toronto. In sediment from Etobicoke Creek (Lake Ontario tributary), approximately 30% of all microplastics found had rigid, opaque, helical forms [36], which resembled those referred to as commercial fragments found in water along the Toronto waterfront [50]. Ballent et al. suggested these forms were derived from deflashing after injection moulding processes [39]. Mapping the locations of plastics-based businesses in the region showed that elevated abundances of microplastics in sediments, and of the helical-shaped particles, were associated with a greater density of plastics industries in the Etobicoke Creek watershed and watersheds of western Toronto in general [39]. Higher abundances of pre-production pellets were found on the beaches of western Toronto [3], and on a Lake Huron beach in Sarnia, Ontario [11, 48]. In both cases, there are a considerable number of industrial users and generators of plastics pellets, and associated transport, in the adjacent watersheds that link the pellets found to industrial sources. These findings provide direction to policy-makers and industry stakeholders as to the types of practices and locations where interventions could reduce microplastics entering the Great Lakes.

Black rubbery particles with sponge-like character were found in lake sediment near Toronto [39] and in urban river sediment in Milwaukee [27], with the authors suggesting tire rubber as the likely source [39], confirmed by pyrolysis-GC analysis [27]. The rubber particles were categorized as foam, and were the dominant morphology in sediments in 2 of the 3 rivers sampled. Given its distinctive character, tire/black rubber particles should be assigned their own category to avoid confusion, and as it is a specific source.

4.2 Pathways

Plastic pollution ends up in rivers, lakes, and oceans in several ways. Aquatic-based sources include dumping of waste in oceans during shipping, and the dumping or loss of fishing gear [87]. For microplastics and litter debris, land-based sources are acknowledged as predominant, and riverine transport is a key pathway (e.g., [88, 89]). Municipal wastewater treatment plants, which can receive plastics via household effluents, industrial discharges, and stormwater in combined sewer systems, are also known pathways of plastics to waterways [90, 91].

4.2.1 Rivers and Stormwater

Rainwater run-off from impervious surfaces is well known to impact water quality, contributing nutrients, suspended solids, and debris to rivers, particularly in urban areas. Litter and debris can enter streams via stormwater [92], and greater concentrations of microplastics were detected during urban wet weather flows in the first such measurements in river waters [93]. Widespread occurrence of microplastics in urban stormwater ponds indicates that they both help trap debris and microplastics and they will also act as a conduit to receiving waters at high flows [94].

The role of stormwater run-off in transporting specific plastics and microplastics has not been well-characterized in the Great Lakes region, as riverine studies in the region have focused more on occurrence and influence of wastewater inputs (described above). In one study that sampled dry and wet weather flows, greater amounts of fragments, foam, pellets, and film were present in urban run-off compared to low flow, but the results were not statistically different given the low number of samples collected, and fiber concentrations were similar in low-flow and run-off conditions [31]. Receiving waters of urban-impacted rivers in Lake Erie and Lake Ontario had greater microplastic abundances when collected after rainstorms due to delivery in stormwater run-off to the lakes [95]. Run-off from agricultural activities within the basin during wet weather and subsequent entry into local watersheds is under investigation [96, 97], given the presence of plastics in land-applied biosolids [98].

4.2.2 Wastewater

Measurements of microplastics in the vicinity of municipal WWTP discharges demonstrate the influence of this pathway in Great Lakes waters. In rivers in the region, microplastic concentrations were greater downstream of WWTPs than upstream in 7 of 9 rivers sampled in the Chicago area, with two statistically significant [30]. The authors found no indication that sand filters (in 5 of 9 WWTPs) affected downstream to upstream concentration ratios. Microplastic abundances were significantly greater downstream than upstream of WWTPs in the North Shore Channel (Chicago) [29] and in the Ottawa River [32]. Abundances were also greater in Great Lakes waters near WWTP discharges [25, 26, 64].

One peer-reviewed study to date includes systematic sampling of WWTP effluents discharging to the Great Lakes, four from western New York state discharging to Lake Erie and two discharging to Lake Michigan from Wisconsin [33]. Average concentrations ranged from 9 to 47 microplastics m^{-3} for the four L. Erie WWTPs and 7–17 microplastics m^{-3} for the two L. Michigan WWTPs. Fragments (21–77%) and fibers (8–68%) were the dominant morphologies across the six plants, with small contributions from film (2–15%), pellets (0–5%), and foam (0–5%). Based on daily WWTP flows, the estimated number of microplastics released ranged from 64,500 to 6.05 million day^{-1} [33]. Microplastic fluxes downstream of WWTPs in nine streams near Chicago ranged from 15,500 to 4.72 million day^{-1} [30]. Currently, insufficient information is available to assess relative loadings from wastewater inputs, riverine contributions, and stormwaters to identify which pathways are most important.

Limited data on microplastics in WWTP effluents have been collected in other studies within the region. Microplastic concentrations up to 100 m^{-3} were measured in an Ontario WWTP effluent discharging to Lake Ontario [95], preliminary concentrations of 4.4 L^{-1} were reported for effluent at a Niagara-area WWTP [97], and a median concentration of 0.05 L^{-1} was measured in effluent tanks at the Ottawa WWTP [32]. Sampling of 3 WWTPs in the Toronto area (4 L; >125 μm) found 0.3–52 microplastics L^{-1}, 90% of which were fibers [34]. A survey of 34 WWTPs in New York State for microbeads from personal care products found that 25 of 34 plants contained microbeads in their effluents [99]. As with surface water sampling, consistent methodologies are needed to better assess abundance, types and sources of microplastic entering the Great Lake through WWTPs.

4.2.3 Air

Atmospheric occurrence and transport of microplastics have not been investigated in the Great Lakes, but microplastics have been measured in atmospheric fallout in large urban centers, such as Paris, France [100], Hamburg, Germany [101], and suspended atmospheric particulate matter in Shanghai, China [102]. Microplastic concentrations in air were greatest near Chinese coastal areas and lower out over Pacific Ocean waters, showing a role of atmospheric deposition of microplastics to water bodies [103]. Transport and deposition of microplastics to remote areas has been documented, including mountain catchments [104] and remote alpine and arctic snows [105]. It is likely that atmospheric transport from urban areas and subsequent deposition over Great Lakes waters is a pathway of microplastics to the lakes, as has been documented for persistent organic pollutants [106, 107].

5 Fate of Microplastics in the Great Lakes Basin

Once microplastics enter aquatic environments, they may be subjected to several processes that influence their movement lakes and rivers. Currents, additives, biofilm formation (e.g., bacteria, algae, and fungi) on their surfaces, ingestion by organisms, sedimentation, and degradation by various mechanisms can all affect whether plastic debris and microplastics end up on beaches, are deposited to lake sediments, or are exported out of the system downstream and ultimately enter the ocean [108–110]. Modeling, laboratory, and field studies are beginning to provide insights into these processes in the Great Lakes region.

5.1 Surface Transport and Distribution

Plastic debris and microplastics entering the lakes and remaining at or near the surface are subject to surface transport within the system driven by wind and water currents. Three Great Lakes modeling studies using Lagrangian models but with varying parameterization (e.g., winds, time scales, particle input, and weighting) have been published [25, 28, 111].

A model encompassing the five Great Lakes assumed inputs of plastic debris from gridded shorelines weighted by shoreline population density [111]. Higher plastics abundances were predicted to occur in southern Lake Michigan, the western basin and south shore of Lake Erie, and in the western portion of Lake Ontario and along its southeastern shore. Good agreement was found between modeled normalized nearshore densities (assuming particles will be beached) [111], and the densities reported for Lake Huron and Lake Erie beach plastics [48]. Model estimates also agreed well with measured open lake surface water abundances [13], although the model did not capture the higher concentrations measured in the eastern portion of Lake Erie [111]. Higher concentrations of fibers were measured in nearshore lake waters in the southern Lake Michigan area compared to nearby inflowing river water, suggesting accumulation in nearshore zone [36], and supporting model predictions of accumulation in southern Lake Michigan and the role of alongshore currents [111]. Applying assumptions for losses of plastic debris from shorelines used in modeling ocean plastics [112], the Great Lakes model estimated that approximately 10,000 t of plastic enter the lakes each year [111]. The model did not account for processes such as beaching or sinking/deposition to sediments.

A hydrodynamic particle transport model developed for Lake Erie included horizontal and vertical diffusion and considered both neutral and buoyant plastic particles [25]. Gyres or patches of higher abundance did not form in Lake Erie under model conditions, and thus did not explain the greater microplastic abundances measured in open waters of eastern Lake Erie [13, 25]. Alongshore currents dominated distribution patterns, with modeled particles distributing east and west along the south shore close to discharge points. In the western basin of Lake Erie, flows take particles across the basin, not alongshore. Plastic density was found to be a factor, as buoyant particles (e.g., PE pellets) had an estimated 1.7 years average residence time, while neutrally buoyant particles averaged 8.1 years estimated residence time, longer than the water residence time of 2.7 years [25]. Processes impacting particle density and sedimentation were also not considered in this model. Using a similar model for Lake Erie over 3 years of data comparisons, similar distributions were predicted, and an estimated 2.6–7.8 metric tons of plastic present in Lake Erie surface waters from year to year [28].

5.2 Degradation

The durability and long life of plastic are among the properties making it an appealing material, but which also give rise to environmental concerns as plastics will remain in the environment for many years. Due to its slow degradation rates, it has been suggested that plastic could be considered a persistent organic pollutant (POP) [113]. Degradation processes for environmental plastics have been reviewed previously [114, 115], and degradation of plastics can proceed both via abiotic and biotic processes. Degradation mediated by ultra-violet (UV) radiation is by far the most important, enabling plastics to become brittle and fragment into smaller pieces, increasing surface area for other processes such as biodegradation to occur. Abrasion (e.g., in sands, against rock) also contributes to the physical breakup of plastics [110, 114]. Factors that limit UV exposure dramatically reduce degradation rates, such as when plastic is in water compared to air [114], and biofilm formation that rapidly reduces UV transmittance [116]. Thus, plastics at depth (lake/river and ocean bottom) will have minimal exposure to UV, inhibiting degradation [110].

Degradation of plastics present in the Great Lakes have been examined on pre-production pellets and fragments obtained from shorelines using scanning electron microscopy (SEM) [11, 48]. Mechanical abrasion was a dominant process in plastics from Lake Huron beaches, with grooves, gauges, pits, flakes, and surface cracks present [11]. Oxidation was apparent in FTIR spectra and suggested that PP particles were more susceptible to degradation under the conditions sampled. The degree of oxidative weathering found on pellets and fragments was similar from

Lakes Huron, St. Clair, and Erie, likely due to similar climatic conditions across these lakes, and was less than that observed on Hawaiian beaches which receive more sunlight [48]. Particles from Lake St. Clair also had less fracturing and mechanical pits than Lake Huron and Erie plastic particles, likely due to more muddy and organic substrates than beach sands. The rate of degradation of various plastics under conditions in the Great Lakes remains an area of needed study.

5.3 Sedimentation

Microplastics with greater buoyancy such as pre-production pellets tend to be distributed along beaches [48]. However, bed sediments are recognized as repositories for microplastics in aquatic systems [117]. Given abundances of microplastics in Great Lakes sediments [3, 37–41], it is apparent that depositional processes readily occur and that they can accumulate near discharge points. Microplastics were captured in settling material in sediment traps located 1 m off the bottom of run-off impacted Lake Ontario waters [39]. In sediments from central Lake Ontario, microplastic levels were approximately 4.7 billion km^{-2} (18 particles in the top 4 cm of a 7 cm diameter core) [3], approximately 700–2,100 times greater than areal abundances in Lake Ontario nearshore surface waters (Table 2) [64], and 20,000 times greater than the average areal abundance of 230,000 particles km^{-2} across Lake Ontario [28]. On volume basis (assuming 4 cm depth for the sediment core, and 8 cm depth for manta trawls), the ratio of particles in surface sediments to surface water ranges 220,000 to 6.3 million, indicating that Great Lakes sediments are a significant sink for microplastics.

Sedimentation processes and factors controlling deposition are not well-understood in freshwater systems, although recent studies are examining these phenomena. In an artificial stream mimicking pulsed releases, microplastics deposited in patterns consistent with natural organic carbon and were related to density and biofilm character [118]. Freshwater laboratory experiments found that microplastic particle transport differed from known sediment transport behavior, needing new empirical equations to describe microplastic transport [119]. Aggregation with phytoplankton biomass [120] and growth of biofilms [121] were important processes contributing to sedimentation and the fate of microplastics in oceans. Particle sizes may also influence depositional behavior. Distributions of smaller microplastics differed from those >500 μm in a Norwegian fiord [122], and the contributions of smaller microplastics increased with depth in a sediment core while larger particles were more likely at the top of the core [123]. The latter has implications for interpreting and tracking depositional trends in sediment cores and needs further investigation. In the Thames River in southern Ontario, greater microplastic abundances were associated with finer grain-sized sediments and those with more organic debris [42]. Large river models suggest that a considerable portion (nearing 100%) of microplastics can be retained in the system during slow flow conditions and in depositional areas, particularly >200 μm [108, 109].

Better understanding of deposition and transport processes will enable mass balance modeling of lake systems to assess roles of sedimentation versus export. The first model to consider input/outputs and sinks in a lake system, Lake Geneva in Switzerland, suggests that sediments contain much of the plastic stock in the lake (580 tonnes) compared to surface waters (0.1 tonnes) [124]. Of the 55 tonnes estimated to enter the lake annually, 40 tonnes were calculated to enter the sediment, 10 tonnes removed via cleanups, and 5 tonnes exits the lake through the outflow. Wet weather river discharges were by far the most important contributors to Lake Geneva (estimated 41 of 55 tonnes year^{-1}) followed by urban run-off (9 tonnes/year), while wastewater effluent contributed only 0.05 tonnes year^{-1}) [124]. Relative contributions may be quite different in the Great Lakes context, and such a modeling exercise is recommended for the lakes.

5.4 Microplastic Fate in Organisms

The interaction of microplastics with and within aquatic organisms are important components of their overall fate in the Great Lakes. Ingestion of microplastics by aquatic life is well documented, particularly in marine environments (e.g., [14, 15]), but also in freshwater fish [125] and invertebrates [126], including Great Lakes fish (discussed above). There is some evidence that fish can be selective in the particles they ingest. Microplastics were rejected by the marine fish, palm ruff (*Seriolella violacea*), in laboratory experiments unless they were associated with food [127]. Ingestion and selectivity can also vary with life stage, as illustrated by the change in selectivity between larval and adult marine medaka (*O. melastigma*) [128].

There has been some examination of the fate of ingested microplastics in freshwater fishes. Goldfish (*Carassius auratus*) fed microbeads and microfibers in food pellets passed through the GI tracts and were egested at time frames similar to food remains [129]. The time of 90% retention was 33 h. Very few particles (0–3 out of 50) remained after 6 days, suggesting little likelihood of accumulation of microplastics. The two particle types did not exhibit significantly different retention rates [129]. A feeding study using juvenile rainbow trout (*Oncorhynchus mykiss*), juvenile white sucker (*Catostomus commersonii*), and adult fathead minnows (*Pimephales promelas*) and a variety of microplastic particle shapes and types found some retention of particles after 24–48 h of clearance, but no significant differences in retention between particle morphologies [130]. For two of the particle types tested, one of eight fish in a treatment class accumulated a much higher number of particles than other fish in the group. Although these were outliers, it may be indicative of how microplastics and plastic debris can impact a select few organisms within a cohort which happen to ingest more than others.

The fate of microplastics within aquatic organisms remains a subject of active research to assess whether microplastics can cross from the GI tract and accumulate in other tissues. To date, there have been no observations of microplastics in tissues other than GI tracts of Great Lakes fish. Several studies have investigated whether translocation from the GI tract can occur in marine and freshwater species. Wild-caught European anchovies (*Engraulis encrasicolus*) were found to contain microplastics in their livers at a high frequency of occurrence, and with particles found up >400 μm in size [131]. In contrast, microplastics were found in the GI tract and gills of the Asian seabass (*Lateolabrax maculatus*), but the muscle and liver samples were equivalent to blanks [132]. If detected, the relative amount of plastic found outside the GI tract to date is quite low.

The uptake of plastic debris and microplastics by seabirds has been an important driver in addressing plastic pollution globally. Early studies, reviewed by Derraik [87], showed impacts of plastics on fat reserves, body condition, transfer to young, and significant mortality in species unable to regurgitate plastic debris. In the Great Lakes region, the occurrence of garbage materials in regurgitated pellets (predominantly) and feces of herring gulls clearly demonstrated not only ingestion, but also the ability to eliminate materials [43]. In Northern Fulmars from Canada's Atlantic coast, fecal precursors contained microplastics in lower amounts than in stomachs but were correlated [133]. Fragments were only found in stomachs, but most other morphologies were found in both, suggesting the ability to excrete most plastics. The presence of plastics in birds such as herring gulls, particularly in regurgitated pellets, has led to suggestions that such pellets would be a useful media for monitoring of plastics on a regional basis and capturing changes through time [78].

6 Conclusions and Future Directions

Knowledge on the occurrence, sources, fate, and transport of microplastics in the Great Lakes basin has been increasing, with more than 25 peer-reviewed studies published over the past 5 years. Microplastics measurements in waters of the five lakes have shown that higher amounts are present close to urban and nearshore areas, particularly near where rivers, stormwater, and wastewater effluents discharge. Greater abundances are found in Lake Erie and Lake Ontario which have larger populations and more sources in closer proximity. Microbeads (spheres), some of which are now banned, contributed to microplastic burden in some studies, but fragments and fibers tended to be the dominant morphologies found. Significant inputs from plastics industry sector emissions were apparent in some regions, as indicated by pellets along shorelines and deflashing/grinding waste present in waters and sediment adjacent to watersheds containing greater numbers of plastics companies. Microplastics, predominantly fibers, are present in the GI tracts of most Great Lakes fish and birds sampled to date. Preliminary modeling of the distribution and transport of plastics shows the importance of alongshore currents in moving plastics around the lakes and provides indications of which shores are likely to have buoyant plastics accumulate to focus cleanup efforts. Lake sediments are likely a major repository of plastics once they enter the lakes, and benthic organisms are likely to experience greater exposures to microplastics.

Several aspects of plastic pollution and microplastics in particularly need consideration for further monitoring and research in the Great Lakes. The adoption of standardized size fractions, morphological categories, and units for reporting of microplastics is needed to facilitate basin-wide assessments and to implement consistent monitoring for the effectiveness of reduction efforts. More efficient methodologies for microplastics analysis are under development, especially for smaller-sized microplastics and nanoplastics. However, these techniques have not been applied to assess occurrence, exposure, and uptake in Great Lakes biota from water, sediment, and in air, the latter likely to be an important exposure route for humans. More investigation is needed on the potential for ecological impacts, especially in areas where abundance in water and sediment is the greatest, and for terrestrial species (e.g., birds), in addition to aquatic organisms. A better understanding of plastic pollution fluxes into and distribution within the lakes is needed, such as mass balance modeling, to evaluate the roles of wastewater, stormwater, and wet weather river flows in delivery of microplastics, helping to ensure source reduction efforts are applied effectively. Sediment cores show promise for tracking long term trends of microplastics in the basin, similar to POPs, but a better understanding of particle dynamics within cores across a range of particle sizes is needed to ensure trends are accurately captured. Given the important role of stormwater in delivering plastics, effective measures of plastics in urban waters are needed to assess local reduction efforts.

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Spatial and Temporal Trends of Metal and Organic Contaminants in the Huron-Erie Corridor: 1999–2014

Ken G. Drouillard, Joseph Lafontaine, Alice Grgicak-Mannion, Kerry McPhedran, and Ewa Szalińska

Contents

Abstract Spatial and temporal patterns of sediment contamination were examined in the Huron-Erie Corridor (HEC) of the Laurentian Great Lakes. Both the St. Clair and Detroit Rivers are designated Great Lakes Areas of Concern (AOCs) and are subject to past and prospective future sediment remediation efforts. Data generated using a system-wide probabilistic sampling design were compiled and contrasted between an early year period (1999–2004) and late period (2008–2014). Contaminants considered included trace metals, organochlorines, polychlorinated biphenyls

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(PCBs), and polycyclic aromatic hydrocarbons (PAHs). The general ranking of sediment contamination across waterbodies was Detroit River > St. Clair River = St. Clair Delta > Lake St. Clair. Canadian and US nearshore areas remained distinct in their pollution signatures as a result of hydraulic barriers formed by shipping channels that longitudinally bisect the system. Canadian segments of the St. Clair River were enriched with hexachlorobenzene (HCB), octachlorostyrene (OCS), and mercury (Hg) and demonstrated a dilution gradient across subsequent downstream Canadian segments. US segments of the Detroit River were enriched with PCBs, PAHs, chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). Temporal trends differed between waterbodies and associated chemicals and explained less overall variation in contaminant concentrations compared to spatial patterns. Most chemicals with concentrations exceeding sediment quality guidelines at the probable effect concentration (PEC) showed little or no difference in sediment contamination between early and late year periods. This study provides support for planned forthcoming sediment cleanup actions in the two AOCs and can serve as a baseline for evaluating future recovery of the system.

Keywords Contaminated sediments, Detroit River, Hazard assessment, Huron-Erie Corridor, St. Clair River

Acronyms

4,4′-Dichlorodiphenyldichloroethylene (p,p′-DDE)	An organochlorine compound
Analysis of variance (ANOVA)	A univariate statistical test used to compare differences in chemical concentrations or PCA scores between groups
Area of concern (AOC)	A designated region of water in the Laurentian Great Lakes identified by the International Joint Commission to have impairments in one or more beneficial uses. All AOCs are assigned remedial action plans to support actions that will lead toward delisting and removal of the AOC status
Arsenic (As)	Chemical element
Cadmium (Cd)	Chemical element
Chromium (Cr)	Chemical element
Copper (Cu)	Chemical element
Gas chromatography-electron capture detection (GC-ECD)	Instrument platform used to measure organochlorine chemicals
Gas chromatography-mass selective detector (GC-MSD)	Instrument platform used to measure polycyclic aromatic hydrocarbons

Hexachlorobenzene (HCB)	An organochlorine compound
Huron-Erie Corridor (HEC)	Specifies the connecting channel waters linking Lake Huron and Lake Erie. It consists of the St. Clair River, Lake St. Clair, and the Detroit River
Inductively coupled plasma-optical emission spectroscopy (ICP-OES)	Instrument platform used to measure trace element concentrations
Iron (Fe)	Chemical element
Lead (Pb)	Chemical element
Lowest effect level (LEL)	Sediment quality guideline generated by Ontario's Ministry of the Environment, Conservation and Parks. The LEL is the chemical concentration in sediment associated with potential loss of sensitive benthic invertebrate species
Mercury (Hg)	Chemical element
Nickel (Ni)	Chemical element
Non-detected (ND)	Concentration of a given chemical analyzed for but was below the method reporting limit
Octachlorostyrene (OCS)	An organochlorine compound
Organochlorine chemicals (OCs)	Class of organic chemicals that contain chlorine as substituents usually referring to legacy pesticides and industrial chemicals
Polycyclic aromatic hydrocarbons (PAHs)	Class of organic chemicals characterized by one or more aromatic rings and containing only carbon and hydrogen
Polychlorinated biphenyls (PCBs)	A class of organochlorine compounds containing two biphenyl rings and one or more chlorine substituents
Principal component analysis (PCA)	Multivariate statistical ordination technique used to reduce the dimensionality of a multivariate dataset
Probable effect concentration (PEC)	Consensus-based sediment quality guideline recommended by MacDonald et al. [20] generated from weight of evidence assessment of sediment quality guidelines used in different jurisdictions. The PEC represents the lowest chemical concentration in sediment that is likely to generate toxicity to benthic invertebrates inhabiting them

Severe effect level (SEL)	Sediment quality guideline generated by Ontario's Ministry of Environment, Conservation and Parks. The SEL is the chemical concentration in sediment associated with potential loss of tolerant and sensitive benthic invertebrate species
Sediment quality guideline (SQG)	A criteria for chemical concentrations in sediments used to assess the quality of sediments as it relates to potential toxicity to benthic invertebrates or other fauna exposed to sediments
Threshold effect concentration (TEC)	Consensus-based sediment quality guideline recommended by MacDonald et al. [20] generated from weight of evidence assessment of sediment quality guidelines used in different jurisdictions. The TEC represents the highest chemical concentration in sediment where toxicity to benthic invertebrates inhabiting them is unlikely
Tukey's honestly significant difference test (Tukey's HSD)	An a posteriori test used to determine between group differences. It is used in conjunction with ANOVA
Zinc (Zn)	Chemical element

1 Introduction

The Huron-Erie Corridor (HEC) includes the St. Clair River, Lake St. Clair, and Detroit River which collectively hydraulically link Lakes Huron and Erie of the North American Laurentian Great Lakes. Both the Detroit and St. Clair Rivers are identified as International Areas of Concern (AOC) by the Great Lakes Water Quality Agreement and have binational remedial action plans associated with them. In addition, the HEC receives inflow from other AOCs including the Clinton River AOC, which in turn drains into Lake St. Clair, and the Rouge River AOC that drains into the Detroit River. Within each remedial action plan, the AOC is assessed across 14 standardized beneficial use impairments developed to monitor change in the chemical, physical, or biological integrity of the system causing impaired human uses, loss of ecosystem services, proliferation of nuisance species or toxicity, and impaired performance of organisms living and dependent on the system of study. Contaminated sediments are a major factor in the cleanup strategies for both the St. Clair and Detroit River remedial action plans due to their direct and indirect linkages to several beneficial use impairments assessed in each system [1–3]. Lake

St. Clair was the first Great Lakes location to have its commercial fishery closed due to mercury (Hg) contamination of fish in the 1970s and continues to have elevated Hg in its sediments [4, 5]. Lake St. Clair and the St. Clair and Detroit Rivers have each been subject to surveys of contaminated sediments [1, 2, 6–13]. These studies identified subregions with high contamination including the upper to middle near-shore Canadian sections of the St. Clair River [1, 14], a large mass of mercury in the center of Lake St. Clair [5], and multi-pollutant contamination of lower US sections of the Detroit River [6, 7, 9, 11]. However, fewer studies have examined sediment quality throughout the HEC to allow broader identification of spatial and temporal trends at the corridor scale [1, 11].

Past surveys of HEC sediment contamination also differ with respect to the types of sampling designs employed. The two main designs implemented in the HEC include (a) point source tracking (judgmental) and (b) probability-based sampling designs. Point source tracking designs designate sampling location based on previous information or expert knowledge concerning the potential location of sources and known/anticipated depositional zones within the study system. Designs of this type are best suited for small sampling scales as they can maximize sample resolution and density in perceived priority locations. This design was applied during the Upper Great Lakes Connecting Channels studies [15] and in more recent sediment surveys of the St. Clair River [2] and is commonly used to designate areas for cleanup or to monitor local improvement following specific cleanup and mitigation activities [16]. However, surveys of this type can provide a biased perspective of the overall system health, especially when collated in weight of evidence assessments since regions of sampling are typically concentrated at known/perceived polluted locations. Probability-based designs randomize sampling locations throughout the study system, usually under a pre-designated stratified random sampling design. Probability-based sampling designs are more appropriate when applied at the system scale, enable unbiased statistical comparison of contamination between sampled strata, compute regional and global mass balance inventories, and can identify previously unknown contaminated and/or reference areas in the system [7, 13]. However, these designs can suffer from sampling resolution deficiencies depending on the scale of system being studied and degree of heterogeneity in sediment contamination patterns that occur within the study system [13].

The first large-scale probability-based sediment survey in the HEC was implemented in 1999 in the Detroit River [1, 7]. This survey included 150 sampling stations that covered the entire AOC boundary, distributed samples equally in US and Canadian waters, and further stratified the AOC into upstream, midstream, and downstream reaches. Priority contaminants analyzed included trace metals, total Hg, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorines (OCs) along with sediment characteristics such as grain size and loss on ignition. In 2004, a second probability-based survey was generated for the Huron-Erie Corridor that included 104 sampling stations distributed in St. Clair River, Lake St. Clair, and Detroit River using a similar design [1]. Additional probability-based surveys have been implemented in the Detroit River since 1999

[13], and the present study describes and combines the results of these past surveys with a new HEC sediment quality survey implemented in 2013–2014.

The objective of this study is to provide a spatial and temporal assessment of multi-pollutant sediment contamination of the HEC applying system-wide and regional assessments. Data from previous probability-based sediment surveys conducted in the HEC were compiled and collated along with the most recent survey data (2013–2014). Temporal changes in sediment quality were compared between data compiled in the early year period (1999–2005) versus the late period (2008–2014). Spatial patterns were delineated at the system scale, waterbody scale, and US versus Canadian jurisdictions of each waterbody. A novel approach taken herein was to apply multivariate ordinations of all study chemicals across different space scales and the two time periods in order to detect covarying chemical groupings diagnostic of multi-pollutant source types and/or common environmental fate and transport characteristics. This differs from the conventional approach of describing spatial/temporal patterns of selected contaminants independently providing another dimension of source characterization and between system contrasts. In addition to concentration changes, priority pollutant inventories were generated for each waterbody using a mass balance approach. System-wide mass balances of this type enable local cleanup activities to be placed into context and provide a baseline from which to compare future systemic improvements. Both the St. Clair and Detroit Rivers have been subject to past sediment cleanup actions [2, 17], and each AOC is currently in the planning phase of new sediment remedial activities targeting contaminated sediments. When coupled with future HEC surveys of equivalent design, the results from this study can thus serve as a baseline to monitor ecosystem recovery occurring as a result of previous and future restoration actions.

2 Methods

2.1 Study Area

The HEC is a 157 km waterway linking Lake Huron to Lake Erie (Fig. 1). It flows through urbanized, industrialized, and agricultural areas. The Detroit River and St. Clair River AOCs, as well as Lake St. Clair, receive pollution inputs currently and historically from a complex array of point, nonpoint, tributary, and upstream sources. The St. Clair River is 65 km in length, drops 1.5 m, and has an average flow of 5,200 $m^3\ s^{-1}$ [15]. It mostly consists of a single deep channel with depths from 8 to 15 m except where obstructed by Stag Island and Fawn Island in the middle reaches. Apart from the very nearshore regions and the islands above, there are few depositional locations in the St. Clair River before it reaches the St. Clair Delta. Upon reaching the Delta, flow decreases, and the river splits into multiple channels averaging 11 m in depth, while shallow bays create depositional zones and complex shoreline of islands covering 80 km^2 [1]. The eastern side of the Delta (Chenal Ecarte, Johnston Channel) includes narrow, shallow waterways carrying lower water

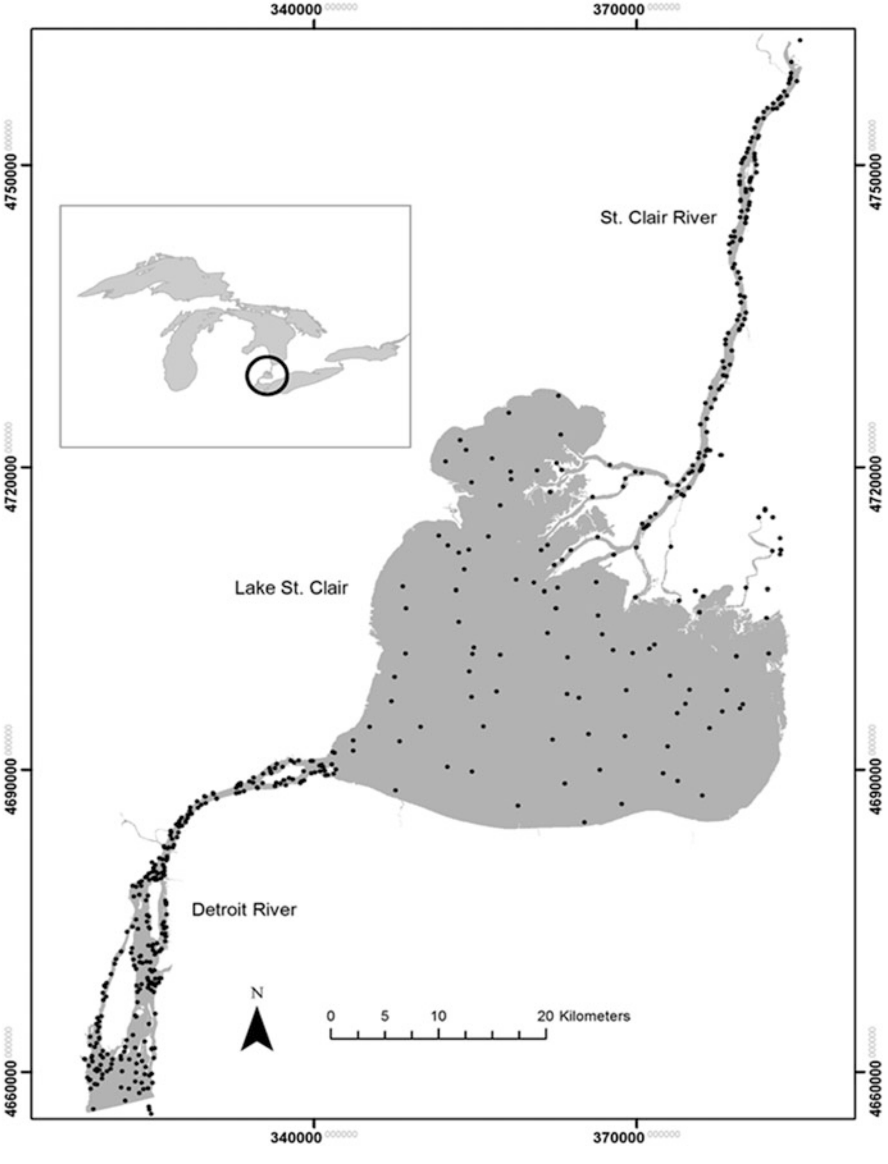

Fig. 1 Map of Huron-Erie Corridor and location of sediment sampling stations from early and late period sediment chemistry surveys

volumes. The western side of the Delta (North, Middle, and South Channels) account for most volume to Lake St. Clair [18]. Lake St. Clair is shallow averaging 3.7 m depth except where bisected by an 8.3 m shipping channel. The Detroit River is 51 km in length, drops 0.9 m, and has an average flow of 5,240 $m^3\ s^{-1}$

[15]. The upper portion of the Detroit River is heavily channelized and narrow containing two islands (Belle Isle and Peche Island). The lower river contains an abundance of large and small islands breaking the river into channels, bays, and harbors with the average depth decreasing to 3 m except for dredged navigational channels. Owing to the depth of shipping channels relative to nearshore areas and most of the surface area of the lake, the shipping channels act as hydraulic barriers attenuating water and sediment mixing between US and Canadian nearshore jurisdictions [1, 7].

2.2 Sample Collection and Chemical Analysis

Sediment chemistry data were collected from six separate surveys completed throughout the HEC over the last 18 years by the Great Lakes Institute for Environmental Research (GLIER). Each survey followed a similar stratified random sampling protocol except for Canadian waters in the St. Clair Delta under the jurisdiction of Walpole Island. The latter followed a directed sampling design**.** The surveys were completed as follows: 1999 and 2008/2009 Detroit River surveys (river-wide surveys with $n = 150$ and $n = 65$ sampling points), 2004 full corridor (emphasizing St. Clair River and Lake St. Clair with $n = 108$), 2005 and 2012 St. Clair Delta ($n = 38$ and $n = 48$), and the 2013/2014 full corridor survey ($n = 223$). Individual sampling protocols and laboratory techniques have been described elsewhere [1, 7, 11–13].

The stratified random sampling design used in each survey segmented the river and/or corridor into upstream-downstream reaches as well as US and Canadian waters. Coordinates for sampling were randomly pre-assigned throughout each segment with equal numbers of sample stations allocated in US and Canadian waters, but unequal sample numbers were used among individual river/lake reaches. The deviation from this sampling design was the Walpole Delta studies conducted in 2005 and 2012 representative of portions of the St. Clair Delta. These studies involved a directed sampling approach where triplicate sediment samples were collected from the same locations in both 2005 and 2012. In all surveys, sample stations were accessed by boat which was moored within 150 m of the preselected sample location. Surface sediment samples were collected using a petite ponar grab sampler ($6 \times 6''$). Multiple sediment grabs were performed until a total volume of 2 L of sediment was collected at the sample site. Duplicate samples (2×2 L volumes) were collected at every fifth site in the 2013/2014 surveys for quality assurance. Where sufficient sediment could not be collected owing to incompatible substrate type (e.g., rocks), the boat was moved by approximately 200 m, and a new sample was attempted for collection with the revised location coordinates noted. Following collection, samples were mixed and stored in plastic bags at 4°C until processing. At processing, samples were sieved to <2 mm and physically mixed. Subsamples of homogenates were taken for analysis of trace elements, total mercury (Hg), PCBs, PAHs, and organochlorines.

For trace elements, sediments were digested by concentrated nitric acid and hydrochloric acid. The digestate was heated to 100°C for 5 h, allowed to cool, and filtered through a Whatman #4 filter paper where it was brought to a sample weight of 100 g with Millipore water. Metals were detected by inductively coupled plasma-optical emission spectrometer (ICP-OES) (1999–2012 used a model: IRIS #701776, Thermo Jarrell Ash Corporation; 2013–2014 used a 700 Series, Agilent Technologies ICP-OES instrument) both under similar protocols and quality control procedures. Metals measured included arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), and zinc (Zn). Certified reference materials (National Research Council-MESS3 and S-PACS2), along with three method blanks, were analyzed with every 40 samples including 1 duplicate sample chosen at random. Detection limits for metals were in the range of 0.005–14 $\mu g\ g^{-1}$. Sample recoveries in reference materials were typically 85–110% across trace elements and checked for compliance with quality assurance protocols that mandate a minimum of 70% recovery.

Total mercury (Hg) concentrations for the 1999, 2004, and 2005 surveys were measured by atomic absorption spectrophotometer (AAS-300, Varian) equipped with a single element hollow cathode lamp and a vapor generation accessory unit (VGA-76, Varian) as described in [11]. Total Hg for the 2008/2009, 2012, and 2013/2014 surveys was measured using a DMA-80 Direct Mercury Analyzer (ATS Scientific INC., Burlington, ON). Despite differences in the method for total Hg between surveys, common sediment reference materials (National Research Council MES-3, LSKD-4) and in-house references were analyzed with each sample batch of 30 samples along with replicate and duplicate samples to ensure method compatibility. Detection limits for Hg were 0.007–0.03 $\mu g\ g^{-1}$. The recoveries of certified standards run with batches of samples ranged from 90 to 108%.

Organic contaminant extraction was performed according to Drouillard et al. [7]. Twenty grams of wet sediment was dried with 100 g anhydrous sodium sulfate and ground by mortar and pestle. The homogenate was transferred to a glass thimble, spiked with surrogate recovery standards (chlorinated biphenyl IUPAC #34 and brominated diphenyl either IUPAC #71) and extracted using 300 mL acetone-hexane (1:1 volume) by Soxhlet for 24 h. Extracts were back extracted using a separatory funnel containing 20% sodium chloride in 200 mL Millipore water and hexane over three solvent washings to remove acetone. Hexane extracts from each wash were collected, combined, and eluted through a glass chromatography column (35 cm × 2.5 cm) containing 80 g anhydrous sodium sulfate and further eluted with 200 mL of hexane. The hexane eluant was evaporated to 2 mL and transferred to a Florisil column (35 cm × 1 cm column prepared with 6 g of activated Florisil) for cleanup. Analytes were eluted from the Florisil column with 50 mL hexane (fraction 1) followed by 50 mL of 15% dichloromethane/85% hexane (fraction 2). Following elution, 5 mL of isooctane was added to each fraction as a keeper, and extracts were evaporated to 2 mL. To remove sulfur, activated copper (0.2–0.5 g) was added to each extract and allowed to sit overnight. Where copper was found to be blackened, the processes were repeated until added activated copper failed to further react. Extracts from each fraction were transferred into separate 2 mL autosampler vial.

Gas chromatography analysis was performed using a Hewlett-Packard 5890 chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD), a 60 m × 0.25 mm × 0.1 μm DB-5 column, and Hewlett-Packard 7673a auto sampler as described in [19]. Each Florisil fraction was injected separately and examined for their associated contaminants. Where analytes were found in both fractions, their areas were added prior to concentration calculation. Additional quality assurance procedures involved running duplicate standards and isooctane blanks between samples within GC-ECD runs. Forty individual and co-eluting PCB congeners from tri- to nonachlorobiphenyls were characterized by retention time and quantified using working standards derived from a certified standard mixture (Quebec Ministry of Environment PCB congener mix). The PCB congeners commonly available across individual surveys included IUPAC #s 28, 31, 44, 49, 52, 70, 74, 82, 87, 101, 99, 105, 110, 118, 127, 128, 132, 138, 149, 151, 153, 157, 170, 171, 158, 180, 183, 187, 194, 195, 206, and 208 with sum PCBs calculated as the sum of the above congeners. Organochlorines (OCs) were characterized on the same extracts and quantified against the instrument response of a working standard generated from a certified standard (Custom OC Pesticide mix from AccuStandard, New Haven, CT). OCs quantified included hexachlorobenzene (HCB), octachlorostyrene (OCS), transnonachlor, and p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE).

Following injection onto GC-ECD, fractions 1 and 2 were combined and added to a new GC-sample vial for analysis of PAHs. PAH analysis was performed using a Hewlett-Packard 5890/5979 gas chromatograph with a mass selective detector (GC-MSD) in selective ion monitoring mode, a 60 m × 0.25 mm × 0.1 μm DB-5 column and 7673 autosampler. Further details of GC conditions, oven program, and ion windows are described in [19]. Analysis of 15 priority PAHs included naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene/triphenylene, benzo(b) fluoranthene, benzo(a)pyrene, indeno(1,2,3,-c,d)pyrene, dibenzo(a,h)anthracene, and benzo-(g,h,i)perylene. Individual PAHs were quantified based on a five-point standard calibration curve using working standards generated from a certified standard (PAH mix standard from AccuStandard, New Haven, CT). Throughout the text, PAHs are reported as the sum of the 15 priority PAH concentrations analyzed above.

For organic contaminants, each batch of 5–7 samples was accompanied by co-extraction of a method blank and certified reference sediment (NIST-SRM 1944) to monitor laboratory performance and ensure quality assurance. For all contaminants, individual survey detection limits, blank corrections, and quality assurance parameters can be found elsewhere [1, 7, 11–13]. The 2013 survey detection limits were in the range of 0.01–0.15 ng g^{-1} for PCBs, 0.02–0.12 ng g^{-1} for PAHs, and 0.01–0.06 ng g^{-1} for OCs. Surrogate standard recoveries were between 70 and 140% for PCB 34 and BDE 70. Where surrogate standard recoveries were less than 70%, the sample was re-extracted until satisfactory recoveries were obtained. Quality assurance procedures for recoveries of PCBs, selected OCs, and PAHs in the certified reference material, run with each batch, required that recoveries were within 2 standard deviations of their certified values.

2.3 Data Analysis

Due to variation of measured analytes between surveys, some adjustments to standardize common chemical parameters (e.g., list of common PCB congeners implemented across all surveys) into one database were required. Data were tested for normality using a Shapiro-Wilk test. Some parameters adhered to log-normal distributions and others did not. As a result, the median and 5–95 percentiles are reported as measures of central tendency and variation throughout the text. Concentrations of individual contaminants were contrasted against sediment quality guidelines to facilitate hazard assessment. Where possible, contaminants were compared against the consensus-based sediment quality guidelines described in MacDonald et al. [20]. These sediment quality guidelines define the threshold effect concentration (TEC) below which adverse effects on benthic invertebrates are not likely to occur and a probable effect concentration (PEC) above which toxic effects are likely to occur. In the case of Fe and HCB, the sediment concentrations were compared to the Ontario sediment quality guideline [21] since this chemical has no guideline value described in MacDonald et al. [20]. The Ontario sediment quality guidelines define a low effect level (LEL) representative of a sediment concentration that is likely to produce toxicity only in sensitive benthic invertebrate species and a severe effect level (SEL) likely to produce toxicity in most benthic invertebrates. The LEL and SEL values for Fe and HCB were considered equivalent to TEC and PEC and interpreted in the same manner.

Principal component analysis (PCA) was performed on log-transformed data using a correlation matrix to determine pollutant intercorrelations and reduce the dimensionality of the dataset. PCAs were completed using PAST statistical software [22]. Although some individual chemical parameters did not conform to log normality, the $\log_{10}$-normalized dataset did comply with multivariate normality assumptions. Thirty samples were discarded from the PCA analysis because they were incomplete with respect to the analysis of all chemical groups, and PCA necessitates a completed data matrix. Chemicals having a detection frequency of less than 60% across sample locations were also removed from the PCA to limit the effect of non-detection data substitutions. For the non-excluded chemicals, non-detections were replaced with the chemical detection limit. During interpretation of the PCA, chemicals with loadings onto a given PCA axis greater than 0.6 were considered affiliated with that axis, while those with loadings >0.7 were considered strongly affiliated with the axis. PCAs were completed on the full corridor dataset, corridor-wide data broken into early (1999–2004) and late periods (2008–2014), and for data subsets associated with individual waterbodies in order to describe major spatial/temporal patterns at the corridor and individual waterbody scales.

Analysis of variance (ANOVA) was used to test for differences in PCA scores from selected PCA analyses to detect differences in axes-affiliated chemicals across time, between waterbodies, or between waterbody segments within individual waterbodies. Tukey's post hoc comparisons were used to test individual groups within each treatment. A probability of <0.05 was used to test for significant differences between groups. ANOVA and Tukey's tests were completed using SYSTAT 13 statistical software.

System-wide mass and waterbody-specific balance were calculated for surface sediments similar to that described by [13]. The Detroit River and St. Clair River were each split into six zones: upstream, midstream, and downstream reaches that were further split into Canadian and US segments. Both Lake St. Clair and the St. Clair Delta were split into Canadian and US segments. For each specific zone, a mass balance was calculated according to:

$$M = C \cdot \rho \cdot A \cdot D \tag{1}$$

where M is the total mass of chemical in each given zone (kg). C represents the mean chemical concentration in that zone (kg/kg dry sediment weight), p is the dry bulk density (kg dw/m^3), A is the surface area of each zone (m^2), and D represents the depth (m) of sampled surface sediments (fixed at 0.1 m for all sample stations). The assignment of bulk sediment densities was according to [13] as 1,378 kg/m^3 for particles $<$0.150 mm and 1,426 kg/m^3 for particles $>$0.150 mm determined for each sample location based on measured grain size distributions. Area measurements of each strata were computed using ArcGIS (ESRI 2016) by splitting a high-resolution shoreline polygon of the HEC into the respective zones of analysis. Chemical mass balance in each waterbody was determined by summing the chemical masses in each zone. Error estimates for chemical mass balances was estimated by a Monte Carlo procedure as described in [13]. The mean and standard deviation values of zone-specific chemical concentrations, sediment moisture contents, and dry bulk density were incorporated as model inputs having error. Monte Carlo simulations were performed using Oracle Crystal Ball Software under an assumed log normal distribution of each variable and run for 100,000 model trials. The median and 5–95 percentiles of the HEC or waterbody-specific chemical mass balances were subsequently computed from the Monte Carlo trial values.

3 Results and Discussion

Fourteen priority contaminants (HCB, OCS, p,p′-DDE, PCBs, PAHs, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn) were above detection limits in more than 60% of samples analyzed (detections across samples ranged from 80.1 to 99.5% of samples) and were selected for examination of temporal and spatial patterns at the HEC scale. Table 1 summarizes the HEC median and 5–95 percentile concentrations, as well as HEC-wide surficial sediment mass inventories, for each contaminant during early and late time periods.

Table 2 summarizes exceedances of sediment quality guidelines for individual contaminants except for OCS for which guidelines were not available. The proportion of sediment quality guidelines related to probable effect concentrations (PEC) was always less than 10% across HEC samples for the early year period

Table 1 Median and 5–95 percentile concentrations of selected contaminants in surficial sediments and mass inventory (*t*) of pollutants in the Huron-Erie Corridor

Chemical	Early period concentration (μg g^{-1} dry wt)	Late period concentration (μg g^{-1} dry wt)	Early period total mass (metric tonnes)	Late period total mass (metric tonnes)
HCB	0.0023 ($1.8e^{-4}$–$9.2e^{-3}$)	0.0006 $5.0e^{-5}$–$1.4e^{-2}$	1.53 0.66–4.30	0.17 0.08–0.49
OCS	0.0003 $1.0e^{-5}$–$9.3e^{-3}$	0.0004 $1.0e^{-5}$–$8.8e^{-3}$	0.11 0.05–0.26	0.15 0.06–0.50
p,p′-DDE	0.0006 $2.0e^{-5}$–$8.7e^{-3}$	0.0004 $5.0e^{-5}$–$5.6e^{-3}$	0.20 0.09–0.57	0.09 0.04–0.27
Sum PCB	0.014 $5.4e^{-4}$–$5.2e^{-1}$	0.014 $1.3e^{-3}$–$2.0e^{-1}$	2.89 1.35–8.64	2.71 1.47–5.80
Sum PAH	0.72 0.04–41.2	0.78 $3.1e^{-4}$–$1.7e^{1}$	171.2 71.2–478.8	172.9 80.1–434.9
As	2.67 0.10–30.73	3.17 1.13–11.94	470.2 302.6–822.0	584.3 326.4–1,123.8
Cd	0.59 0.15–3.04	0.67 0.10–2.95	62.22 41.89–94.09	112.8 66.9–223.7
Cr	113.81 5.14–58.27	15.34 6.58–48.00	2,114.7 1,541.8–2,926.6	2,597.5 1,828.5–3,904.3
Cu	18.01 3.59–72.98	11.00 1.91–49.06	2,606.3 1,787.9–3,959.8	1,486.7 932.7–2,573.5
Fe	1253.4 563–3446	1.03 0.34–3.17	187,138.9 $1.4e^{5}$–$2.6e^{5}$	167,364.1 $1.2e^{5}$–$2.4e^{5}$
Hg	0.19 0.02–1.15	0.13 0.01–0.69	47.09 23.80–101.63	22.76 12.25–49.95
Ni	14.51 5.46–42.74	10.70 3.95–36.60	2,044.0 1,495.6–2,999.2	1,493.1 985.9–2373.4
Pb	7.52 2.09–83.29	6.89 2.37–47.07	1,158.0 715.9–2,201.4	1,127.2 741.0–1,848.4
Zn	47.18 16.74–228.74	39.17 14.05–182.81	7,548.9 5,428.5–10,527.7	6,088.2 4,282.3–9,470.1

Table 2 Exceedance of consensus-based threshold effect concentration (TEC) and probable effect concentration (PEC) sediment quality guidelines in the Huron-Erie Corridor

Chemical	TEC value (μg/g dry wt)	PEC value (μg/g dry wt)	Early period TEC exceedance % (*n*)	Late period TEC exceedance % (*n*)	Early period PEC exceedance % (*n*)	Late period PEC exceedance % (*n*)
HCB	0.02	24	9.1 (34)	2.8 (7)	0 (0)	0 (0)
OCS	NA	NA	NA	NA	NA	NA
p,p′-DDE	0.00316	0.0313	15 (42)	8.2 (29)	0.4 (1)	1.1 (4)
Sum PCB	0.0598	0.676	19.5 (53)	17.9 (63)	2.9 (8.0)	1.4 (5)
Sum PAH	1.61	22.80	33.5 (91)	30.9 (109)	8.8 (24)	3.7 (13)
As	9.79	33.00	19.5 (53)	7.9 (28)	4.4 (12)	0 (0)
Cd	0.99	4.98	32.4 (88)	38.0 (134)	0.4 (1)	2.0 (7)
Cr	43.40	111.00	7.4 (20)	6.5 (23)	0.4 (1)	0.9 (3)
Cu	31.60	149.00	24.6 (67)	11.3 (40)	1.5 (4)	1.1 (4)
Fe	20,000*	40,000*	0 (0)	0 (0)	0 (0)	0 (0)
Hg	0.18	1.06	50.7 (138)	35.1 (124)	5.9 (16)	2.0 (7)
Ni	22.70	48.60	26.1 (71)	17 (60)	2.6 (7)	2.3 (8)
Pb	35.80	128.00	8.8 (24)	6.5 (23)	2.6 (7)	1.4 (5)
Zn	121.00	459.00	15.8 (43)	8.5 (30)	0.7 (2)	1.7 (6)

Sediment quality guidelines obtained from MacDonald et al. [20]

Sediment quality guidelines for HCB and Fe refer to lowest effect level (LEL) and severe effect level (SEL), respectively. They are derived from Ontario Ministry of Environment limits as described by Fletcher et al. [21]

% Exceedance represents the proportion of sample sites in the HEC exceeding the TEC or PEC concentration, respectively

n is the number of sample sites in the HEC exceeding the TEC or PEC concentration, respectively

*$p < 0.05$ for significance testing

(1999–2004) and less than 4% for the late year period (2008–2013). Nine of 14 chemicals had fewer PEC exceedances in the late period compared to the earlier period with the exception of p,p′-DDE, Cd, Cr, and Zn. The proportion of TEC exceedances was higher than PEC exceedances and ranged from 0 to 50.7% (total Hg) in the early period and from 0 to 38.0% (Cd) in the late period, respectively. Most chemicals also exhibited fewer TEC exceedances in the late year period with the exception of Cd. Mercury, Cd, and PAHs were among the top three contaminants with highest TEC exceedance frequencies in both early and late years. For the latter three chemicals, TEC exceedances were above 30%. Overall, the generally low prevalence of PEC exceedances but moderate level of TEC exceedances implies that sediments at the HEC scale have moderate to low contamination levels that could impact the most sensitive invertebrate species but have less likelihood of impacting tolerant benthic invertebrate species.

Table 3 Chemical associations with individual principle component axes

Dataset used in PCA	PCA axis	Eigenvalue (% variance)	Affiliated chemicals[a]
Huron-Erie Corridor Early and late periods	PCA1 PCA2 PCA3	6.61 (47.2%) 1.82 (13.00) 1.04 (7.4)	p,p′-DDE, **PCBs**, **PAHs**, Cd, **Cr**, **Cu**, Fe, **Ni**, **PB**, **Zn** HCB, OCS **As**
Huron-Erie Corridor Early period only	PCA1 PCA2 PCA3 PCA4	6.88 (49.1%) 1.95 (14.0%) 1.12 (8.0%) 0.96 (6.8%)	PCBs, **PAHs**, **Cd, Cr, Cu, Fe**, **Ni, Pb, Zn** **HCB**, OCS **p,p′-DDE** **As**
Huron-Erie Corridor Late period only	PCA1 PCA2 PCA3	6.81 (48.7%) 1.86 (13.3%) 1.34 (9.5%)	**p,p′-DDE, PCBs**, PAHs, **Cr, Cu, Ni, Pb, Zn** **HCB**, OCS **As**
St. Clair River only	PCA1 PCA2 PCA3 PCA4	5.3 (37.5) 2.8 (20.3) 1.3 (9.2) 1.1 (8.1)	As, **Cr, Cu, Fe, Ni, Pb, Zn** **HCB, OCS, PCBs,** Hg Cd **PAHs**
St. Clair Delta only	PCA1 PCA2	6.3 (44.6) 2.7 (19.1)	PCBs, **PAHs**, **Cu, Fe, Hg, Ni, Pb, Zn** **As, Cd,** Cr
Lake St. Clair only	PCA1 PCA2 PCA3 PCA4	6.5 (46.2) 2.1 (15.3) 1.5 (10.9) 1.2 (8.3)	p,p′-DDE, **PCBs**, Cr, **Cu**, Fe, **Ni, Pb, Zn** **As, Cd** PAHs OCS
Detroit River only	PCA1 PCA3	6.7 (47.7) 1.2 (8.3)	p,p′-DDE, **PCBs, PAHs**, Cd, **Cr, Cu, Hg, Ni, Pb, Zn** **As**

[a] Chemicals with loading coefficients greater than 0.6 were considered affiliated with a given axis Chemicals in bold have loading coefficients greater than 0.7 and are strongly associated with a given PCA axis

3.1 Inter-chemical Correlations and Data Reduction

PCAs were performed on the complete chemistry dataset as well as subsets of data to identify groups of contaminants with similar behavior across study periods. Table 3 presents eigenvalues, variance explained, and chemical associations on significant PCA axes (those with eigenvalues >1) for each PCA run. Consistency in contaminant grouping across PCA analyses indicates strong inter-chemical correlation patterns across scale implying common sources and/or environmental fate throughout the system. However, when there are deviations in groups of chemicals loading together across PCA analyses, this suggests scale effects of major pollutant patterns indicative of waterbody-specific differences in pollutant sources and loads.

For the full HEC PCA, the first three PCA axes explained 77% of the variance with all subsequent axes having eigenvalues less than 1 and no strongly affiliated chemicals loading onto lesser axes. PCA1 affiliated chemicals consisted of p,p′-DDE, PCBs, PAHs, Cd, Cr, Cu, Fe, Ni, PB, and Zn. The PCA2 was strongly affiliated with HCB and OCS, while the PCA3 was affiliated with As. The second and third PCA runs were restricted to corridor early or late period data. These analyses generated similar amounts of variance explained by the first three PCA axes as well as similar trends in chemical loadings. In both cases, PCBs, PAHs, and metals, Cr, Cu, Ni, Pb, and Zn, loaded onto PCA1 in common with the full dataset. PCA2 was also associated with HCB and OCS in each run (Table 3). However, there were differences in chemical loadings to PCA3 between early and late corridor datasets. PCA3 was affiliated with p,p′-DDE in the early period PCA, while As was associated with this axis in the late year PCA. Other differences in chemical loadings between the PCA analyses were a lack of affiliation of p,p′-DDE to axis 1 (early period PCA) and lack of Cd and Fe affiliation to axis 1 for the late period PCA. Thus, at the corridor scale, the organic contaminants (PCBs, PAHs) and selected metals (Cr, Cu, Ni, Pb, Zn) tended to exhibit similar patterns as one another and were the main drivers of spatial/temporal patterns at the corridor scale.

The next set of PCAs was completed on individual waterbodies inclusive of early and late year periods (Table 3). PCAs performed on individual waterbodies produced different sets of axes-chemical affiliations as compared to the HEC scale (Table 3). This suggests differences in waterbody-specific chemical loadings to each system and the nature of multi-pollutant sources. Some similarities were however evident. For St. Clair River, Delta, Lake St. Clair, and Detroit River, there was a common PCA1 association of metals that included Cu, Ni, Pb, and Zn across each PCA, indicative of similar sources or similar patterns of environmental deposition and fate for this group of contaminants. Other contaminants showed distinct differences between the systems. For example, in the St. Clair River, HCB, OCS, PCBs, and Hg grouped together on PCA2 indicating different sources of the organics with the PCA1-associated metals. In contrast, for the Detroit River, PCBs, PAHs, and p,p′-DDE were grouped together along with PCA1-affiliated metals. Given that the Detroit River PCA bore the strongest resemblance in its PCA1 chemical associations to the HEC PCA, this suggests that the Detroit River was the main driver of spatial/temporal patterns at the corridor scale, while HCB and OCS, characteristic of the St. Clair River, were the second most important pattern on a HEC-wide basis.

3.2 *Spatial and Temporal Trends at the Corridor Scale*

An ANOVA was performed on PCA scores for the first two PCA axes to test for differences in affiliated chemical concentrations present in the system between study periods and between waterbodies. Scores along PCA3 were not examined due to the inconsistent loadings of affiliated chemicals in the early and late period PCAs. There was a highly significant ($p < 0.01$; ANOVA) decrease in PCA1 scores from the early to late study periods for the corridor-wide data. However, the apparent temporal decreases were not consistent for all PCA1-affiliated chemicals. Median HEC-wide sediment PCB, PAH, and Cr concentrations were 0.4, 20.8, and 11.6% higher in the late period as compared to the early period, whereas Cu, Ni, Pb, and Zn exhibited declines in median concentrations between early and late periods of 38.7, 25.8, 8.7, and 16.5%, respectively (Table 4). There was also a significant ($p < 0.05$; ANOVA) decrease in PCA2 scores between the early and late study periods. In this case, median HCB concentrations decreased by 74.0%, whereas median OCS concentrations increased by a marginal 6.6%. Thus, while the ordinated data implies system-wide decline in overall sediment contamination, the strengths of such temporal patterns were less apparent than spatial patterns of pollutants across the waterbodies described below. Figure 2 presents box and whisker plots of PCA scores for the two major axes from each waterbody. Data were further separated into early and late time periods for data presentation purposes. PCA1-affiliated chemicals were highly significantly ($p < 0.01$; Tukey's HSD) elevated in the Detroit River compared to the other waterbodies in both time periods. PCA1 scores remained similar to one another for the remaining waterbodies with the exception that Lake St. Clair was significantly lower ($p < 0.05$; Tukey's HSD) than the St. Clair River and Delta in the late period (Fig. 2 top graphic).

PCA2-affiliated chemicals (HCB and OCS) exhibited a dilution pattern from St. Clair River and Delta through the rest of the corridor (Fig. 2 bottom graphic). This pattern was most evident in the early year period where there were significantly ($p < 0.05$; Tukey's HSD) higher scores generated for St. Clair River and Delta compared to Lake St. Clair and the Detroit River. However, it was also observed that significant decreases ($p < 0.05$; ANOVA) in PCA2 scores occurred for these two waterbodies such that the significant differences between waterbodies in PCA2 scores were no longer retained in the late period.

Figure 3 compares the frequency of exceedance of sediment quality guidelines at the PEC and TEC values for individual contaminants. For simplicity of presentation, exceedance frequencies are presented on the combined early and late periods. Contaminants were arranged in order of increasing exceedance frequency in the most contaminated waterbody (Detroit River). Iron was excluded because it did not exceed TEC or PEC at any sampling location. The pollutants Cd, PAHs, and Hg exhibited the highest frequency of >TEC concentrations for the Detroit River but also had elevated exceedances in other waterbodies (mainly Hg and Cd; Fig. 3 top graphic). TEC exceedances of Cd, PAHs, and Hg ranged from 45.5 to 58.6% of samples collected from the Detroit River, from 6.2 to 31.7% in the St. Clair River, 5.5 to 56.0% in the Delta, and 3.7 to 28.4% in Lake St. Clair. Apart from the Detroit River, sediment concentrations >TEC were generally less than 10% from a given waterbody for the remaining pollutants. For the Detroit River, all PCA1 compounds exceeded TEC at a frequency of 11% or higher. Figure 3 bottom graphic presents PEC exceedances by waterbody. The majority of PEC exceedances were also observed for the Detroit River but with a different rank order of pollutants. In this case, PCBs, Ni, and PAHs had concentrations >PEC in 4.5–12.4% of samples. Concentrations >PEC were generally less than 4% for the remaining PCA1 compounds in the Detroit River. There were no PEC exceedances in Lake St. Clair. PEC exceedances in the St. Clair River and Delta were limited to Hg (range 4.8–6%), HCB (1%), Pb (St. Clair only 0.7%), and PAHs (St. Clair River only

Table 4 Median concentrations (5–95 percentiles) of selected pollutants in the St. Clair River (SCR), St. Clair Delta (Delta), Lake St. Clair (LSC), and Detroit River

Chemical	SCR Early period	SCR Late period	Delta Early period	Delta Late period	LSC Early period	LSC Late period	DR Early period	DR Late period
HCB	0.0024 $5.0e^{-5}$–$1.6e^{-1}$	0.0005 $5e^{-5}$–$2.1e^{-2}$	0.006 $2.3e^{-4}$–$4.9e^{-2}$	0.003 $5.0e^{-5}$–$1.2e^{-2}$	0.0011 $4.5e^{-4}$–$1.3e^{-2}$	0.0003 $5.0e^{-5}$–$2.1e^{-3}$	0.0021 $2.4e^{-4}$–$3.8e^{-2}$	0.0006 $5.0e^{-5}$–$7.3e^{-3}$
OCS	0.00027 $1.0e^{-5}$–$5.1e^{-3}$	0.00031 $1.0e^{-5}$–$1.3e^{-2}$	0. $1.0e^{-5}$–$1.4e^{-2}$	0.00045 $4.9e^{-5}$–$0.9e^{-1}$	0.00009 $1.0e^{-5}$–$7.9e^{-4}$	0.00024 $1.0e^{-5}$–$3.6e^{-3}$	0.0030 $1.0e^{-5}$–$3.4e^{-3}$	0.00041 $4.4e^{-5}$–$4.4e^{-3}$
p,p′-DDE	0.00042 $2.0e^{-5}$–$2.4e^{-3}$	0.00030 $6.8e^{-5}$–$2.2e^{-3}$	0.00002 $2.0e^{-}5$–$1.3e^{-3}$	0.00033 $7.3e^{-5}$–$1.3e^{-3}$	0.0005 $4.8e^{-5}$–$2.7e^{-3}$	0.00018 $2.0e^{-5}$–$6.5e^{-4}$	0.0012 $2.0e^{-5}$–$1.3e^{-2}$	0.0012 $1.4e^{-4}$–$1.2e^{-2}$
PCBs	0.012 $1.8e^{-3}$–$3.5e^{-2}$	0.012 $1.6e^{-3}$–$9.0e^{-2}$	0.010 $6.1e^{-4}$–$3.0e^{-2}$	0.011 $1.6e^{-3}$–$3.7e^{-2}$	0.0058 $1.6e^{-3}$–$2.0e^{-2}$	0.0044 $1.3e^{-4}$–$2.1e^{-2}$	0.021 $2.5e^{-4}$–$6.7e^{-1}$	0.031 $4.0e^{-3}$–$4.7e^{-1}$
PAHs	0.44 0.01–2.41	0.94 0.11–6.42	0.39 0.04–1.82	0.46 0.05–1.25	0.13 $1.0e^{-4}$–$7.8e^{-1}$	0.27 $2.3e^{-4}$–$9.3e^{-1}$	1.63 0.10–69.06	2.64 0.09–31.42
As	1.57 0.10–4.26	3.95 1.83–9.30	2.02 0.1–3.74	3.50 1.91–14.47	1.70 1.25–2.96	2.49 1.17–9.65	4.48 1.02–38.56	3.18 0.10–7.88
Cd	0.43 0.26–0.71	0.40 0.10–1.16	0.40 0.20–0.72	1.50 0.21–2.90	0.24 0.05–0.41	0.35 0.10–1.49	1.05 0.19–3.30	1.32 0.37–5.17
Cr	7.56 4.37–12.60	12.65 6.50–48.00	11.22 4.11–26.18	22.22 7.00–38.54	9.64 6.87–18.05	11.91 5.98–25.20	18.83 8.90–70.12	24.39 8.58–84.25
Cu	5.51 0.79–18.03	11.31 4.39–24.50	14.96 2.20–32.45	7.00 1.15–13.49	13.66 6.90–24.05	5.88 0.30–14.30	26.63 8.12–100.12	19.79 4.24–108.87
Fe	768.5 $5.4e^{2}$–$1.7e^{4}$	1,013 $5.1e^{2}$–$2.8e^{3}$	955 $4.1e^{2}$–$2.2e^{3}$	0.57 0.29–1.03	983 $6.1e^{2}$–$1.5e^{3}$	868 $3.0e^{2}$–$1.6e^{4}$	1,673 $0.70e^{2}$–$4.24e^{4}$	1,796 $4.4e^{2}$–$3.54e^{3}$
Hg	0.05 0.02–1.23	0.04 0.01–0.78	0.29 0.04–1.18	0.20 0.03–0.71	0.10 0.02–0.91	0.083 0.01–0.40	0.18 0.014–0.81	0.17 0.03–0.66
Ni	7.33 3.95–16.24	9.82 4.38–36.32	12.75 4.39–27.00	7.05 3.41–13.59	8.99 5.33–17.67	6.82 2.41–13.98	19.67 8.14–47.46	18.34 6.39–51.28
Pb	3.7 1.88–9.03	6.38 2.87–19.49	8.99 5.34–17.67	4.51 2.43–7.40	3.85 2.47–12.89	4.60 1.67–10.24	14.32 3.07–122.86	13.86 3.14–89.89
Zn	32.06 16.95–66.19	39.95 17.37–73.03	14.31 3.07–122.86	30.09 11.64–41.55	33.90 17.31–55.25	28 9.98–45.81	68.05 20.28–368.77	69.08 17.04–418.86

Concentrations expressed in $\mu g\ g^{-1}$ dry weight

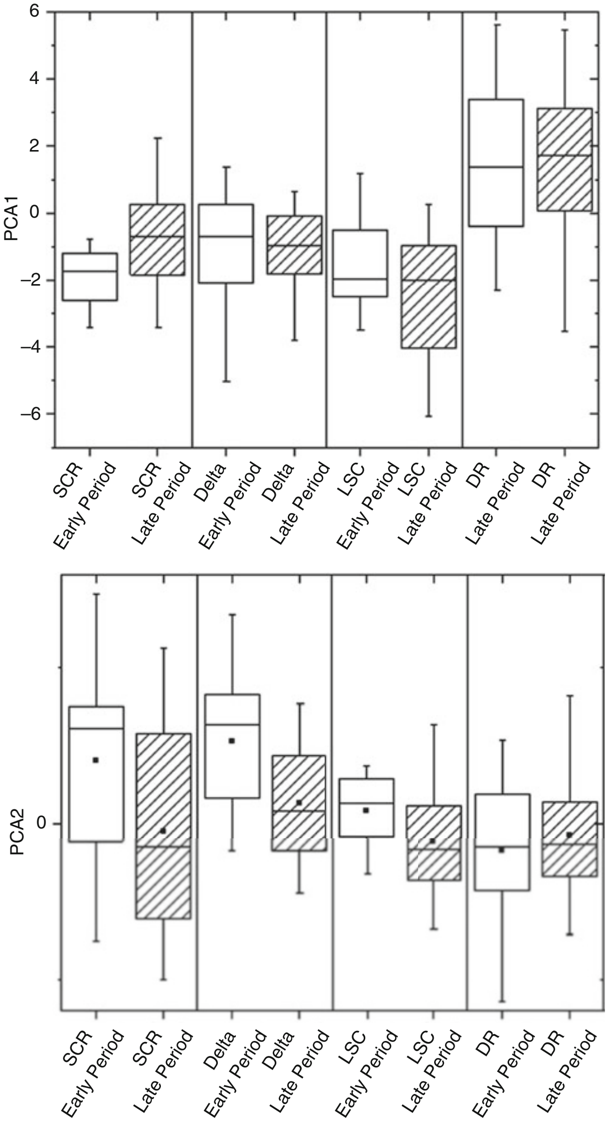

Fig. 2 Mean and distribution of PCA scores in individual segments of the Huron-Erie Corridor. Top graphic presents PCA1 scores, and bottom graphic presents PCA2 scores. Squares denote median, horizontal line inside box is the median, box edges are 25 and 75 percentiles, and whiskers are 5 and 95 percentiles. Hollow boxes are early period (1999–2004), hatched boxes are late year period (2008–2014) data. SCR, Delta, LSC, DR refer to St. Clair River, St. Clair Delta, Lake St. Clair, and Detroit River, respectively

0.7%). Hg and HCB were the only contaminants where PEC exceedances were higher in the St. Clair River and Delta compared to the Detroit River.

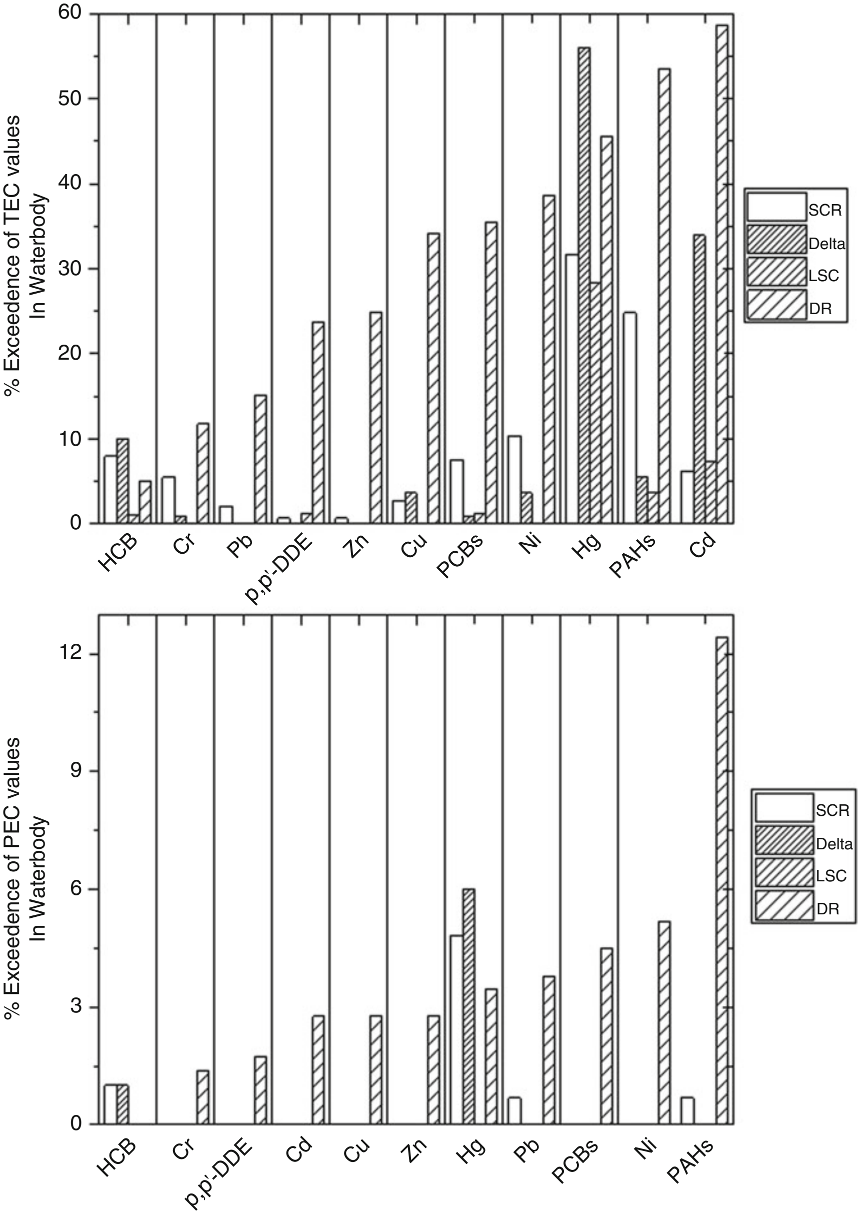

Fig. 3 Frequency of sediment concentrations exceeding threshold effect concentration (TEC; top graphic) or exceeding probable effect concentration (PEC; bottom graphic). SCR, Delta, LSC, DR are St. Clair River, St. Clair Delta, Lake St. Clair, and Detroit River, respectively

3.3 Spatial and Temporal Trends Within the AOCs

ANOVAs were performed on PCA scores from PCAs completed on individual waterbodies in order to test for spatial-temporal patterns at the waterbody scale. Emphasis was placed on the two AOCs (St. Clair River and Detroit River) because of the larger sampling intensity, greater heterogeneity of these systems, elevated contamination relative to the Delta and Lake, and their interest from the perspective of remedial action plans.

3.3.1 St. Clair River

Figure 4 presents box and whisker plots of PCA1 and PCA2 scores for the St. Clair River divided into four strata (Canadian upper and lower strata and US upper and lower strata) during early and late time points. Between study periods, there was a highly significant ($p < 0.01$; ANOVA) increase in PCA1 scores (affiliated chemicals: As, Cr, Cu, Fe, Ni, Pb, and Zn) but no difference in PCA2 scores (HCB, OCS, PCBs, and Hg). As with the HEC-wide temporal trend, the apparent increase in PCA1 scores for the St. Clair River was not consistent across PCA1-affiliated chemicals. Increased median sediment concentrations between early and late periods occurred for As, Cr, and Cu on the order of 44.4, 12.8, and 3.4%, respectively (Table 4). Conversely, Fe, Ni, Pb, and Zn were decreased in their median sediment concentrations by 3.2, 16.1, 8.5, and 14.9%, respectively. Thus, the temporal trend generated by the St. Clair PCA1 appears to be most strongly dictated by the increase in As concentrations between study periods.

There was no difference in PCA1 scores between river segments during the early period and the increase in PCA1 scores between study periods for the St. Clair River occurred across all strata of the AOC (Fig. 4 top graphic). Such a pattern is not consistent with an increase in localized loadings of As, or other PCA1 chemicals, occurring within the AOC itself. PCA1 pollutants did not undergo systemic increase in the Detroit River samples which were analyzed over similar time periods as St. Clair River samples although increases were apparent for As and Cr (but not Cu) in the Delta and Lake St. Clair. Olawoyin et al. [23] identified enriched Cr, Ni, Pb, and Zn in atmospheric particulate matter from air samples collected near Sarnia. The authors identified Cr, Pb, and Ni in atmospheric particles as being derived from both anthropogenic and crustal sources based on moderate enrichment factors but also concluded that atmospheric As, Cd, Cu, and Fe were primarily of crustal origin due to low enrichment factors. Although Pb concentrations showed marginal increase between early and late periods, the median St. Clair River Pb concentration (6.4 μg/g) during the late period was 4.5- to 5.4-fold lower than the river-wide means of Pb reported in surveys conducted during the mid-1980s [24, 25]. Other PCA1 chemicals (Cr, Cu, Ni, and Zn) were within a factor of 2 of their 1985 concentrations reported in [25].

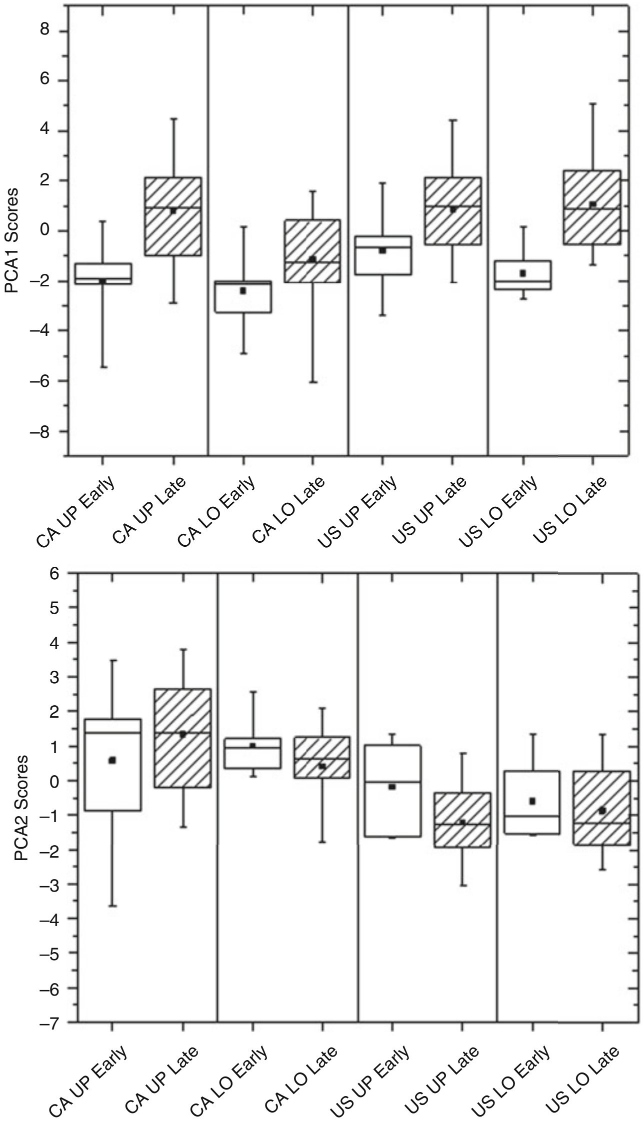

Fig. 4 Mean and distribution of PCA scores in individual segments of the St. Clair River. Top graphic presents PCA1 scores, and bottom graphic presents PCA2 scores. Squares denote median, horizontal line inside box is the median, box edges are 25 and 75 percentiles, and whiskers are 5 and 95 percentiles. Hollow boxes are early period (1999–2004); hatched boxes are late year period data (2008–2014). CA UP, CA LO, US UP, and US LO refer to Canadian upstream and downstream reaches and US upstream and downstream reaches, respectively

Venteris et al. [26] reported background As concentrations in Ohio soils in the range of 10–20 μg/g above the global soil background of 4.7 μg/g. The median As concentrations for the HEC (2.67–3.17 μg g^{-1}) and late period St. Clair River (3.95 μg g^{-1}) were in general concordance with the global soil background As concentrations and less than the reported Lake Huron background concentration of 4.7 μg/g [27]. The highest site-specific As concentration in the late period St. Clair River (18 μg g^{-1}) was consistent with the Lake St. Clair maximum (14.5 μg g^{-1}; [8]). One factor that may explain the apparent differences in PCA1 chemical concentrations in the St. Clair River between early and late periods is the difference in sampling resolution between the 2004 and 2014 survey years. The early year survey consisted of only 27 samples distributed throughout the St. Clair River, while the late year survey contained 118 samples. There were also a greater number of early year survey sites distributed closer to nearshore areas, while the 2014 survey incorporated more offshore and channel sites. Among the waterbodies tested, only Lake St. Clair and the St. Clair River had large differences in sampling resolution between survey periods.

Exceedance of sediment concentrations >PEC by PCA1 chemicals were rare in the St. Clair River. Pb exceeded PEC at only one station. Despite the previously noted increase in St. Clair River As concentrations with time, no stations were >PEC for As whereas concentrations while >TEC exceedances remained at 6% or less for all strata. Figure 5 top graphic presents exceedances of PCA1-affiliated chemicals against TEC values for the four St. Clair River strata. The greatest number of TEC exceedances occurred in lower US strata for Ni and Cr at 15.2% of samples. Nickel exhibited moderately high TEC exceedances >10% in upper Canadian and US strata. Given the small number of sediment concentrations >TEC and >PEC for PCA1 chemicals, these contaminants were not considered major hazards to sediment quality of the AOC.

PCA2-affiliated compounds in the St. Clair River included HCB, OCS, PCBs, and Hg that have been previously designated as priority chemicals in the AOC [2]. PCA2 scores for the St. Clair River are provided in Fig. 4 (bottom graphic). There were no significant differences in PCA2 scores by strata for the early year dataset, whereas highly significant differences ($p < 0.001$; ANOVA) in PCA2 scores between strata were present in the late period data. Overall spatial patterns were similar in the early and late period data (Fig. 4 bottom graphic) indicating that the failure to detect between strata differences in the early year data was most likely due to the lower sampling resolution of the early year survey. For the late period data, the upper and lower Canadian strata were significantly elevated in PCA2 scores relative to their US counterparts ($p < 0.001$; Tukey's HSD). There was no significant difference between the Canadian upstream and Canadian downstream strata ($p > 0.05$; Tukey's HSD) nor between the two US strata ($p > 0.8$; Tukey's HSD).

Previous studies on the St. Clair River have reported enhanced contamination of HCB, OCS, and Hg in Canadian waters of the AOC especially in nearshore areas near the Sarnia industrial complex and downstream of this region to Stag Island [2, 10, 14]. HCB and OCS were associated with the "blob," a chemical spill of perchloroethylene discovered in bottom sediments of the river in 1985 near the

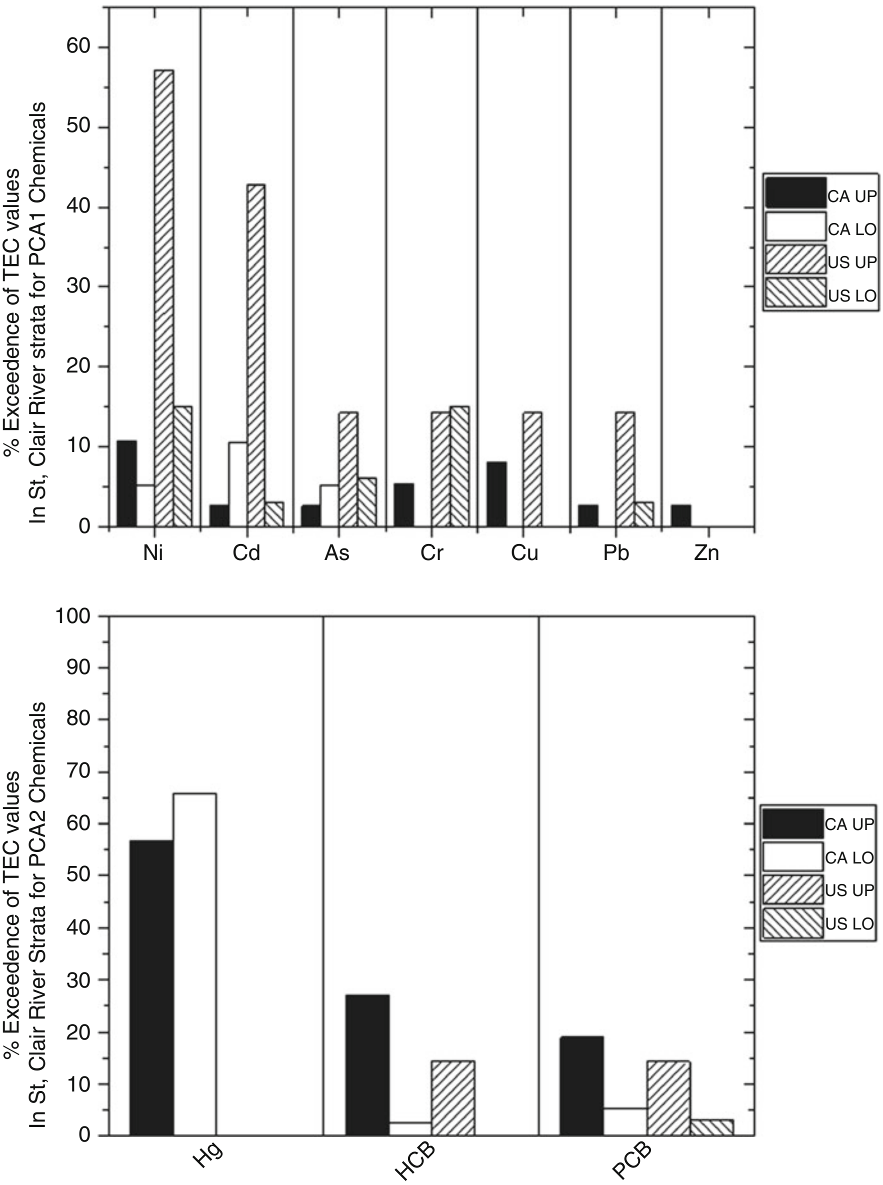

Fig. 5 Frequency of sediment concentrations exceeding threshold effect concentration (TEC) for PCA1-associated chemicals (top graphic) or PCA2-associated chemicals (bottom graphic) in the St. Clair River. CA UP, CA LO, US UP, US LO refer to Canadian upstream and downstream reaches and US upstream and downstream reaches of the St. Clair River, respectively

former Dow Chemical Company Canada facility and has since been subject to sediment cleanup efforts [2, 28, 29]. Pugsley et al. [10] reported mean OCS concentrations in Canadian waters of the St. Clair River of 14.8 ng/g dry weight and a maximum concentration of 79.5 ng/g near Stag Island. These concentrations were higher than the median river-wide values of 0.3 and 0.2 ng/g in the early and late period from the present research, but similar to the mean upper Canadian OCS concentration observed during the late period of 9.8 ng/g dry weight. The highest OCS value of 100 ng/g from the present late period survey, located in Canadian waters near the old Dow Canada facility, was similar to the reported high of Pugsley et al. [10]. Richman and Milani [2] reported OCS at its highest concentration of 1,400 ng/g near Stag Island. Similarly, HCB in contaminated zones of St. Clair River during 2006–2008 ranged from not detected to 400 ng/g with the median concentration of 27 ng/g [2]. The same station with high OCS values from the present research also contained HCB at 437 ng/g comparable to the maximum reported in [2], although the former high sample location was described to occur at the downstream end of Stag Island while the present high finding was located near the former Dow Canada facility. There were six additional stations in the upper Canadian St. Clair River segment which had HCB concentrations exceeding the Ontario 20 ng/g TEC value. The median HCB concentration in the upper Canadian strata from the present research was 3.2 ng/g or 8.4 times lower than Richman and Milani's [2] median estimate. However, these differences reflect the different sampling designs between studies. Richman and Milani [2] focused their sampling efforts in previously designated contaminated zones of the AOC in order to provide supporting data for future sediment mitigation efforts, whereas the present survey considered the AOC as a whole in its sampling.

Mercury release to the St. Clair River has been ascribed to occur largely from a chlor-alkali plant operated at the former Dow Canada site. Murdoch and Hill [14] reported total Hg concentrations as high as 16 μg/g in the St. Clair River during 1986 with elevated concentrations in the nearshore areas near Sarnia and downstream of the city. Richman and Milani [2] reported even higher surficial sediment total Hg concentrations in Canadian nearshore areas of the St. Clair River consistent with the previously designated contaminated zones. Their highest recorded total Hg concentration was 41 μg/g and greatly exceeded the maximum value of 2.94 μg/g observed presently. Richman and Milani [2] also reported that there was little change in surficial sediment Hg concentrations in the contaminated zones of the AOC between 1990–2001 and 2006–2008, although data from sediment cores implied decreases from early period maxima. The above spatial and lack of distinct temporal patterns for total Hg in St. Clair River sediments are consistent with the current observations.

Exceedance of PEC values for PCA2 chemicals in the St. Clair River was observed for Hg at seven stations in the upper Canadian waters. Figure 5 bottom graphic presents exceedance of TEC values for PCA2 chemicals. Of the remaining PCA2 chemicals, Hg had the highest frequency of TEC exceedances followed by HCB and PCBs. All three chemicals had higher numbers of TEC exceedances in Canadian strata. TEC exceedances for Hg occurred exclusively in Canadian strata and ranged from 56.8 to 65.8% of samples collected. TEC exceedances of HCB and

PCBs were distributed mainly in the upper Canadian strata, while Hg shows a more even distribution throughout the Canadian portion of the AOC and into Lake St. Clair.

Table 5 presents chemical mass balances in surficial sediments and changes in mass inventories between early and late periods on a waterbody-specific basis. Statistical differences in mass inventories are similar to changes in concentration data described above. For source identification purposes, the % mass inventories for each contaminant were contrasted against % surface area associated with a given areal segment. Segments where the % chemical mass exceeded the surface area of the segment by fourfold or more-fold were flagged as potential source regions and/or contaminant deposits. For the early time period, source regions/deposits were identified for HCB and OCS in the St. Clair River and St. Clair Delta (OCS for the Delta only). Similar patterns occurred for HCB and OCS in the late period, but no system-wide source areas were apparent for other contaminants in the late period. HCB was the most enriched in the upper St. Clair River Canadian strata (60- and 16-fold higher % mass relative to % area of the corridor segment in early and late year periods, respectively). Similarly, the OCS inventory was 17- and 8-fold higher compared to surface area in the upper Canadian St. Clair River and Canadian St. Clair Delta during the early period dropping to 8-fold and <2-fold in the late period. Hg was enriched by 6-fold in the Canadian St. Clair River during the early period, and this fell to 3.4-fold enrichment in the late period. Thus, both the concentration trends and mass inventories point to major contaminant deposition zones, particularly for PCA2 chemicals in the upper Canadian waters of the St. Clair River. While the St. Clair River has reportedly undergone significant declines in sediment contamination between the 1970s and 1990s [2, 4], evidence for continued increases in sediment quality post the 2000s has been limited. Given the lack of temporal change in PCA2 chemicals observed for the St. Clair River over the 2004–2014 study period, as well as within designated contaminated zones of the river [2], it is anticipated that planned future sediment cleanup efforts designated for the upper Canadian segment will generate additional benefits to reduce risks of PCA2 chemicals in this AOC.

3.3.2 Detroit River

Similar to the St. Clair River, the Detroit River was divided into four strata consisting of upper and lower Canadian and US strata with Fig. 6 presenting box and whisker plots of PCA1 and PCA2 scores. There were no significant differences in PCA scores throughout the Detroit River between the two study periods. The PCA1-affiliated compounds in the Detroit River included p,p′-DDE, PCBs, PAHs, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. PCA1 scores demonstrated highly significant differences between some strata in the early year dataset. For both upper and lower reaches, US PCA1 scores were significantly elevated compared to their Canadian counterparts ($p < 0.001$; ANVOA; both contrasts). There were also upstream/downstream differences in each jurisdiction such that elevated PCA1 scores were present in the lower reach as

Table 5 Median surficial sediment mass balance (5–95 percentiles) of selected pollutants in the St. Clair River (SCR), St. Clair Delta (Delta), Lake St. Clair (LSC), and Detroit River

Chemical	SCR Early period (*t*)	SCR Late period (*t*)	Delta Early period (*t*)	Delta Late period (*t*)	LSC Early period (*t*)	LSC Late period (*t*)	DR Early period (*t*)	DR Late period (*t*)
HCB	0.42 0.09–2.66	0.013 0.003–0.098	0.16 0.04–0.71	0.05 0.017–0.137	0.34 0.10–1.25	0.010 0.003–0.098	0.17 0.03–1.45	0.018 0.004–0.096
OCS	0.011 0.003–0.061	0.013 0.004–0.046	0.050 0.014–0.169	0.030 0.006–0.130	0.020 0.006–0.067	0.060 0.015–0.346	0.010 0.003–0.040	0.012 0.002–0.083
p,p′-DDE	0.004 0.002–0.008	0.0025 0.0013–0.0055	0.010 0.003–0.023	0.010 0.003–0.020	0.130 0.042–0.461	0.030 0.012–0.074	0.040 0.013–0.174	0.033 0.007–0.205
PCBs	0.098 0.054–0.207	0.100 0.042–0.292	0.19 0.08–0.42	0.19 0.05–0.65	0.94 0.31–4.50	0.89 0.37–2.61	1.27 0.42–5.48	0.85 0.21–3.64
PAHs	5.63 2.18–20.17	6.85 2.97–22.22	7.74 2.66–28.28	4.93 1.85–13.29	27.65 7.12–138.53	45.15 13.15–140.30	111.5 33.9–390.2	65.15 16.8–281.1
As	11.71 6.44–22.86	20.70 13.51–35.99	29.71 14.21–66.54	97.7 48.5–221.0	251.8 145.5–517.3	399.14 167.98–929.05	144.7 65.1–408.3	37.89 19.36–70.82
Cd	3.23 2.36–4.91	2.28 1.46–4.04	7.72 4.99–12.59	22.62 12.96–39.37	29.09 14.99–55.44	60.04 24.34–165.96	19.29 10.10–40.31	16.71 7.00–44.40
Cr	54.28 38.89–77.12	77.03 48.55–126.18	187.7 100.1–372.0	342.4 218.4–538.2	1,437.1 942.9–2,202.7	1,747.9 1,064.9–2,911.1	370.9 220.2–720.7	293.5 135.4–847.0
Cu	49.62 25.36–103.46	63.53 41.39–98.45	255.1 133.9–502.4	130.6 79.2–245.8	1,892.2 1,141.8–3,185.8	847.3 395.7–1,768.3	307.2 134.2–890.6	247.5 98.4–685.3
Fe	6,403.6 $4.2e^3$–$1.3e^4$	5,934.2 4,108.4–8,456.9	17,095.5 $1.1e^4$–$3.1e^{-4}$	12,640.8 $7.9e^3$–$2.1e^4$	130,199.8 $8.9e^4$–$2.1e^5$	119,037.4 $7.2e^4$–$1.9e^5$	27,338.5 $1.7e^4$–$4.8e^4$	20.022.3 $1.0e^4$–$4.6e^4$
Hg	2.05 0.83–6.64	0.84 0.41–2.23	5.96 2.22–16.45	3.27 1.42–8.44	32.25 11.31–87.34	13.89 5.27–39.23	3.97 1.75–11.16	2.34 0.86–7.23
Ni	57.61 38.44–90.60	59.72 36.78–99.15	215.4 116.5–377.7	139.2 84.5–237.3	1,365.3 863.0–2,292.9	962.6 530.5–1,803.1	350.2 221.9–581.4	222.5 110.9–499.5
Pb	32.91 22.04–59.31	38.46 23.59–84.81	91.1 51.2–170.5	86.0 56.2–132.3	679.2 344.6–1,625.6	643.8 327.9–1,173.0	289.1 133.4–810.0	184.9 81.5–557.6
Zn	245.2 175.1–375.1	206.0 150.4–295.3	770.0 449.6–1,265.6	549.1 383.3–783.6	4,797.8 3,124.6–7,355.2	3,734.8 2,278.4–6,202.1	1,439.5 7,32.5–3,503.7	1,015.7 378.9–3,310.0

All concentrations expressed in $\mu g\ g^{-1}$ dry weight

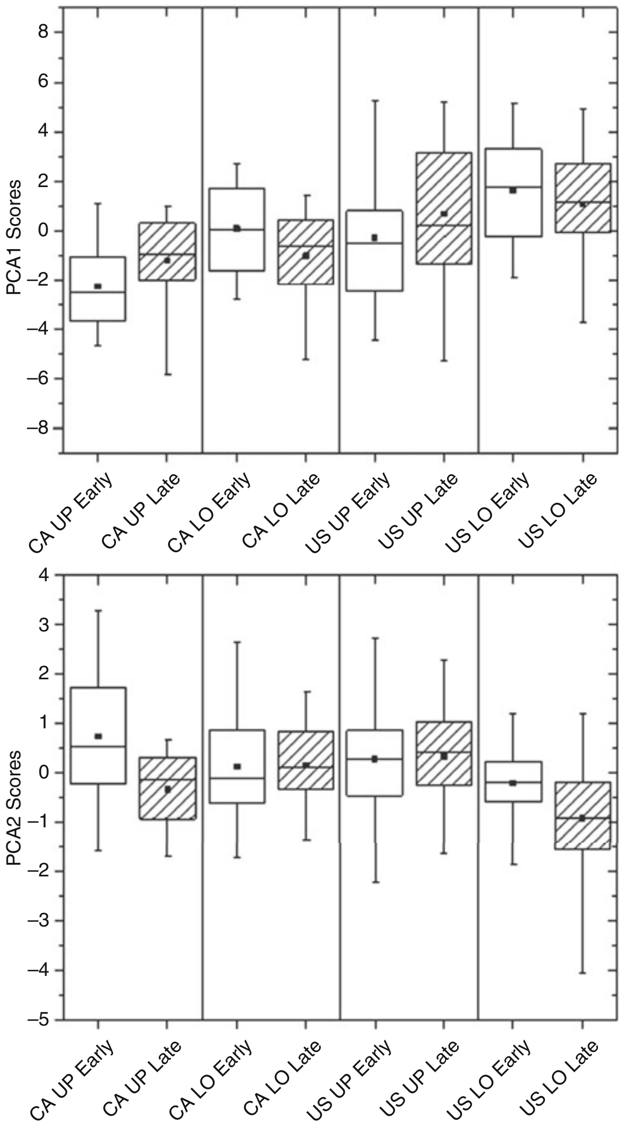

Fig. 6 Mean and distribution of PCA scores in individual segments of the Detroit River. Top graphic presents PCA1 scores, and bottom graphic presents PCA2 scores. Squares denote median, horizontal line inside box is the median, box edges are 25 and 75 percentiles, and whiskers are 5 and 95 percentiles. Hollow boxes are early period; hatched boxes are late year period data. CA UP, CA LO, US UP, and US LO refer to Canadian upstream and downstream reaches and US upstream and downstream reaches of the Detroit River, respectively

compared to the upper reach of a given jurisdiction. A somewhat different pattern occurred in the late period data. In this case the US and Canadian strata differences were maintained for the upper and lower reaches. However, the within-country differences between upper and lower strata were no longer evident.

Figure 7 presents exceedance frequencies of TEC and PEC values for PCA1-associated chemicals. Pollutants are ordered from lowest to highest frequency of exceedance present in the lower Detroit River. Sediment concentrations >TEC were most prominent for PCBs, Cd, and PAHs where the lower US strata exhibited >TEC concentrations ranging from 73.9 (PCBs) to 83.7% (PAHs) of samples compared to 39.7 (PCBs) to 54.0% (Cd and PAHs) in the upper US strata. For the Canadian strata, the highest frequency of concentrations >TEC for PCA1 compounds was observed for Cd (43.0%), Hg (47.0%), and Ni (43.4%). However, values >PEC for PCA1 chemicals were mostly restricted to US strata. The highest frequency of >PEC concentrations occurred for PAHs in the upper US strata (28.6%) followed by the lower US strata (19.6%). All other >PEC prevalence for PCA1 compounds were less than 10% except for Ni at 10.9% in the lower US strata.

Median concentrations of PCA1 chemicals in the Detroit River were compared to past literature reports. Murdoch [30] reported mean Detroit River values of Cu, Zn, Ni, and Pb based on 20 samples collected from outfalls and industrial areas of the system from the 1980s. Copper remained stable in the system with the 1980s mean reported at 36 μg/g (range 1–52 μg/g) compared to early and late year period median river concentrations (20–27 μg/g and range of 4–109 ng/g across survey periods). However, Zn and Pb demonstrated considerably lower contamination in the present study compared to river-wide means reported for the 1980s with 8.8- and 4.9-fold decreases in Pb and Zn values from the 1980s to present. Similar results were obtained when data were compared to Nichols et al. [25] Detroit River trace element concentrations collected in 1985. In this case stable long-term river-wide concentrations were noted for Cd, Cr, Cu, and Ni which were within a factor of 2–3 between 1985 and 2014. In contrast, Hg, Zn, and Pb decreased by 8.9-, 4.7-, and 3.9-fold over the same time period. Total PAHs reported by Furlong et al. [31] from samples collected in US downstream sections of the Detroit River in 1986 had a median concentration of 22 μg/g dry weight (range 0.350–130 μg/g) that was just over double the median downstream US PAH concentration from the combined early and late period (9.44 μg/g dry weight; range 0.03–82.02 μg/g). A larger improvement was observed for total PCBs in the lower US segment which had a 1986 median concentration of 0.62 μg/g (range ND to 14.00 μg/g; [31]) compared to the present US downstream survey median of 0.11 (range <0.01 to 1.43 μg/g). Overall, the spatial patterns of the contamination of PCA1 chemicals in the Detroit River remain consistent with past observations [4, 6, 7, 9, 16]. While significant decreases in priority pollutants accompanied specific areas of cleanup activities in the system [6, 32, 33] and long-term improvements for some contaminants such as Hg, Zn, Pb, and PCBs appear to have occurred in US segments of the river, evidence of further declines in priority pollutants after the 2000s remains limited.

Only As had affiliation with PCA2 scores for the Detroit River. There was a highly significant decrease ($p < 0.01$) in PCA2 scores between the two study

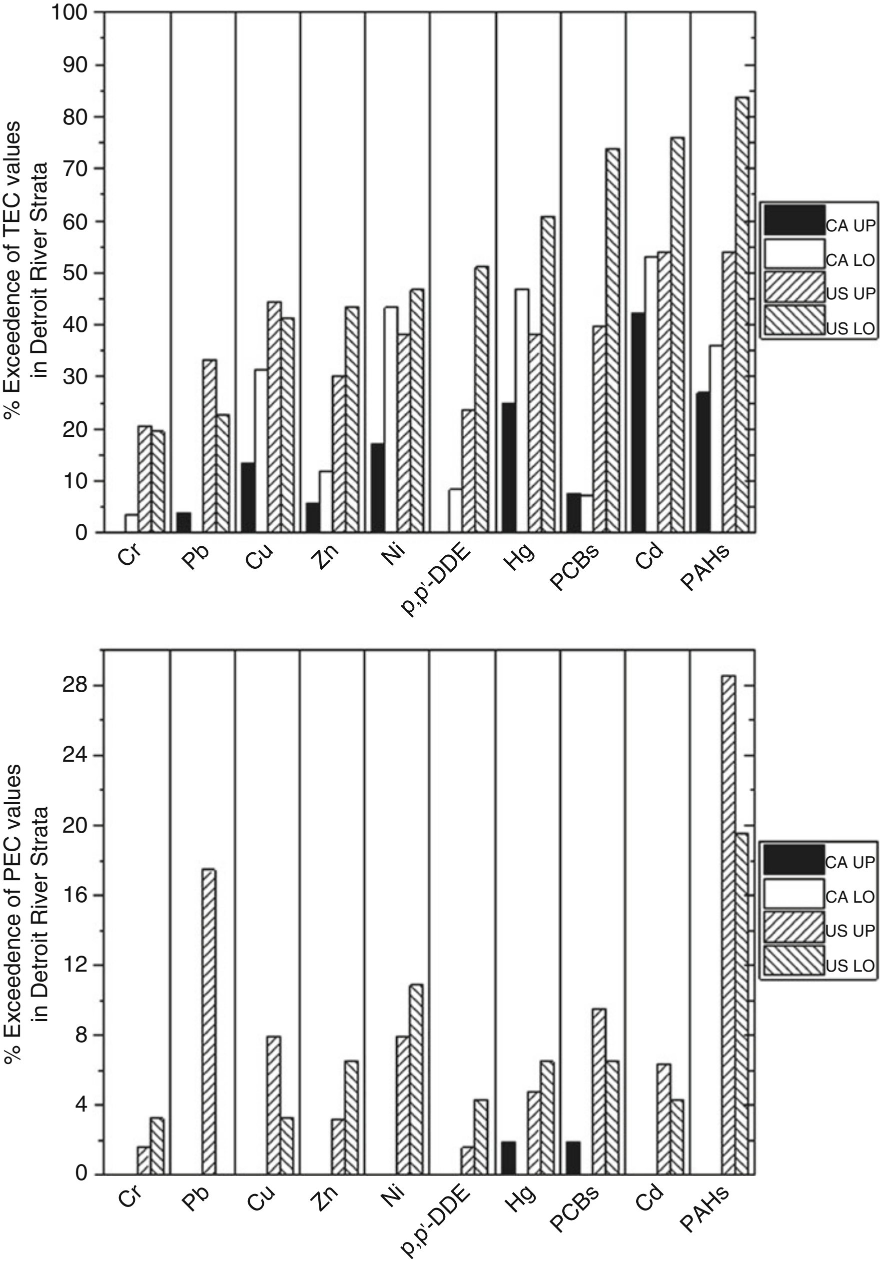

Fig. 7 Frequency of sediment concentrations exceeding threshold effect concentration (TEC) for PCA1-associated chemicals (top graphic) or sediment concentrations exceeding probable effect concentrations (PEC; bottom graphic) in the Detroit River. CA UP, CA LO, US UP, US LO refer to Canadian upstream and downstream reaches and US upstream and downstream reaches of the Detroit River, respectively

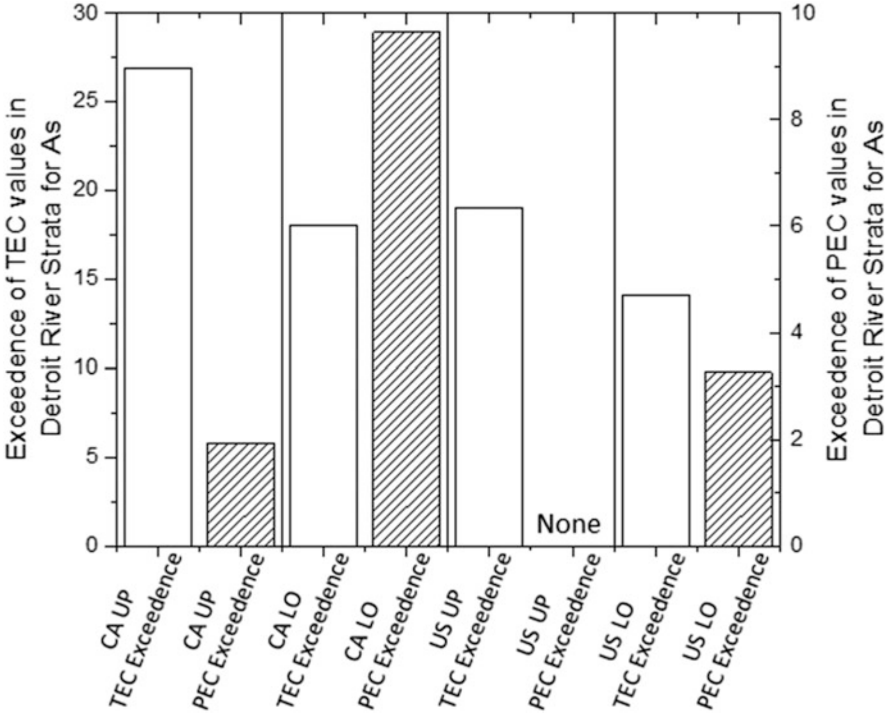

Fig. 8 Frequency of sediment arsenic (As) concentrations exceeding threshold effect concentration (TEC; left axis) or exceeding probable effect concentrations (PEC; right access). CA UP, CA LO, US UP, US LO refer to Canadian upstream and downstream reaches and US upstream and downstream reaches of the Detroit River, respectively

periods, the opposite of the pattern noted for As in St. Clair River. The decrease was mostly evident in the upper Canadian and lower US strata (Fig. 6 bottom graphic). For the early period, pairwise comparisons indicated a significant difference ($p < 0.05$; Tukey's HSD) between the upper and lower Canadian PCA scores but no other between-strata differences. For the late period, significantly lower scores ($p < 0.001$; Tukey's HSD) occurred in the lower US strata as compared to the upper US and lower Canadian strata. Figure 8 presents exceedance frequencies of TEC and PEC values for As in each strata of the Detroit River. Exceedance of TEC values occurred to the greatest extent in upper Canadian waters (26.9%) followed by equivalent exceedances in the Canadian lower and US upper reaches (18.1 and 19.4%) and lowest exceedances in the lower US reach (14.1%). Concentrations >PEC were highest in the Canadian lower reach approaching 10% but were less than 3% in the remaining reaches. The median late period As concentration in the Detroit River was 3.18 μg/g and similar in magnitude to the median concentration described for the St. Clair River and background As concentration for Lake Erie (3.7 μg/g; [34]). Despite the observed exceedances of SQGs, the As concentrations observed throughout the HEC remain consistent with global soil mean for this element.

The reason for the distinct contamination pattern for this pollutant remains unknown and, as with St. Clair River, implies a different source of potentially geochemical origin unconnected to nearshore point sources.

Table 5 presents chemical mass balances in surficial sediments and changes in mass inventories between early and late periods for the Detroit River. Using the same criteria as the St. Clair River, river segments where the % mass exceeded the % area by more than fourfold were flagged as potential source and/or deposition areas of contaminants. The Detroit River was identified as a source/deposition region for PCBs, PAHs, As, and Cd. HCB was also enriched by sixfold in the lower US segment of the Detroit River early period but did not exceed the fourfold criteria in the late period. For PCBs, mass/area enrichment was 12- and 9-fold higher and 4- and 11-fold higher in the US Detroit River upper and lower segments during early and late time periods, respectively. PAHs showed a similar pattern with mass/area enrichment of 13- and 11-fold and 9- and 15-fold enrichment in the early and late US upper and lower Detroit River segments. For As, enrichment ratios of 5 were evident in Canadian waters of the Detroit River in the early period, but no enrichment was apparent in the later period. Cadmium showed a fivefold enrichment in the lower US Detroit River for the early period, but this fell to a threefold enrichment in the late period. Lead was enriched by six- and fourfold in the upper and lower US Detroit River segments in the early period and was nine- and fourfold enriched in the late period. Zn was also enriched in the upper and lower US Detroit River (fivefold in both cases) in the early period but was only above fourfold enrichment for the lower US Detroit River in the late period.

4 Conclusions

The present study contrasted sediment contamination and surficial sediment mass inventories of priority pollutants between early (1999–2004) and late year (2008–2014) study periods in the Huron-Erie Corridor (HEC). By adopting a stratified random sampling design across individual surveys, we were able to provide less biased examination of changes in sediment pollutant inventories over time and across different spatial scales. At the HEC scale, spatial patterns of sediment contamination dominated over temporal trends. The strongest spatial pattern in the HEC was observed for the group of contaminants represented by PCBs PAHs, Cr, Cu, Ni, Pb, and Zn which were enriched in sediments from US waters of the Detroit River relative to concentrations present in the other waterbodies. The organic contaminants represented by HCB and OCS were the second strongest spatial pattern present in the HEC showing enrichment in the upper Canadian segment of the St. Clair River consistent with known legacy contamination from the Sarnia industrial complex. From a hazard perspective, probable effect concentrations (PEC) were exceeded to the greatest extent in the US sections of the Detroit River for the widest diversity of pollutants including PAHs, Ni, PCBs, Pb, Hg, Zn, Cu, Cd, p, p′-DDE, and Cr. In the St. Clair River, exceedance of PEC values was limited to

HCB, Pb, PAHs, and Hg. The majority of PEC exceedances in the St. Clair River occurred for Hg in the upper Canadian segment consistent with past legacy sources. Hg and HCB were the only pollutants with higher frequencies of PEC exceedances in the St. Clair River as compared to the Detroit River. Mass inventories and comparison of mass/area ratios within individual waterbodies and waterbody segments reinforced statistical patterns detected for surface sediment contaminant concentrations and provide an overall contamination ranking of Detroit River $>$ St. Clair River $=$ St. Clair Delta $<$ Lake St. Clair.

Spatial patterns for some contaminants such as Hg were lost within multivariate analyses owing to inconsistency between pollutant correlations across systems. For example, Hg failed to load to a PCA axis in the HEC-wide dataset despite its strong association with organic chemical pollutants (HCB, OCS, and PCBs) in the St. Clair River, along with strong affiliation to PCBs and PAHs in the Detroit River. The differences in multi-pollutant associations between systems reflect the different industrial sources and pollutant use patterns in the Sarnia industrial and Detroit industrial complexes. The upper Canadian segment of the St. Clair River appears to impact all downstream Canadian segments for Hg, HCB, and OCS generating a classic dilution from source gradient of sediment contamination. However, US sources of Hg, PCBs, PAHs, and several metals entering the Detroit River obscure the source-dilution pattern when applied to the Detroit River AOC as a whole.

Temporal patterns differed across the waterbodies. For the St. Clair River, there was an apparent increase in As, Cr, and Cu between the study periods. However, these trends were ascribed to artifacts associated with changes in sampling resolution between early and late period surveys, with the latter incorporating a threefold higher sampling resolution that included more offshore and channel stations as compared to early period surveys. Given the high degree of spatial heterogeneity of sediment contamination in both AOCs, future surveys of sediment quality should include no less than 100 sampling stations in order to adequately describe regional patterns or to examine temporal changes. By contrast, As declined in the Detroit River between the two time periods. Exceedance of PEC values for As did not occur in the St. Clair River but approached 10% in lower Canadian waters of the Detroit River. Obvious sources for As in the AOCs were not apparent, spatial patterns of this contaminant remained distinctly different from other trace elements linked to industrial sources, and concentrations were generally consistent with the global soil background value as well as estimated background As levels for Lakes Huron and Erie.

There was some evidence for long-term improvement of certain pollutants in the AOCs. In both the St. Clair and Detroit Rivers, Pb showed improvement in mean AOC concentrations from surveys conducted in the 1980s. There was also some evidence for long-term improvement of Hg, Zn, and PCBs in the lower US Detroit River between the 1980s and present. In addition, the number of PEC exceedances was observed to decline for many priority contaminants between the early and late study periods. However, changes in sediment contamination between early and late periods for OCS, HCB, or Hg were not evident between 2004 and 2014. Similarly, PCA1 chemicals (p,p′-DDE PCBs, PAHs, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in the Detroit River, also linked to poor sediment quality in the AOC, showed little evidence for change during the 2000s. Additional sediment mitigation efforts are being planned and anticipated to occur in Canadian upstream sections of the St. Clair River as well as in large sections of US nearshore waters of the Detroit River. The data from the present work provides support for these planned sediment cleanup activities and can serve as a baseline to evaluate system-wide improvements in pollutant concentrations, hazards, and mass inventories in the future.

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A Review of Heavy Metals Contamination Within the Laurentian Great Lakes

Ewa Szalinska

Contents

Abstract Heavy metals are ubiquitous in the Great Lakes basin at a wide range of concentrations. Their historical sources are associated with geological settings of the area, while contemporary ones are attributed to anthropogenic activities of the watershed's inhabitants. Four heavy metals in particular can be credited with the development of this area: copper, iron, lead, and mercury. Copper has been mined and processed in the Lake Superior basin for almost 10,000 years, while the iron industry history impacts are relatively new, dating back to the nineteenth century. It was iron however, which first prompted widespread development of the region, due to its high demand and extensive use. Also, lead and mercury can be credited as elements marking critical moments in local economic progress: lead, as an exponent of the auto-moto industry, and mercury as a side pollutant of coal burning and as a determinant of the chlor-alkali industry. The following description of the Great Lakes status in relation to metals has been drawn based mostly on sediment contamination, since this compartment of the environment is considered

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an “archive” for most of the aquatic pollutants. A review of metal loadings in the Great Lakes shows a fascinating history of the civilizational progress and efforts and also scientific accomplishments in metal research. Temporal patterns of metal concentrations showed the highest values around the 1950s, followed by a generally decreasing trend attributed to notable achievements in emission reduction and remediation efforts. Although such a trend is a most desirable attainment and conclusion, still much remains to be considered in this field, especially in light of potential future climatic changes.

Keywords Contamination level, Cycling, Monitoring, Sources, Spatial-temporal changes

1 Historical and Contemporary Sources

The Great Lakes basin has a long and complex geologic history which affects metal legacy and distribution of contemporary contaminated areas. Briefly, the bedrock geology of this basin consists of two substantially different rock formations overlain by unconsolidated glacial deposits. Bedrock of the northern part is composed of Precambrian metamorphosed igneous and sedimentary rocks, while Phanerozoic sedimentary remnants of the ancient seas fill out the southern part of the basin (Fig. 1). Within the Precambrian rocks, there is a notable occurrence of minerals, including those associated with volcanogenic massive sulfide and iron deposits, gold and platinum group metals (PGMs), copper, nickel, and others. The Phanerozoic formations bear mostly sandstone, shale, limestone, dolostone, and salt deposits, with addition of some hydrothermally deposited minerals [1].

Indigenous metal mining activity dates back to the period between 8,000 and 5,000 years BP when an intensive native copper industry was maintained by the inhabitants of the Lake Superior area (Keweenaw Peninsula and Isle Royale). High interest in this metal had shaped societies and traditions associated with the Old Copper Complex and left a lasting environmental legacy preserved within the natural geological records [2, 3]. The arrival of European settlers approx. 420 years BP fueled a native copper demand, and resulted later in the first major mining rush of North America, in Michigan’s Keweenaw Peninsula (mid-1840s). The same period brought also iron ore mining development, originally at Michigan’s Upper Peninsula, followed by widespread iron mines in all parts of the Lake Superior iron district. After iron, gold fever in Minnesota, Ontario, and Michigan’s Upper Peninsula further fast-tracked evolution of the Great Lakes region [4].

During the 1860s, the Civil War increased the need for Lake Superior iron, and intense mining of high-grade ores (50–70% of iron) lasted until the 1930s. Moreover it also rapidly accelerated development of shipping and railroad transport services, since the excavation areas were distant from the markets. Extensive extraction

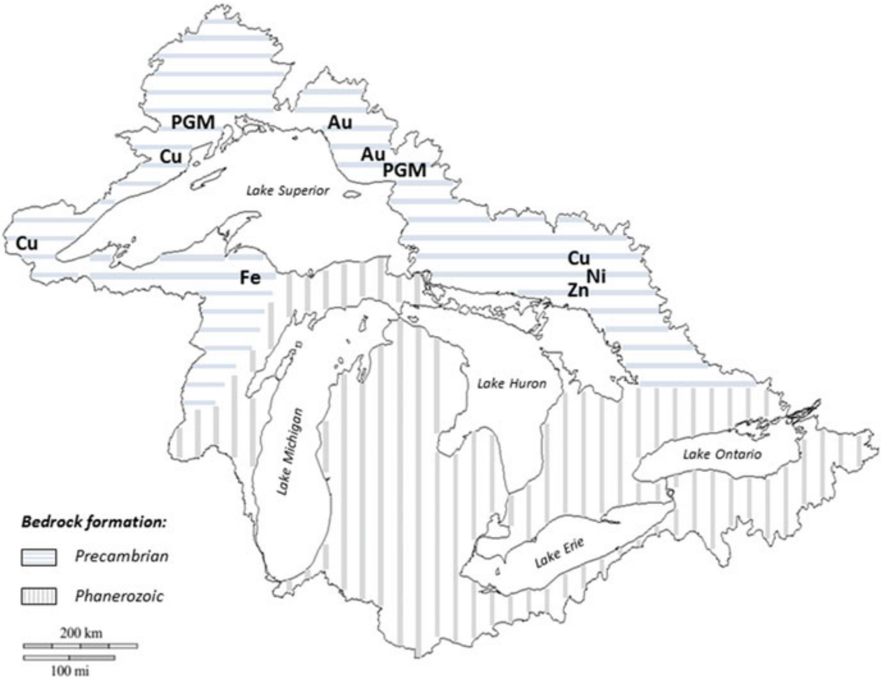

Fig. 1 Approximate range of bedrock formations and metal deposits in the Great Lakes basin (Au, gold; Cu, copper; Fe, iron; Ni, nickel; Zn, zinc; PGM, platinum group metals). Modified after [1, 6, 7]

of low-grade ores (taconite), which required expensive beneficiation (i.e., crushing, screening, grinding, and separation), started around the 1950s when higher-grade hematite ores became depleted. The opening of the first effective and profitable taconite processing facility in 1955 soon resulted in tailing pollution of Lake Superior [5]. Contemporary mining activities still continue to be a prosperous sector of the Great Lakes area industry, with 29 precious (gold and PGMs) and base (nickel, copper, zinc) metal mines in Ontario, with a production worth CAD$ 7.4 billion in 2015 [6]. As for the metal production in Michigan state, only two iron and nickel-copper mines are currently under operation [7].

Booming ore mining and metal processing in the twentieth century prompted a massive industrial expansion of the Great Lakes area resulting in the automobile industry becoming the largest sector of the American economy. Application of assembly techniques, mastered by Henry Ford and other auto pioneers, led to a clustering of all processes within a single area and was concentrated in Southeast Michigan. The Ford River Rouge Complex, established in 1917, became an example of the efficient auto production facility, heavily relying on the river as a means of transportation, a water source, and receiver of wastewaters [8]. Metallic materials were originally responsible for about 80% of total automobile weight, including mainly steel and cast iron. Since the 1950s the relative use of ferrous materials has dropped significantly in favor of lower mass density materials (aluminum and magnesium alloys and metal-based composite materials) [9]. The dramatic increase of vehicle production contributed also to the increase of lead in the environment. The impact of widespread burning of tetraethyl-leaded gasoline, introduced in 1923 to improve engine performance, has been observed in the Great Lakes sediment records [2]. Despite discontinuation of leaded gasoline use in vehicles after the 1970s, alkyl leads are still used in aviation gasoline, and this additive is still being produced and used in the Great Lakes basin as in the other parts of the world [10].

Massive production requires a major source of energy, which through the history of the Great Lakes region was mainly obtained from coal burning. Coal-fired power plants remain a main source of mercury emission into the atmosphere despite the fact that many plants in this area have made an approach to fully eliminate coal for producing electricity [11, 12]. Once released into the atmosphere, mercury is transported and enters freshwater systems through direct atmospheric deposition (wet and dry) and watershed surface runoff. This phenomenon has been widely observed in the upper Great Lakes, while industrial sources dominate the mercury records in the lower lakes [13]. The industrial discharges of mercury contamination are usually attributed to chlor-alkali facilities, localized mainly in the areas of the major connecting channels including the Niagara River [14]. However, the presence of other mercury anthropogenic sources with individual emissions exceeding 50 kg/year is recognized in the Great Lakes area, including other fuel combustion sources, waste incinerators, metals and mining sources, and manufacturing facilities. Although substantial progress was made in reducing point-source discharges, only a partial decline in mercury concentrations has been observed in the area [15].

As for the other metals being detected in the Great Lakes aquatic environment compartments (e.g., manganese, cadmium, zinc), the local industrial and municipal discharges are generally considered as the main source. However, the natural presence of metals in the Earth's crust and subsequent release as a result of mining and other industrial activities should be also considered in some cases (e.g., arsenic) [16].

2 Contamination Status

To describe metal historical legacy and present contamination within the Great Lake basin, a lake-by-lake description has been prepared based on the State of the Great Lakes 2017 Technical Report [12] and available research data published in scientific journals. Besides the five main lakes, contamination of the Huron-Erie Corridor (St. Clair River, Lake St. Clair, and Detroit River) as a main route connecting the upper and lower Great Lakes has been described. The contamination by copper, iron, lead, and mercury is the primary focus of this chapter; however, depending on local conditions, results for other metals are also discussed. A short compilation of the collected data for each lake sediments has been presented in Table 1.

Table 1 Range and average metal concentrations (μg/g) in sediments from the Great Lakes including probable effect level (PEL) and threshold effect level (TEL) values

Lake	Copper	Iron	Lead	Mercury
PEL/LEL [17]	35.7/196.6	–	35/91.3	0.174/0.486
Superior	2.3–215 avg. 98 [18]	4,483–40,639 avg. 25,760 [19]	5.8–95 avg. 47 [18]	0–0.328 avg. 0.088 [18]
Michigan	0–82 avg. 31 [18]	3,000–100,000 μg/g [20]	0–165 avg. 67 [18]	0.002–0.264 avg. 0.0077 [18]
Huron	0.85–86 avg. 32 [18]	1,402–76,958 avg. 7,940 μg/g [19]	0.95–120 avg. 34 [18]	0.01–0.37 avg. 0.043 [18]
Erie	3.1–68 avg. 36 [18]	75th percentile of lake avg. 3,300 [21]	4.4–105 avg. 41 [18]	0.006–0.94 avg. 0.187 [18]
Ontario	3.7–110 avg. 59 [18]	75th percentile of lake avg. 2,980 [21]	5.2–200 avg. 72 [18]	0–1.4 avg. 0.586 [18]

2.1 *Lake Superior*

Lake Superior is the largest, coldest, and deepest of the Great Lakes and constitutes mainly a single depositional zone that is subdivided into ten interconnected basins [22]. Longer contaminant cycling times (173 years water residence) and lower rates of volatilization result in lower rates of decrease in concentrations for some legacy contaminants, compared to the other Great Lakes. However, typical offshore deepwater sediment contaminant concentrations are very low [12].

Within the Lake Superior watershed, there are recognized historical anthropogenic sources for copper, with numerous tailing piles and smelting facilities. It has been estimated that smelters along the Keweenaw Waterway refined five million metric tons of local native copper from 1889 to 1968, and between 1952 and 1995, an additional 1.8 million metric tons of copper and silver were smelted in this area [23]. The copper industry is responsible for the elevated sediment concentrations still detected in Lake Superior sediments, exceeding both the background concentrations and the probable effect level and threshold effect level (PEL/TEL; [17]) values (Table 1) [18, 19]. Currently, 14 mines operate in the direct Lake Superior basin, extracting copper but also gold, silver, platinum, palladium, nickel, zinc, lead, and iron ores [24]. As for the other investigated metals present in the Lake Superior sediments, e.g., lead or zinc, observed concentrations [18] rarely exceeded PEL (Table 1). Moreover, these values were considered the lowest among the Great Lakes.

Local mining is historically intertwined with atmospheric mercury contributions, since this element occurs naturally in solid solution within ores and is commonly used for amalgam extraction of gold and silver [23, 25]. The mercury levels in specific nearshore locations within Lake Superior are also heavily influenced by shoreline-based urban and industrial activities, e.g., coal-burning power plants, slimicides from pulp and paper mills, chlor-alkali plants, and municipal incinerators. Therefore, mercury concentrations detected in sediment of this lake frequently exceed TEL values [19, 26]. A recent study claims that atmospherically derived mercury is the dominant contributor to Lake Superior sediment, though watershed sources are significant near river mouths, such as the St. Louis River and Thunder Bay [13]. It should be noted, however, that considerable achievements have been made since 1990 in reducing the emissions and discharges of legacy chemicals from within the Lake Superior basin, with an 80% reduction in mercury itself [24].

2.2 Lake Michigan

Lake Michigan is the third largest of the Great Lakes (residence time: 62 years) and is conjoined with Lake Huron through the wide Straits of Mackinac (Lake Michigan-Huron); however the two lakes are typically represented in environmental studies as separate water bodies. Due to the presence of a rock feature running under Lake Michigan, known as the Milwaukee Reef, the lake is separated into two distinct basins (northern and southern). Each of the basins features different characteristics, promoted also by a lake-long stretch from north to south (494 km), which supports diverse climatic and ecological conditions. The northern basin is surrounded by dolomite rocks, and this part of the watershed is mostly covered by forests. Here the relatively shallow Green Bay is separated by a peninsula and chain of islands. The southern portion of the watershed is characterized by vast sand dunes created by the last glacial retreat and surrounded mostly by agricultural areas. However, the southern lake shoreline is extensively developed, hosting large urban and industrial centers (e.g., Chicago) [20, 27].

Most of the sediment surveys show a higher degree of metal contamination for Green Bay than the open-lake areas, since its watersheds have had a long history of exploitation. Originally, the economy of the region was based on the fur trade and lumber industry. Afterward, economic development shifted to papermaking and manufacturing [28]. Therefore, Green Bay has relatively high mercury records in its surficial sediments, with an average of 0.360 μg/g, while the rest of the lake does not exceed 0.080 μg/g [18]. Rates of mercury accumulation in sediment show the highest values from the mid-1950s; then a substantial decrease during the past half century, in response to effluent controls and reduced industrial use of mercury, has been observed [15]. The elevated mercury levels originating from industrial and watershed-derived sources have been also detected in the southern part of the lake (mouth of the Grand River) [13].

As for the other metals, the presence of lead in sediment cores should be noted. The legacy sources of lead to Lake Michigan are attributed to mining and smelting of lead and zinc ores in the Upper Mississippi Valley deposits and its subsequent long-range atmospheric transport. The lead sources located in the direct vicinity of the lakeshore include lead smelters, coal combustion, and leaded gasoline and are dependent on the degree of industrial development. As a result, southern basin sediments hold higher levels of lead pollution. Concentrations peaked around the late 1950s, and again lead loads have recently diminished due to reduced coal use and a phaseout of leaded gasoline [29, 30].

2.3 Lake Huron

Lake Huron comprises the easterly portion of Lake Michigan-Huron (residence time: 21 years), and its waters drain into the St. Clair River, which subsequently flows toward the lower Great Lakes. Within this lake are several individual depositional basins: St. Marys River; North Channel; Georgian Bay; Michigan's western shores, Main Basin; Saginaw Bay; and Ontario's southeast shore. In each basin individual bedrock control or glacial features can be distinguished [31]. Northern and southern lake features and basin land use activities are distinctive and directly influence the quality of the aquatic environment. In the north, Precambrian shield rocks cover the shores of Georgian Bay, and the North Channel contains extensive base metal deposits and hosts intense industrial activity related to ore mining and processing, e.g., Sudbury area. Due to the heavy share of forest, and complex shoreline with multiple islands, this region has also high recreational value and makes highly popular tourist destination. In the south, glacial deposits of sand, gravel, and till predominate, and this part is dominated by agricultural land use. However, the anthropogenic coastal development footprint (e.g., Sarnia) should also be noted [32].

Relatively high nickel concentrations of up to 287 μg/g recorded in sediments of the western end of the North Channel result from extensive nickel mining in Sudbury [19]. As for the other metals, the lake-wide average values are relatively low compared to the other lakes, except for copper which still exhibits elevated values due to the local geological background [18].

Recent levels of mercury in Lake Huron water (0.29 ng/L) and sediments (0.04 μg/g) are the lowest compared to the other lakes [19, 26, 33], and no apparent spatial pattern of sediment or water contamination exists, which is likely associated with recent reductions in Lake Huron mercury sources and loadings. Historical studies have indicated that mercury contamination in Saginaw Bay and Georgian Bay further acted as sources of mercury to southern Lake Huron and Lake St. Clair [34]; however recent data indicate that these sources are no longer significant [14, 15, 33] and mercury presence should be attributed to atmospheric deposition [13].

2.4 Huron-Erie Corridor

The Huron-Erie Corridor is a 157-km-long waterway connecting the upper Great Lakes (Lakes Superior, Michigan, and Huron) with Lakes Erie and Ontario. Within the corridor, water flows from Lake Huron through the St. Clair River and enters Lake St. Clair. Prior to entering Lake St. Clair, a broadening of the river occurs, providing an extensive depositional area known as the St. Clair Delta. Lake St. Clair drains into the Detroit River, which constitutes the last portion of the corridor. The navigable channel (part of the St. Lawrence Seaway) created through the Huron-Erie Corridor (HEC) serves as a major trade artery and also constitutes a border between Canada and the United States. Due to its function as a shipping channel, the corridor's watershed has developed into one of the most industrialized and environmentally altered areas within the Great Lakes basin. Both fluvial reaches of the HEC receive only a few contaminants from the upstream lakes but have been extensively affected by point and diffuse source inputs from urban centers, multiple industries, hazardous waste sites, and sewage treatment plants located on both sides of the St. Clair and Detroit Rivers [35].

Mercury is still considered as one of the most prominent contaminants for the Huron-Erie Corridor due to historical sources, mainly chlor-alkali production localized within the St. Clair and Detroit Rivers catchments [14, 36]. The substantial reductions in these contaminants' concentration in the St. Clair River and Lake St. Clair over the past few decades have been observed in both sediments and biota [37–39]. These reductions can be attributed to the successful management actions taken to reduce contaminant loadings to Lake St. Clair and sediment remediation [40]. Geovisualization techniques show that presently the mercury spatial pattern within Lake St. Clair still displays higher levels in deeper parts of the lake, in the dredged shipping route, and in proximity to the main outflow channels through the St. Clair Delta [41], which is considered an important depositional zone for the corridor [42].

As for the last portion of the Huron-Erie Corridor, mercury, arsenic, copper, lead, and zinc are key pollutants in Detroit River sediments. Elevated metal concentrations observed in the middle and lower reaches were attributed to sources localized along the river and accumulation associated with flow conditions, especially in the broad lower reach of the Detroit River [16]. Among these sources, mainly industrial activity is being credited; however urban point sources should also be recognized [43]. The sediment contamination of this river has been linked to degradation of benthos and exceedance of water quality standards and is described as an exposure vector to biota that results in restrictions on fish and wildlife consumption, degradation of fish and wildlife populations, and fish tumors and other deformities. The extent and severity of sediment contamination was the main reason for cleanup efforts completed under Remedial Action Programs for the Detroit River [44, 45].

2.5 Lake Erie

Lake Erie is a relatively shallow and narrow water body, receiving around 80% of its waters from the Detroit River. The lake waters empty into Lake Ontario through the Niagara River, with an average residence time of 2.7 years. Lake Erie is naturally divided into three distinct but interacting water bodies: the western basin, central basin, and eastern basin [46]. Lake Erie's basins include the largest percentage of agricultural land in the Great Lakes, particularly along Erie's western and northern shores. The southern shores of Lake Erie are densely populated, with large metropolitan areas on the US shore, e.g., Toledo, Cleveland, and Buffalo [47].

From the contamination point of view, the western basin has gained the most attention due to its unique conditions. The Detroit River is the primary vector delivering pollutants to this basin, including metals associated with water and sediments. These contaminants originate mainly from the lower portion of the river, traditionally recognized as an industrial hub [16, 21]. Moreover nutrient-rich agricultural runoff creates perfect conditions for harmful and nuisance algal blooms (HNABs) regularly plaguing Lake Erie and paralyzing regional tourism, fishing industries, and the drinking water supply [48].

Since the automobile industry dominates the economy, along with natural gas, salt, and sandstone mining, large arrays of metals are being detected in sediments, with concentrations exceeding TEL. As for the spatial distribution pattern, an apparent concentration decrease following lake water flow from west to east and from south to north of the central basin has been observed [21, 49]. Sources of mercury contamination in Lake Erie are primarily attributed to loadings from historical sources, including chlor-alkali production in the Detroit and St. Clair Rivers [14]. Contemporary studies of isotopic mercury pattern confirm that elevated mercury concentrations in this lake's sediments are still linked to industry and urbanization [13]. As for temporal patterns, a substantial decrease after peak levels from the 1950s to 1970s has been commonly observed and attributed to source reduction and/or remediation programs [14, 21].

2.6 Lake Ontario

Water flowing from Lake Erie (and the upper Great Lakes) through the Niagara River accounts for roughly 80% of inflows into Lake Ontario. After approximately 6 years of retention time, 90% of this water drains through the St. Lawrence River toward the Atlantic Ocean [50]. From the depositional point of view, three major basins can be distinguished within the lake, i.e., Niagara, Mississauga, and Rochester basins. A fourth minor basin (Kingston basin) is located at the outflow of Lake Ontario to the St. Lawrence River and receives reduced sediment loadings from the main lake due to the presence of a major topographical barrier (Duck-Galloo sill) [51, 52]. Among all the Great Lakes, Lake Ontario is the most heavily influenced by industrial activity localized mainly along the Canadian western and northern shores (e.g., Hamilton and Toronto) and the Niagara River area. Moreover, in contrast to the other Great Lakes, Lake Ontario is more significantly impacted by local contaminant sources, compared to atmospheric deposition [49, 52].

The Niagara River remains the main vector for particle-associated contaminant delivery, due to the lack of depositional areas for fine particles within the river [53]. These contaminants originate mainly from the historical and contemporary industrial facilities localized in its basin (Buffalo and Niagara Falls), including two chlor-alkali plants [54]. Therefore, the observed mercury concentrations in the western part of the lake are higher compared to the eastern one [13, 14]. As for the other metals (lead and copper), concentrations above the PEL are mainly observed in all three deep lake basins with the values decreasing in the expansion of this areas [49, 52]. Within the lake, concentrations exceeding provincial and/or federal sediment quality guidelines are being reported for local contaminant hot spots. Among them, Hamilton Harbour as a steel production center, and as a confined embayment discharging a large urban/industrial watershed, remains a major concern due to the high pollutant concentrations continuously being detected, including metals [55]. For the other areas, an improvement in sediment quality since the 1960s has been reported from various studies [21, 49, 52].

3 Fate and Environmental Impact

As described in the previous chapters, metals are being transferred to the Great Lakes system from various natural and anthropogenic sources via different pathways. Wastewater discharges are usually considered as the primary path; however surface runoff from the industrial/urban catchment is also recognized as an important metal migration vector. Additionally, metals released even from remote sources enter this freshwater system through atmospheric dry and wet deposition [13, 26, 56]. Once metals enter the water of the Great Lakes, they are subject to variable and multiple cycles of uptake, aggregation, settling, decomposition, and resuspension. The periodic redox cycles during sedimentation and resuspension allow metals in sediment to be mobilized and released into the water column. The subsequent transfer, transport, and settling within the basin are facilitated mainly by local hydraulic and geochemical conditions, e.g., organic matter content or grain-size distribution, but also by anthropogenic factors [35, 57].

Many metals are essential in small quantities for aquatic organisms (e.g., copper, iron, manganese, nickel, and zinc), but they are often toxic at higher concentrations, while others, biologically nonessential (e.g., cadmium, lead, and mercury), may cause adverse effects even in small concentrations or interact with the metabolism of essential metals. Metals occur in the freshwater environment predominantly in three forms (dissolved, colloidal, and particulate) which differ in terms of bioavailability and toxicity for aquatic organisms. In general, dissolved metals are considered as most bioavailable and toxic, while particle bounded elements are generally not easily available for organisms. However, in actual aquatic conditions, metal bioavailability and toxicity are controlled by various processes and factors, e.g., metal speciation, pH, organic carbon content, dissolved oxygen, redox potential, hardness, salinity, and presence of ligand complexes [58–60]. Once present in the aquatic environment, metals may enter the food web and amplify in animal tissues as they move up the food chain. Both diet and exposure to aqueous concentrations are sources of metals for aquatic organisms, but sources differ greatly among metals. Usually, diet is considered as the main path of contamination to upper trophic levels. Metals transferred through aquatic food webs to fish, piscivorous animals, and humans are of serious environmental and human health concerns [61, 62].

Since biota can integrate contaminant exposure from the area they occupy, and may accumulate contaminants to a higher level than their surrounding media, they can provide a good indication of the extent of the contamination problem. In the Great Lakes, several formal contaminant biomonitoring programs have been carried out since the 1970s, with the general focus on two broad issues: (1) overall environmental contamination, ecosystem status, and/or risk to wildlife and (2) direct risk to humans. To cover the first issue, several types of species encompassing different trophic positions, diets, and habitats are included in the programs. Examples of biomonitors include caged mussels, forage and top predatory fish, birds (herring gull and bald eagles), snapping turtles, and other wildlife such as mink. However, other benthic organisms are also investigated under likewise oriented research programs (e.g., mayflies). For the programs designed specifically to protect humans, sport fish are the main target since they are considered as the major transfer point between contaminants in the aquatic system and human exposure [63, 64]. The main focus of these programs is on persistent, bioaccumulative, and/or toxic chemicals of concern. Therefore, mercury is a prominent example from the metal/metalloid group due to its ability to transform into the more toxic form, methylmercury. The subsequent selection of metal bioaccumulation cases intends to cover main metal contaminants and main food web components and is based on the selected previously published research papers.

As for the lower food web components, mussels are mainly used to monitor waterborne concentrations of metals due to the large volumes of water which they filter. Moreover, due to their ability to transfer suspended particles over a large size range and eject them to the bottom sediments as pseudofeces, they are also used to investigate the impact of polluted sediment on the aquatic web [65, 66]. The results of studies with use of the zebra mussels (*Dreissena polymorpha*) displayed site-to-site and year-to-year differences in metal contamination of soft body tissues which can be attributed to the spatial and temporal variability between sampling sites. Specifically, zebra mussels show higher concentrations of metals when collected from sites where sediment concentrations of these metals are higher. There is however usually no significant statistical relationship between metal concentration in their tissues and sediments [66].

Sediment burrowing organisms demonstrate a much stronger relationship between sediment contamination and food web uptake. Mayfly nymphs have a prolonged residency in sediment making them susceptible to uptake and accumulation of present pollutants, and thus, they are commonly used to investigate heavy metal transfer. Indeed, it has been shown that spatial representation of heavy metal concentrations in burrowing *Hexagenia* mayflies from Lake Erie exhibited a similar pattern to the spatial distribution of heavy metals and organic matter in sediments. Moreover, visibly higher concentrations were detected in mayflies residing in regions of elevated metal contamination [67]. As for the higher food web components, due to the decreasing metal contamination pattern in the Great Lakes, selected metals (e.g., copper, cadmium, and lead) are being found in fish tissue but only occasionally at levels requiring consumption restrictions. Therefore, the main monitoring and research focus remains mainly on mercury [19, 64, 68, 69].

Mercury in atmospheric deposition, water, soils, and sediments exists mainly in inorganic forms. However, nearly all of the mercury bioaccumulation by fish and higher trophic organism levels are related to its organic form, i.e., methylmercury [70, 71]. In most aquatic ecosystems, in situ production of methylmercury (methylation) is the prevailing source of this form, but the reverse process (demethylation) is also possible. These processes are controlled by various biotic and abiotic factors and can occur in various compartments of aquatic ecosystems, including sediment, periphyton, and water. In natural aquatic environments, biotic methylation in sediment and photodemethylation in water are suggested to be the main components of the mercury aquatic cycle [72, 73]. While already in an organic form, mercury is readily bioavailable and due to its ability to cross biological membranes has been demonstrated to biomagnify to high concentrations [64, 74].

Although methylmercury has been detected in the Great Lakes' higher trophic organisms, e.g., common loons (*Gavia immer*) [75] and free-ranging minks (*Neovison vison*) [76], the major concern is related to fish and the subsequent transfer to humans. Sensitive populations, such as women of childbearing age and children, and highly exposed populations, including families of recreational anglers and aboriginal subsistence fish consumers [68], are a particular concern. It has been estimated that in the United States, more than four million adults consume a variety of fish harvested from the Great Lakes every year, and in Ontario, Canada, the Great Lakes are the preferred fishing venue for more than one million anglers. According to the provincial monitoring datasets (Ontario Ministry of the Environment and Climate Change, OMOECC), mercury concentrations in predatory fish are generally declining in the upper Great Lakes (Superior and Huron), where mercury is occurring largely due to natural abundance and/or atmospheric input. Conversely, in the lower Great Lakes (Erie and Ontario) where mercury is derived mainly from local point sources, these concentrations are recently experiencing either flat or weak increasing trends [77]. Moreover, the projected 2050 mercury levels in fish can pose a potential implication to the health of human consumers [78]. To prevent this threat, fish consumption advisories are issued and updated regularly by the province of Ontario for the Canadian waters and by the Great Lakes states for US waters. Although PCBs are the major drivers of the restrictive fish consumption advisories for this area, mercury remains an equally important cause of restrictions, where recommendations are given on consumption rates per month for a particular size and type of fish from a specific location [79]. Despite the existing guidelines and advisories, the mercury from fish consumption has been detected in the blood of the local anglers and fish eaters [80], with levels exceeding the reference dose (US EPA) in those not following the guidelines [81].

4 Monitoring and Remediation Actions

The first comprehensive surveys of metal pollution in the Great Lakes started in the 1970s when the growth of public concern in occurrence of toxic chemicals in the air, water, soil, and food chains in the Great Lakes basin was noted. Public interest was particularly aroused by the excessively high levels of mercury in fish which forced the closing of the commercial fishery in Lake St. Clair and the western part of Lake Erie [82]. Since then mercury and other metals have been included in various monitoring and research initiatives, and detailed descriptions of metal sources, fate, and distribution have been provided for all the Great Lakes.

The majority of actions aiming to restore and protect water quality and aquatic ecosystem health of the Great Lakes are conducted under the frame of the Great Lakes Water Quality Agreement (GLWQA). Through this agreement the concerted actions of Canada and the United States have been organized since 1972. Mercury was originally recognized as one of the chemicals of mutual concern (CMC) under the GLWQA and therefore targeted by binational strategies and the development of aquatic environment quality standards, objectives, criteria, and guidelines. The other metals have been subjected to research and monitoring interest as being included in water quality standards developed for the Great Lakes watershed. Moreover, they are also targeted as part of a sediment pollutant list.

The amendment of the GLWQA from 1987 brought designation of areas of concern (AOCs) within the Great Lakes basin, as “geographic areas that fail to meet the general or specific objectives of the GLWQA where such failure has caused or is likely to cause impairment of beneficial use of the area’s ability to support aquatic life.” The beneficial use impairments (BUIs) are understood as a reduction in the chemical, physical, or biological integrity of the waters of the Great Lakes and a cause for specific problems related to environmental and human health (e.g., restrictions on fish and wildlife consumption, or restrictions on dredging activities). Although contaminated sediments are not designated as a specific BUI in the AOCs, they are recognized as a major cause of environmental problems as well as a key factor in restoring 11 of the 15 impairments under the GLWQA. Sediment contamination is linked directly to the degradation of benthos and exceedance of water quality standards/objectives BUIs [83, 84]. Indirectly, contaminated sediments provide an exposure vector to biota that result in restrictions on fish and wildlife consumption, degradation of fish and wildlife populations, and also fish tumors and other deformities [85].

For all the designated AOCs in the Great Lakes basin, a cleanup plan is required, i.e., a Remedial Action Plan (RAP) which is run and prepared separately for each AOC. Generally, RAPs are focused on measures to be taken to restore the BUIs and management actions necessary for the AOC delisting. A majority of these activities lead to local cleanup actions, including contaminated sediment remediation, followed by monitoring activities. The cleanup actions for Canadian AOCs have been supported by the Government of Canada since 1987, and since then approx. $130 million have been spent to fund these activities. To date, over 900 restoration projects have been completed by the Environment and Climate Change Canada (ECCC) and community partners in the AOCs to enhance water quality, restore fish and wildlife populations and habitats, improve management of municipal wastewaters, and investigate and develop options to manage contaminated sediments. Contaminated sediment management projects have been completed in the St. Lawrence River (Cornwall), Niagara River, Detroit River, Bay of Quinte, and the Peninsula Harbour Area of Concern. Randle Reef in the Hamilton Harbour AOC is the largest Canadian contaminated sediment site within the Great Lakes with a cleanup being underway, with an estimated total cost of sediment remediation at approximately $140 million [86]. The contaminated sediments on the US side have been addressed under the Great Lakes Legacy Act (GLLA), with approximately $565 million invested by the US Environmental Protection Agency (US EPA) and nonfederal sponsors since 2002. The significant resources to remediate and restore the Great Lakes are also provided through the Great Lakes Restoration Initiative (GLRI), with approx. $700 million spent on AOC-related projects between 2010 and 2014 [87, 88].

The most extensive information on metal levels in the Great Lakes waters stems from the Great Lakes Surveillance Program. This program is delivered as part of Canada's commitment to the GLWQA and also responds to the needs of the binational Cooperative Science and Monitoring Initiative, the Lakewide Management Plans, the Binational Toxics Strategy, and the Integrated Atmospheric Deposition Network. In total, 27 trace metals and mercury concentrations have been investigated in approx. 100 sampling stations since the 1970s [89], and these data have been used in multiple publications (e.g., [18]). As a result of the GLWQA, several long-term monitoring programs using biota (or biomonitors) were initiated in both Canada and the United States since the 1970s. Since these programs intended to address persistent, bioaccumulative, and/or toxic chemicals, they also included mercury with a focus on different species encompassing different trophic positions [63].

5 Temporal Changes and Future Prospects

Evaluation of temporal changes of aquatic environment contamination is crucial to address questions about the state of the system, i.e., whether it has improved and/or benefited from the completed remediation actions. However, tracking temporal changes in large lacustrine and riverine systems presents many logistic and technical challenges. Such systems exhibit complex hydrological properties confounded by many natural and anthropogenic factors identified at micro- and macroscales. Moreover, changes in sampling designs and assessment techniques across surveys conducted in different years have to be considered when discussing contamination changes in time [44, 45]. Therefore, assessment of temporal changes is more feasible when data originate from the long-term monitoring programs. Indeed, the existing almost 50-year-long monitoring data, resulting from activities conducted and supported by ECCC and US EPA, allow to draw overall conclusions on temporal changes of metal contamination in the Great Lakes, demonstrating a decreasing trend in trace metals and mercury both in water and sediment, when comparing contemporary data with measurements from the late 1960s and 1970s. Primary contributors to this change include major management actions, such as phasing out leaded gasoline, remediating contaminated sites, reducing and/or eliminating discharges from industrial facilities, reducing open-lake disposal of contaminated sediments, and reducing loadings from atmospheric sources [14, 18, 26].

When temporal changes are being assessed in the smaller scale within the Great Lakes, e.g., to address AOCs' status or local "hot spots," usually sediment contamination is discussed since sediments serve as repositories for organic and inorganic contaminants [56]. The dispersal of sediment-borne metals in aquatic environments is dictated by a number of interrelated factors and processes. Commonly hydraulic and geochemical-related parameters are taken into consideration when a description of spatiotemporal patterns is involved, e.g., bottom current velocity, fine fraction (<0.063 mm), aluminum, and organic matter. Moreover, the resolution of anthropogenic sources should be also argued in such studies [35]. To assess decadal changes of the system-wide metal contamination in the Detroit River (sampled in 1998 and 2008/2009), a stratified random sampling design was implemented during both surveys. Sampling sites were selected to encompass the entire boundary of the river, and sampling was performed in six strata of the river. Strata consisted of upstream, midstream, and downstream reaches each divided by width into Canadian and US waters [90]. Randomized sampling enabled use of a variety of statistical tools to establish river-wide chemical mass balance estimates of priority contaminants, to compare changes in contamination in selected areas, and to delineate locations of contaminated and clean zones within the river. The results of this study showed that a majority of the examined metals demonstrated little or no trends with respect to sediment contamination over the time interval of 1999 to 2008/2009. However, observed increases in cadmium and zinc concentrations in the less contaminated upstream region of the Detroit River suggested a possible influence of upstream anthropogenic sources [45].

Additional confounding factors have to be addressed when considering contaminants which can be transformed among elemental, ionic, and organic species as they cycle within and among air, water, land, and the biosphere. Regional temporal trends of mercury generally show declines in recent decades. However, reversals in this downward trend to show increasing concentrations have been observed in some biota since the mid-1990s and early 2000s [71, 91]. Results of the isotopic studies showed that in the upper Great Lakes (Lakes Huron, Superior, and Michigan), mercury sediment signature is dominated by atmospheric sources, while watershed-derived and industrial sources dominate in Lakes Erie and Ontario sediments. Moreover, they indicate that atmospherically derived mercury may be a more important source of methylmercury to higher trophic levels than legacy sediments in the Great Lakes [13]. Therefore, mercury temporal trends may differ not only from species to species but also from lake to lake in this large system [92, 93].

Among the factors responsible for the nondecreasing or increasing mercury trend in the Great Lakes biota in recent years are changes in climate [91, 94]. Over the past 50 years, air temperatures have increased, and heavier precipitation events have become more frequent in the Great Lakes area, with these trends projected to continue [95, 96]. Changes in precipitation, which is one of the primary pathways for atmospheric mercury entering the aquatic environment, will impact wet deposition and subsequent mercury inputs into the Great Lakes watershed and lakes. Warmer temperatures may alter the structure and function of the lakes' food webs which may be responsible for processes that influence concentrations of mercury at higher trophic levels [97], including methylation through phytoplankton uptake [98].

Future metal studies in the Great Lakes waters will likely be dominated by climate change, especially since variable responses among the Great Lakes system can be expected. There is a need, however, to highlight the other important issues in upcoming research. For instance, the presence and date of metal-based engineered nanoparticles and nanomaterials in in situ conditions should be assessed, particularly since their transformations in the aquatic environment may affect their physiochemical properties, reactivity, bioavailability, and toxicity [99]. Moreover, a growing interest in rare earth elements (REEs) has been noticed, since Canada has significant rare earth resource potential [100] with some deposits located directly in the Great Lakes catchment (e.g., Eco Ridge). REE is the collective name for a group of 17 metallic elements, comprising 15 elements of the lanthanide group, plus scandium and yttrium. Since, REEs have excellent electronic, optic, catalytic, and magnetic properties, they are useful for a wide range of high-tech applications, from cell phones to hybrid cars and nuclear batteries [101, 102]. In nature, REEs occur together in numerous ore/accessory minerals (e.g., silicates, carbonates, oxides, and phosphates), and usually they are not concentrated in economic viable quantities. Moreover, association with naturally occurring radioisotopes (e.g., thorium and uranium) can create environmental issues during REE exploration [101]. Although, the total Canadian REE resources are estimated for 830,000 tons (in terms of rare earth oxides) [102] currently, there is no rare earths production or refining in Canada. Alongside technical problems related to REE technologies, the current REE market situation has to be considered when potential future mining project is debated. The monopolistic position of China in REE mining, refining, and corresponding know-how critically affects economic feasibility of REE industry in any other part of the world [103]. However, investments in process know-how shall be pursued initially in order to achieve an independent REE supplies in Canada in future.

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Part II
Ecological Impact

Binational Efforts Addressing Cyanobacterial Harmful Algal Blooms in the Great Lakes

Katelyn McKindles, Thijs Frenken, R. Michael L. McKay, and George S. Bullerjahn

Contents

Abstract Cyanobacterial harmful algal blooms (cyanoHABs) are a recurring impairment in many of the lakes and connecting water bodies that make up the

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Laurentian Great Lakes. In many of these lakes, eutrophication during the twentieth century resulted in shifts in summer phytoplankton populations to communities dominated by harmful and noxious colonial and filamentous cyanobacteria. Nutrient pollution of Lake Erie was an important factor behind the implementation of the 1972 Great Lakes Water Quality Agreement between the USA and Canada. While the GLWQA has been effective in targeting point sources of nutrient loading, nonpoint source contributions related to agricultural activity have increased in recent decades. Re-eutrophication as experienced in parts of western Lake Erie and portions of the other Great Lakes is exacerbated by global climate change with these factors collectively contributing to a resurgence in the frequency and severity of cyanoHABs. As the Laurentian Great Lakes are shared waters between the USA and Canada, successful mitigation of cyanoHABs will require increased binational coordination.

Keywords Cyanotoxins, Eutrophication, Great Lakes, Harmful algal blooms, Lake Erie

1 Cyanobacterial Blooms as Contaminants in the Great Lakes

Freshwater is North America's most abundant natural resource, yet our freshwater resources are at risk. Nowhere is this more apparent than the Laurentian Great Lakes and their watersheds. Home to >35 million people distributed across two nations whose citizens rely on this freshwater resource for potable water, employment, sustenance, and recreational opportunities, environmental concerns are a recurring theme, compromising beneficial uses of the lakes and posing a threat to a combined GDP of US $6 trillion across the Great Lakes region [1–3]. Whereas environmental issues in the twentieth century often concerned industrial pollution affecting sediment quality and the health of fish and wildlife, in recent decades, cyanobacterial harmful algal blooms (cyanoHABs) have directly impacted humans by compromising the quality of drinking water as well as leading to deaths of pets or animals in husbandry.

CyanoHABs recur annually in many locations throughout the Great Lakes, often transcending national borders (Figs. 1 and 2). As the Great Lakes are a shared resource, this issue requires binational cooperation and policy, a recent example of which is the amendment made to Annex 4 of the US-Canadian Great Lakes Water Quality Agreement (GLWQA) calling for reductions in phosphorus target loads to western Lake Erie (detailed in [4, 5]).

CyanoHABs accumulate biomass and form dense surface scums and benthic mats contributing to impairment of beneficial use including reduced water transparency, decreases in gas exchange, and, during bloom decomposition, increased consumption

Fig. 1 Less than a month following the August 2014 Toledo Water Crisis, a cyanoHAB encroached upon the shores of Pelee Island in Canadian territorial waters leading to a water use ban by the local county health unit affecting >1,800 residents and tourists and prompting this cartoon that appeared in the *Sandusky (Ohio) Register*. Copyright Don Lee, donleecartoons.com

of oxygen contributing to hypoxia. CyanoHABs likewise compromise the safety of freshwater resources through production of toxins (e.g., microcystins, saxitoxins, anatoxins) that are potentially harmful to humans, livestock, and wildlife [6–10]. Each year, there are multiple reports of dogs succumbing to cyanotoxins following exposure to cyanoHABs in ponds, lakes, and rivers, including recent fatalities in summer 2019 reported in Georgia [11], Nevada [12], and New Brunswick [13].

2 History of CyanoHABs in Lake Erie

From the mid-1900s, researchers reported rapid increases in nutrient concentrations (eutrophication) in the lower Great Lakes, eventually manifested through shifts in the fish populations of Lake Erie [14–16]. Focusing on the lower food web, shifts in phytoplankton species composition (mainly diatoms) and abundance in Lake Erie during the 1950s were hypothesized to be related to the increased trophic status of the lake, most probably as a result of the use of fertilizers and an increased runoff of nutrients from farmlands into local rivers that ultimately end up in Lake Erie [17]. Data collected from Lake Erie by the Division Avenue Pumping Station and Filtration Plant in Cleveland, OH, from 1919 to 1963 showed a steady increase in average phytoplankton numbers from 1927 and that the spring

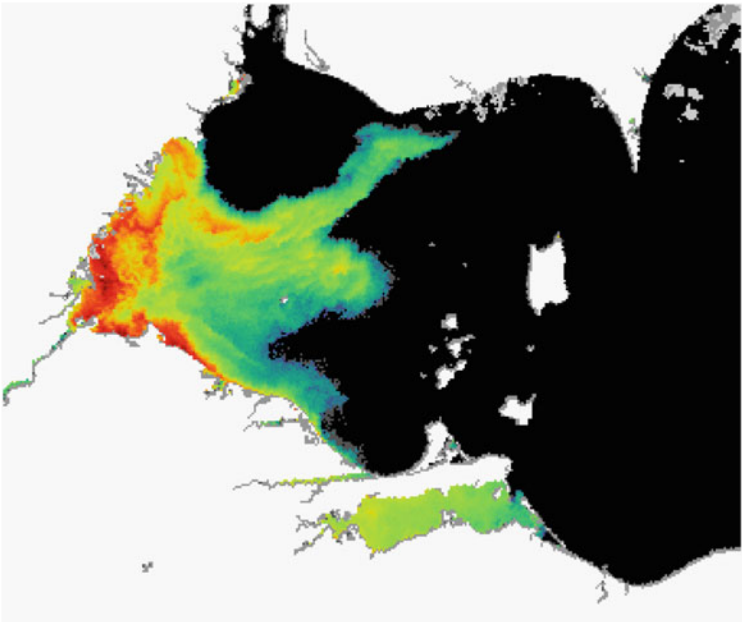

Fig. 2 A satellite-derived cyanobacterial index for western Lake Erie for 4 August, 2019. While centered in coastal waters of Ohio, the bloom extends into the waters of Michigan and the Canadian province of Ontario. Image credit: the image was derived from Copernicus Sentinel-3 satellite data from the European Organisation for the Exploitation of Meteorological Satellites (EUMETSAT) and was processed to convert lake color to cyanoHAB abundance by NOAA, National Centers for Coastal Ocean Science

maxima were more marked and longer over the years, while the fall minima became shorter [18]. The same study also observed increased phytoplankton diversity from 1948 as colonial green algae and filamentous cyanobacteria (*Anabaena*) became more prevalent in their monitored stations. From the 1950s [19], a strong presence of *Microcystis* and other filamentous cyanobacteria, including *Anabaena*, *Aphanizomenon*, and *Oscillatoria*, was observed in Lake Erie.

Widespread recognition of changing trophic state of each of the Lake Erie basins came only in the early 1970s. Basin-wide values for chlorophyll-*a* biomass and particulate phosphorus were evaluated by Dobson et al. [20], who classified the eastern basin as meso-oligotrophic, the central basin as mesotrophic, and the western basin as eutrophic. Around the same time, Munawar and Munawar [21] used maximum phytoplankton biomass to classify the eastern basin as strictly mesotrophic, the central basin as mesotrophic leaning towards eutrophic, and the western basin as hypereutrophic.

Addressing eutrophication of the lower Great Lakes, the 1972 binational GLWQA targeted loading of phosphorus [22]. The specific objective of this agreement in relation to phosphorus was to limit loading to "prevent nuisance growths of algae, weeds, and slimes that are or may become injurious to any beneficial water use" [23]. The GLWQA is a continuing commitment between the USA and Canada to protect the shared waters of the Great Lakes. It was designed as a framework for identifying priority regions and outlining actions to improve overall water quality. The agreement was amended in 1983, 1987, and again in 2012, where the agreement was updated to address water quality programs to ensure the "chemical, physical, and biological integrity" of the Great Lakes [23].

3 Reemergence of CyanoHABs in Western Lake Erie

Implementation of the GLWQA was successful, especially in terms of reducing phosphorus inputs from point source pollution into Lake Erie [24, 25], resulting in reduced total phosphorus (TP) loads, water column TP concentration, increases in water clarity, and clear decreasing trends in algal biomass through the 1980s [24, 26, 27]. Average biomass of phytoplankton declined as compared to conditions before nutrient reduction [28, 29], although these objectives were likely expedited through establishment of invasive dreissenid mussels [30–32]. However, in recent decades, while total phosphorus loadings have decreased, loadings of bioavailable phosphorus within some parts of the western basin have increased (Fig. 3), attributed mainly to nonpoint source pollution [33–35]. Coincident with increasing phosphorus in these regions has been a rise in phytoplankton and cyanobacterial biomass, especially during summer [36].

Whereas the cyanobacterial community in the 1970s was dominated by filamentous nitrogen-fixing taxa such as *Anabaena* (syn. *Dolichospermum*) and *Aphanizomenon* [21], most of the summer cyanobacterial biomass evident in the western basin since the mid- to late 1990s consists of the non-nitrogen-fixing cyanobacterium *Microcystis* [37]. For the past two decades, summer *Microcystis* blooms in Lake Erie have recurred annually [38], with record-breaking blooms observed between 2011 and 2017 [39–42]. There has also been a tendency for annual bloom formation to start earlier in the year and extend later in the season [43].

Whereas *Microcystis* dominates cyanoHABs in Lake Erie's western basin, a bloom dominated by the filamentous cyanobacterium, *Planktothrix agardhii*, recurs each summer in Sandusky Bay, a 165 km^2 drowned river mouth along the Ohio shoreline located at the transition between western and central basins of the lake [35, 44–46]. *P. agardhii* has also been reported in tributaries to Lake Erie and Lake St. Clair where it occasionally forms microcystin-producing blooms [47–49]. Like *Microcystis*, there is no evidence to support nitrogen fixation for *P. agardhii*, yet recent studies on the Sandusky *Planktothrix* bloom revealed this taxon to be highly adapted to nitrogen-depleted waters, and such conditions arise in the bay due to high rates of denitrification [46]. Compared to *Microcystis*, *P. agardhii* is a more efficient scavenger of scarce nitrogen, contributing to its success in yielding bloom conditions, often persisting from May to October, in Sandusky Bay [50].

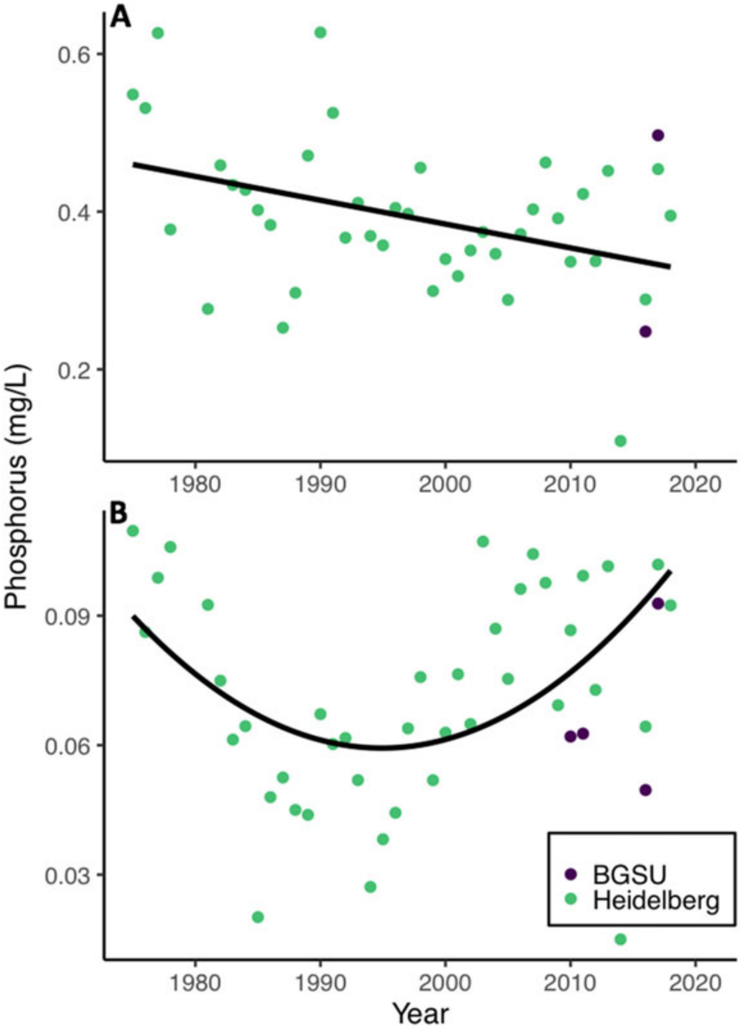

Fig. 3 Phosphorus loads entering Lake Erie from the Maumee River as (**a**) total phosphorus (TP) and (**b**) soluble reactive phosphorus (SRP), represented as annual flow-weighted mean concentrations (FWMC) from 1975 to 2019. Phosphorus data come from two locations, Mary Jane Thurston State Park (river km 55; BGSU sampling) and Waterville, OH (river km 33; Heidelberg sampling). The latter are collected as part of the Tributary Loading Program maintained by the National Center for Water Quality Research at Heidelberg University (OH). This site is located 3.2 km upstream of the US Geological Survey gauging station 04193500 (41° 30′ 00″ N, 83° 42′ 46″ W) from which discharge data were obtained. FWMC is calculated as the total yearly load divided by the total yearly flow. (**a**) TP FWMC is variable although with the trend decreasing since 1975. (**b**) SRP FWMC sharply decreased from 1975 to 1990, followed by an increasing trend from 1990 to present

Cyanobacteria can produce a diverse array of compounds, with varying toxicological effects, and thus represent a health risk to humans and animals [51–54]. CyanoHABs also lower the recreational value of aquatic resources (e.g., for fishing, boating; [3]) and may also reduce biodiversity and decreased water quality [55]. For example, during the 2014 cyanoHAB, the cyanotoxin concentration in the intake water exceeded the treatment capacity of the Collins Park Water Treatment Plant in Toledo, Ohio. This event may have been exacerbated by a large-scale viral lytic attack targeting the *Microcystis* bloom resulting in transformation of the toxin pool from the particulate to soluble phase [56]. This contamination of processed water resulted in a "do not drink" advisory lasting >48 h which affected >400,000 residents [35] and resulted in an economic loss in the region totaling at least $65 million [57]. Recognizing the prevalence of cyanobacterial blooms in western Lake Erie during the early twenty-first century, the open waters of the western basin within the state of Ohio were formally declared as impaired under Section 303(d) of the Clean Water Act [38].

4 Effects of Global Change on CyanoHABs

Blooms of cyanobacteria are mainly a result of the growth strategies of these bacteria, their superior competitive resource acquisition strategies, and a lack of top-down control by grazers [58–60]. Bloom frequency, duration, but also severity are expected to increase in response to climate change. Different climate change factors will contribute, of which temperature, CO_2, and eutrophication are likely to dominate.

4.1 Temperature

Results of multiple analyses conclude that temperate lakes, including the Laurentian Great Lakes, are warming [61, 62]. Multiple drivers are behind this trend [63] including multi-decadal trends in ice phenology [64], enhanced heat accumulation during mild winters, and pronounced increases in air temperature across the Great Lakes region that are projected to continue through the twenty-first century [65]. Together, these factors result in the earlier onset of thermal stratification and increased surface-water temperatures with effects most pronounced in Lake Superior where summer surface temperatures have increased 3.5°C over the past century [66, 67].

Consistent with warming surface waters, growth rates of mesophilic microbes are expected to increase [68]. Therefore, warming is also generally expected to lead to enhanced growth of cyanobacteria. Rising temperatures indeed seem to favor cyanobacteria [69, 70]. Although warmer lakes do not necessarily harbor higher phytoplankton biomass, the percentage of the total phytoplankton biovolume attributable to cyanobacteria increases steeply with temperature [71]. Likewise, recent evidence suggests that lake warming may undermine efforts to combat cyanobacterial blooms through nutrient management [72]. In addition, increasing temperature may promote the growth of toxigenic over non-toxigenic populations of cyanobacteria, leading to blooms with a higher toxin content [73]. Indeed, a pan-European study recently showed that both direct and indirect effects of rising temperature were the main drivers of the spatial distribution in the toxins produced by the cyanobacterial community, the toxin concentrations, and the toxin quota [74]. Alternatively, some recent studies on cultured *Microcystis* showed an increase in cellular microcystin quota at lower growth temperatures [75]. Clearly more work is needed to assess the interplay of temperature and toxin production as climate change continues.

4.2 CO_2

Rising atmospheric CO_2 concentrations will likely alter phytoplankton community composition and intensify cyanobacterial blooms in nutrient-rich waters [76–79], increasing phytoplankton productivity up to twofold [80]. In nutrient-rich waters, increasing partial pressure of CO_2 in surface water (pCO_2) is expected to increase the carbon-to-nitrogen and carbon-to-phosphorus ratios of phytoplankton, which may change toxin profiles of cyanobacterial blooms [81–83]. Consequently, effects of rising CO_2 might not be restricted to only the phytoplankton community; it is very likely that the entire aquatic food web is affected through cascading effects [84]. How the effects of rising CO_2 will influence ecosystem-scale processes in the Great Lakes is largely unknown. Some projections have looked at the role of rising pCO_2 on lake acidification where projections based on worse-case emission scenarios predict a decline in pH by 0.29–0.49 units by the year 2100 [85]. While this would have serious consequences for many organisms [86], recent analyses for Lake Erie [35] and Lake Superior [87] suggest that lake alkalinity, and hence buffering capacity, has been increasing in recent decades, which, combined with projected increases in lake surface-water temperatures, may counter the direct effects of rising atmospheric CO_2.

4.3 Eutrophication

Primary production in freshwater ecosystems is often limited by nitrogen and phosphorus or co-limited by multiple elements [88, 89]. Hence, increasing inputs of nutrients from, for instance, agricultural fields into freshwaters can trigger cyanoHAB formation [90, 91]. Despite decades of legislation aimed at reducing phosphorus loading into Lake Erie, portions of the lake including Maumee Bay have entered into a period of re-eutrophication [25, 36, 92, 93]. Further, not only the amount of nutrients put into aquatic systems is important, but their elemental balance (i.e., elemental stoichiometry) is also an important factor governing toxicity of cyanobacterial blooms. In this case, the amount and species of nutrients present can affect the dominance of toxigenic over non-toxigenic strains [94]. For instance, if the amount of nitrogen is enriched relative to phosphorus, the production of nitrogen-rich toxins (e.g., microcystin) may be stimulated [81, 83]. As a result, adoption of dual-nutrient management strategies targeting both nitrogen and phosphorus is advocated to control occurrence and toxicity of cyanoHABs [35, 95, 96].

5 Beyond Lake Erie: Examples of CyanoHABs in Other Laurentian Great Lakes

Blooms are on the rise throughout the world [72], so it comes as no surprise that they are not restricted to Lake Erie's western basin but are also reported in other regions of the Great Lakes affecting both Canadian and US waters. Whereas the blooms are geographically distinct, the affected regions share characteristics that promote bloom formation, namely, high levels of nutrient loading into a shallow embayment or lake that warms rapidly and serves as a bioreactor. As is the case in western Lake Erie [97, 98], most blooms occurring elsewhere in the Great Lakes are influenced by nutrients delivered by tributaries that drain predominantly agricultural watersheds.

5.1 Green Bay, Lake Michigan

Having a surface area >4,000 km^2, Green Bay is the largest embayment of Lake Michigan and the largest freshwater estuary on Earth. The Fox River, which drains >40,000 km^2 of predominantly agricultural watershed, enters Green Bay from the south and is responsible for roughly one-third of the phosphorus input into Lake Michigan [99]. For well over a century, the Fox River and Green Bay suffered from extensive environmental degradation related to the combined effects of pulp and paper production, agriculture, and insufficient wastewater management infrastructure [100]. High phosphorus loading resulted in a distinct trophic gradient, existing to present, ranging from hypereutrophic-eutrophic within the International Joint Commission (IJC)-designated Area of Concern (AOC) encompassing the Fox River mouth and extending into the lower bay and transitioning to mesotrophic further north [101, 102]. Blooms of *Aphanizomenon* were noted as early as the 1930s, and cyanoHABs intensified following invasion of Green Bay by dreissenid mussels in the early 1990s [103]. Whereas point sources of phosphorus loading into Green Bay have been largely addressed through changes to municipal infrastructure [100], agricultural nonpoint source loadings continue to promote annual cyanoHABs consisting of *Aphanizomenon*, *Anabaena* (syn. *Dolichospermum*), and *Microcystis* [102, 104, 105] responsible for the production of microcystins and other cyanobacterial peptides that contribute to impairment of Green Bay for drinking water and recreational use [106].

5.2 Saginaw Bay, Lake Huron

Saginaw Bay is a large embayment (~3,000 km^2) located on the southwestern side of Lake Huron. The bay receives inflow from four sub-watersheds whose combined 23,000 km^2 catchment is the largest in the state of Michigan. Point source phosphorus loading to Saginaw Bay from the Saginaw River was significantly reduced in the late 1970s [107]; however, with 65% of the watershed allocated to agricultural use, nonpoint source phosphorus loading has continued [108], and cyanobacteria continue to bloom during summer following a trophic gradient from the river mouth leading to the outer bay [105, 109, 110]. Like Green Bay, invasion by dreissenid mussels has likely contributed to the intensification of cyanoHABs that are dominated now by *Microcystis*, facilitated by selective grazing on competing taxa [111, 112].

5.3 Hamilton Harbour and Bay of Quinte, Lake Ontario

Hamilton Harbour is situated on the southwestern tip of Lake Ontario, an embayment between the cities of Hamilton and Burlington, ON, with a legacy of concentrated industrial activity. The bay is connected to Lake Ontario via a small shipping channel. In the 1980s, the IJC designated Hamilton Harbour as an AOC, mainly due to contamination resulting from steel production and hyper-eutrophication as a result of sewage discharge [113, 114]. Although the GLWQA was successful in reducing nutrient inputs from point sources, and water quality indices have generally showed an improvement [115, 116], cyanobacterial blooms continue to recur [7, 114] and may be promoted by discharge from combined sewer overflows into tributaries leading into Hamilton Harbour [117].

Situated in eastern Lake Ontario, the Bay of Quinte is a long, narrow embayment on the Ontario shore that is prone to regular cyanobacterial blooms of *Microcystis*, yielding detectable microcystin toxin most years. Additionally, blooms of *Dolichospermum* have also been reported [118–120]. The emergence of *Microcystis* as a dominant bloom-forming taxon in the Bay of Quinte parallels to some degree the pattern of blooms in western Lake Erie, in which phosphorus reductions from point sources, followed by dreissenid invasions, preceded the presence of *Microcystis* cyanoHABs.

5.4 Lake St. Clair

Lake St. Clair is a shallow, polymictic lake that is part of the Huron-Erie corridor. The lake contains two distinct water masses that rarely mix: one in the northwest which is more influenced by input of oligotrophic water from Lake Huron delivered by the St. Clair River and one in the southeast, influenced by input from nutrient-rich water from the Thames and Sydenham Rivers which drain predominantly agricultural watersheds (87% and 89% agriculture, respectively) in southwestern Ontario [121, 122]. Consistent with this, the southeastern Canadian sector of the lake displays enhanced productivity [121, 123]. Indeed, while the Lake St. Clair phytoplankton community was historically dominated by diatoms and chrysophytes [124], more recently, the presence of the nuisance benthic cyanobacterium *Lyngbya wollei* has been documented along the Michigan shoreline [125], and *Microcystis* is now commonly reported along the southern shore of the lake [126].

5.5 Apostle Islands, Lake Superior

Recently, episodic reports describe recurrences of a cyanobacterial bloom consisting of *Dolichospermum* sp. along the southern shore of Lake Superior stretching from Superior, WI, to the Apostle Islands [127]. The emergence of blooms in Lake Superior is surprising, mainly due to the fact that the lake is characterized as ultraoligotrophic, with the phytoplankton assemblage co-limited by phosphorus and iron [128]. In the case of Lake Superior cyanoHABs, climate change has likely improved conditions favorable for cyanoHABs through a combination of lake warming [66, 67] and nutrient delivery. Nutrient input in this area is likely associated with increased intensity and frequency of extreme rain events, including several recent "500-year" flood events in the Lake Superior basin that resulted in elevated nutrient loading to the nearshore regions [129].

6 Cyanotoxins Produced in the Great Lakes

Different cyanobacterial taxa can produce different types, and amounts, of toxins. On top of that, toxins often have a different activity or toxicologic effect. Here we discuss some of the toxins potentially produced by taxa occurring in the Great Lakes, building on the recent review of Miller at al [130].

6.1 Microcystins

Microcystin-LR (MC-LR) is a cyclic heptapeptide that is produced by several cyanobacterial species, including multiple variants of *Microcystis* spp. This genus includes the most common bloom-forming, toxin-producing taxa throughout the Great Lakes [131]. Therefore, it is unsurprising that this is the most commonly detected cyanotoxin in the Great Lakes [130].

The most common route of exposure for humans is through the consumption of contaminated seafood, cattle liver, and roots of edible plants that have been irrigated with cyanobacterial toxin-contaminated water, through dietary supplements that contain blue-green algae, or through the drinking of water during recreational activities or using untreated surface waters as a primary source of drinking water [132].

MC-LR can have different effects on an individual depending on the amount of exposure. Acute toxicity has been linked with nausea and vomiting, weakness, gastroenteritis, and acute liver failure through hepatic necrosis [132], while small doses over a long period of time lead to tumor formation and metastasis. At the cellular level, the toxin will cause cell blebbing, loss of membrane integrity, and the formation of apoptotic bodies [133]. Cells take in the toxin via organic anion transporting polypeptides, which are expressed in the liver, gastrointestinal tract, kidney, and brain [132]. Once inside the cell, the toxin has tumor-promoting activity and can induce cytoskeleton rearrangement, promote DNA damage through the formation of reactive oxygen species (ROS), and inhibit DNA repair [132].

6.2 Cylindrospermopsins

Cylindrospermopsin is primarily produced by *Cylindrospermopsis raciborskii*, which is now considered an invasive species in the Great Lakes region [45, 134]. Cylindrospermopsin production has also been linked to other cyanobacteria species found in the Great Lakes system, such as *Aphanizomenon flos-aquae* [135], *Dolichospermum planktonicum* [136], *Lyngbya wollei* [137], and some *Oscillatoria* spp. [138]. Despite the presence of these taxa in the Great Lakes, there are only a few isolated reports of cylindrospermopsin detection [131]. One of these comes from a synthesis of results from the Monitoring and Event Response for Harmful Algal Blooms in the Lower Great Lakes (MERHAB-LGL) program between 2000 and 2004 that reported a limited number of low-level (>0.01 µg/L) detects in Lake Erie and Lake Ontario [139].

Cylindrospermopsin is known to cause liver and kidney damage via inhibition of protein synthesis and glutathione production, leading to cell death [140]. There is also a link between cylindrospermopsin and tumor production, as cylindrospermopsin-treated cells showed increased levels of gene markers responsible for the downregulation of the P53 tumor suppressor protein [141].

As an example, in 1979, an outbreak of severe gastrointestinal illness and acute liver failure occurred on Palm Island, Northern Queensland, Australia, which was linked to cylindrospermopsin [142]. The outbreak was triggered when the water supply was treated with copper sulfate, which is known to lyse cyanobacterial cells and releasing toxins. When tested on mice, the cell lysate caused massive hepatocyte necrosis in the liver and lesions in the kidneys, adrenal glands, lungs, and intestines [143].

6.3 Saxitoxins

Saxitoxins are well-known secondary metabolites of some dinoflagellates where they are implicated in paralytic shellfish poisoning associated with "red tide" events in coastal marine systems [144]. As the name implies, toxicity to humans can come through consumption of shellfish that accumulate the toxins through filter feeding. Saxitoxins are neurotoxins characterized as Na+ channel blockers and can result in paralysis of both voluntary and involuntary (e.g., diaphragm) muscles. Surprisingly, saxitoxins are also produced by a subset of filamentous freshwater cyanobacteria with most recent evidence suggesting a polyphyletic origin for toxin production [145]. Among known cyanobacterial saxitoxin producers, several taxa, likely recent invaders, are found in the Great Lakes including *Cylindrospermopsis raciborskii* [45] and *Lyngbya wollei* [146]. Whereas these taxa are present, to date, saxitoxin has not been detected in the Great Lakes. Recently, however, *sxtA*, a gene required for saxitoxin production, was detected by qPCR associated with recurrent blooms of *Dolichospermum* in Lake Erie's central basin during June and July, prior to the onset of large-scale *Microcystis* blooms [147]. Results from this study were derived using integrated (8 m) water column samples, thus reducing bias for surface scums. Had surface scums been sampled directly, it is possible that saxitoxin concentrations would have exceeded the threshold for detection.

6.4 Anatoxins

Anatoxin-a, also known as "very fast death factor," was first characterized from cultures of *Anabaena* (syn. *Dolichospermum*) *flos-aqua*e isolated from Burton Lake, SK, Canada [148]. The toxin is a neurotoxin acting as a cholinergic agonist that mimics the neurotransmitter acetylcholine binding with high affinity to nicotinic acetylcholine receptors and resistant to degradation by acetylcholinesterase. Symptoms of intoxication begin with convulsions, leading to paralysis and finally death due to suffocation by respiratory arrest.

While anatoxin-a-producing taxa are commonly reported in temperate freshwater lakes and rivers including inland lakes of the Great Lakes basin [131], there are limited reports of toxin-producing taxa in the Great Lakes. The MERHAB synthesis reported elevated levels of anatoxin-a (>1 μg/L) from Lake Champlain and lower levels (>0.1 μg/L) associated with eutrophic embayments in Lake Ontario and the western basin of Lake Erie [139]. More recently, a survey of municipal water treatment plants in the Great Lakes region, including Lake Erie and the Bay of Quinte, demonstrated the presence of anatoxin-a across all stages of the treatment process including finished water at the Lake Erie site at 0.6 μg/L [149].

7 Binational Efforts Addressing CyanoHABs

Joint Canada-US efforts to monitor water quality parameters of the Great Lakes are guided by the GLWQA which is administered by the International Joint Commission (IJC), a binational organization established under the 1909 Boundary Waters Treaty [22, 150–152]. The GLWQA provides recommendations for monitoring as well as ensuring compliance with environmental objectives, including those outlined through Lakewide Action and Management Plans (LAMPs) which integrate priority issues from GLWQA Annexes, serving as blueprints to guide management decisions aimed at protecting and restoring water quality in the Great Lakes. Whereas surveys conducted by university scientists as well as state and provincial agencies are typically restricted to territorial waters, federal agencies that conduct water quality surveys, including the US Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA), Fisheries and Oceans Canada (DFO) and Environment and Climate Change Canada (ECCC), frequently carry out transboundary surveys, sometimes even coordinating activities such as intercomparison studies (e.g., [153]). While each agency maintains their own data repositories, binational teams of scientists from these agencies often work together drawing upon their respective datasets to provide joint analyses of long-term trends in water quality parameters [154–156].

Strengthening binational cooperation, the Cooperative Science and Monitoring Initiative (CSMI), implemented under the Science Annex of the GLWQA, was developed in 2002 to better coordinate science activities identified as priorities by LAMP Management Committees among agency scientists, academic researchers, non-governmental organizations, and tribal governments in support of management actions in the Great Lakes [157]. The CSMI Steering Committee is co-chaired by representatives of ECCC, and the US EPA-Great Lakes National Program Office (GLNPO) and the Initiative proceeds through a 5-year cycle, whereby each of the Great Lakes is studied in depth with research focused on the unique challenges and data gaps associated with each lake. CSMI 2019 focused on Lake Erie and was the fourth such rotation through the lake. Consistent with the recurring trend of cyanoHABs in western Lake Erie, research on nutrient dynamics and cyanoHABs has been prioritized during each Lake Erie CSMI including 2019 [49].

New to the 2019 Lake Erie CSMI was the HABs Grab, a binational survey event conducted on 7 August, 2019, involving research vessels and aircraft representing seven universities; four federal agencies (NOAA, NASA, DFO, ECCC); the municipality of Toledo, OH; and LimnoTech, an Ann Arbor, MI-based environmental engineering and science company. Also involved was the Cooperative Institute for Great Lakes Research (CIGLR), a consortium of binational research partners who collectively support NOAA's mission in the Great Lakes. The goal of HABs Grab was to provide a snapshot of the extent and toxin profile of the 2019 Lake Erie cyanoHAB. Over a period of 4 h, 8 research vessels simultaneously sampled 175 discrete sites from a predetermined sampling grid covering Erie's western basin to determine cyanoHAB biomass through measures of chlorophyll *a* and the cyanobacterial-specific pigment phycocyanin, microcystins, and nutrients. The bloom was also imaged by a binational fleet of three aircraft conducting hyperspectral imaging. While the cyanoHAB was most concentrated in Ohio waters, it extended into the waters of Michigan and through some locations in Canadian waters (Fig. 2). Overall, HABs Grab yielded a detailed survey of a large-scale bloom at a level of resolution never before achieved and brought a high level of public awareness to the issue through extensive press coverage (e.g., [158–160]).

Also new to the 2019 Lake Erie CSMI was participation by the Great Lakes HABs Collaboratory, a "collective laboratory" established in 2015 by the Great Lakes Commission in partnership with the US Geological Survey (USGS) – Great Lakes Science Center [161]. The HABs Collaboratory is directed by a binational steering committee of agency and academic scientists who seek to improve cooperation, establish a common knowledge base among the HABs science community, and identify and support through seed funding, policy-relevant research priorities. This is accomplished through publication of fact sheets, webinars, and regular meetings among Collaboratory members.

Water quality sondes measuring in situ temperature, pH, dissolved oxygen, conductivity, and photopigments provide data indicative of cyanoHAB formation useful in guiding conventional sampling efforts and informing water plants of cyanoHAB events that require more extensive chemical treatment. The sondes are deployed on buoys in sites traditionally affected by blooms, as well as at water plant intakes to provide an early warning system for cyanobacterial blooms. Over 20 YSI EXO2 water quality sondes (YSI Inc., Yellow Springs, OH, USA) are presently deployed in the western basin of Lake Erie and integrated through the Great Lakes Observing System (GLOS) to provide real-time data to water treatment plant operators and the public at large [35]. These sensors distributed through at-risk areas are at the core of a cyanoHAB early warning system (EWS) being developed by GLOS along with agency and academic partners as part of a Smart Lake Erie initiative [162]. The system also features an Environmental Sample Processor (ESP) which functions as "a lab in a can," autonomously collecting water samples and measuring microcystins in near real time [163, 164]. While GLOS is US-based, it is a participating organization in the Group on Earth Observations (GEO), specifically providing support to GEO-Great Lakes, a binational partnership under the lead of the USGS and ECCC.

Binational efforts to address cyanoHABs are not restricted to the agency and academic scientific community. Promoting innovation to accelerate technology solutions to address environmental problems in Lake Erie, Erie Hack [165] recently completed a second successful competition in 2019. Led by the Cleveland Water

Alliance and funded by private partnerships, Erie Hack led regional competitions in Great Lakes hubs in both Canada and the USA, and many of the teams competing showcased technology to address and mitigate nutrient loading from our watersheds and proliferation of cyanoHABs in Lake Erie.

CyanoHABs in the Great Lakes proliferate mainly as a result of human activities on land, namely, agriculture. Whether in Canada or the USA, the issues are similar across Great Lakes watersheds: nutrient runoff related to agricultural activity promotes blooms of potentially harmful cyanobacteria [35]. While the solutions are clear, they are not easily achieved and will require coordinated efforts across different jurisdictions [166]. These will include the collective efforts, will, and binational cooperation of the scientific community, resource managers, community stakeholders, and our elected representatives to successfully address this environmental threat.

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Impacts of Invasive Species in the Laurentian Great Lakes

Emma M. DeRoy and Hugh J. MacIsaac

Contents

Abstract The Laurentian Great Lakes are subject to numerous anthropogenic perturbations, among which invasive species are notable. Sequential invasions of non-indigenous species have had profound effects within the basin's ecosystems. Invasive species have altered ecosystem functioning, trophic dynamics, and nutrient

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cycling. They have similarly been implicated in affecting contaminant dynamics, including their transport and bioaccumulation. This work is a regional synthesis of aquatic invasive species-induced changes to ecosystem functioning in the Great Lakes and their tributaries. We have highlighted several species whose impacts on legacy contaminant, nutrient, and food web dynamics in these lakes have been particularly strong. Profiled species included filter feeders [zebra mussels (*Dreissena polymorpha*) and quagga mussels (*D. rostriformis bugensis*)], a fish [round goby (*Neogobius melanostomus*)], and two invasive plants [common reed (*Phragmites australis*) and cattail (*Typha* spp.)]. Collectively, these species showcase invasive species' ecosystem-wide effects. The Great Lakes have a long invasion history. Despite extensive research efforts, complex food web interactions and synergies between invasive species and concomitant stressors can obscure causality. These interactions underscore the need for long-term, spatially resolved studies to understand invasive species' direct and indirect effects on invaded ecosystems.

Keywords Contaminant, Food web, Impact, Invasive species, Laurentian Great Lakes

1 Introduction

The Laurentian Great Lakes provide valuable ecosystem services and harbor the earth's largest freshwater reservoir. The lakes are, however, subject to numerous stressors including toxic chemicals, nutrient loading, and climate change [1], which may interact synergistically [2]. These stressors have caused extensive but often unpredictable changes over the past few decades. Invasive species – non-indigenous species that cause ecological, economic, or health problems – are one of the most important stressors in the Great Lakes [1, 3]. As such, they serve as one of nine high-level indicators of water quality and ecosystem health for the basin [4].

The Great Lakes are a classic example of a mass biological invasion [5]. The system contains the greatest number of non-indigenous species of any studied freshwater system [6] (Fig. 1), whose annual economic impacts exceed $800 million [7]. Commercial shipping during the twentieth century spurred non-indigenous species' introductions [8], whose ballast water has been the dominant transportation vector in recent decades [6]. This invasion rate has increased over the past two centuries owing to greater economic activity (i.e., introduction effort) [9] and, possibly, facilitation between non-indigenous species (an "invasional meltdown") [9, 10].

Studies of invasion have historically focused on terrestrial ecosystems at the expense of the aquatic [11]. However, high invasion rates in freshwater habitats underscore the need to better characterize their effects [6]. Freshwater systems are also extremely sensitive to anthropogenic stressors and harbor a greater proportion

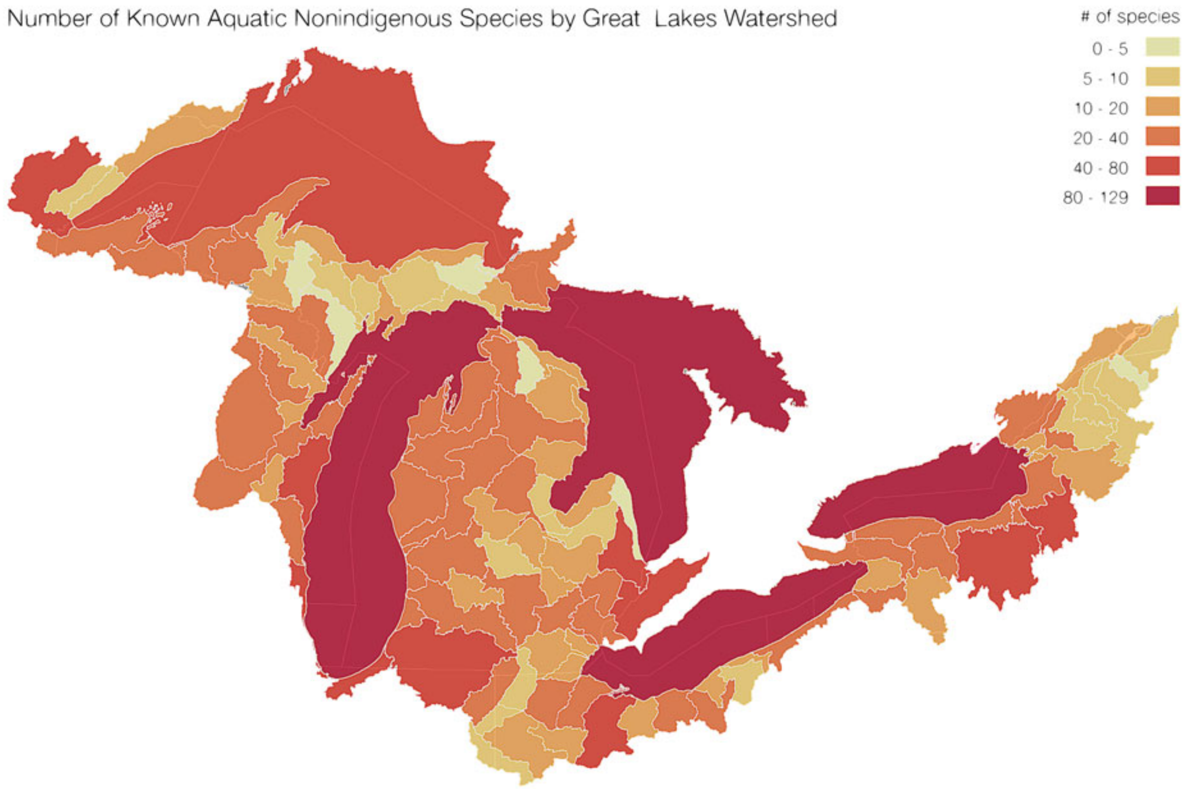

Fig. 1 Distribution of non-indigenous species throughout the Laurentian Great Lakes and their tributaries. Reproduced with permission from NOAA-Great Lakes Aquatic Nonindigenous Species Information System (GLANSIS). https://www.glerl.noaa.gov/glansis/graphics/glansisMap.png

of high-impact invasive species relative to their marine counterparts [11]. Over one-third of non-indigenous species in the Great Lakes have significant ecological or socioeconomic impacts [12, 13], which are cumulatively deteriorating the basin's state [4]. These impacts are appreciably broad. Many invasive species are prey for native predators or predate upon native species. Thus, they have the potential to induce food web shifts [14–16], alter energy pathways [17], and trigger trophic cascades [18]. Lake Erie's food web structure has been most significantly impacted at the hands of anthropogenic activity, in part due to the presence of invasive species [19].

On the heels of regulations to restore their health [20], the Great Lakes have undergone numerous changes [21, 22]. Many such changes were facilitated by reductions in nutrient point loading [21] and anthropogenic mercury (Hg) deposition to the basin [reviewed in 23]. Despite these efforts, the basin is still plagued by a myriad of contaminant-related issues. Nearshore algal blooms persist [4], and contaminant burdens in many fish have either plateaued or increased [15, 23–25]. Indeed, these contaminant levels still often exceed consumption guidelines [4, 26]. Invasive species are implicated in many of these trends [23–25].

Invasive species may occur alongside (i.e., additive) or interact with (i.e., synergistic) other environmental stressors, including nutrient loading and toxic chemicals [1, 2, 11] (Fig. 2). Synergies between invaders may further exacerbate their effects on nutrients and other contaminants in this system [10, 27]. Long-term ecosystem changes, nutrient trends, and contaminant dynamics have been monitored through various government-led programs (reviewed in [22, 28–31]). These and other datasets may be used to examine invasive species' effects on contaminant dynamics in the Great Lakes basin.

The purpose of this chapter is to explore recent findings with respect to invasive species' direct and indirect effects on nutrient and legacy chemical contaminant dynamics in the Great Lakes and their tributaries and to highlight current knowledge gaps. We utilized an indicator species approach, including species such as benthic filter feeders (*Dreissena polymorpha* and *D. rostriformis bugensis*), a benthic fish (*Neogobius melanostomus*), and two invasive wetland plants (*Phragmites australis* and *Typha* spp.). Each of the aforementioned is a model invasive species, having demonstrably affected the structure and function of Great Lakes ecosystems. Furthermore, these species occupy different components of the food web, allowing us to explore implications of their presence on benthic, pelagic, and coastal ecosystems. Collectively, they underscore the breadth of invasive species' impacts on contaminant dynamics and nutrient cycling. In this chapter, we examined effects on stable isotopes, nutrients, and a range of legacy contaminants including polychlorinated biphenyls (PCBs) and heavy metals, highlighting alterations in cycling, availability, magnification, and ratios. We constrained our scope to developments over the past 5 years.

To identify relevant papers published during the period of interest (2014 through November 2019 inclusive), we conducted a systematic literature review using ISI Web of Knowledge and Scopus for the terms: ("invasive species" or "non-native species" or "alien species" or "non-indigenous species" or "exotic species") and

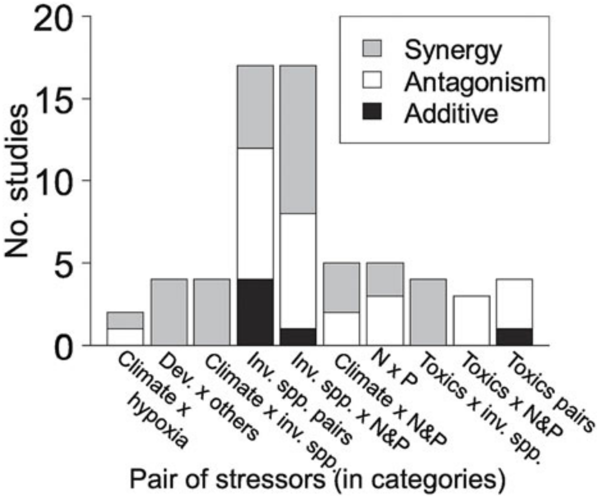

Fig. 2 Interactions between concomitant stressors in the Great Lakes basin and the frequency of their study, separated by interaction type. Interactions have been partitioned into synergies, antagonisms, and additive effects. Interactions between invasive species – and with other stressors – are depicted. *Inv. spp.* invasive species; *N* × *P* nitrogen loading × phosphorus loading, *climate* climate change, *Dev.* coastal urban development. Reprinted from Ecological Indicators, Vol 101, Smith SDP, Bunnell DB, Burton Jr. GA, Ciborowski JJH, Davidson AD, Dickinson CE, Eaton LA, Esselman PC, Evans MA, Kashian DR, Manning NF, McIntyre PB, Nalepa TF, Pérez-Fuentetaja A, Steinman AD, Uzarski DG, Allan JD, Evidence for interactions among environmental stressors in the Laurentian Great Lakes, 203–211, 2019, with permission from Elsevier

(“contamina*” or “nutrient” or “environmental chemistry” or “isotope”) and (“great lakes”). We restricted our focus to studies on the aforementioned focal species. Using the complement of studies derived from this search, we added additional papers cited therein, as well as recent papers of which we were aware.

2 Dreissenid Mussels (*Dreissena polymorpha* and *D. rostriformis bugensis*)

2.1 Overview

Dovetailing the Great Lakes Water Quality Agreement between Canada and the United States [20], nutrient abatement programs successfully suppressed point loading of phosphorous (P) throughout the Great Lakes, with major declines between 1980 and 2008 [32]. Despite ongoing management efforts, basin-wide nutrient conditions are deteriorating [4, 33], which have in part been attributed to invasive mussels.

The zebra mussel (*Dreissena polymorpha*) and its congener the quagga mussel (*D. rostriformis bugensis*) (hereafter dreissenid mussels) were introduced to the Great Lakes shortly after the binational agreement was ratified. Invasive dreissenids were first detected in Lake Erie – zebra mussels in 1986 [34] and quagga mussels in 1989 [35] – after which both species spread widely. Dreissenids have demonstrably affected the Great Lakes, to the extent that they have been classified as the top environmental stressor [36]. As ecosystem engineers [37], dreissenids have had significant top-down and bottom-up effects throughout the Great Lakes. Below we highlight many of the changes to nutrient, stable isotope, and legacy contaminant dynamics associated with these species.

2.2 *Phosphorous*

Dreissenid mussels (*Dreissena polymorpha* and *D. rostriformis bugensis*) have affected waterbodies throughout the basin both directly and indirectly. In the former, dreissenids amplify the rate at which particulates are removed from the water column and sequestered into the sediment [38, 39]. In the latter, dreissenids assimilate P in their soft tissues and shells or excrete it as feces or pseudofeces into the sediment-water interphase [40–42]. Excreted P subsequently stimulates primary production in the nearshore benthic region [37, 42].

By tying up available nutrients in the nearshore and impeding offshore availability for primary producers, dreissenids have created “feast and famine” conditions in primary production [4] and an aptly termed “nearshore shunt” [37, 43]. Consequently, dreissenids are concomitantly implicated in eutrophication of the nearshore benthic zone and oligotrophication of the offshore pelagic zone [39–42, 44, 45]. Observed decreases in total P offshore are consistent with bottom-up effects of dreissenids [38, 39, 46] and are concordant with their spread [47]. Ultimately, low P concentrations offshore may impede the basin’s ability to support productivity [4, 46]. Continued nutrient loading from tributaries may further exacerbate this dichotomy [48], highlighting the complex interactions between dreissenids and other anthropogenic stressors.

2.3 *Stable Isotopes*

Stable isotope analyses can help assess invasive species’ food web changes [49] and have recently been co-opted to quantify long-term effects of dreissenids to aquatic ecosystems. The dreissenid invasion has resulted in the predominance of nearshore energy channels (described above). This has altered trophic dynamics of food webs within the basin, particularly in Lake Michigan [17]. Long-term datasets for lakes Michigan, Huron, Ontario, and Erie have reported dramatic declines in *Diporeia*, an amphipod involved in energy cycling [4, 50, 51]. These declines were coincident with the dreissenid invasion and spread [4, 14, 50, 51] which may have inhibited *Diporeia* foraging [52]. Through reduced prey availability, dreissenids appear to have forced dietary shifts in top predatory species, increasing the reliance of pelagic fish on nearshore benthic energy channels [14, 17]. This has corresponded to δ13C enrichment and δ15N declines in the pelagic and profundal fish community relative to baseline [17]. Similar benthic energetic shifts have been reported elsewhere for Lake Michigan [53] and Lake Ontario [54]. These phenomena underscore the extent to which these mussels have contributed to restructuring food webs basin-wide.

2.4 Carbon, Nitrate, and Silica

Dreissenids have caused extensive basin-wide changes to carbon (C) dynamics and biogeochemical cycling [55]. In particular, lakes Michigan, Huron, Erie, and Ontario have undergone carbon dioxide (CO_2) supersaturation, with the most demonstrable changes occurring in Lake Michigan's heavily infested waters [55]. Observed increases in the partial pressure of CO_2 ($p CO_2$) have also been attributed to the dreissenid invasion [55].

In addition to the above-described impacts, decreases in particulate C in both Lake Michigan and Lake Huron [38, 41], increases in dissolved inorganic C in Lake Ontario [56], and increases in nitrate (NO_3) and silica throughout the basin [38, 41] have similarly been reported. These changes have likewise been ascribed to dreissenids and are concurrent with their spread [38, 41, 57]. Dreissenids have similarly produced ecosystem-wide effects on nutrient dynamics in smaller, inland lakes [42], though these effects appear to be highly context-dependent. In offshore waters of lakes Michigan and Huron, dreissenids' indirect effects predominate over those attributed to direct grazing [41]. In Saginaw Bay, Lake Huron nutrient loading appears to have a stronger influence on the food web than do dreissenids [58]. Green Bay, Lake Michigan, also varies from typical patterns, as the response to the dreissenid invasion is seemingly overwhelmed by nutrient inputs [59].

2.5 Legacy Contaminants

Dreissenids are sentinel organisms for chemical contaminants and bioaccumulative pollutants owing to their prolific filter feeding [60]. Dreissenids mobilize and biomagnify sediment contaminants, whose filtration increases sedimentation of contaminants like titanium dioxide [61] and PCBs [62]. They may thus provide an entry point to benthic food webs [62] once ingested by sediment-dwelling amphipods and chironomids [15].

Dreissenids may act as a conduit for Hg bioaccumulation and accelerate its methylation [63]. Dreissenid-induced shifts in energy pathways have stimulated the proliferation of filamentous benthic green algae (*Cladophora glomerata*), whose growth is facilitated by dreissenid pseudofeces [64]. In Lake Michigan, the nearshore benthic zone supports dense dreissenid-*Cladophora* assemblages in which heightened levels of methylmercury (MeHg) are found [63]. Decaying mats of *Cladophora* support MeHg production [65, 66] and facilitate its entry into food webs [63]. Nearshore dreissenids that cohabit with and consume *Cladophora* harbor greater MeHg concentrations relative to offshore mussels [63]. In this way, dreissenids may act as a vector for MeHg bioaccumulation once consumed by top predators, which now disproportionally feed on prey in nearshore benthic regions [17]. By hindering offshore productivity and initiating declines in *Diporeia* populations, dreissenids may also contribute to truncated growth rates and higher Hg loads of top predatory fishes throughout the basin [14, 27, 53].

3 Round Goby (*Neogobius melanostomus*)

3.1 Overview

Non-indigenous fishes can have significant consequences to food web dynamics [67]. The invasive round goby (*Neogobius melanostomus*) is a striking example. The fish was first documented in the St. Clair River in 1990 [68]. By 1999, the species was well-established throughout the Great Lakes [69], whose proliferation appears to have been facilitated by zebra mussels introduced several years prior [70]. As the most abundant non-indigenous vertebrate in the Laurentian Great Lakes-St. Lawrence River basin [71], they have drawn concern over their long-term effects on ecosystem functioning [72]. Below we present an overview of their effects on stable isotopes and legacy contaminants.

3.2 Stable Isotopes

Top predatory fish within the basin have flexibly responded to recent changes in prey availability. In the Great Lakes, round goby (*Neogobius melanostomus*) are heavily predated by piscivores, including brown trout (*Salmo trutta*) [73, 74], smallmouth bass (*Micropterus dolomieu*) [16], steelhead (*Oncorhynchus mykiss*) [75], burbot (*Lota lota*) [76], and lake trout (*Salvelinus namaycush*) [27, 73, 77]. Consequently, foraging patterns of top pelagic predators have shifted to exploit this abundant prey source. Diets of many fishes now include significant contributions from nearshore carbon energy sources in lakes Superior, Huron, and Ontario [27, 74, 77]. Given these dietary shifts, many predatory fishes have lower δ15N and higher δ13C values relative to pre-invasion scenarios [73]. Round goby (*Neogobius melanostomus*) has similarly become the dominant prey item for native benthic lake sturgeon (*Acipenser fulvescens*) in Lake Ontario. δ15N enrichment in sturgeon has been linked to the round goby introduction [78].

3.3 Legacy Contaminants

Synchronized invasions of dreissenids and round goby (*Neogobius melanostomus*) have generated otherwise absent connections between benthic and pelagic food webs in the Great Lakes [79]. Round goby (*Neogobius melanostomus*) serves as a conduit for contaminant uptake and transfer via dreissenid consumption [73], the latter of which act as sentinels for contaminants (as described above). Together, these species have mobilized sequestered pollutants [62, 79] and precipitated changes in contaminant bioaccumulation in upper trophic levels [80]. More specifically, these species have engendered community-wide shifts in contaminant transfer toward the nearshore benthos [17, 27]. This shift has significant implications for fish contaminant burdens. In Lake Erie, round goby (*Neogobius melanostomus*) is the prominent prey for smallmouth bass [16]. This reliance is purported to drive increases in smallmouth bass polybrominated diphenyl ether (PBDE) levels in future years [79].

3.3.1 Hg

Round goby (*Neogobius melanostomus*) is a strong vector for persistent contaminants such as Hg. Round goby (*Neogobius melanostomus*) and dreissenid mussels (*Dreissena polymorpha* and *D. rostriformis bugensis*) have collectively been associated with recent trend reversals in fish Hg concentrations within the basin [81]. For instance, total Hg concentrations in Lake Ontario walleye have remained constant over the past 40 years despite reduced contaminant emissions, due in part to food chain lengthening by invasive species [26]. Round goby (*Neogobius melanostomus*) has also been linked to elevated Hg levels in fish in lakes Huron [27], Michigan [53], and Erie [25]. Namely, the goby and dreissenid invasions into Lake Huron coincided with the collapse of prey populations [82, 83]. Top predatory fish subsequently relied on alternative sources of food – including gobies [27] – which contain lower energy density relative to their preferred prey [84]. This trend is particularly salient in lake trout, whose stunted growth rates and higher Hg concentrations have been linked to the round goby (*Neogobius melanostomus*) invasion across multiple lakes [4, 27, 53]. In Lake Michigan, increased lake trout Hg concentrations were reported following the round goby (*Neogobius melanostomus*) and dreissenid invasions [53]. These changes to Hg bioaccumulation manifested in light of decreased emissions over the period surveyed [85, 86]. In turn, these data indicate the disproportionally negative effect of invasive species on lake trout contaminant burdens [53].

4 Common Reed (*Phragmites australis*) and Cattail (*Typha* spp.)

4.1 Overview

Great Lakes coastal wetlands provide essential ecosystem services [87], filtering nutrient-rich runoff prior to entering larger waterbodies [88]. They also serve as C sinks [89] given their high rates of primary production and slow decomposition [90]. These traits make wetlands highly susceptible to plant invasions [91] which are often aided by sediment and nutrient enrichment [4]. In recent years, Great Lakes wetlands have been subject to elevated nitrogen (N) inputs [92]. This has driven C accretion [93] and facilitated plant invasions [94–96]. Invasive plants are ubiquitous in Great Lakes coastal wetlands, dominating up to 70% of total vegetation cover [97]. The cattail (*Typha* spp.) and common reed (*Phragmites australis*, hereafter *Phragmites*) are presently two of the most successful invasive plants in North American wetlands [91].

Three cattail species are found in the Great Lakes: *Typha latifolia*, the European narrow leaf *Typha angustifolia*, and *Typha* × *glauca*, wherein the latter two species are invasive [98–100]. *Typha x glauca* is a hybrid between native *T. latifolia* and introduced *T. angustifolia* [98] (hereafter, both invasive cattail species will collectively be referred to as invasive *Typha*). Invasive *Typha* is abundant throughout the Great Lakes [101]. Actively displacing native wetland communities, it comprises up to 50% of wetland area in Lake Ontario alone and dominates 13.5% total Great Lakes wetland area [97]. *Typha* has significant and well-documented negative effects on native plant diversity [95, 102], impacts that correlate positively with its stand age [102]. Highly dense *Typha* stands produce prodigious amounts of litter, which accumulate for decades following its invasion [103]. Among other effects, its high litter mass may imperil fish community diversity by stimulating anoxic conditions. In a Lake Michigan coastal wetland, *Typha*'s recalcitrant litter led to reductions in fish abundance and diversity by reducing dissolved oxygen levels [104]. *Typha*'s presence may also facilitate the establishment of other aquatic invasive plants [105], further extending the span of observed impacts.

Phragmites is one of the worst invasive species in North American wetlands [106], of which two strains are present in North America [107]. The invasive Eurasian strain is now ubiquitous throughout the Great Lakes [108] where it is particularly abundant in Lake St. Clair, Lake Huron, and Lake Michigan [4]. While the lower Great Lakes are at most immediate risk for further expansion, climate change will likely also increase susceptibility of the upper Great Lakes' coastal zones [109]. *Phragmites* is adept at colonizing nutrient-rich systems, effects of which are extensive. *Phragmites* negatively influences plant biodiversity [95] and threatens 25% of at-risk species in Ontario alone [110].

Relative to native species, *Phragmites* and *Typha* have greater aboveground biomass [96, 111, 112] and produce larger amounts of recalcitrant litter [95, 111]. They also have tremendous capacities for nutrient removal. Indeed, their larger relative sizes may permit access to more resources and portend a competitive advantage relative to comparative natives [94, 113]. Below, we summarize their effects on N and C dynamics and their interactive effects with other anthropogenic stressors.

4.2 Nitrogen

Both invaders alter nutrient cycling regimes [94, 102], promoting greater N retention relative to native species [94, 112]. *Typha* increases inorganic N soil pools [103, 114]. Sites invaded by *Typha* often exhibit higher soil organic matter, NO_3, and ammonium (NH_4^+) concentrations relative to native sites, as demonstrated in coastal wetlands abutting lakes Michigan and Huron [102, 114, 115]. Wetlands dominated by *Typha* also boast higher denitrification potentials relative to those dominated by native species [102]. These effects correlate positively with stand age [102]. Despite the ecosystem services *Typha* confers, benefits must be gauged against their strong negative effects and measured over time [102]. Indeed, *Typha*'s positive ecosystem functions were temporally mediated in a Lake Michigan wetland [115]. Similar trade-offs between ecosystem services are likewise apparent for *Phragmites* [112].

Litter decomposition rates of common reed (*Phragmites australis*) and cattail (*Typha* spp.) are similar [116]. In two inland Michiganian lakes, the invasions of both plants increased organic matter storage and aboveground biomass N stocks [95]. While *Phragmites'* leaves have a higher N content relative to *Typha*, both plants had similar effects on N standing stocks in a Lake Erie coastal marsh [112]. *Typha*'s slow-decomposing plant litter also appears to be disproportionately responsible for its impacts on ecosystem functioning [114]. Their litter increases inorganic N and N mineralization rates and has been implicated in the decline of native plant richness and abundance [114].

Interestingly, [117] found no difference in NO_3, ammonia (NH_3), soil organic matter, or denitrification potentials between inland Lake Michigan wetland areas dominated by invasive *Phragmites* relative its native counterpart. Despite these similarities, *Phragmites* growth in Lake Michigan wetlands was more positively correlated with nutrient availability – in particular, inorganic N [118] – a testament to its efficient resource use.

Both invaders are adapted to nutrient-rich habitats and interact synergistically with nutrient loading [4, 109, 119]. Ecosystem modelling suggests that nutrient loading fuels *Typha* dominance [119] and *Phragmites* presence [109]. However, nutrient effects on *Phragmites* distribution may be lake and context-specific [109, 118]. Notwithstanding potential context dependencies, this synergy suggests that a more nuanced management strategy – reduced external nutrient loading – may provide an attractive alternative to traditional herbicide management [119].

4.3 Carbon

The dominance of both invaders is positively related to aboveground biomass and C standing stocks [95, 112]. Common reed (*Phragmites australis*) and cattail (*Typha* spp.) promote C accumulation in surface litter and soils [102, 111, 112, 116], even under low N levels [93]. In doing so, these invaders have the capacity to significantly alter the structure and function of coastal wetlands [93].

Together, these plants drive wetland C accretion through increased primary productivity [93]. *Phragmites* can affect C cycling through high rates of C assimilation [120] and net primary production [116]. These rates often exceed those of native meadow marsh [112]. Stemming from their greater maximum size, wetlands invaded by *Phragmites* may promote greater C storage relative to *Typha* [93]. *Phragmites* may also disproportionately alter wetland C budgets, whose sediment CO_2 release is greater than in *Typha* sediments [116]. Conversely, *Typha* monospecific stands have greater C mineralization rates and more labile soil organic matter relative to *Phragmites* [95]. Despite these disparities, effects on annual C stocks appear to be similar [112]. While *Phragmites* promoted greater C assimilation relative to native meadow marsh in a Lake Erie coastal marsh, assimilation rates and C stocks were equal to that of *Typha* [112].

Typha soil methane (CH_4) emissions are thrice that of native-dominated mesocosms, due in part to their greater aboveground biomass and productivity [111]. These emission rates also exceed that of *Phragmites,* which may reduce CH_4 emissions from sediments [116]. Importantly, nutrient loading may indirectly facilitate greater CH_4 emissions by stimulating *Typha* productivity [111], exacerbating the already high global warming potential of wetlands [121].

5 Knowledge Gaps

In this chapter, we summarized recent research on several invasive species' effects on legacy contaminant, chemical, and nutrient dynamics in the Great Lakes basin. Disentangling invasive species' effects from the milieu of stressors with which they co-occur continues to be problematic. Several factors complicate cause-and-effect relationships. Other current and sometimes-synergistic anthropogenic stressors – such as nutrient loading – may obfuscate invasive species' relative effects [52, 93]. Modelling may offer one way to unravel ecosystem-level effects of invaders [52], and their application is encouraged.

Invasive species represent an unprecedented energy pathway. However, their influences on contaminant bioaccumulation and biomagnification require further study [27, 79]. Broad effects are difficult to infer given that contaminant trends are often system- and species-specific [122] and affected by among-year variability in fish contaminant loads [26]. Indeed, Hg concentrations may exhibit considerable spatiotemporal variation, both within and among trophic levels [24]. Concomitant stressors are also likely to influence legacy contaminant uptake and accumulation [24, 25]. To further complicate matters, the extent to which natives predate upon invasive species is context-dependent in smaller inland lakes [123]. These complexities may ultimately hinder causal inferences.

There is a pressing need for long-term, high-frequency, high-quality data to clarify the mechanisms of invasive species' impacts on nutrient and contaminant dynamics within the Great Lakes. Given high among-lake variability in contaminant patterns [24, 124], responses to invasive species are likely to vary between systems and spatially and temporally within a system [2, 51]. Differences in temporal resolution [38] and high inter-annual variation in time series data [52] can also obstruct clear trends by providing competing results. These context dependencies are similarly applicable in coastal wetlands [112], wherein impacts of invasive plants often only materialize over time [102]. Such system contingencies can have profound influences on the accurate quantification of invasive species' impacts. These context dependencies emphasize the importance of multi-lake, spatially resolved studies. However, this objective is complicated by the need for binational interagency laboratory cooperation. A coordinated binational strategy is imperative to effectively understand and manage invasive species' impacts throughout the basin. Unfortunately, binational regulations for the management of aquatic invasive species are currently lacking [125].

Data gaps compromise our ability to accurately estimate invasive species' effects on food web dynamics for even the most well-studied lakes [52]. For instance, invasive species' trophic roles are understudied in Lake Michigan, despite being a relatively data-rich waterbody [73]. Furthermore, the paucity of historical baseline diet information for nearshore native predators in Lake Michigan may impede understanding of invasive species' effects on ecosystem processes [73]. In Lake Erie, nutrient dynamics and phosphorous recycling also demand further study [19].

Our review revealed unequally distributed research efforts among our focal species. The recent literature is replete with studies on dreissenid mussels (*Dreissena polymorpha* and *D. rostriformis bugensis*), seemingly at the expense of other invaders. Despite their pivotal role in restructuring ecosystems, such biases may impede a holistic understanding of invasive species' impacts throughout the basin. Research foci within each indicator species also appeared skewed. Round goby (*Neogobius melanostomus*) and dreissenids have collectively shifted food web dynamics, whose impacts are inextricably linked [27, 70, 73, 79, 80]. While frequently reported in unison, future researchers should continue to unravel these species' relative and cumulative influences. Despite being the subject of considerable research, dreissenids' effects on C dynamics are largely unknown (but see [126]). Likewise, the way in which invasive plants influence C accretion – alone and through synergistic interactions with nutrient loading – is unclear [93]. The extent to which *Typha* and *Phragmites* affect nutrient cycling beyond N and C is also ill defined [112]. Collectively, these information gaps have cascading consequences for understanding broad implications of these species' invasions.

6 Conclusion

The Great Lakes have experienced extensive invasive species-induced perturbations in their structure and function. Significant progress has been made over the past several years to understand the extent of these effects. Nevertheless, our review revealed several knowledge gaps, which may impede a comprehensive understanding of invasive species' impacts within the basin. Species' invasions require broad, coordinated approaches in their study and management. Despite recent developments, concerted efforts are essential to further unpack invasive species' ecosystem-level effects on legacy contaminant, nutrient, and food web dynamics.

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Understanding the Ecological Consequences of Ubiquitous Contaminants of Emerging Concern in the Laurentian Great Lakes Watershed: A Continuum of Evidence from the Laboratory to the Environment

Heiko L. Schoenfuss, Lina C. Wang, Victoria R. Korn, Chryssa K. King, Satomi Kohno, and Stephanie L. Hummel

Contents

Abstract Contaminants of emerging concern (CECs) represent a plethora of chemicals only recently recognized as potentially causing harm at environmental concentrations to organisms through diverse modes of action. Studies have confirmed CECs are pervasive in water, sediment, and fish tissues collected from the Great Lakes watershed, corroborating studies from ecosystems worldwide. In some tributaries, CECs exceed water-quality benchmarks or screening values expected to cause adverse effects in fish based on data from single-compound exposures. However, a scarcity of data precludes predictions about the adverse

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effects of long-term exposures of resident fish to complex mixture of CECs. We combine a literature review with recent case studies to explore evidence for the effects of CECs gathered across the continuum from field studies to controlled laboratory investigations. This information is used to identify obstacles to the development of natural resource management practices. Ranking prominent among these obstacles are the dearth of analytical capabilities, paucity of mixture studies, and complexity of integrating CEC effects with additional stressors. Despite these knowledge gaps, using existing water-quality benchmarks and developing screening values from the literature can provide limited directions in identifying CEC sources in need of mitigation. Natural resource managers are encouraged to review data on CEC presence and sources when assessing conservation efforts in Great Lakes tributaries.

Keywords Aquatic toxicology, Endocrine disruptor, Fish, Weight of evidence

1 Introduction

The Laurentian Great Lakes have been at the nexus of economic development, industrialization, and environmental science for over a century. Containing one fifth of the world's surface freshwater, this aquatic ecosystem serves many important ecosystem functions [1]. Multiple areas of the Great Lakes have been designated as US National Wildlife Refuges or US National Estuarine Research Reserves, highlighting the value natural resources contain within its waters. While sustaining human populations, these natural resources have also been under threat by human development and pollution [2]. More recently, potentially detrimental stressors to the ecosystem health of the Great Lakes have been identified as "contaminants of emerging concern" (CECs) and may include pharmaceuticals, personal care products, pesticides, and industrial by-products [3–5].

Many pollutants enter the Great Lakes through its network of tributaries and associated coastal wetlands. These areas serve as critical habitats and fish nurseries and warrant special attention [1, 6]. However, the complexity and relative novelty of CECs has hampered efforts to develop comprehensive resource management approaches despite the rapid advancement in our understanding of CECs [7, 8]. The current work will review evidence for the presence and biological effects of CECs in the Great Lakes watershed and provide two case studies to highlight knowledge gaps concerning the effects of CECs in complex environmental mixtures. By combining multiple lines of evidence and working across the experimental continuum from field studies to laboratory investigations, this manuscript aims to identify obstacles to the development of effective resource management strategies (Fig. 1).

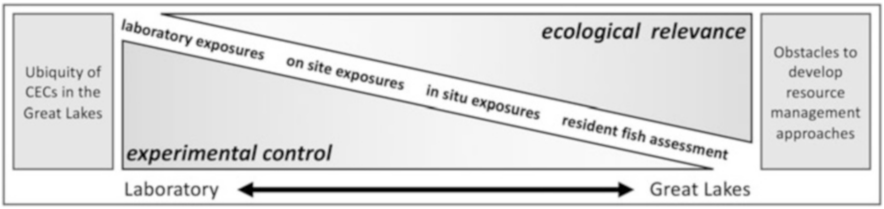

Fig. 1 The continuum of investigations from controlled laboratory environment to field studies with a concurrent increase in ecological relevance and decline in experimental control. The ultimate goal of these studies is to understand the ecological effects of CECs and identify obstacles to the development of resource management strategies

Past studies of the Great Lakes have used this continuum approach to elucidate the causal agents responsible for the decade-long decline of lake trout (*Salvelinus namaycush*) in Lake Ontario and for the poor reproductive health of white sucker (*Catostomus commersonii*) in Canadian Great Lakes tributaries (both examples reviewed in [9]). A series of studies across the experimental continuum found early life stages of lake trout to be sensitive to dioxins and PCBs found in Lake Ontario at concentrations likely to cause population declines [10]. These studies were conducted at a time when many of the CECs found to be causative agents of the fish decline were already being phased out – thus the studies were of retrospective value. In contrast to these retrospective studies, field investigations in Canadian streams causally linked ongoing discharge from pulp and paper mill effluent to altered steroidogenesis and poor reproductive health in white suckers [11]. Similar approaches are needed to assess the current and future impact of CECs on fish species throughout the Great Lakes and their tributaries.

2 CECs in the Great Lakes Watershed

CECs include diverse compounds grouped predominantly by the relative recency of their existence or discovery in the environment or by the recent realization that environmental concentrations may cause adverse effects [12]. In their definition, CECs diverge from prior groupings of environmental contaminants commonly defined by their chemical characteristics (e.g., heavy metals) or common mode of action (e.g., PAHs). Prominent subclasses of CECs include hormones and hormonal mimics that are often estrogenic and in toto may feminize male fish [13]. Similarly, environmental detection of CECs often includes pharmaceuticals with diverse modes of action in sub-categories such as antidepressants, opioids, or antidiabetic drugs [14]. Personal care products, including musks and fragrances, are also frequently found among CECs [15]. Pesticides and industrial by-products such as alkylphenol detergents are considered CECs due to their ability to interact with the endocrine system resulting in physiological alterations [16–18].

CECs have been found in aquatic ecosystems across all populated continents [19, 20], and their presence in the Great Lakes watershed is not surprising. Numerous studies have identified a range of CECs in Great Lakes water and sediment (reviewed in [21]). Perhaps the most comprehensive study to date of CEC distribution in the Great Lakes was conducted by [18] and included almost 300 water and 80 sediment samples collected across seven US tributaries to the Great Lakes. CECs were omnipresent and in complex mixtures containing chemicals from several classes of CECs. Despite the frequency of occurrence, total estrogenicity was generally low (<10 ng/L), and seldom exceeded concentrations that would suggest alterations to exposed biota [22]. However, even low concentrations of estrogenic compounds can have lasting effects on fish populations under chronic conditions, as illustrated by the collapse of a fathead minnow (*Pimephales promelas*) population in an experimentally exposed Canadian lake [23]. Here the collapse of this forage fish population initiated a subsequent decline in predatory fish species [24, 25]. This outcome highlights food web alterations as a result of CEC exposure may impact species not directly affected by contaminants [8]. CECs may also be transferred across trophic levels; Heynen et al. [26] demonstrated the biomagnification potential of the anxiolytic drug oxazepam in the Eurasian perch (*Perca fluviatilis*). A moderate biomagnification factor for oxazepam resulted in reduced wet weight in perch, suggesting trophic transfer in addition to direct exposure may be of relevance to the assessment of CEC effects [26].

Further analysis of CEC data from [18] highlighted the presence of CECs in complex mixtures that reflect surrounding urban or agricultural land use [27]. The pervasive presence of CECs in Great Lakes tributaries and their occurrence in complex mixtures with diverse modes of action presented challenges to elucidate the biological effects of these mixtures on aquatic life. Of particular concern to natural resource managers should be the common exceedance of water-quality benchmarks by CECs at multiple sites in the Great Lakes [18]. These exceedances were often linked to legacy compounds such as PAHs; however detergent metabolites, plasticizers, and pesticides were also found to exceed water-quality benchmarks or screening values at several study sites [28, 29]. Similarly, [30] measured CECs in the Great Lakes at concentrations demonstrated in laboratory studies to cause adverse biological effects.

The multitude of studies documenting presence and concentrations of CECs in the Great Lakes highlight the complexity and site specificity of CECs' occurrence. As a result, further studies and modeling efforts are required to provide resource managers with better tools to evaluate the likelihood that CECs may substantially impede the recovery or conservation of species at any given site. A recent modeling effort by [31] successfully associated broad land-use characteristics with the presence of CECs in tributaries of the Great Lakes. Critically, their models derived more information from land use than from the presence of point sources, suggesting both urban and agricultural runoff are important contributors to CEC presence in the Great Lakes. Many environmental studies of CEC occurrence and effects have focused on point-source pollution, especially the release of treated municipal wastewater effluent. Although this point source is undoubtedly a pathway for CECs to enter the Great Lakes [18, 28, 32], overland runoff as a pathway for CEC pollution to aquatic environments is less understood. A limited number of studies have demonstrated overland runoff may contribute similar estrogenic potencies to receiving waters as wastewater effluent [33] and can match treated municipal wastewater in CEC composition and concentration [34]. Even effluent discharge from residential on-site septic systems, which are common along tributaries to the Great Lakes, have the potential to add CECs to nearby aquatic ecosystems [35, 36]. Collectively, these studies represent convincing evidence that CECs are pervasive throughout the Great Lakes watershed, enter the aquatic environment through overland runoff and point-source pollution, and are biologically available to aquatic organisms at concentrations that may result in adverse health effects.

3 Resident Fish Studies

Over the past 20 years, a plethora of laboratory studies have raised the specter that CECs may adversely affect fish behavior [37–39], morphology [13, 40, 41], physiology [42–45], and reproductive fitness [46, 47]. These laboratory findings have been corroborated by field studies that demonstrated changes to biological functioning in resident fish populations at sites with CEC presence. For example, two studies documented the widespread occurrence of intersex (combined presence of male and female reproductive tissues in a single organism) in fish downstream of wastewater treatment plants in the UK and USA, respectively [13, 48], and also documented the presence of estrogenic CECs known to feminize male fish. The presence of the egg yolk precursor protein, vitellogenin, in male fish at concentrations similar to those in gravid females has become a well-established indicator of acute exposure to estrogenic endocrine CECs [49]. Studies of resident fish in the Great Lakes watershed have also aligned CEC occurrence with adverse biological outcomes. Endocrine-mediated effects of dioxins, PCBs, and pulp and paper mill effluent in Great Lakes fish populations were highlighted by Ankley and Giesy [7]. Niemuth et al. [50] demonstrated that concentrations of the antidiabetic pharmaceutical metformin at concentrations previously documented in Lake Michigan [30] may cause endocrine disruption. Similarly, Kavanagh et al. [51] linked exposure to estrogenic CECs from treated municipal wastewater discharge with high plasma vitellogenin concentrations and incidence of intersex in male fish in Lake Ontario.

Across US tributaries of the Great Lakes, Choy et al. [52] documented the ubiquitous presence of CECs in sediment, water, and fish tissue. In a related study of biological effects, Thomas et al. [5] associated changes in the reproductive health of sunfish (*Lepomis* ssp.) with the presence of CECs in six Great Lakes tributaries. Similarly, Jorgenson et al. [22] linked CEC presence to changes in biological function in resident sunfish, largemouth bass (*Micropterus salmoides*), and white sucker. Interestingly, different species and sexes altered different physiological processes. In the presence of CECs, liver health indices were altered in female bass, while male bass exhibited signs of altered organismal health indices.

In female white sucker, reproductive parameters were affected, while males also exhibited signs of both altered liver function. Organismal health indices were impacted in sunfish of both sexes [22]. However, all of these studies are hampered in their interpretation by the inability to causally link effects observed in resident fish to the documented presence of CECs. This is due in part to the complexity of aquatic systems, the uncertain exposure history of sampled resident fish, environmental variables, and ephemeral occurrence and concentrations of CECs in complex mixtures. Effects of CECs may occur in concert with effects of other environmental stressors or be antagonistic, exacerbating or inhibiting the effects of other environmental stressors [53].

4 Caged Fish Studies

Assessment of resident fish is instructive in determining the combined biological effects of multiple stressors. More controlled studies, using mesocosms or hatchery-reared fish caged in stream for weeks or months, may contribute additional information to approaches' causality [18, 54–56]. The known exposure history of caged fish, the similar length of exposure, and the spatial constraint of their movement through caging provide sufficient evidence to generate a causal linkage between CEC presence, exposure, and biological effects [54, 55].

Caged fish studies conducted in US Great Lakes tributaries illustrate the complexity of multiple stressors and their combined impact on caged sunfish [5]. Hatchery-reared sunfish caged at 27 field sites across six tributaries documented consistent biological effects commonly associated with exposure to CECs, especially high concentrations of the egg yolk precursor protein vitellogenin in the plasma of male fish. These changes were also associated with morphological changes in the liver, the organ responsible for vitellogenin biosynthesis, and a decline in reproductive fitness [5]. Misdirection of energetic resources either to detoxify CECs or to produce unwarranted proteins such as vitellogenin were a common integer in many of the above cited examples. Increased metabolic expense as a result of pollutant stress may interact with other environmental stressors commonly documented in Great Lakes tributaries (e.g., habitat degradation, low dissolved oxygen, invasive species) to raise core energetic needs at the expense of reproductive fitness [57, 58].

An in-depth assessment of sunfish health in a major tributary of the Great Lakes, the Maumee River, confirmed both the frequent presence of CECs in these waterways and the subtle biological effects of sunfish caged at seven sites throughout the watershed [59]. Water, sediment, and fish tissue chemistry identified CECs in every sample with pesticides and pharmaceuticals most commonly detected in all matrices. Biological effects were consistent with a biological stress response and increased at downstream sites where urban influence adds to the agricultural pollutant load of the river [59]. This study compared effects in caged and resident fish and found the latter to be more impacted by exposure, suggesting a temporal component in the expression of adverse effects of CEC exposure.

5 On-Site Laboratory Studies

Assessing biological impacts of CECs across a range of field sites while controlling for other stressors (nutrient availability, dissolved oxygen, etc.) has been accomplished through on-site laboratory studies. This approach has a long and successful history creating causal linkage between exposures and effects (e.g., [60–63]). Using this approach, Hanson and Larsson [64] demonstrated higher 7-ethoxyresorufin-*O*-deethylase (EROD) activity, indicating activation of detoxification pathways, in rainbow trout supplied with leachate contaminated stream water. Minarik et al. [65] used an on-site laboratory trailer in the Chicago metropolitan area to expose male fathead minnows in a flow-through system to environmental waters upstream and downstream of wastewater effluent discharge while controlling for dissolved oxygen, temperature, photoperiod, and diet. Effluent exposure and the presence of estrogenic CECs was linked to high plasma vitellogenin concentrations and reductions in the expression of secondary sex characteristics. Cipoletti et al. [66] exposed fathead minnow breeding pairs to waters from eight sites along the Maumee River (Lake Erie) and documented reduced fecundity as the most sensitive exposure endpoint. This was a surprising finding as the total estrogenic potential of the water was low and as there were only subtle changes in other biomarkers frequently associated with endocrine disruption [66] suggesting that overall pollutant stress may have diverted metabolic energy from reproduction.

To build on the existing literature, a case study was conducted in 2017 and repeated in 2018 in the Milwaukee River watershed (Lake Michigan) to assess the effects of land use on CEC presence and biological consequences. Breeding pairs of fathead minnows were exposed to waters collected from six field sites (Fig. 2a) and two controls for 21 days while monitoring reproduction and indicators of fish health (body condition factor, plasma vitellogenin). Twenty breeding pairs of fathead minnows were employed per treatment (=site) in 2 L aquaria and exposed to site-specific waters through daily 50% static renewal exchanges following previously developed methodology [65, 66]. Weekly water analysis identified a range of CECs corresponding to land-use characteristics ranging from agricultural to densely urban and industrial (Fig. 2b).

Analysis of CEC presence and concentrations at each field sampling site (Fig. 2b, composite of three weekly samples) indicates more CECs were present and at higher concentrations in 2017 than 2018. This finding held true at all field sites and highlights the ephemeral and multisource nature of CECs. Rain preceded the 2017 field season which may have resulted in the transport of CECs from the landscape into the aquatic environment. In contrast, little precipitation prior to or during the exposure in 2018 may explain the reduced presence of CECs in the second study year. Despite these annual differences, most field sites tracked closely together in total chemical composition across the 2 years of study (Fig. 2c) suggesting that despite the ephemeral nature of CECs, site-specific conditions may prevail for years. Only the KKL site differed considerably from all other sites and also differed considerably in land use as it was the only densely industrial site assessed in this study. Densely industrial sites, commonly located near river estuaries around the

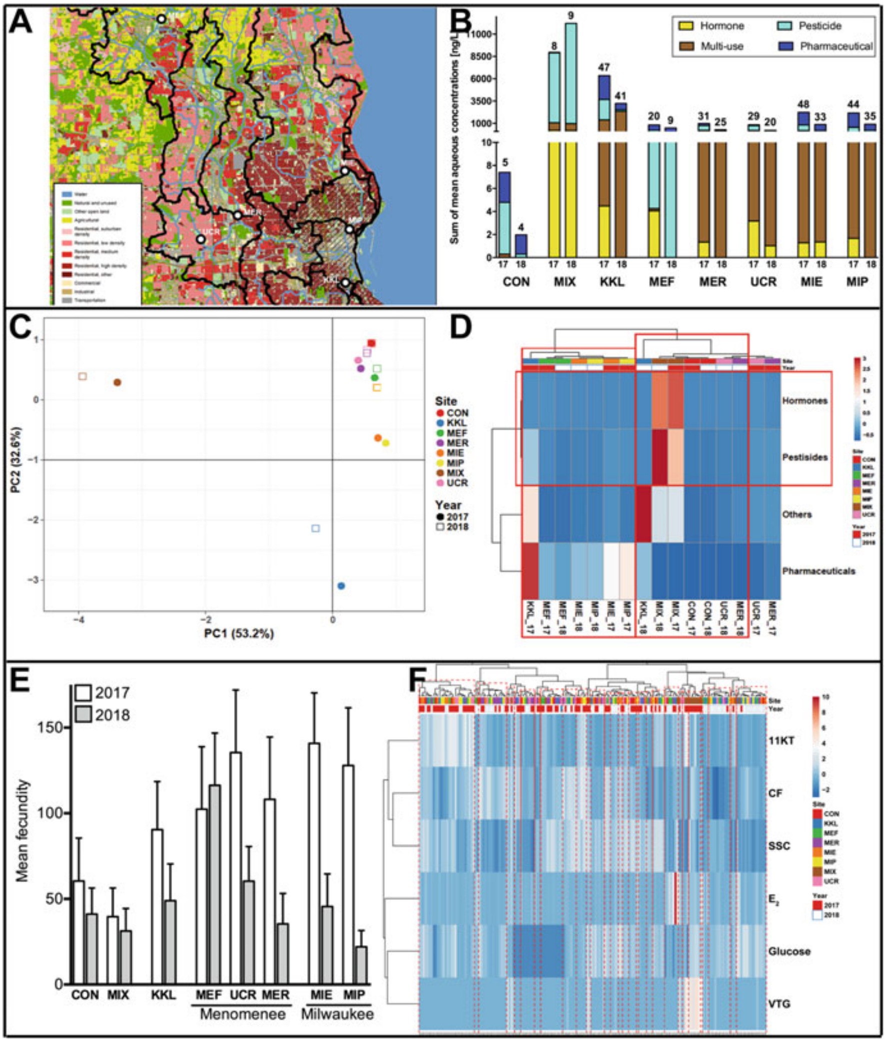

Fig. 2 On-site laboratory exposure studies to ascertain site-specific exposure effects using river water samples. (**a**) Six sites in Milwaukee River watershed were assessed in 2017 and in 2018 together with a negative and positive control water. (**b**) Confirmatory chemistry with CECs grouped into four categories. (**c**) Principal component analysis (PCA) of chemistry by site. (**d**) Cluster analysis by site and CEC category. (**e**) Mean (and standard error) fecundity of female fathead minnows exposed for 21 days to site-specific waters in 2017 and 2018. (**f**) Cluster analysis of biological effects by site for male fathead minnows. All data standardized by endpoint and analyzed using ClustVis [67] for PCA and hierarchical clustering with heat map. Pvclust package [68] on R Studio [69] identified significant differences among clusters using approximately unbiased probability ($p < 0.05$) based on a multiscale bootstrap of 10,000 times using average distances and a correlation matrix

Great Lakes and in proximity of harbors, are seldom studied in the context of CEC effects and may require more attention in the future, especially give their proximity to ecologically critical fish habitats. A cluster analysis of chemical categories and sites (Fig. 2d) reveals a grouping of hormones and pesticides and offsets these two chemical categories from pharmaceuticals and other CECs. These clusters persisted across study years.

A surprising biological finding of this case study was the stimulating effect of all environmental water mixtures to fathead minnow fecundity when compared to controls (Fig. 2e). Counterintuitively, control females had lower fecundity than females from all environmental treatments in 2017 and from most environmental treatments in 2018 (except MIP). At any given site, fecundity was significantly lower for females exposed to environmental samples from most field sites in 2018 even though control fecundity did not differ significantly between study years. Especially female minnows exposed to waters from urbanized and industrial sites (KKL, MER, MIE, MIP) experience significantly reduced fecundity in 2018 despite the lower concentration of CECs when compared to 2017. Lastly, a cluster analysis of all measured biological effects across years and field sites (Fig. 2f) provided little resolution, suggesting that the observed effects were either widespread or subtle.

6 Controlled Laboratory Studies

Although on-site laboratory studies may constrain many stressors, the physico-chemical conditions prevalent at each field site are impossible to fully control for in a laboratory setting. In addition, it is logistically difficult to maintain temporary laboratory infrastructure at field sites for long periods of time. To further control for environmental conditions, laboratory exposure studies have frequently been employed. In the past two decades, thousands of fish exposure studies have been conducted to elucidate the detrimental effects of CECs [70–73]. Often these studies have utilized standard laboratory model species such as fathead minnow and Japanese medaka (*Oryzias latipes* [63]). The majority of these studies used short-term exposures (days to weeks) with one chemical at multiple concentrations or simple mixtures of a limited number of chemicals with assumed similar modes of action [74, 75].

Estrogenic CECs including natural and synthetic estrogens (estrone, 17β-estradiol, ethynylestradiol) and alkylphenolic detergents have been shown repeatedly to feminize male fish [13, 42, 43, 61]. Mood-altering pharmaceuticals are known to alter fish behavior and reduce survival [39, 76]. Relatively few studies, however, have examined the complexity of environmental mixtures of multiple modes of action (reviewed by [77, 78]). When fish are exposed to complex mixtures of CECs, effects are rarely readily predictable from individual compound exposure and may be additive, antagonistic, and in rare cases synergistic [53, 74, 78]. At the same time, chemical mixtures, especially containing multiple pharmaceuticals, may present a “therapeutic effect” where the observed effect superficially appears to be positive [39, 79].

A paucity of life cycle studies further complicates the assessment of complex mixtures of CECs at environmentally relevant concentrations. Life cycle studies often document greater sensitivity than short-term acute exposure studies. For example, life cycle exposure of fathead minnows to the synthetic estrogen ethynylestradiol yielded lowest observed effects concentrations below 1 ng/L – well below prior estimates from short-term exposure studies [47]. Elliott et al. [80] exposed early life stages of fathead minnows and sunfish to 17β-estradiol at environmentally realistic concentrations and documented physiological and reproductive fitness effects that differed across generations and species. Using a mixture of multiple pharmaceuticals in a pond-like system [81] highlighted the prolonged bioavailability of some, but not all, pharmaceuticals under seminatural conditions.

To comprehensively investigate the effects of complex mixtures of CECs as they commonly occur in the environment [27], multi-chemical multigenerational exposures are needed. A case study was conducted utilizing the extensive chemical data set established by [18]. A cluster analysis identified a complex mixture consisting of 11 CECs commonly occurring in Great Lakes tributaries associated with urban land use. Fathead minnows were exposed over subsequent generations to this mixture at six concentrations representing a 220-fold increase in concentration from environmentally common to worst-case scenarios (Fig. 3a and Table 1). Breeding pairs of mature fathead minnows were randomly assigned to 5 L aquaria containing a spawning tile and aeration. Twenty spawning pairs (F1 generation) were assigned to each treatment and received contiguous flow-through exposure to the corresponding CEC mixture for the duration of the study (~300 days). Following 21 days of exposure, fecundity of each spawning pair was tracked for the next 40 days. Larvae obtained during this time were used to establish the F2 generation. Upon reaching maturity, second-generation fathead minnows, which had been exposed for their entire life cycle, were paired, and fecundity was again monitored for 40 days similar to F1 generation adults. Adults from both generations were euthanized at the end of their respective spawning period and assessed for changes in physiological parameters.

The resultant physiological data indicate that male fathead minnows respond to the estrogenic nature of the CEC mixture through the biosynthesis of vitellogenin soon after the exposure commences (Fig. 3b). However, this response was absent in the second generation of exposure where vitellogenin returns to baseline (control) concentrations suggesting a compensatory response or lack of responsiveness in adopted (survived) fish. Similarly, female fathead minnows produce less plasma vitellogenin following CEC exposure in the F1 generation but also rebound to control (high) concentrations in the F2 generation. These data highlight the often transient nature of CEC exposure effects at environmentally relevant concentrations and emphasize the ability of exposed organisms to adapt to adverse CEC conditions over time. An anecdotal field study of a thriving carp population trapped in an estrogenic effluent similarly demonstrated robust population size despite overt signs of estrogenic CEC exposure [65].

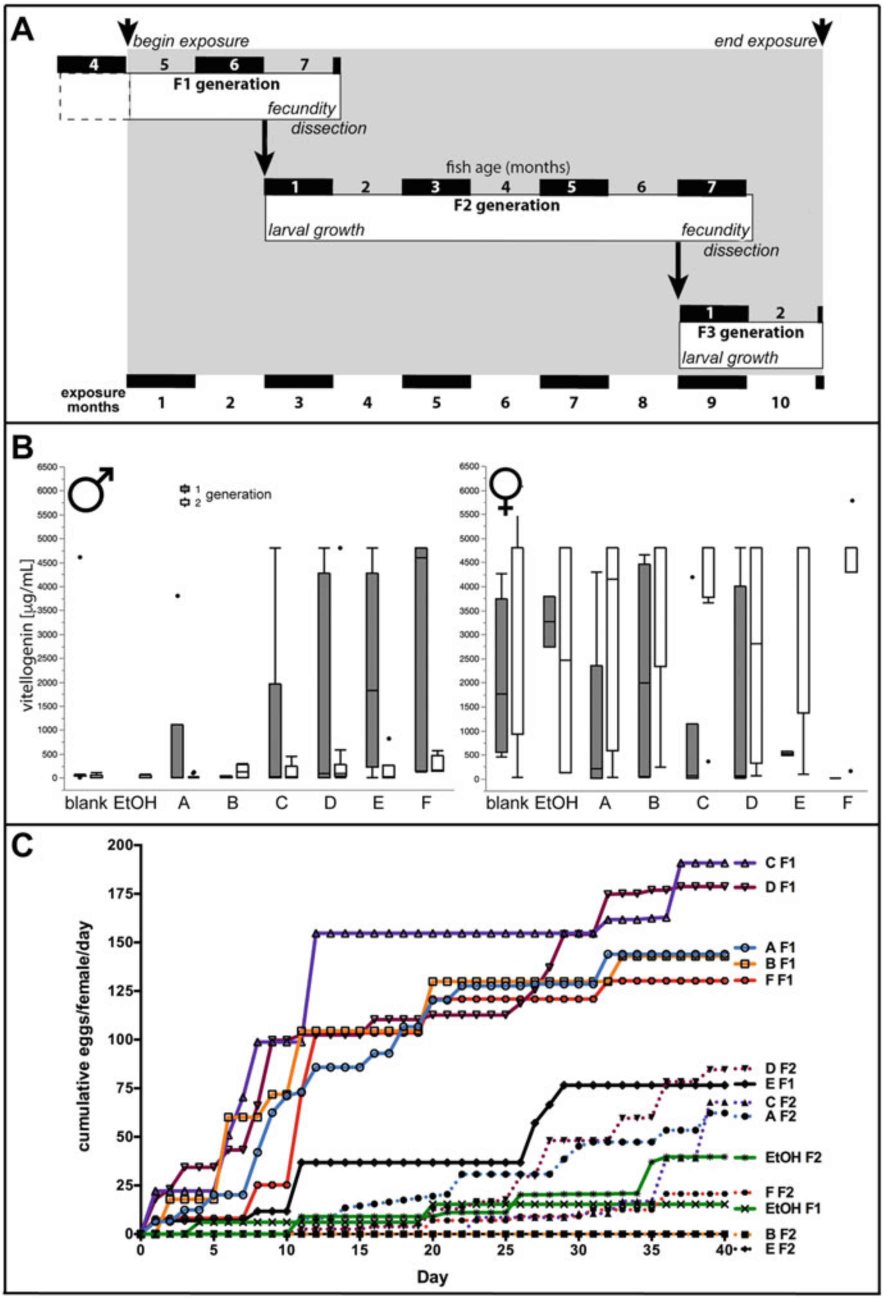

Fig. 3 Multigenerational laboratory exposure of fathead minnows to mixtures of CECs. (**a**) Experimental design; (**b**) plasma vitellogenin concentrations in male (left) and female minnows across two generations of exposure; (**c**) reproductive success monitored over 40 days each in minnows (ANOVA with Holm-Sidak multiple comparison correction). Mixture concentration increases from a total of 721 ng/L (sum of 11 CECs; mixture *A*) to 158,087 ng/L in the highest concentration mixture (*F*). Mean CEC concentrations in Table 1

Table 1 Mean and standard deviation of measured concentrations (ng/L) of each chemical in mixture: 4-nonylphenol, 5-methyl-1H-benzotriazole (5-MeBt), bisphenol-A (BPA), desvenlafaxine, estrone, fexofenadine, hexahydrohexamethyl cyclopentabenzopyran (HHCB), metformin, *N*,*N*-diethyl-3-methylbenzamide (DEET), sulfamethoxazole, and tributoxy ethyl phosphate (TBEP) across ethanol carrier control (EtOH), and six complex mixtures (solutions *A*–*F* with chemical concentrations in solution *D* equals highest measured environmental concentration)

	Treatment	EtOH	*A*	*B*	*C*	*D*	*E*	*F*
	Head tank (*n*)	7 (6)	4&8 (27)	1 (12)	6 (25)	3&5 (39)	9 (11)	2 (25)
4-Nonylphenol (detection limit = 100)	Average ± SD	6 ± 0	44 ± 98	133 ± 104	322 ± 895	1,202 ± 956	3,154 ± 3,662	9,243 ± 11,261
5-MeBt (DL = 5)	Average ± SD	0 ± 0	137 ± 286	143 ± 494	2,821 ± 10,237	3,174 ± 2,477	19,297 ± 24,707	49,054 ± 3,429
BPA (DL = 100)	Average ± SD	0 ± 0	132 ± 327	30 ± 104	164 ± 182	1,817 ± 1,492	7,555 ± 8,490	17,961 ± 26,958
Desvenlafaxine (DL = 5)	Average ± SD	0 ± 0	38 ± 81	17 ± 51	246 ± 790	492 ± 367	2,893 ± 4,089	5,658 ± 5,226
Estrone (DL = 20)	Average ± SD	nm	nm	nm	nm	nm	m	nm
Fexofenadine (DL = 20)	Average ± SD	0 ± 0	69 ± 135	43 ± 107	302 ± 651	966 ± 645	5,280 ± 5,789	10,332 ± 8,994
HHCB (DL = 50)	Average ± SD	0 ± 0	2 ± 12	20 ± 68	69 ± 170	1,396 ± 5,457	1,852 ± 2,430	3,613 ± 3,663
Metformin (DL = 20)	Average ± SD	0 ± 0	45 ± 113	35 ± 121	249 ± 690	997 ± 674	4,460 ± 4,804	9,591 ± 7,641
DEET (DL = 5)	Average ± SD	0 ± 0	87 ± 133	67 ± 83	202 ± 256	1,263 ± 938	4,413 ± 5,010	10,127 ± 11,109
Sulfamethoxazole (DL = 10)	Average ± SD	0 ± 0	10 ± 24	12 ± 26	19 ± 61	122 ± 101	656 ± 697	1,814 ± 2,035
TBEP (DL = 100)	Average ± SD	0 ± 0	157 ± 357	941 ± 1,885	838 ± 1,041	11,284 ± 37,638	19,126 ± 17,714	40,694 ± 44,790
Sum of concentrations		6	721	1,441	5,232	22,713	68,686	158,087

Effects of CEC exposure on reproductive output in fathead minnow spawning pairs over two generations were equally complex (Fig. 3c). In the first generation, all CEC solutions appeared to have a stimulatory effect on reproduction in fathead minnow spawning pairs by increasing fecundity above solvent control concentrations. However, this effect was muted in the second generation where females exposed to the two highest concentration CEC mixtures produced less eggs than solvent control females. The stimulatory effect observed in the first generation mirrors observation from the Milwaukee River watershed case study described above. This effect previously has been coined “therapeutic effect” to highlight that seemingly beneficial enhanced egg production as a result of an artificial stimulus such as CEC presence. However, this effect may not be sustainable in the absence of improved habitat conditions [79].

7 Strategies to Link CECs to Observed Biological Effects

The ubiquity of CECs, complex mixtures throughout the Great Lakes watershed, and paucity of effects/causation of CEC impacts from field investigations to laboratory studies challenge the prioritization of CECs. The development of water-quality benchmarks and screening values may assist natural resource managers in assessing risk to fish populations and developing management recommendations to achieve restoration or conservation goals.

Gefell et al. [82] developed screening values for 14 CECs in water (Table 2). A set of comprehensive and population-relevant SV_{HIGH} and SV_{LOW} values was developed for each CEC using all adverse effects reported in peer-reviewed literature. SV_{LOW} was the threshold concentration defined at or below which a CEC is unlikely to cause an effect to fish, while SV_{HIGH} was defined as the threshold concentration at or above which a fish is likely to encounter an adverse effect. Water-quality benchmarks have been developed by environmental agencies and have been used to assess potential impacts of CECs to aquatic resources [28]. However, these benchmarks and screening values only represent a fraction of the CECs being detected in aquatic systems. Indeed, the effort to develop screening values by [29, 82] was limited by the lack of sufficient data for many other CECs (Gefell, pers. comm.). For example, pharmaceuticals such as statins, mood altering drugs, and antidiabetic medications lack sufficient adverse effect data to derive screening values despite their common detection in the environment.

Despite their limited number, the available benchmarks and screening values represent valuable tools for assessing adverse biological effects to fish as they allow for the ranking of stream segments based on CEC measurements. In addition, [82] grouped literature results into five effect categories for population-relevant screening values (behavioral, developmental, growth, mortality, and reproductive) and seven detailed effect categories for comprehensive screening values (circulatory/blood constituents, endocrine, genotoxicity, gross pathology, histopathology, neurological, physiology/metabolism; Table 2). These focused effect categories can provide

Table 2 Comprehensive and population-relevant SV_{HIGH} and SV_{LOW} values with the associated effects categories for each CEC, as developed in Gefell et al. [29, 82]

	Comprehensive		Population-relevant		Effect category											
CEC	SV_{HIGH} (µg/L)	SV_{LOW} (µg/L)	SV_{HIGH} (µg/L)	SV_{LOW} (µg/L)	Circulatory/ blood constituents	Endocrine	Genotoxicity	Gross pathology	Histopathology	Neurological	Physiology/ metabolism	Behavioral	Developmental	Growth	Mortality	Reproductive
4-Androstene-3,17-dione	0.852	0.000204	3.23	0.00127										X		
Bisphenol A	118	0.0318	177	0.062				X				X	X	X	X	X
Carbamazepine	139	0.00865	299	0.0788	X				X	X	X	X	X	X	X	X
Citalopram	0.222	0.000102	0.237	0.000254								X				
DEET	22	0.0236	7,098	0.00127	X	X									X	
Diphenhydramine	1.26	0.00846	3.35	0.0527								X	X			
Estrone	0.00665	0.0000144	0.0186	0.000115							X	X	X			X
HHCB	21.3	0.0649	60.2	0.91							X	X	X	X	X	
Ibuprofen	10.5	0.0153	0.822	0.00417	X	X	X				X		X		X	X
Lidocaine	890	2.4	949	5.98								X				
β-Sitosterol	18.4	0.0604	101	0.171	X							X	X			
TBEP	267	0.448	511	1.67								X	X		X	
Triclosan	12.8	0.00254	40.8	0.00286								X	X		X	X
Venlafaxine	0.155	0.000638	0.285	0.0026		X			X			X			X	X

natural resource managers with insights into possible linkages between the occurrence of specific CECs and adverse health effects observed in fish populations (Table 2).

Observed exceedances of water-quality benchmarks and screening values [28, 29] direct natural resource managers toward individual and population-relevant endpoints. For example, atrazine and BPA have been shown to elicit changes in reproductive biology and physiology of a variety of species [83]. Gefell et al. [29] also observed hazards associated with developmental, growth, reproductive, and gross pathology effect categories in greater than ten project locations across the Great Lakes basin due to BPA exceeding screening value thresholds.

However, linking screening values and water-quality benchmarks to observed biological effects may be challenging especially when mixtures of CECs are present. Aquatic ecosystems are complex and variable by season in terms of biological activity, contaminant occurrence, concentrations, and mixtures [8, 18, 28, 84–89]. In addition, biological or physiological changes observed in individual fish or populations may not be solely caused by CEC exposure. Thus, it is prudent to use water-quality benchmarks or screening values in concert with other monitoring efforts to better understand the contribution of CEC exposure to fish health.

8 Obstacles to Resource Management Solutions

The presence of CECs and their known biological effects present challenges for natural resource managers in their quest to assess, remediate, mitigate, reverse, or arrest the effects of CECs in ecosystems. Many of the CECs currently being evaluated are inherently involved in the health and sustainment of human life and will likely remain a presence in aquatic ecosystems. Therefore, it is critical for natural resource managers to have a variety of realistic management actions available to cope with the presence of CECs and meeting fish population restoration and conservation objectives.

Nilsen et al. [8] examined the challenges associated with determining effects of CECs on organisms and aquatic food webs and identified data gaps. These include the complexity of CEC mixture effects, sublethal exposure effects, multigenerational CEC exposure, multi-stressor impacts, and CEC effects across food webs [8]. Many of these data gaps stifle the development of effective resource management tools.

Natural resource managers also face practical obstacles such as CEC analysis cost when developing management solutions for CEC. Analyzing for diverse CECs may cost several thousand dollars per sample. This imposes a significant financial burden for natural resource managers with a limited budget. For example, if a watershed or wildlife refuge manager would develop an monitoring protocol to included 50 water and 50 sediment samples, the budget could easily exceed $500,000/year. Natural resource managers need to constrain which CECs should be monitored based on putative upstream pollutants sources and observed environmental effects. Several common CEC mixtures have been identified [18, 88], and hydrological models have been developed to predict the presence of CECs based on land-use characteristics [31]. These findings could guide resource managers as to which CECs might be best targeted for monitoring.

However, given the paucity of water-quality benchmarks and screening values for the plurality of CECs, it remains unclear which are most harmful in the aquatic ecosystem. Using water-quality benchmarks and screening values provides a point of departure to determine if CECs may pose a risk to aquatic ecosystem health, but they are not the definitive tool for answering the question "do CECs impose adverse risk to fish populations?". Davis et al. [45] examined metabolic effects in an effort to help prioritize CEC assessments. While promising, it is still unclear if changes in metabolomics observed were due to CEC exposure or other environmental factors and at what concentrations metabolic responses signal potential population level effects. However, several studies described above highlighted metabolic stress and the associated diversion of energy from reproductive process [5, 56, 59] signaling potential population level effects. The next step is to determine which CECs or mixtures of CECs pose the greatest risk to individuals or populations [8] and to then determine how mitigating those effects will lead to better natural resource management solutions.

The need for monitoring of CECs in conjunction with long-term population and community assemblage assessment is needed to determine the effects of CECs in environmental systems. Real-world monitoring of systems being managed for fish population conservation or restoration efforts will provide insight into how stressors acting in concert with CECs are impacting fish populations. Translating the current scientific literature on individual impacts into population-relevant effects also remains a challenge. Literature which focuses on impacts to individuals, while valuable for understanding effects of CECs, frequently does not extrapolate to population-relevant impacts [17, 38, 45, 46, 51, 88, 89]. Answering the questions "do individual effects lead to population level effects or are these individual effects then represented in compensatory mortality in populations?" will lead to the formulation of better solutions for natural resource managers.

Understanding how chemicals change and degrade once they enter aquatic ecosystems and assessing the toxicity of those by-products presents additional challenges. For example, phototransformation products of naproxen are more toxic than the parent compound when present singularly or in mixtures with each other and naproxen [90]. Metcalfe et al. [87] also found evidence of CEC parent and derivative compounds persisting in the environment in complex mixture and accumulating in fish tissues. A greater understanding of how CECs behave in aquatic ecosystems from "cradle to grave" is needed to fully understand the effects from CEC exposure on aquatic organisms.

Differences in effects of CECs between freshwater and marine organisms have been found along with differences in effects at different life stages with younger organisms often showing increased impacts [22, 24, 88]. Where the water-quality benchmark or screening values are sufficient to protect the most sensitive species and population is uncertain [91]. Utilizing in vitro transactivation assay customized for each species [92] may provide a tool extrapolate effects across species, especially to those of special conservation status, to directly address management concerns for species found in each management area. Better understanding how different species are affected by CECs can lead to better species-specific management recommendations.

The paucity of scientific literature on the effectiveness of remedies to CEC presence or remediation in the environment remains an additional challenge for the development of meaningful natural resource management solutions. Much of the current scientific literature for contaminant remediation is on legacy contaminants, mining contaminants, or single incident contaminant remediation [93–96]. Solutions such as dredging, substrate removal, capping, or eliminating point sources, while effective for the cleanup of superfund sites or single incident contamination release [93–95], are not plausible solutions for CEC remediation. CECs are pervasive in aquatic systems because of their continual use in daily human life and are therefore released continually into the environment creating pseudo-persistent conditions [97]. Phytoremediation or wetland treatment ponds have been effective at removing contaminants associated with agricultural processes and other hazardous chemicals [95, 98, 99], but their effectiveness for CEC removal has not been evaluated. Having plausible and economically feasible solutions that are grounded in sound scientific evidence ready for natural resource managers is needed to ensure best management practices are being developed. The lack of these solutions has left natural resource managers with the question of “How do we overcome the impacts of CECs on fisheries conservation strategies?” still remains to be resolved.

9 Conclusions

CECs are a ubiquitous presence in all matrices throughout the Great Lakes watershed with little expectation of unimpacted reference sites to be used as calibration points for the impacts of CECs on aquatic life. CEC composition and concentrations likely increase along an upstream to downstream gradient with many Great Lakes tributaries being defined by agricultural land-use upstream and urban/industrial land use in downstream reaches. The complex mixture of CECs, especially in riverine estuaries and lakeshore wetlands, presents a challenge to natural resource managers as evidence is accumulating for the presence of some CECs at concentrations exceeding aquatic health benchmarks or screening values indicative of adverse effects. Evidence for the biological effects of CEC exposure to fish populations residing in Great Lakes tributaries is also building and being contributed to from a continuum of studies spanning the range from resident fish assessment to controlled laboratory exposures. It is clear that CECs, their complex mixtures, and their interactions with other environmental stressors may impact fish morphology, physiology, and behavior, ultimately diverting energy from exposed organisms that otherwise would be available to enhance reproductive fitness. Natural resource managers will be tasked with evaluating the effects of CECs while planning actions to support or restore fish populations. Screening values and water/sediment quality benchmarks are valuable tools natural resource managers can use to assess potential risks to fish exposed to CECs. They can help guide managers to expected impacts and effects possibly caused by CECs or be used as early warning signals for when impacts may occur if used in conjunction with monitoring activities. Using these values in concert with recently developed hydrological models for the occurrence of CECs in Great Lakes tributaries may narrow the range of CECs to be submitted for expense chemical analysis. But currently screening values and water/sediment quality benchmarks only exist for a small handful of CECs. Further development of these values for individual chemicals or for mixtures of chemical is needed to better guide natural resource managers of risks and impacts associated with CECs. Areas still in need of development for successful natural resource management solutions include cost-effective analyses, prioritization of CECs for monitoring, development of additional benchmarks and screening values, scientific evidence for successful remediation actions, and scientific evidence for technology upgrades to water treatment facilities.

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Part III
Monitoring and Modelling

Geochemical Approaches to Improve Nutrient Source Tracking in the Great Lakes

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Abstract Water quality issues that lead to freshwater eutrophication are a rapidly intensifying global concern, and the recent increase in eutrophic conditions in the Great Lakes has gained international attention. The Great Lakes account for over 85% of North America's freshwater supply and have had a history of water quality problems that peaked in the early 1970s with cultural eutrophication in Lake Erie. Despite many coordinated efforts that attempt to link eutrophication to phosphorus, it is becoming clear that knowledge gaps exist in understanding nutrient dynamics and their relationship to cyanobacterial biomass development across temporal and spatial scales. New geochemical approaches (compositional and isotopic) can improve our understanding of the relationships between the fundamental processes regulating nutrient dynamics from terrestrial and aquatic sources (biotic and abiotic) and the adaptive metabolic responses that promote cyanobacteria growth in different environmental conditions. An understanding of the underlying mechanisms responsible for the fate and transport of nutrients from point and non-point source emitters through to their final point of deposition (or metabolic uptake) will expose the causal links that drive primary production at each stage of the system and provide strategic targets to control eutrophication. A comprehensive understanding of the chemical and environmental factors that influence the measurement, monitoring, and identification of pollution sources responsible for water quality issues will lead to better policy decisions and long-term protection of our freshwater resources.

Keywords Chloride, CSIA, Isotope, Lake, Nitrate, Nutrient, Phosphate, Watershed

1 Introduction

Over the past century, rapid human population growth and widespread impacts of human activities on global environmental processes have caused a geochronological transition from the Holocene to the Anthropocene [1]. Atmospheric nitrogen deposition from fossil fuel combustion and industrial and agricultural sources have increased tenfold over background levels in vast regions of North America [2]. Elemental cycles and metabolic processes within ecosystems are changing, and the long-term effect of these changes on large lake systems is a concern. The Laurentian Great Lakes account for 21% of the world's and 85% of North America's supply of freshwater. They have had a history of water quality problems that peaked in the early 1970s with cultural eutrophication in Lake Erie. Carbon, nitrogen, and phosphorus inputs were studied as contributing elements, which stimulated changes in environmental policy to reduce phosphorus inputs into the Great Lakes [3]. These policy changes led to a decline in eutrophication through to the 1990s; however, increased frequency and severity of cyanobacterial blooms have occurred in some regions, particularly in Lake Erie and Lake St. Clair from the mid-1990s to 2015 [4]. The causes of these recent increases in cyanobacteria populations are not well understood, and their impacts have become a focus in recent studies [4–9].

Geochemical indicators (compositional and isotopic) can be used to identify sources, transport pathways, and biodegradation mechanisms of nutrients in freshwater. However, there is a wide range of biotic and abiotic processes that affect the transport, the recycling, and the fate of nutrients [10] that contribute to water quality issues in the Great Lakes. In many cases, phosphate (H_3PO_4, $H_2PO_4^{-}$, HPO_4^{2-}, PO_4^{3-}, denoted as PO_4) concentrations appear to be a controlling factor for cyanobacterial biomass development [11–13]; however, nitrate (NO_3^{-}) [14] and carbon dioxide (CO_2) concentrations [15–18] can be important factors for marine phytoplankton growth and may influence species composition in freshwater systems when PO_4 concentrations are not limiting [19].

The release of nutrients from lake sediments under anoxic conditions near the lake bottom is a recognized internal source of PO_4 (i.e., internal P-loading) [20]. Biological processes in sediments can be contributing factors to internal P-loading through gas production and consumption (methane, oxygen, and CO_2) [21], co-metabolism of nutrients [22, 23], and sediment agitation that can release nutrients from sediments [24–26]. Additional pressure from the deposition of organic matter from algal blooms leading to oxygen depletion can also cause a shift in metabolic pathways from the favored oxygenase pathway to the carboxylation pathway, which could enhance enzyme efficiency and growth of cyanobacteria [18, 27]. Although internal and external phosphorus loading may trigger cyanobacterial blooms, it is becoming clear that other nutrients, carbon and iron (Fe), are likely involved in controlling cyanobacterial species composition and other symptoms of eutrophication including the production of cyanotoxins [28].

Naturally occurring components of the water cycle can be used as environmental indicators to identify nutrient and contaminant sources as well as their transformation pathways in lakes and watersheds [29–32]. They differ from artificial tracers that are injected into the water cycle for the purpose of an investigation or experiment [10] and pollution or contaminant indicators, which are introduced into the water cycle from anthropogenic activity [31]. While not natural to the water cycle, contaminant indicators are often introduced in the same manner (point and non-point sources) as environmental indicators. Determining point and non-point sources of nutrients and contaminants using their geographical distribution of concentrations is difficult because seasonal variability can have a major impact on the indicators and physical circulation is dynamic in the Great Lakes [33]. The added complexity of seasonal variability on concentration-dependent indicators often requires large datasets comprised of densely sampled, multi-year monitoring programs to provide the insight needed to confidently address environmental concerns [34, 35]. New approaches that integrate stable isotope analysis of nutrients and contaminant indicators are growing in popularity as an effective way to track contaminants and their degradation products through the water cycle [36].

Compound-specific isotope analysis (CSIA) has been widely used as an approach to understand the fate and transport of natural and contaminant indicators in a wide range of environmental and industrial applications [37–42]. Geochemical processes that involve chemical bond-breaking will often produce a measurable change in the stable isotope ratio of environmental and contaminant indicators [43]. The change in isotope ratio arises from the difference in the reaction rates between indicators with heavy versus light isotope atoms, where a faster reaction rate for the light isotope results in heavy atom enrichment of the environmental and/or contaminant indicator as the geochemical processes proceed. The temporal change in isotope ratio over the course of the chemical process generates an enrichment value (ε) that is constant, concentration-independent, and only sensitive to processes that involve changes in chemical bonds [42, 44, 45]. Therefore, isotope measurements can provide a diagnostic of geochemical processes that overcomes many of the limitations associated with concentration-dependent indicators, often providing definitive environmental assessments without the need for multi-year monitoring programs [32].

Conservative indicators are typically more inert to chemical reactivity and isotopic fractionation. Distinct isotope ratios for conservative indicators can provide a robust approach to characterize source contributions and transport mechanisms in the environment. Alternatively, non-conservative indicators are typically metabolites and/or chemical species that are produced by different mechanisms/pathways and/or sensitive to chemical bond-breaking and isotope fractionation [35, 36]. Sensitivity to chemical bond changes can provide key insight into the processes (abiotic and biotic) impacting the environmental fate of these indicators through the hydrogeological cycle [35, 46]. Multi-indicator approaches combining concentration-independent/concentration-dependent and isotopic indicators can be used to develop a comprehensive understanding of the fate and transport of environmental and contaminant indicators for processes, residence times, and groundwater flow [10, 47].

2 Nitrate and Ammonia

Increasing concentrations of nitrogen from anthropogenic sources in Canada's surface and groundwater is a growing concern. NO_3^- concentrations in drinking water are a problem because of the severe health hazards associated with ingestion [48–50]. In 2013, Health Canada set the maximum acceptable NO_3^- concentration in drinking water at 45 mg/L [51]. However, cases have been observed linking adverse health effects with NO_3^- contaminated water at levels below this regulatory limit [50]. Ammonia (NH_3) and ammonium (NH_4^+) can be toxic to aquatic species at concentrations >19 μg/L [52, 53]. Over the past century, NO_3^- concentrations in the Great Lakes have increased substantially, with a fivefold increase observed in Lake Superior from the early 1900s to 2010s [54–56]. Based on available data from 1966 for Lake Ontario, 1968 for Lake Huron, and 1983 for Lake Michigan to 2013, NO_3^- and nitrite (NO_2^-) concentrations have become more stable in the later years [57], which may indicate greater nitrogen uptake and accumulation on the landscape. Lake Michigan NO_3^- concentrations are currently stable after experiencing a threefold increase in nitrogen concentrations between 1900 and 2000, and in Lake Ontario tributaries, a 60% increase in NO_3^- concentrations was observed between 1970 and 2000 [56, 58]. In both lakes, the increase in NO_3^- was attributed to various human activities including changes in land use and agricultural application of synthetic fertilizers [59]. In tributaries of Lake Erie which are influenced by greenhouse and traditional agricultural activity, concentrations of NO_3^-, other dissolved macronutrients, and metals have been found to be higher compared to traditional agriculture alone [35]. Although non-greenhouse and greenhouse influenced streams are still located within watersheds dominated by conventional grain and row-crop agriculture, recent research has illustrated how different agricultural practices can influence nutrients in rivers disproportionately to their spatial coverage in watersheds [35]. Lake Erie has the highest levels of primary productivity of all the Great Lakes, resulting in the highest biological uptake rates and reduction of NO_3^- contamination [60], although NO_3^- concentrations are also the highest [57]. Elevated NO_3^- concentrations in Lake Erie may require more stringent maintenance [55, 60, 61] with careful consideration for managing the relative abundance of nitrogen to phosphorus, which can influence the composition of toxin-producing cyanobacterial species [62, 63].

2.1 Stable Isotope Analysis: Nitrate and Ammonia

Nitrogen has two stable isotopes, ^{14}N and ^{15}N, with approximate abundances of 99.6% and 0.4%, respectively [10]. One of the benefits of using NO_3^- is that both nitrogen and oxygen stable isotopes are accessible as an isotopic indicator. Oxygen has three stable isotopes ^{16}O, ^{17}O, and ^{18}O with respective abundances of 99.76%, 0.04%, and 0.2% [64, 65]. Although the heavier isotope is less abundant in the natural environment, increased abundances are observed from anthropogenic sources [66, 67].

Dual-isotope CSIA (nitrogen and oxygen) is providing new insight into the characterization of the sources, fate, and transport mechanisms of NO_3^- in the environment [10, 68, 69]. Oxygen isotope exchange was an early concern with the use of NO_3^- isotopes in environmental systems. Equilibrium isotope fractionation between NO_3^- and water could scramble source signatures, limiting the use of this indicator. Soils were reported to have measurable oxygen exchange between water and NO_3^- [70]. It is not unexpected that biogeochemical processes will either use oxygen from water to generate NO_3^- or catalyze equilibrium exchange of the oxygen atom for NO_3^- in reversible processes. These processes could change source signatures as NO_3^- is transported through the watershed. However, direct abiotic equilibrium exchange between NO_3^- and water is too slow under typical environmental conditions to be a limiting factor in the use of NO_3^- isotopes as a geochemical indicator [69]. The slow abiotic exchange rates suggest that NO_3^- isotopes will be stable in the absence of biotic processes and will not have a major impact on $\delta^{18}O$ values. The non-conservative nature of nitrates as an environmental indicator may be a limitation to its application if the processes that affect the reported isotopic values are not well understood [71]. However, although complicated, the combined conservative nature for abiotic processes and non-conservative nature for biotic processes of NO_3^- isotopes provides new opportunities to use this indicator to track the fate, the transport (including residence times), and the microbial dynamics of NO_3^- through the watershed. An improved understanding of these dynamics can also be used as a proxy to better understand co-migrating nutrients and contaminants in the Great Lakes.

The use of NH_4^+ as an isotopic indicator has been proposed due to its natural abundance in surface water from fish excretion [72], decomposing organic matter [72], and runoff from livestock production [73]. NH_4^+ is less commonly used as an indicator due to its relatively quick conversions in the nitrogen cycle and vulnerability to larger isotopic effects than other nitrogen compounds [74]. However, both NO_3^- and NH_4^+ are frequently studied to develop site-specific management plans and implement remediation efforts [48]. Determining the origins of both NO_3^- and NH_4^+ can be complicated by the wide range of isotopic compositions originating from the multiple oxidation states of these nitrogenous compounds, which range from +5 for NO_3^- to −3 for NH_4^+ (ammonium) [75]. In the surface water of the Great Lakes, approximately 95% of all oxidized nitrogen is in the form of NO_3^- or NO_2^- [76]. The remaining 5% of total nitrogen content in water is composed of other compounds such as nitroxyl (HNO), nitrogen gas (N_2), hydroxylamine ($HONH_2$), and NH_4^+ [76, 77].

2.1.1 Nitrate Isotopes

Isotopic analysis for NO_3^- in water can be completed by both biological and chemical methods. Cascotti et al. proposed the biological denitrifier method, which uses the bacteria *Pseudomonas aureofaciens* to denitrify NO_3^- into nitrous oxide (N_2O) before analyzing $\delta^{18}O_{NO3^-}/\delta^{16}O_{NO3^-}$ [78]. However, Coplen et al. stated that $\delta^{15}N_{NO3^-}$ values may be overestimated by *P. aureofaciens* conversion to N_2O by 1–2 parts per thousand (ppt) due to preferential conversion of atmospheric NO_3^- [79]. The authors further suggested that the use of *Pseudomonas chlororaphis* as a denitrifying bacteria increases conversion of NO_3^- from water resulting in lower respective uncertainties of ±0.2 and ±0.3 ppt for $\delta^{15}N_{NO3^-}$ and $\delta^{18}O_{NO3^-}$ [79]. It is more common, however, for isotopic analysis of NO_3^- to be completed using gas chromatography-isotope ratio mass spectroscopy (GC-IRMS) [78–80].

A common chemical method of analyzing $\delta^{15}N$ in freshwater samples involves releasing the nitrates from the ion exchange collection method with hydrochloric acid (HCl) before bringing the solution to a neutral *p*H with silver (I) oxide (Ag_2O) [75]. This forms solid silver (I) chloride (AgCl), which can be filtered before the produced silver nitrate ($AgNO_3$) is combusted into N_2 [75]. An analysis method for $\delta^{18}O_{NO3^-}$ was described by Amberger and Schmidt where potassium (K) salts were added to produce KNO_3 before combustion with $Hg(CN)_2$ to make CO_2 [81]. This method was found to have a standard deviation of ±0.5‰ when laboratory standards were analyzed with mass spectroscopic analysis [75, 81]. Newer chemical methods determined $\delta^{15}N$ and $\delta^{18}O$ for NO_3^- and NO_2^- with standard deviations below +0.2‰ and +0.5‰, respectively [82]. First, NO_3^- is reduced to NO_2^- using spongy cadmium (cadmium and zinc) before reduction to N_2O under weakly acidic conditions with sodium azide [82]. An automated system is used to isolate the produced N_2O before it is analyzed by continuous flow GC-IRMS [82]. In comparison, the bacterial method is far more operator friendly and produces fewer toxic by-products than chemical methods making it the preferential analytical measurement technique for many researchers. More recently, a new chemical approach using titanium has emerged with a comparable precision to the bacterial and cadmium methods that gave reproducible $\delta^{15}N$ and $\delta^{18}O$ isotopic results as low as 50 ppb (3.5 μM) of NO_3^- [83]. The titanium reduction method is completed in a single step, has a lower toxicity, and does not require anaerobic bacterial cultures. The titanium method will likely be widely adopted for NO_3^- isotope analysis [83].

2.1.2 Ammonia Isotopes

There are three main methods to analyze $\delta^{15}N_{NH4^+}$ in water samples including (1) diffusion, (2) distillation, and (3) chemical methods. Diffusion methods bind NH_4^+ to acidified papers [84] or Teflon membranes [85] before combustion conversion into N_2 for mass spectrometric analysis. Steam distillation is used to remove N_2 from the sample before purification in a furnace with copper (Cu) and copper oxide (CuO) [84, 86]. The efficiency of distillation techniques is lower than diffusion methods as a result of the additional stability from hydrogen bonding between NH_4^+ and water [86]. More recently, chemical methods have been used to release N_2O gas for analysis methods that are comparable to NO_3^- isotopic analysis. Liu et al. proposed oxidation by hypobromite (BrO^-) to produce NO_2^- before using $HONH_2$ in the presence of a strong acid [87]. The resulting N_2O gas can be analyzed with purge and trap GC-IRMS, even in nanomolar concentrations, with a standard deviation of ±0.3‰ [87, 88].

For the purpose of source detection in surface and groundwater, source-representative samples must be characterized. Depending on the sample type, preparation for isotopic analysis may require deviations from standard procedures. Sampling procedures must be adapted to account for factors that may affect $\delta^{15}N$ contaminant material in the environment. For example, fertilizer or manure sources typically have variable isotope signatures due to nitrification and NH_3 volatilization which occurs following application to soil [75]. Soil samples for $\delta^{15}N$ of surface-applied manure may need to be collected from beneath the soil surface to limit the potential variability of the true source signature while collecting additional surface samples to account for localized variability from biotic processes [75]. Furthermore, care must be taken to exclude further contamination and isotope fractionation effects among samples collected from different media (e.g., water versus soil) and hold times ahead of laboratory analysis.

2.2 Reaction Pathways

Nitrogen reaction pathways and their effects on $\delta^{15}N$ in a water system are summarized in Fig. 1. Nitrate and NH_4^+ depositions are categorized under natural or anthropogenic sources. Nitrate dynamics in the water cycle is impacted by four main processes: nitrogen fixation, ammonification, nitrification, and denitrification [77]. There are many anthropogenic factors that influence microbial regulation of these reaction pathways, such as land use activities and climate change [89, 90]. When determining the source of nitrogen, it is important to consider that nitrogen sinks represent pools of accumulated nitrogen that are less accessible, such as in terrestrial soils, forest biomass, and marine sediments [90]. Less accessible nitrogen in the watershed can complicate source identification by either appearing as a different source or transitioning point sources to non-point sources over time. Other uncontrolled processes should also be considered, such as long transit times and legacy deposition for nitrogen that can result in delayed isotopic detection of effluxes from monitored sources [91].

Nitrogen reactive processes are dependent on microbial communities and the source of nitrogen. In Eq. (1), microorganisms use the nitrogenase enzyme to convert atmospheric nitrogen into a useable form [77, 92, 93]. Nitrogen fixation follows this process by converting atmospheric nitrogen into an active form before reacting with hydronium ions to produce NH_3 [92]. This process typically produces NH_3 that is depleted in ^{15}N relative to atmospheric nitrogen due to preferential fixation of the lighter isotope ^{14}N by plants and bacteria [75]. However, the extent of this fractionation is dependent on the microbial species, initial concentrations, and environmental conditions [75].

$$\underset{\text{NITROGEN GAS}}{N_2} + \underset{\text{HYDRONIUM}}{8\,H^+} \rightarrow \underset{\text{AMMONIA}}{2\,NH_3} + \underset{\text{HYDROGEN}}{H_2} \tag{1}$$

Nitrous oxides originating from the burning of fossil fuels are released directly into the atmosphere where they are converted into aqueous NO_3^- in precipitation or sorbed onto particulate matter [2, 77]. These wet and dry forms of nitrogen can be deposited directly into water bodies, and/or they can be deposited on the landscape and runoff into surface waters [94]. Nitrate from soils and fertilizers can directly enter the water system through surface runoff or leaching into the groundwater [77]. Plants contribute to biological fixation as they take up nitrogen sources to make chlorophyll for photosynthesis and different proteins [77]. Equation (2) depicts ammonification where organic nitrogen, such as proteins and nucleic acids from decaying organisms or animal waste, is converted into NH_4^+ [77, 95]. The fungi and bacteria that initiate this process use the enzyme glutamine dehydrogenase to catalyze the reaction [93]. During the ammonification process, there is typically a ^{15}N-depletion in the NH_4^+ product relative to the pool of organic nitrogen due to preferential use of the lighter isotope by microbial activity [75, 96].

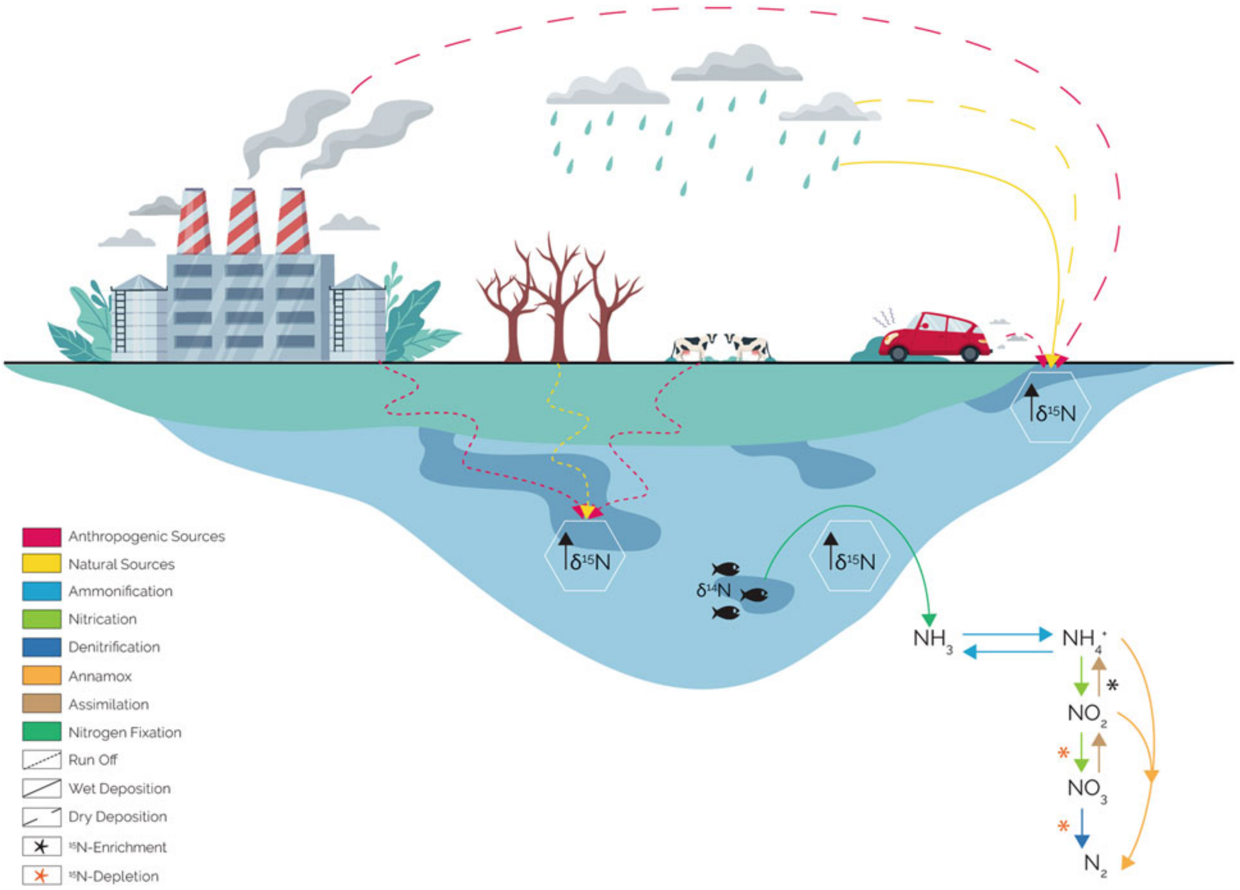

Fig. 1 Diagram linking isotopic nitrogen deposition of nitrates and ammonia from common anthropogenic and natural sources through the nitrogen reaction pathway

$$\underset{\text{ORGANIC NITROGEN}}{R\text{-}NH_3} \rightarrow \underset{\text{AMMONIUM}}{NH_4^+} + \underset{\text{BYPRODUCT}}{R} \tag{2}$$

Ammonia sources go through a nitrification process (Eq. 3) where proteobacteria (*Nitrosomonas*) oxidize NH_4^+ into NO_2^- [75, 77, 95]. The oxidation of NH_4^+ to NO_2^- typically leads to a ^{15}N-depletion in the product [97]. Equation 4 shows the conversion of NO_2^- into NO_3^- by *Nitrobacter* microorganisms [75, 77, 95]. The further oxidation of NO_2^- to NO_3^- typically leads to a ^{15}N-depletion in the product relative to the starting material [98].

$$2\,NH_4^+ + \underset{\text{OXYGEN}}{3\,O_2} \rightleftarrows 2\,\underset{\text{NITRITE}}{NO_2^-} + \underset{\text{HYDRONIUM}}{4\,H^+} + \underset{\text{WATER}}{2\,H_2O} \tag{3}$$

$$NO_2^- + 0.5\,O_2 \rightleftarrows \underset{\text{NITRATE}}{NO_3^-} \tag{4}$$

Nitrate assimilation (reverse reaction of Eq. 4 and Eq. 3) can incorporate nitrate reactive species back into the environment using enzymes. A large portion of nitrate assimilation is done by microbial activity, phytoplankton, and other organisms. In this case, the enzyme nitrate reductase converts NO_3^- into NO_2^- followed by nitrite reductase to facilitate conversion to NH_4^+ [93]. The distribution of nitrogen isotopes among intermediates in the nitrogen cycle adds complexity to interpreting the fractionation; however, it is has been proposed that a ^{15}N-enrichment can be observed in NH_4^+ [75].

Denitrification is carried out by microbial organisms where nitrates are reduced to nitrogen that is released into the atmosphere [92]. In this step, a carbon or a sulfur source reduces nitrates into gases such as nitrogen or N_2O [77, 92]. The reduction of NO_3^- to N_2 typically results in an enrichment of $\delta^{15}N$ in the residual reactant species relative to the starting material [99]. Both carbon and sulfur sources create CO_2, but carbon sources release water as a product and sulfur sources produce sulfate (SO_4^{2-}) [77]. Low total concentrations of 1.9 to 5 mg of sulfur per gram of sediment core were reported for the Great Lakes [100]. It follows that carbon sources such as glucose are more abundant than sulfur as shown in Eq. 5 [77, 92]. Simultaneously, anaerobic ammonium oxidation (anammox) also produces N_2 from NO_2^- and NH_4^+ [98].

$$\underset{\text{GLUCOSE}}{5\,C_6H_{12}O_6} + 24\,NO_3^- + 24\,H^+ \rightarrow \underset{\text{CARBON DIOXIDE}}{30\,CO_2} + \underset{\text{WATER}}{42\,H_2O} + 12\,N_2 \tag{5}$$

2.3 Source Identification

The Great Lakes contribute billions of dollars to the Canadian and American economies through ecosystem services including tourism, fishing, and public freshwater distribution systems, which are threatened by increasing NO_3^- contamination [76, 94, 101, 102]. Anthropogenic emissions combined with the high solubility of nitrates are contributing to NO_3^- pollution [68, 102, 103]. Nitrate can enter the environment through dry or wet deposition which may complicate source tracking using isotope detection [56, 89, 94]. Dry deposition involves gaseous or particulate NO_3^- adhering to particle surfaces in the atmosphere [89], whereas wet deposition occurs when nitrogen leaves the atmosphere through precipitation [89]. Dry deposition was more prevalent when atmospheric concentrations of nitrogen were relatively high in colder climates [89]. Differences in land use activities, proximity to water bodies, and the number of source pools of nitrogen result in unique isotopic signatures across geographic regions [35, 94].

2.3.1 Natural Sources

Natural sources of nitrates globally contribute to approximately 300–500 teragrams (10^{12}) per year (TgN/year) [94]. Microbial fixation was identified as the primary natural source of NO_3^-, accounting for approximately 200–300 TgN/year [94]. Other natural sources of NO_3^- originate from organic materials in soil, algal biomass in water, and terrestrial plant matter [48, 104]. Soil NO_3^- produced by microbial nitrification typically has a $\delta^{18}O$ value of less than +15‰ with a $\delta^{15}N$ value of −3.0 to +5.0‰ [10, 67]. Ammonia in soil has a somewhat larger range in $\delta^{15}N$ of −5.0 to +5.0‰ [67], which is dependent on moisture content from 0 to +33.2‰ [105]. Subsurface freshwaters tend to have a $\delta^{18}O$ value of approximately −10.0‰ [81], whereas $\delta^{15}N$ is more variable depending on the type of water body [106]. Microbial productivity in lake water was reported to lead to greater variability in $\delta^{15}N_{NO3^-}$ and $\delta^{18}O_{NO3^-}$ compared to groundwater [106], and evidence suggests that variability in $\delta^{15}N$ of NO_3^- and NH_4^+ may depend on microbial species composition [107]. However, earlier studies demonstrated that microbial denitrification in groundwater near forested and agricultural areas contributed to higher $\delta^{18}O_{NO3^-}$ values (+40–50‰) and lower $\delta^{15}N_{NO3^-}$ values (+1–4‰) compared to surface water [108]. Temperate forests were identified as a significant natural source of NO_3^- in groundwater and surface water [104]. Nitrate export from forests is increased by stress or damage, such as from atmospheric acid deposition and acidification [109]. Atmospheric values of $\delta^{15}N$ and $\delta^{18}O$ ranged from −10.0 to +8.0‰ and +30 to +80‰, respectively [10]. Natural processes such as lighting and volcano eruptions contribute around 10 TgN/year of NO_3^- to the atmosphere, resulting in wide isotopic ranges in atmospheric $\delta^{15}N$ and $\delta^{18}O$ [94, 109, 110].

2.3.2 Anthropogenic Sources

Anthropogenic sources of NO_3^- such as fertilizers, pesticides, animal and human wastewater, and runoff from urban areas [111] are the leading causes of NO_3^- pollution in surface and groundwater [48, 76, 94, 103, 112]. Synthetic fertilizers have a distinct isotopic signature of approximately 0‰ to +3.0‰ for $\delta^{15}N$ and +19‰ to +25‰ for $\delta^{18}O$ [10, 67]. Sources of NH_4^+ are on the lower end of the $\delta^{15}N$ range with values of −2.8 to +0.9‰, whereas $\delta^{15}N_{NO3^-}$ is +1.9 to +3.5‰ [75]. Leaking sewage systems was identified as a major anthropogenic source of NO_3^- water contamination [112]. Manure and sewage were found to have similar $\delta^{15}N$ values of +7.0 to +20‰, but could be distinguished by lower $\delta^{18}O$ values in sewage [10, 113].

It is largely accepted that the primary source of NO_3^- contamination in surface water is due to the burning of fossil fuels [48, 94]. Fossil fuel sources have different isotopic signatures based on their formation process; nitrates from vehicle exhaust had $\delta^{15}N$ values of −13 to −2.0‰, whereas coal burning produced values from +6.0 to +13‰ [114]. Atmospheric deposition from vehicle and industrial exhausts had unique isotopic signatures on nearby plants [115], and similar results with higher dry NO_3^- depositions were observed in proximity to a major roadway [116]. The variability in these sources adds to the complexity in characterizing sources and the fate and transport of NO_3^- in watersheds.

2.4 Fractionation and Other Isotopic Limitations

Many studies have found that using only nitrogen isotopes for source determination is challenging due to the overlapping values of many nitrate sources, including different NO_3^- and NH_4^+ sources [10, 113, 117]. This poses a challenge for source detection in water systems where multiple contaminant sources are often mixed and all impacted by various biogeochemical processes. It has been proposed that ^{15}N is useful for obtaining information about nitrogen conversions in the hydrosphere, but it has limited value as a standalone isotopic indicator [118]. However, due to the high abundance of nitrogenous compounds in the environment, oxygen isotopes can be used to distinguish between other intervening nitrogen sources to improve the accuracy of source detection [10]. This combined interpretation of nitrogen and oxygen isotopes may provide a means to further differentiate sources in watersheds [119].

Another challenge with using NO_3^- isotopes for source determination is that NO_3^- and NH_4^+ are vulnerable to isotopic effects such as fractionation. Typically, in low temperature environments such as freshwater lakes, kinetic effects dominate over thermodynamics [75], and the effects of diffusion fractionation are negligible [75]. Kinetic fractionation effects are influenced by multiple factors such as reaction rate, concentrations, intramolecular interactions, and, in some cases, competition between light and heavy isotope binding [43]. In faster reactions, reactants are quickly turned into products resulting in less fractionation [75]. However, rate-determining steps such as denitrification have higher energy barriers and greater isotopic discrimination, resulting in larger fractionation effects [75]. Due to the heterogeneous nature of contaminants and the mixture of multiple water sources in the Great Lakes, a dispersive correction factor may be needed to account for some deviation in isotope values for distinct sources [43].

2.4.1 Phytoplankton Processes

The link between isotopic fractionation and the energetics and nutritional requirements of phytoplankton are not well understood, which causes challenges for nutrient source tracking using stable isotopes. Phytoplankton are an essential regulator of NO_3^- nitrogen fixation and assimilation in aquatic environments [120, 121]. Multiple factors moderate phytoplankton productivity including phosphorus and nitrogen availability, light, temperature, and other micronutrients including Fe and silica (SiO_2), thereby controlling the efficiency of NO_3^- uptake from water bodies [72, 93, 121–126]. Variations in algal metabolism contribute to a wide range of $\delta^{15}N$ fractionation from −27‰ to 0‰ [75, 127].

Fractionation of $\delta^{15}N_{NH4}{}^+$ is often larger than for $\delta^{15}N_{NO3}{}^-$ due to preferential usage of NH_4^+ in biological processes [74]. Preferential depletion of $\delta^{15}N_{NH4}{}^+$ among nine agricultural plant species when NO_3^- fertilizers were applied was attributed to higher cellular transportation [74]. The benefit of using NO_3^- isotopes in aquatic environments was demonstrated to track nitrogen cycling from phytoplankton to zooplankton grazers because $\delta^{15}N_{NO3}{}^-$ is stable over time compared to nitrogen isotopes from organic matter [128].

CSIA shows promise for improving estimates of phytoplankton population growth rates and nitrate assimilation rates in the Great Lakes. Understanding factors that influence isotope fractionation will be critical for improving CSIA methods. However, effects of environmental factors on isotope fractionation within algal and bacterial populations can be complex and will require advances in research in this area [92].

2.4.2 Microbial Processes

Isotopic fractionation often occurs due to enzymatic breaking of bonds during nitrogen conversions [98]. Nitrogen undergoes more chemical changes than oxygen, so larger fractionation effects are apparent for processes like anammox, where oxygen is absent [67, 98]. When using both $\delta^{18}O$ and $\delta^{15}N$, fractionation is more prevalent during denitrification as compared to nitrogen fixation or nitrification [67]. This is attributed to less reversibility in the denitrification step resulting in a larger effect on isotope values [67]. Fractionation effects can also be amplified by the increasing number of reactions occurring [75]. However, the potential for fractionation depends on numerous other factors such as temperature, *p*H, and microbial species [75].

Considering that organisms preferentially consume lighter isotopes, fractionation is a predictable function of microbial processes acting upon nitrates in water [75]. Microbial activity drives many processes in the nitrogen cycle [94, 129]. However, different geographical regions have unique hydrological processes that create distinct microbial assemblages with unique isotopic signatures [94, 129]. Microbial activity is most prevalent in the nitrogen cycle during nitrification where NH_4^+ conversion to NO_2^- and then to NO_3^- is regulated by *Nitrosomonas* and *Nitrobacter* bacteria [77, 95]. Slower reaction kinetics associated with *Nitrosomonas* are associated with greater isotopic fractionation [75]. Equilibrium effects disproportionately select for ^{18}O during nitrification, where higher fractionation was explained by additional processes such as assimilation [130]. In contrast, a study of three bacterial species (*Nitrococcus*, *Nitrobacter*, and *Nitrospira*) found that less than 3% of ^{18}O atoms were exchanged with NO_3^-, but instead were preferentially incorporated in water [131]. This demonstrates the importance of understanding site-specific environmental and microbial processes acting upon isotopic indicators when studying the source and pathways of nutrients and contaminants.

Ammonia oxidation in freshwater tends to be primarily regulated by archaea species rather than bacteria due to their dominance in many microbial assemblages [132]. Ammonium-oxidizing archaea bacteria in the Great Lakes tend to be species *Nitrosomonas oligotropha* and *Nitrosomonas communis* with multiple species from the genus *Nitrosospira* [132]. Archaea genera *Nitrososphaera* have been found to be most common in Lake Erie, whereas *Nitrosopumilus* and *Nitrosotalea* are known to be dominant in Lake Superior [132]. Granger and Wankel found that $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ values can be overestimated by bacteria during nitrification and anammox, which must be taken into consideration when they are used as indicators in the Great Lakes [98].

2.4.3 Physical and Hydrological Processes

Physical and hydrological processes affect nitrogen cycling reaction rates and isotopic fractionation [43]. For example, hydrological factors such as site topography, slope direction, and surface runoff rates can influence deposition and movement of NO_3^- and optimal sampling points for nutrient and contaminant indicators [94]. Lower temperatures in cooler climate regions may lead to slower denitrification rates resulting in greater ^{15}N fractionation [133]. In contrast, fractionation is reduced when there are low concentrations of bioavailable nutrients, which limits enzymatic reactions resulting in decreased NO_3^- assimilation rates and lower fractionation [48]. On a larger scale, drought in Central Ontario, due to increased Pacific Ocean temperatures, has been linked with reduced soil nitrification rates that are dependent on moisture content [33].

Human remediation activities have also caused unexpected changes in NO_3^- cycling processes [120]. For example, liming treatments used to increase stream *p*H and offset the effects of anthropogenic atmospheric acid deposition can also reduce NO_3^- concentrations in water by stimulating microbial activity [109]. Increased nitrogen uptake can propagate further changes by altering nutrient availability for downstream microbial communities. Furthermore, fractionation effects of liming and other remediation methods are still poorly understood for NO_3^- due to the complexity of nitrogen cycling. Variability in NO_3^- isotopes was proposed to be related to differences in hydraulic residence time in the presence of sediments with varying biogeochemical conditions [134]. Across the Great Lakes watersheds, tributaries, and lake basins, wide isotopic variation among sampling locations highlights the need to understand site-specific reaction chemistry to determine baseline isotope values.

2.5 Nitrates Affecting Other Processes

In contrast to other contaminants, even less information is available to establish links between NO_3^- concentrations and other biogeochemical processes within the Great Lakes. Linkages have been established between high phosphorus and low iron (Fe) concentrations in lake sediments, which can cause increase frequency and intensity of cyanophyte blooms in freshwater [133]. NO_3^- and sulfur are implicated in this process by acting in an indirect synergistic manner to promote phytoplankton productivity. That is, NO_3^- can mobilize SO_{42}^- in agricultural soils, which can thereby increase transportation of phosphorus to surface waters [135]. Nitrate also simultaneously immobilize Fe^{2+}, which preferentially binds to sulfides resulting in lower phosphorus binding efficiency [135]. This ultimately results in the decomposition of more organic matter in soils, further stimulating NO_3^- mobilization [135].

In contrast, lower NO_3 concentrations result in reduced SO_{42}^- mobilization, which can lead to more Fe availability [123]. Cyanobacteria growth is associated with seasonal internal Fe loading from lake sediments, which can cause low oxygen conditions near lake sediments that further promotes denitrification [123].

Due to the complexity of NO_3^- and NH_4^+ interactions in the environment, these indicators are limited in their application for nutrient source tracking when used in isolation. Fractionation effects for NO_3^- are poorly understood and can be extensive when relying on $\delta^{15}N$ or $\delta^{15}N/\delta^{18}O$ isotope ratios. To mitigate these problems, multi-indicator approaches are gaining popularity where a combination of $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ is used alongside other indicators such as chlorides (Cl^-) and boron ($\delta^{11}B$) [113, 136].

3 Chloride

The complicated behavior of NO_3^- and NH_4^+ in the water cycle suggests combinations with other indicators, such as Cl^-, could provide more insight into source identification in hydrogeological investigations. Chloride may be used to track water flow paths and monitor inland water ecosystems, as it remains mostly unaffected by biotic and abiotic processes during its movement through the hydrological cycle. Furthermore, Cl^- concentrations have been rising due to soil cultivation, increased use of road salt, and other anthropogenic activities leading to the contamination of shallow groundwater and freshwater resources. In recent years, numerous publications have provided evidence for rivers and groundwater salinization by road salt runoff affecting the quality of surface waters [137–139]. In 2018, the US government used 42 million tonnes of salt where 43% of it was used for highway de-icing [140]. Environment Canada estimates that almost five million tonnes of salt is used for de-icing roads annually in Canada [141]. In the city of Toronto, within the Highland Creek watershed, groundwater Cl^- concentrations reached approximately 275 mg/L in autumn, exceeding the US EPA secondary standard of 230 mg/L [142]. Due to the inherent conservative nature of Cl^-, it is an excellent candidate to be used as an isotopic indicator to identify contaminant sources.

Chlorine isotopes range from ^{28}Cl to ^{51}Cl, but of the 24 isotopes, only ^{35}Cl and ^{37}Cl are stable isotopes with 75.76% and 24.24% abundance, respectively [143]. All Cl^- radioactive isotopes have a half-life of <1 h except ^{36}Cl with a half-life of 301,000 years [144]. Chlorine has two stable isotopes which are found commonly in oceans and evaporite deposits with limited presence in the atmosphere [145]. Chloride isotopes are conservative in nature, highly soluble, and mobile making them good candidates as hydrological indicators in environmental studies [46]. The radioisotope of chlorine (^{36}Cl) is used to infer information regarding the age of water in aquifers [146]. ^{36}Cl is also used for groundwater dating and is found along with stable chlorine isotopes. The $^{36}Cl/[Cl]_{TOT}$ ratio is used to report ^{36}Cl concentration over total chloride concentration in groundwater, where a lower ratio is observed in subsurface groundwater compared to the meteoric ratio [146]. Variation in $^{36}Cl/[Cl]_{TOT}$ results from temporal changes in local groundwater recharge, evaporation, transpiration, interactions between water and rocks, biological uptake, and input of Cl-rich water [147, 148]. Due to the non-volatile nature of ^{36}Cl, it can be useful in limited applications to date groundwater samples as well as to trace preferential flow transport through the vadose zone [46, 146]. In the Great Lakes, halogen elements including Cl^- are not limited to natural sources or influenced by evaporation [29]. Thus, the overall conservative nature of Cl^- isotopes makes them a promising geochemical tool for studying the origin, pathway, and processes affecting the distribution of nutrients in watersheds.

3.1 Stable Isotope Analysis: Chlorine

IRMS using the dual inlet or continuous flow mode is the most common Cl^- isotopic analysis technique [145]. The sample is prepared by initially precipitating Cl^- from the solution as AgCl and converting it to methyl chloride gas via reaction with excess CH_3I (g). Uncertainties as low as ±0.1‰ and 0.2‰ in Cl^- isotopic measurement are achievable for dual inlet and continuous flow, respectively [149]. Although continuous flow has greater analytical error, it significantly reduces the amount of sample required relative to the dual inlet IRMS [150].

Chlorine isotopic measurements can also be completed using thermal ionization mass spectrometry (TIMS) [151]. TIMS analysis is carried out in negative (nTIMS) ion mode measuring Cl^- or positive (pTIMS) ion mode measuring $CsCl_2^+$. This process is driven by drying the sample on a high purity filament, such as tungsten, rhenium, or tantalum, before vaporizing and ionizing it by resistive heating [152, 153]. Although nTIMS provides higher sensitivity using only several hundred ng of a Cl^- sample compared to pTIMS (several μg of sample) [154], common loss of precision (error $\geq$ +0.9‰) has been observed during nTIMS measurements [153, 155]. On the other hand, pTIMS has shown poor reproducibility in solid samples measured with IRMS, which is attributed to the fractionation occurring during the ionization process [156].

Secondary ion mass spectrometry (SIMS) is another technique developed for isotopic analysis of Cl-rich samples (>200 ppm) [157]. Secondary ions of the samples are generated through Cs^+ ion bombardment before they are accelerated toward the mass spectrometer. The analytical error is typically larger (1.5‰); however, recent advances continue to improve the reproducibility in $\delta^{37}Cl$ measurements with this technique [157, 158].

3.2 Chlorine Isotopes and Fractionation

Chlorine isotopes are typically considered a conservative indicator because they have limited isotopic fractionation. Negligible variation in $\delta^{37}Cl$ values has been observed in groundwater, formation waters, evaporates, and sedimentary basins [145, 159]; however more $\delta^{37}Cl$ variation has been observed in terrestrial samples (−2.0‰ to +2.0‰) [144]. In biotic systems, the Cl^- isotopic fractionation (−15.8‰ ± 4.0‰) of perchlorates (ClO_4^-) has been characterized from microbial respiration [160]. Differences in isotope values can be exploited using $\delta^{37}Cl$ of natural versus synthetic ClO_4^- in groundwater, where $\delta^{37}Cl$ of imported Chilean natural fertilizer was −14.5‰, whereas locally accumulated atmospheric ClO_4^- was −9.2‰ [161].

Chloride tends to move faster than the average velocity of water in soil [162]; however, complications in Cl^- behavior might be observed if it is sequestered by organic material or minerals at low *p*H [163]. Other abiotic processes involving Cl^- include formation of volatile HCl complexes at low *p*H, precipitation as AgCl in the presence of silver ions, and formation of minerals with ferric ions. Chlorine transport through a watershed can also be limited by uptake and retention in plant tissue, dependent on plant species, where Cl^- is later released into soil by decomposition [146].

In a review of theoretical chlorine equilibrium fractionation, in a -1 valence state, fractionations in geological samples should only be a few per mil and decrease with warmer temperatures [144, 145]. Under higher oxidation states, however, greater fractionation of Cl^- and Cl_2 is expected [144]. Several processes are known to contribute to Cl^- kinetic fractionation such as molecular diffusion, ion filtration, and ion exchange; these processes have been comprehensively reviewed [144, 145]. Thus, although Cl^- has been considered to be a conservative indicator, fractionation in groundwater is possible due to the filtration effect of clay and/or various diffusion rates of ^{35}Cl and ^{37}Cl [145, 164]. This non-conservative behavior of Cl^- has been the subject of several other studies [165–167], which illustrate the potential reactivity of Cl^- in various environments. In a study of 32 forested catchments in eastern North America and Europe, Cl^- behaved conservatively at locations with high Cl^- input and non-conservatively at locations with low Cl^- input [168].

3.3 Chlorine in the Environment

Understanding the source of salinity in surface water and groundwater is important for preserving water quality [169]. Chloride salts such as sodium chloride (NaCl) are prevalent in saline groundwater [170]. Factors contributing to salinization of aquifers include evaporation resulting in the concentration of salts, irrigation agriculture causing increased mobilization of salts through runoff and evapotranspiration by crop plants, and addition of solutes to water through rock weathering and atmospheric deposition [171]. Isotopes have been successfully used to evaluate source and transport. For example, $^{36}Cl/[Cl]_{TOT}$ measurements from upper and lower regions of the Jordan River, in Lebanon and Israel, showed a decrease in $^{36}Cl/[Cl]_{TOT}$ due to downstream dilution [172]. However, this data was also used to calculate that almost 70% of Cl^- found in upstream spring tributaries and more than 90% in downstream water was leached from rocks in the upper Jordan River watershed [172].

In the Ibusuki coastal area of southwest Japan, $\delta^{37}Cl$ of geothermal fluids have high salinity and different ion compositions than seawater [173]. An average $\delta^{37}Cl$ value of $-0.15‰$ (combined with a correlation between $\delta^{2}H$ and $\delta^{18}O$ of water) suggested that groundwater contained a mixture of seawater and local meteoric water [173]. Musashi and his colleagues observed a hyperbola mixing of at least two Cl^- sources while investigating the correlation between $\delta^{37}Cl/\delta^{11}B$ and the [Cl]/[B] molar ratio in Ibusuki area [173]. The first source of Cl^- appeared to originate from an interaction between seawater and rocks because ^{37}Cl was depleted and the

[Cl]/[B] molar ratio was high. The second Cl^- source had a magmatic volatile signature that was enriched in ^{37}Cl and low in [Cl]/[B] [173].

In some cases, Cl^- isotopes can be integrated into interpretations with other indicators. Isotope indicators were used to study the sources of salinity in the Upper Rio Grande–Rio Bravo River, along the Mexico and US border, where salinity has been increasing over the past 75 years [171]. $^{36}Cl/[Cl]_{TOT}$ and [Cl]/[Br] ratios were used along with, [Ca]/[Sr], $^{87}Sr/^{86}Sr$, and $\delta^{234}U$ to show that groundwater from a sedimentary brine source was responsible for the increase in salinity, rather than agricultural activities [171]. Distinct $^{36}Cl/[Cl]_{TOT}$ ratios are expected for different salt sources; thus, $^{36}Cl/[Cl]_{TOT}$ ratio $< 1 \times 10^{-15}$ could be indicative of aquifer contamination by road salt from salt domes, and $5–15 \times 10^{-15}$ could be sourced to oilfield brines compared to high $^{36}Cl/[Cl]_{TOT}$ ratio of meteoric origin [46].

Along the shoreline of Lake Ontario, near Frenchman's Bay and the City of Pickering, the impact of road salt on Lake Ontario was evaluated using a Cl^- mass balance model and hydro-chemical analysis [174]. Chlorine concentrations as high as 1,600 mg/L were observed in groundwater where 1,700 t of salts were deposited into Frenchman's Bay and its catchments through road runoff. This mass accounted for ~50% of total road salt used in winter in the local watershed.

In a study of 14 sites in central Ohio rivers, water was analyzed for ^{36}Cl, [Cl]/[Br], and dissolved ion concentrations to determine anthropogenic sources of Cl^- [137]. Comparison of analyzed sample results to previous data from the same area indicated that halite formations contributed the highest proportion of Cl^- into rivers annually, whereas road salt was the main source of increased Cl^- concentrations in late winter. In addition to road salt, agricultural fertilizer runoff also contributed to increased [Cl]/[Br] and NO_3^- concentrations.

The studies highlighted above emphasize the impact of road salt on ground and surface drinking water resources. Stable isotope databases for common environmental contaminants are becoming more widely available [175–177]. For example, a comprehensive review of isotope studies on frequently used salts, including de-icing road salts, showed that $\delta^{37}Cl$ ranged from −2.0‰ to +1.0‰ [178]. However, further research is required to expand these databases to include multiple isotope indicators and CSIA data, which will improve the accuracy and precision of isotopic methods for tracing non-point source pollutants.

4 Use of Isotope Indicators in the Great Lakes

4.1 Nitrates and Ammonia

Water quality in some regions of the Great Lakes is declining as a result of pollution from synthetic fertilizers, urban runoff, and livestock manure [48]. The influx of NO_3^- and excess PO_4 can exacerbate symptoms of eutrophication, where decomposing biomass from algal blooms starve water of oxygen in large regions near the lake bottom [122, 133, 179]. Although there has been almost a century of limnological research on the Great Lakes, there is a lack of cohesion in ever-expanding biogeochemical and ecological datasets, which could be used to advance research on nutrient source tracking and impacts on these vast ecosystems [8].

4.2 Chlorine

Chlorine inputs have increased in the Great Lakes over the past 150 years [180]. Chloride concentrations increased in Lake Michigan and Lake Huron (and to a lesser extent in Lake Superior), starting in the early 1900s, and reached maximum values in the 2000s. Chlorine concentrations in Lake Erie and Lake Ontario reached maximum levels in the 1960s and 1970s, but subsequently declined mainly due to more stringent industrial regulations. Transport among lakes was shown to be an important factor, as 35% of Cl^- in Lake Huron was attributed to input from Lake Michigan. Lake Erie contributed 45% of Cl^- to Lake Ontario, although concentrations within Lake Erie were attributed mostly to its own watershed. As of 2006, Cl^- concentrations were predicted to continue increasing as a result of unabated road salt use in all of the Great Lakes.

In 1970, using a steady-state model and published data from 1965 [181], O'Connor and Mueller estimated that pre-European settlement Cl^- concentrations in Lake Superior and the other Great Lakes combined were ~ 2 and ~ 3 mg/L, respectively [182]. However, these calculations did not consider that large regions of the Great Lakes watersheds had already been developed prior to 1850. Chapra et al. used average outflow data from 1860 to 1899 and estimated lower pre-settlement Cl^- concentrations for Lake Superior (0.93 mg/L), Lake Michigan (1.86 mg/L), Lake Huron (1.58 mg/L), Lake Erie (1.75 mg/L), and Lake Ontario (1.87 mg/L) [180]. With the exception of Lake Superior (1.4 mg/L), by 2006 large increases in Cl^- concentrations were reported in Lake Superior (11.4 mg/L), Lake Michigan (6.6 mg/L), Lake Huron (8.4 mg/L), and Lake Erie (22.3 mg/L) compared to pre-settlement estimates [180].

The impacts of salinity in the Great Lakes are readily observed in their tributaries. Sediment and water samples were collected from 21 lakes adjacent to highways in the Toronto area and around Lake Ontario. They found that samples containing >400 mg/L salt (> 800 μS/cm conductivity) were mostly populated by Arcellacean species common in brackish water, although species composition was also affected by nutrient concentrations and other local factors [183]. Widespread impacts observed in their study highlighted the need for more comprehensive research on possible effects of road salts on Great Lakes ecosystems.

$\delta^{37}Cl$, $\delta^{81}Br$, and water isotopes δ^2H and $\delta^{18}O$ were used to assess the origin and mobility of saline groundwater and the physical stability of a rock formation in a deep geological repository (DGR) [184]. They used six samples from the Upper Silurian, Middle Silurian (Guelph formation), and Cambrian formations from two cored boreholes (DGR-3 and DGR-4) under the Bruce Nuclear Power Plant site on the eastern shore of Lake Huron [184]. In the Upper Silurian formation, δ^{37}Cl values ranged from −0.03‰ to −0.05‰, which was higher but similar to the range (−0.40‰ to −0.20‰) reported by Skuce et al. who analyzed samples taken from the same formation [185]. These subsurface studies provide potential end members for Cl^- because formation brines have been used as road salt in in the Great Lakes watershed.

The isotope δ^{37}Cl can also be used to determine the source of ClO_4^- pollution found in aquifers [186]. Perchlorates are stable environmental contaminants which are highly water soluble and are derived from anthropogenic and natural sources [187, 188]. Among all five Laurentian Great Lakes, in 2017 and 2008, Poghosyan et al. observed that ClO_4^- concentrations ranged from 0.05 to 0.13 μg/L, whereas ClO_4^- δ^{37}Cl ranged from +3.0‰ to +4.0‰ [189]. Concentrations of ^{36}Cl (reported as $^{36}Cl/[Cl]_{TOT} \times 10^{-15}$) ranged from 6.7×10^{-11} to 7.4×10^{-12} and were greatest in Lake Superior because it has the longest water renewal time (191 years). Elevated $^{36}Cl/[Cl]_{TOT}$ was attributed to ^{36}Cl generated by atmospheric testing of nuclear bombs over the Pacific Ocean during the cold war era. However, perchlorate Cl^- isotopic results in combination with oxygen stable isotope data (i.e., δ^{18}O and $^{17}O/^{16}O$) suggested a predominantly natural origin for ClO_4^- in the Great Lakes [189].

4.3 Applied Multi-indicator Approach in the Great Lakes

The complexity of interconnected basins and watersheds is impacted by numerous and widespread land use activities in large lake systems [190]. Nutrient sources are typically mixed, biologically influenced, and impacted by widely variable regional water flow. This is especially relevant within the Lake Huron, Detroit River, and Lake Erie corridor. The Detroit River supplies 90% of water to the western basin of Lake Erie through average annual discharge of around 5,300 m^3/s. Although there has been ongoing water quality monitoring, very recently, there have been considerable modelling efforts that are providing new insight into the nutrient dynamics along this corridor [191–195].

Multiple indicator approaches combining measurements of elemental concentrations and stable isotope analysis have demonstrated that with smaller “snapshots” of data, important insights can be achieved into the sources of nutrients in spatially complex aquatic ecosystems [32, 34, 48]. As an example, Detroit River water and sediment samples were taken from 21 sites on 8 east to west transects between Lake St. Clair and Lake Erie on November 14, 17, and 22 in 2016. However, limited information can be obtained in a single sampling campaign from the relationship between NO_3^- and PO_4 concentrations (Fig. 2a). This is not surprising since these nutrients can have point source and non-point source inputs with many physical and biological processes that will differentially impact their concentrations. The limited biological cycling of Cl^- and sodium (Na^+) can provide insight into the physical

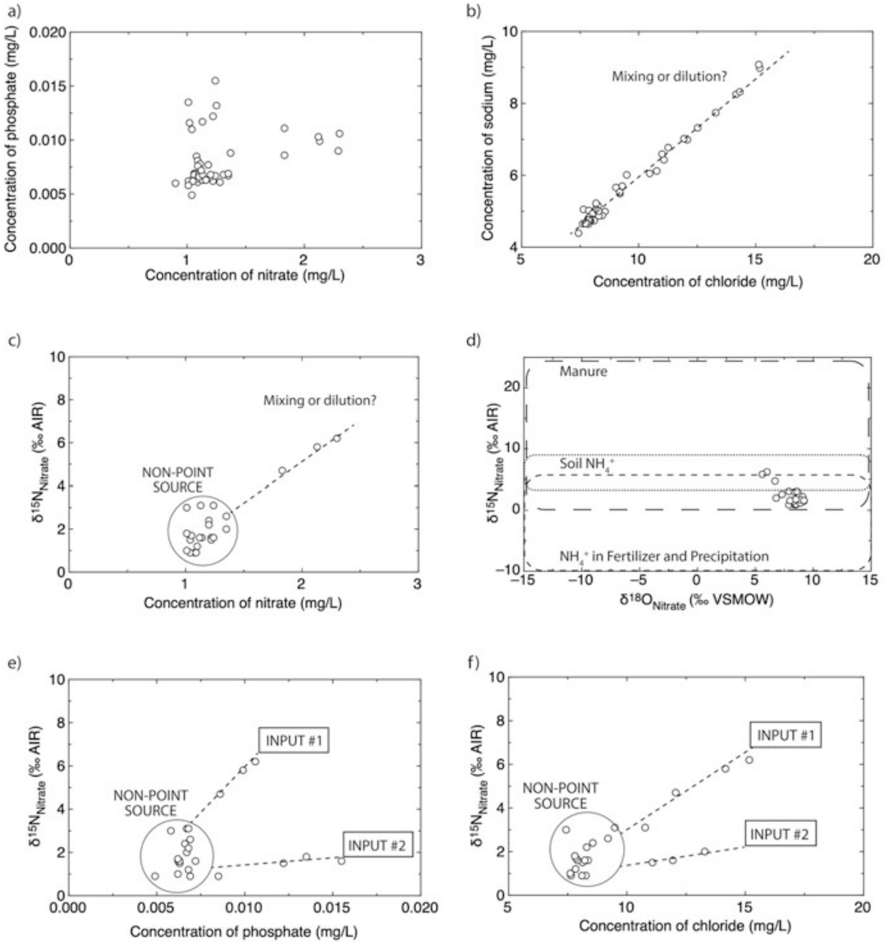

Fig. 2 Detroit River water samples analyzed to compare (**a**) PO_4 concentration (mg/L) versus the NO_3^- concentration (mg/L), (**b**) Na^+ concentration (mg/L) versus Cl^- concentration (mg/L), (**c**) the $\delta^{15}N_{NO3}^-$ values (‰ AIR) versus NO_3^- concentration (mg/L), (**d**) the $\delta^{15}N_{NO3}^-$ values (‰ AIR) versus the $\delta^{15}N_{NO3}^-$ values (‰ AIR) versus the $\delta^{18}O_{NO3}^-$ values (‰ VSMOW), (**e**) the $\delta^{15}N_{NO3}^-$ values (‰ AIR) versus PO_4 concentration (mg/L), and (**f**) $\delta^{15}N_{NO3}^-$ values (‰ AIR) versus Cl^- concentration (mg/L) [32]

processes impacting their concentrations in the system, where a linear relationship may implicate mixing and/or a dilution trend throughout the river system (Fig. 2b). Similarly, the relationship between NO_3^- concentrations and the $\delta^{15}N$ values of NO_3^- may suggest mixing between sources and/or a dilution trend (Fig. 2c). Additional linear relationships for crossplots of the inverse NO_3^- concentrations with the $\delta^{15}N$ values support mixing or dilution trends, whereas crossplots of the natural logarithm of NO_3^- concentrations with the $\delta^{15}N$ values suggest the possibility that they are impacted by denitrification (not shown) [196]. The $\delta^{18}O$ and $\delta^{15}N$

isotope values of NO_3^- suggested fertilizer inputs and atmospheric deposition were the dominant sources of nitrate; however, several samples were indicative of a different soil-based and/or wastewater source along the upper Detroit River supporting a source mixing hypothesis in (Fig. 2a–d) [32].

Although PO_4 and Cl^- are concentration-dependent indicators, crossplots with indicators such as the $\delta^{15}N$ values of NO_3, can provide new insight to identify sources in the watershed. For example, if NO_3 sources are different and/or impacted differently by physical and biological isotope fractionating processes, so long as their isotope values are distinct, they will mix with other nutrients in the watershed and move through the watershed with a co-migrating multi-indicator signature. However, if signatures are sufficiently different at the point of mixing and the environmental changes do not cause them to merge signatures, they can be used to distinguish sources. In this case, the relationship between Cl^- concentrations, PO_4 concentrations, and $\delta^{15}N$ of NO_3^- suggested that there could be two distinct sources of nutrients in addition to the anticipated non-point sources along the Detroit River (Fig. 2e, f) [197]. Overall, higher concentrations of Na^+, Cl^-, and PO_4 appear to be associated with the Little River and Rouge River outflows [32, 34]. However, at the time of sampling, the input near Little River (Input #1, Fig. 2) has ^{15}N-enriched $\delta^{15}N$ values for NO_3^- with slightly lower concentrations of PO_4 and slightly higher concentrations of Cl^- compared to the nutrient input near the Rouge River (Input #2, Fig. 2). Although much more work is needed to understand these systems, integrating concentration-independent stable isotope indicators can provide unique insight into the sources of nutrients in a watershed with limited data. These isotope techniques are not meant as a replacement for the multi-year and comprehensive modelling approaches. Instead, they are needed to guide policy as they may provide regulators and stakeholders with earlier insight and/or a means to “spot check” watersheds with a “snapshot” of data.

Statistical analysis of aqueous constituents and isotopic indicators in river water combined with sediment chemical, isotopic, and contaminant indicators can be used to identify nutrient sources in the Detroit River. Using a principal component analysis (PCA) paired with a hierarchical clustering of loadings, a combination of archival and novel data is used to distinguish point sources, non-point sources, and upgradient water bodies to identify sources of nutrients and contaminants to the Detroit River [34]. Urban point sources are well defined, containing NH_4^+ along with sediment metals, PAH, PCB, and pesticides. The inclusion of dissolved PO_4 with urban point sources suggested it may be a contributing source to the Detroit River. Previous work in the Laurentian Great Lakes region typically indicated agriculture is the primary source of riverine PO_4 [57]. More recently, the origin of PO_4 within the Detroit River was shown to be from mixed urban and agricultural sources [32]. The grouping of PCA loadings suggests that the primary driver of aqueous PO_4 in the Detroit River could be urban point source discharges, introducing the possibility that urban land use within the Detroit River watershed may play an important role for water quality within the river and potentially the western basin of Lake Erie [198].

5 Conclusion

Unabated NO_3^- and PO_4 pollution in the Great Lakes will have serious implications for the sustainability of these unique ecosystems. Temporal and spatial variability in nutrient sources, transport, and biogeochemical processing will provide challenges for detection of NO_3^- origins using isotopic methods. The extent of this variability may result in some overlap in isotopic signatures of $\delta^{15}N$. Based on the information available, it is recommended that site-specific statistics are used to determine which isotopic indicators are suitable for analysis. Properties such as climate, rainfall, and topography have been shown to influence NO_3^- contamination in the environment, so it is beneficial to have a management plan that is calibrated for NO_3^- contamination in a specific region. However, bacterial and algal uptake and processing of NO_3^- might be somewhat coordinated across regions of the Great Lakes because climate trends are spatially correlated within this network of interconnected basins. Linkages between road salt application and the increase of Cl^- in the Great Lakes ensure a unique opportunity to introduce this specific tracer for monitoring contaminants in the Great Lakes.

There is a critical lack of information about the current state and predicted trends for future NO_3^- pollution in the Great Lakes. Tentative management plans have been developed for some lakes in the region. However, these plans do not consider the interconnections among watersheds and lake basins, nor do they account for potential negative unintended effects of remediation. The use of multiple chemical and isotopic indicators for environmental fingerprinting offers unique opportunities to identify potential origins of contaminants in the Great Lakes.

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Advances in Remote Sensing of Great Lakes Algal Blooms

Caren E. Binding, Richard P. Stumpf, Robert A. Shuchman, and Michael J. Sayers

Contents

Abstract Many regions of the Great Lakes now see recurring cyanobacterial harmful algal blooms (cyanoHABs), with documented repercussions for ecosystem services, public health, and ecosystem integrity. Early detection and comprehensive monitoring of cyanoHABs are fundamental to their effective management and mitigation of detrimental impacts. Satellite remote sensing has provided the means by which algal blooms in the Great Lakes can be observed with unprecedented frequency and spatial coverage. Algorithms have been developed and validated; fully automated data processing streams have been rendered operational; and

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stakeholders have been engaged in order to develop user-friendly end products. Such products have been integral in providing near-real-time monitoring of bloom conditions, documenting spatiotemporal trends, improving understanding of environmental drivers of blooms, and guiding nutrient management actions. In this chapter we present background information on remote sensing of algal blooms, document the current state of knowledge with a focus on Lake Erie, and discuss remote sensing products available to the Great Lakes community.

Keywords Algal blooms, Electromagnetic spectrum, Hyperspectral, Phytoplankton, Spatiotemporal trends, Surface scum

1 Background

The potential of satellite remote sensing of water quality in the Great Lakes was first documented in the 1970s, with Landsat data being explored in the identification of particulate contaminants [1], whiting events [2], and chlorophyll-a [3]. Since then, increasingly sophisticated satellite sensor technologies, novel algorithm development, and considerable improvements in data availability and image processing capabilities with modern computational power have resulted in major advancements in remote sensing of the Great Lakes. For example, cloud-based parallel computing tools available via Google Earth Engine have substantially reduced the time and resources required to process and analyze remote sensing imagery [4]. The combination of an increasing number of aquatic color satellite missions, the adoption by space agency data providers of service models supporting free and open data, and widespread availability of open source software applications have enabled unprecedented access to remote sensing data. The benefits of remote sensing are numerous: imagery delivers synoptic water quality observations over large areas, providing lake-wide views of dynamic features simply not possible using ground-based observations; frequent revisit times provide observations suitable for time series analysis and targeted event-based monitoring; and archive historical data allow for retrospective analysis up to several decades. A demonstrable increase in the confidence in satellite-derived water quality parameters has led to an increase in the uptake of those products into research and monitoring applications and a move toward near-real-time operational product delivery.

As reviewed in detail by Mckindles et al. [5], cyanobacterial harmful algal blooms (cyanoHABs) are recurring events within the Great Lakes and notably the western basin of Lake Erie [6–8], with often severe detrimental impacts on drinking and recreational waters. Binational in situ monitoring of algal blooms is conducted on Lake Erie by federal, state/provincial, and municipal levels of government as well as multiple research facilities within the watershed. Even with regular monitoring programs, however, analysis of lake-wide conditions or long-term trends is often hampered by fragmented datasets and inconsistencies in the timing of surveys [9]. This lack of spatial and temporal consistency in in situ datasets of algal blooms often impedes abilities to resolve short- and long-term variance in cyanoHAB events and develop robust management strategies for their mitigation. With budgetary pressures and logistical constraints on traditional monitoring programs, remote sensing therefore offers a cost-effective solution for large-scale spatiotemporal monitoring of algal blooms in the Great Lakes. Increasingly, remote sensing has been used to report on algal bloom conditions on Lake Erie, providing near-real-time alerts, supporting operational forecasting systems, and furthering our understanding of ecological trends and underlying drivers of spatial and temporal bloom variability [4, 6, 10, 11].

This chapter provides an overview of remote sensing of algal blooms on the Great Lakes, with a particular focus on Lake Erie and the remote sensing products produced binationally by the Environment and Climate Change Canada (ECCC), the US National Oceanic and Atmospheric Administration (NOAA), and Michigan Tech Research Institute (MTRI). As a number of sources of satellite-derived algal bloom products are available to the Great Lakes community, this chapter aims to consolidate information on the most frequently used satellite sensors, algorithms, and products, as well as some of the applications which they have supported, and the limitations of this technology.

2 Satellite Sensors

Remote sensing of algal blooms is based on the concept that variations in algal or cyanobacterial biomass cause measurable changes in the color of the water, which can be detected by passive optical sensors on board remote platforms such as satellites or aircraft. Satellite aquatic color platforms come with a diverse suite of spatial, temporal, and spectral resolutions (Table 1), which depend on the sensor specifications and satellite orbit. Spatial resolution determines the smallest feature a sensor can detect, described as the image pixel size at maximum resolution (e.g.,

Table 1 Current and past aquatic color satellite sensors appropriate for observing algal blooms in the Great Lakes

Sensor	Spatial resolution	No. of bands[a]	Revisit time	Years of operation
Landsat (1–8)	30 m	4–6	16 days	1972–present
SeaWiFS	1.1 km	8	Daily	1997–2010
MODIS (A/T)	250 m-1 km	13	Daily	1999/2002–present
MERIS	300 m	13	2 days	2002–2012
VIIRS	375–750 m	9	Daily	2011–present
OLCI (S-3 A/B)	300 m	17	Daily[b]	2016/2018–present
MSI (S-2 A/B)	10–60 m	9	5 days[b]	2015/2017–present

[a] In the visible-NIR portion of the spectrum, 400–865 nm
[b] With two sensors in constellation

300 m for Envisat's MEdium Resolution Imaging Spectrometer (MERIS) and its successor Sentinel-3's Ocean and Land Colour Instrument (OLCI)). The pixel size is determined by the sensor's instantaneous field of view, viewing angle to the ground, and satellite altitude. Temporal resolution, or revisit time, is the time between consecutive views of the exact same area of the earth. Spectral resolution defines the number and width of wavebands measured across the visible and near-infrared domains of the electromagnetic spectrum, with sensors ranging from multi-spectral (measuring at multiple discrete wavelengths) to hyperspectral (measuring near continuously across the full spectrum). Historically, optical satellite sensors were designed for either land or global ocean observing; therefore inland water applications relied upon either ocean color sensors that lacked sufficient spatial resolution or high spatial resolution land sensors that lacked sufficient spectral and radiometric resolution [12, 13]. With the onset of the European Space Agency's Copernicus program, and the launch of multiple satellites in constellation (Sentinel-3A and B, Sentinel 2A and B), we have entered an era of unprecedented data availability, with higher spatial resolution, increased frequency of observation, and spectral bands specifically targeting applications for algal bloom detection.

2.1 Multi-mission Data and Product Continuity

The lack of consistency in spectral, spatial, and temporal resolution between many of these remote sensing platforms means that products often require assessment for continuity before multi-sensor time series can be relied upon. Binding et al. [14] demonstrated broad consistency in the SeaWiFS (Sea-viewing Wide Field-of-View Sensor) and MODIS (Moderate Resolution Imaging Spectroradiometer) sensors in a study of water clarity across the Great Lakes, while Sayers et al. [15] investigated the coherence of SeaWiFS and MODIS-based cyanoHAB products in a time series of bloom extent for western Lake Erie. Wynne et al. [16] modified the Cyanobacteria Index (CI) algorithm, first defined for the MERIS spectral configuration, for application to MODIS, and showed generally good agreement between HAB distributions from the two. Similarly, Zeng and Binding [17] used a neural network solution to provide consistency in the measurement of bloom extent on Lake Erie with multi-mission data of varying spectral resolutions. Ho and Michalak [4] evaluated multiple Landsat 5 algorithms to estimate phytoplankton blooms and compared the results with those obtained from MERIS and MODIS CI products. Moving forward there is an increasing commitment from space agencies to ensure data continuity, with multiple near-identical sensors operating in constellation, therefore reducing the need for refining algorithm solutions to accommodate differences in sensor specifications.

3 Bloom Detection Algorithms

Numerous methods have been developed and adapted to determine chlorophyll-a concentrations or cyanoHAB conditions in Lake Erie [18–25]. Algal bloom detection algorithms take many forms but are driven by expected variations in the shape and/or magnitude of the spectral water-leaving radiance or reflectance signal detected by the satellite sensor (Fig. 1) which can then be empirically or analytically related to a specific measure of the bloom (e.g., chlorophyll-a or phycocyanin concentrations, cyanobacterial biomass/biovolume, etc.). Algorithms may be categorized broadly into either empirical (data-driven) approaches that span from regression methods to complex neural network simulations [26] or physics-based solutions that range from those involving empirical tuning (e.g., the absorption-based band ratio approach [19, 27]) to semi-analytical approximations of the underlying radiative transfer and optical property theory [21].

The Great Lakes are typically considered optically complex waters [28], due to the suite of organic and inorganic materials that interact with light through absorption and backscattering to determine the water's color signature. Chlorophyll retrieval algorithms based on blue to green band ratios (B:G), designed for the relative simplicity of the open ocean, perform poorly in optically complex waters due to the confounding interference of suspended minerals and dissolved organic materials on the optical properties. In addition, water reflectance (Rw) is used for many algorithms, and the atmospheric correction needed to retrieve Rw becomes more difficult in optically complex waters, leading to error and uncertainty in the resulting products [29–31]. Nevertheless, regionally tuned B:G algorithms have shown success for low-moderate phytoplankton biomass and offshore waters of the Great Lakes [19]. However, under conditions of turbid, eutrophic water (as typically observed in Lake Erie), the combination of algorithm saturation and amplified uncertainty from atmospheric corrections can lead to erroneous bloom retrievals from this algorithm approach [24].

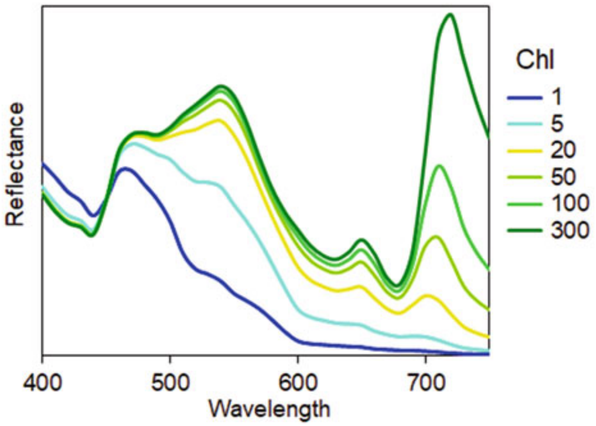


Fig. 1 Variation of spectral reflectance properties of a cyanobacterial bloom with increasing chlorophyll-a (μg/L). Reflectance is simulated using radiative transfer modeling in the absence of non-algal materials for qualitative representation only

Algorithm approaches exploiting the red and near-infrared (R-NIR) portion of the spectrum perform well in turbid eutrophic waters [32]. Line height algorithms such as the Maximum Chlorophyll Index (MCI) and Cyanobacteria Index (CI) capture phytoplankton absorption and scattering features in the R-NIR and are the basis for bloom detection algorithms used by ECCC [33] and NOAA [34], respectively. MTRI-derived chlorophyll products are the output of a semi-analytical bio-optical algorithm (CPA-A [21]) that simultaneously optimizes estimated concentrations for three color-producing agents (chlorophyll, suspended minerals, and dissolved organic matter). These methods are all based on bio-optical characteristics of water under algal bloom conditions, such as differential absorption by chlorophyll-a in specific red and blue bands.

Phycocyanin (PC) is a frequently used cyanobacteria marker pigment and forms the basis of many proposed remote sensing algorithms for detecting cyanobacteria (e.g., [35]). Satellite derivation of PC concentrations, however, is challenging due to the lower contribution to absorption from PC relative to chlorophyll-a and the significant overlap in their absorption properties [36–38] leading to an estimated fourfold difference in the sensitivity of remote sensing of PC relative to chlorophyll-a [39]. Consequently, these approaches are often used only as an indicator of cyanobacteria presence rather than a quantitative measure of PC concentration [40–42].

A few studies have used the Landsat series of sensors for bloom detection and monitoring on Lake Erie [4, 43]. However, the limited number and broad bandwidth of available spectral bands, combined with the low radiometric sensitivity of historical sensors, present challenges. Atmospheric corrections are less effective for Landsat and algorithms cannot be specific to the unique spectral properties of phytoplankton or cyanobacteria. For example, the red band (630–690 nm) spans many of the specific optical features used in bloom discrimination algorithms for other sensors (i.e., chlorophyll-a absorption at ~670 nm and fluorescence at ~685 nm), while no band exists for the detection of phycocyanin absorption at 620 nm. Furthermore, Landsat's long revisit time (~16 days) combined with data loss from cloud cover makes it difficult to reliably capture changes in highly dynamic bloom conditions [15, 22, 40, 44]. Notwithstanding those limitations, Ho and Michalak [4] assessed 11 simple band ratio and band difference algorithms for Landsat and subsequently assessed Lake Erie bloom extent back to 1984, considerably extending observations that were otherwise limited to the ocean color generation of satellite sensors, SeaWiFS, MODIS, and MERIS, beginning in 1997 [6, 15].

Some algorithm approaches attempt to decompose the bloom community composition, for example, Wang et al. [45] applied inverse modeling approaches using Gaussian decomposition and spectral optimization to retrieve multiple pigments. Others adopt a varimax-rotated principal components analysis (VPCA) approach to decompose spectral reflectance into information about the underlying color-producing agents [25, 46]. Although promising approaches, they are yet to be fully validated, often require hyperspectral resolution, are computationally demanding such that prompt access to operational products may be challenging, or have yet to be distilled into end user products readily interpretable by the broader Great Lakes community.

4 Products and Applications

Recognizing the large number of algorithms and sensors available to users, the focus here is on three processing streams of operational remote sensing products for Lake Erie algal blooms delivered by ECCC, NOAA, and MTRI. Figure 2 shows select cloud free images of 2019 bloom conditions in the western basin of Lake Erie, from July through to early September. Despite different algorithm approaches and different sensors used by these three processing streams, there is good consistency in daily products to track the bloom on Lake Erie. Those image products are made web-accessible to the public in near real time [47–49], providing prompt access to information on bloom conditions that can support immediate action for drinking water treatment and recreational activities, and are the foundation of outreach material disseminated to the user community (e.g., cyanoHAB bulletins, seasonal forecasts, and summary reports).

Beyond maps of chlorophyll or cyanobacteria biomass, remote sensing is increasingly being used to deliver quantitative information of algal bloom conditions through a suite of bloom indices, documenting bloom intensity and severity [6, 10, 33], spatial extent [15, 22, 33, 44, 50], duration [33], or frequency [51, 52]. Many studies have used remote sensing data to determine that annual bloom extent on Lake Erie is increasing [6, 15, 22, 44, 53]. These bloom indices are at the core of binational efforts to report on seasonal and interannual variability in bloom conditions on Lake Erie (Fig. 3) and contribute to the determination of recommended phosphorus load reductions to meet commitments under the Great Lakes Water Quality Agreement [53]. Ongoing satellite detection and reporting of bloom conditions will provide important metrics to study the lake's response to implemented nutrient abatement strategies as well as the influence of climate change on the Lake's anticipated recovery.

Satellite products have been used to gain further insight on the environmental drivers of bloom conditions. For example, Wynne et al. [20] analyzed the western basin bloom of 2008 in relation to meteorological conditions, making note of the effects of lake temperature and wind mixing on bloom intensity. Sayers et al. [22] showed a relationship between sediment resuspension events and annual bloom extent. Satellite imagery and statistical models have also demonstrated the link between bloom intensity and spring discharge and total phosphorus loads to the western basin of Lake Erie [6, 10, 22, 54, 55]. Unravelling the complex relationships between watershed, meteorological, and in-lake processes and bloom conditions on Lake Erie has been integral in the development of both short-term forecasting capabilities [11, 56] and seasonal forecasting [10]. By forecasting where blooms are likely to exist over the course of a few days, water resource and public health managers may be better prepared to take the necessary immediate actions to mitigate

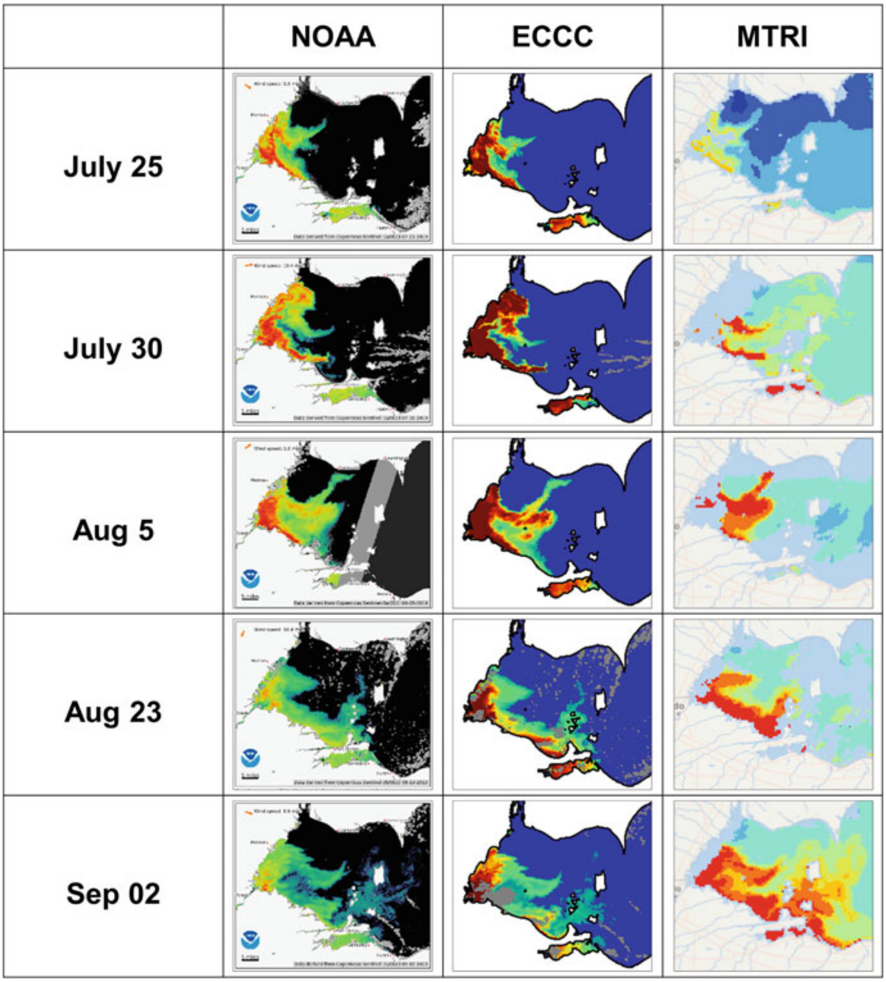
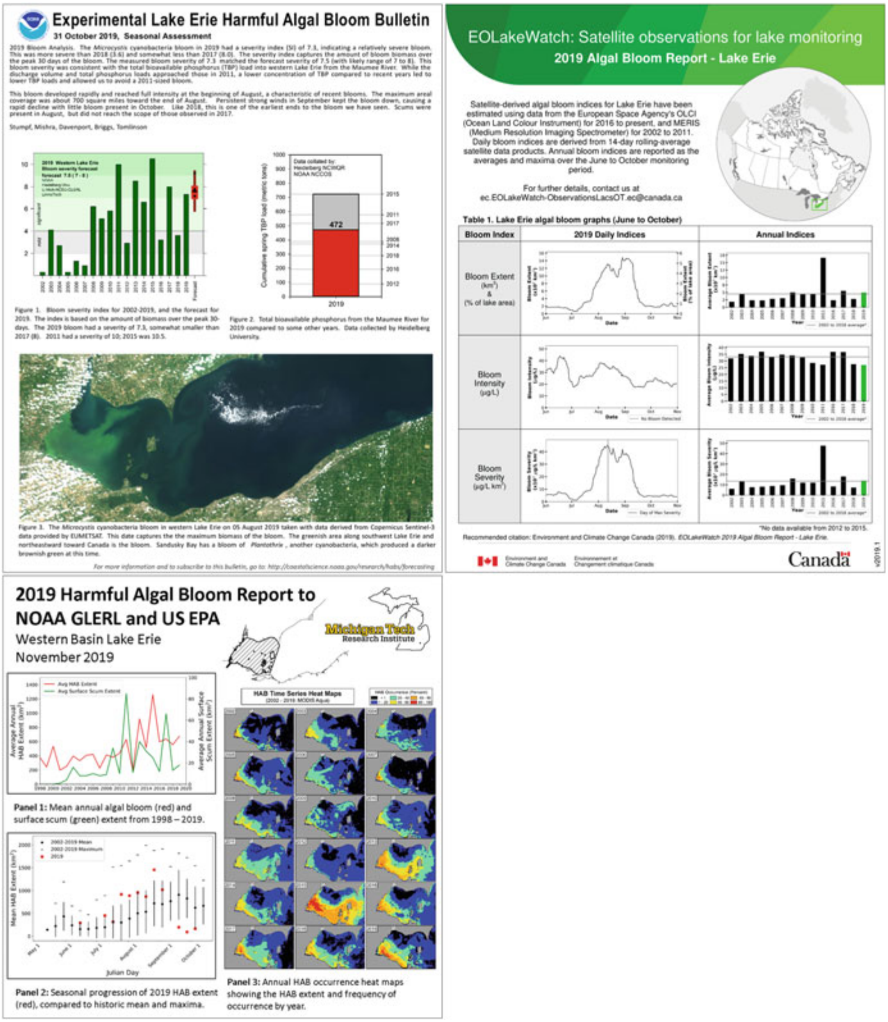


Fig. 2 Select images of algal bloom conditions on Lake Erie in 2019 from NOAA, ECCC, and MTRI processing streams

any potential detrimental impacts [11]. Seasonal forecasts of bloom severity allow public water suppliers and agencies concerned with toxin monitoring to plan ahead for the bloom season and for local businesses to anticipate possible effects on the summer tourism economy [10].

4.1 Consistency in Bloom Products

Despite consistency in the core bloom retrieval products shown in Fig. 2, differences exist in the algorithms and analytical approaches used by each organization which



Experimental Lake Erie Harmful Algal Bloom Bulletin

31 October 2019, Seasonal Assessment

2019 Bloom Analysis. The Microcystis cyanobacteria bloom in 2019 had a severity index (SI) of 7.3, indicating a relatively severe bloom. This was more severe than 2018 (3.6) and somewhat less than 2017 (8.0). The severity index captures the amount of bloom biomass over the peak 30 days of the bloom. The measured bloom severity of 7.3 matched the forecast severity of 7.5 (with likely range of 7 to 8). This bloom severity was consistent with the total bioavailable phosphorus (TBP) load into western Lake Erie from the Maumee River. While the discharge volume and total phosphorus loads approached those in 2011, a lower concentration of TBP compared to recent years led to lower TBP loads and allowed us to avoid a 2011-sized bloom.

This bloom developed rapidly and reached full intensity at the beginning of August, a characteristic of recent blooms. The maximum areal coverage was about 700 square miles toward the end of August. Persistent strong winds in September kept the bloom down, causing a rapid decline with little bloom present in October. Like 2018, this is one of the earliest ends to the bloom we have seen. Scums were present in August, but did not reach the scope of those observed in 2017.

Stumpf, Mishra, Davenport, Briggs, Tomlinson

Figure 1. Bloom severity index for 2002-2019, and the forecast for 2019. The index is based on the amount of biomass over the peak 30-days. The 2019 bloom had a severity of 7.3, somewhat smaller than 2017 (8). 2011 had a severity of 10; 2015 was 10.5.

Figure 2. Total bioavailable phosphorus from the Maumee River for 2019 compared to some other years. Data collected by Heidelberg University.

Figure 3. The Microcystis cyanobacteria bloom in western Lake Erie on 05 August 2019 taken with data derived from Copernicus Sentinel-3 data provided by EUMETSAT. This date captures the the maximum biomass of the bloom. The greenish area along southwest Lake Erie and northeastward toward Canada is the bloom. Sandusky Bay has a bloom of Planktothrix, another cyanobacteria, which produced a darker brownish green at this time.

For more information and to subscribe to this bulletin, go to: http://coastalscience.noaa.gov/research/habs/forecasting

EOLakeWatch: Satellite observations for lake monitoring

2019 Algal Bloom Report - Lake Erie

Satellite-derived algal bloom indices for Lake Erie have been estimated using data from the European Space Agency's OLCI (Ocean Land Colour Instrument) for 2016 to present, and MERIS (Medium Resolution Imaging Spectrometer) for 2002 to 2011. Daily bloom indices are derived from 14-day rolling-average satellite data products. Annual bloom indices are reported as the averages and maxima over the June to October monitoring period.

For further details, contact us at ec.EOLakeWatch-ObservationsLacsOT.ec@canada.ca

Table 1. Lake Erie algal bloom graphs (June to October)

Bloom Index	2019 Daily Indices	Annual Indices
Bloom Extent (km²) & (% of lake area)		
Bloom Intensity (µg/L)		
Bloom Severity (µg/L km²)		

*No data available from 2012 to 2015.

Recommended citation: Environment and Climate Change Canada (2019). EOLakeWatch 2019 Algal Bloom Report - Lake Erie.

Environment and Climate Change Canada Environnement et Changement climatique Canada

Canada

v2019.1

2019 Harmful Algal Bloom Report to NOAA GLERL and US EPA

Western Basin Lake Erie

November 2019

Michigan Tech Research Institute

Panel 1: Mean annual algal bloom (red) and surface scum (green) extent from 1998 – 2019.

Panel 2: Seasonal progression of 2019 HAB extent (red), compared to historic mean and maxima.

Panel 3: Annual HAB occurrence heat maps showing the HAB extent and frequency of occurrence by year.

Fig. 3 NOAA Lake Erie HAB Bulletin 2019 Seasonal Assessment, ECCC EOLakeWatch 2019 Lake Erie Annual Bloom Report, and MTRI 2019 Algal Bloom Report

lead to some variation in reported bloom metrics. The approaches taken by ECCC, NOAA, and MTRI in their bloom reporting are summarized below.

ECCC produces maps of MCI-derived chlorophyll-a as daily and 14-day rolling average products (in order to minimize uncertainties introduced by cloud cover). The algal bloom flag is raised on a pixel by pixel basis when derived chlorophyll-a concentrations are in excess of 10 μg/L. This threshold follows the World Health Organization guideline levels for relatively low probabilities of adverse health effects of 20,000 cyanobacterial cells/mL (corresponding to 10 μg/L of chlorophyll-a under conditions of cyanobacterial dominance). ECCC reports on daily bloom indices: bloom intensity as the average chlorophyll-a content of the area flagged as a bloom; bloom spatial extent as the total area covered by that bloom flag; and bloom severity as the product of bloom intensity and extent. Annual bloom indices are then reported as their maxima and average over the June to October monitoring period, therefore intrinsically accounting for bloom duration.

NOAA identifies presence of cyanobacterial blooms with the CI product obtained between June and the end of season. The CI is related to *Microcystis*, with 10^8 cells/mL = 1 CI unit. The non-detect limit is 0.0001 CI (~10,000 cells/mL). The World Health Organization [57] has identified 20,000 cells/mL (CI ~ 0.0002) as mild risk and 100,000 cells/mL (CI ~ 0.001) as moderate risk. The state of Ohio uses the satellite data with CI $>$ 0.002 (20,000 cells/mL) as a threshold for assessing the impairment of open waters of western Lake Erie [58]. In addition, NOAA produces a severity metric each year based on a composite of the imagery. Composites are made of the maximum observed CI value at each pixel in imagery taken within 10-day windows (e.g., July 1–10, July 11–20). Because *Microcystis* typically floats to the surface on calm days, the composite is mostly likely to capture the maximum biomass at each pixel, as well as reducing data loss from clouds. The severity is then based on the three 10-day periods with the greatest total biomass in the western lake [6]. Further development of that severity index aims to integrate over the bloom season to capture bloom duration [59].

MTRI identifies cyanobacterial presence based on the CPA-A-derived chlorophyll-a concentration and water temperature. An empirical relationship was derived from in situ data from the Great Lakes showing that phycocyanin was abundant when chlorophyll-a concentrations were greater than 18 μg/L and water temperature was greater than 20 °C [22]. This difference in bloom threshold definition explains the lower documented bloom extent reported by MTRI compared with ECCC. Additionally, MTRI estimates the presence of cyanoHAB surface scum (floating biomass) using a modified NDVI approach [22]. Maps are created for cloud-free images from the MODIS, VIIRS, and SeaWiFS sensors on a per pixel basis, which are used to generate a suite of cyanoHAB products detailing the intra- and interannual bloom extent and frequency that are reported to the US EPA and other interested stakeholders.

5 Challenges and Limitations of Remote Sensing

5.1 Product Validation

CyanoHABs vary from localized to basin-wide events and can be highly dynamic in space and time [60–62], thus are difficult to adequately capture with conventional sampling methods (discrete water samples). For the same reason, validating remote sensing retrievals with discrete samples can often misrepresent algorithm accuracy due to the non-homogeneity of bloom biomass within a single co-located pixel (an area of ~0.09 km^2 for OLCI). Nevertheless, discrete measurements have been made throughout the Western Basin across multiple years to capture bloom spatial and temporal variability and compare well to remote sensing-derived products [22, 24].

5.2 Algal Bloom Toxicity

Cyanotoxins cannot be directly detected by remote sensing due to the lack of any discernible optical signature, and therefore any potential for bloom toxicity determination from space relies upon potential proxy-based approaches. Direct comparison of satellite data to toxicity is problematic, because the toxin production by cyanobacteria cells changes through the bloom and changes between years [39]. A method to overcome this is to use a relationship of toxin concentration to pigment concentration, derived in the field, and updated frequently through the season, and combine that with the satellite-observed pigment concentration.

5.3 Vertical Bloom Variability

Cyanobacteria are well known for their ability to regulate their buoyancy and move vertically in the water column to exploit optimal light and nutrient conditions [63]. Satellite retrievals, however, represent only bloom conditions within the surface layer as defined by the first optical depth, which is determined by the combined attenuation of light by dissolved and particulate matter [64]. The vertical distribution of cyanobacteria in the water column therefore has a significant impact on what proportion of the total biomass the remote sensing signal captures [20, 65–67]. This can be seen clearly in satellite imagery during intermittent periods of wind mixing, where the bloom seemingly decreases in intensity during a wind event but in fact is simply mixed from the surface layers [20, 65]. While mapping of the surface extent of cyanobacterial blooms is relatively straightforward, with variable depth distributions of cyanobacteria throughout the water column, quantitative mapping of total cyanobacterial biomass with remote sensing is more challenging [67]. Efforts to account for that variability in the vertical distribution of phytoplankton biomass have centered on the integration of remote sensing observations with hydrodynamic modeling [56, 68] and more recently on the application of LIDAR [69]. Rowe et al. [69] describe a short-term forecast system for cyanoHAB abundance and distribution in Lake Erie, including a method to simulate vertical distribution of buoyant cyanobacteria, while Soontiens et al. [56] documented the sensitivity of hydrodynamic models to phytoplankton buoyancy velocity and vertical distribution in their simulation of western Erie HABs.

5.4 Variable Optical Properties

One of the largest sources of uncertainty in satellite retrievals is the variability of local inherent optical properties (IOPs) of the dissolved and particulate materials that contribute to the remote sensing reflectance signal. A number of studies have documented large spatiotemporal variability in the optical properties of the western basin blooms [24, 70, 71], driven in large part by variations in phytoplankton community composition. Cyanobacteria blooms often exhibit unique backscatter and absorption features due to the presence of gas vacuoles [72], colonial aggregation [73], and specific pigmentation [74]. For example, Binding et al. [24] documented elevated backscattering coefficients associated with Maumee Bay *Microcystis*-dominated blooms, resulting in higher MCI and CI per unit chlorophyll compared with typically *Planktothrix*-dominated Sandusky Bay blooms. Better characterization of the spatial and temporal variability of IOPs would result in more robust remote sensing algal bloom retrievals.

6 Conclusions

Remote sensing of algal blooms in the Great Lakes has reached a level of maturity where products are routinely accepted and utilized by Canadian and US stakeholders, including government, industry, academia, and the public. Outreach material providing near-real-time updates on bloom conditions, seasonal forecasts, and post-season summaries has proven invaluable to policy-makers and water resource managers. The recognized limitations of remote sensing (cloud cover, image frequency) are often mitigated by the integration of hydrodynamic and ecological modeling and novel analytical solutions. Moving forward, remote sensing algal bloom products are being enhanced by greater sensor capabilities, improved understanding of optical properties, and improved knowledge of the Great Lakes ecosystem. Furthermore, with future satellite missions (hyperspectral, geostationary, LIDAR) comes the potential for the development of an advanced suite of products (e.g., particle size, bloom community composition, and vertical bloom distributions).

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Part IV
Management

Land Use, Land Cover, and Climate Change in Southern Ontario: Implications for Nutrient Delivery to the Lower Great Lakes

M. Catherine Eimers, Freddy Liu, and Jennifer Bontje

Contents

Abstract Southern Ontario is home to over a third of the Canadian population and is also one of the most productive agricultural areas in the country. This mosaic of a large and growing urban population and prime agricultural land creates particular challenges for soil and water resource management. While urban areas continue to expand in southern Ontario, changes in agricultural cover and practices within the headwaters are also important to consider. There have been dramatic increases in tile-drained cash crop production (principally grain, corn, and soybean) in southern Ontario over the past few decades, largely at the expense of pasture and forage land. Urban populations will continue to expand into the future, but there is considerable scope for further agricultural change in the headwaters as well. Expansions in urban land cover and intensification of agriculture affect the hydrologic response to extreme events as well as water quality and nitrate leaching in particular. It is important to consider the effects of shifts in both types of land cover on stream

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flow and water quality in the variable landscape and climatic conditions of the lower Great Lakes.

Keywords Agriculture, Land use change, Nutrients, Water quality

1 Population of Southern Ontario

Ontario is Canada's second largest and most populous province (13.4 million), accounting for 38% of the nation's population in 2016 [1]. Over 90% of the Ontario population lives within the approximately 84,000 km^2 area known as southern Ontario, shown in Fig. 1, concentrated within several larger urban centers that are located primarily along the northern shoreline of Lake Ontario. The Toronto census metropolitan area (CMA) alone accounts for almost half of the Ontario population (5.9 million) and 1 in 5 of all Canadians resides within the Toronto CMA (Fig. 1). Southern Ontario is also one of the fastest expanding areas in the country, with an overall population increase of 6.2% between 2011 and 2016 compared with a national growth rate of 5% [1]. The majority of future population growth in Ontario is expected to occur within southern Ontario, and if current rates of growth continue, the population is expected to grow by 30%, or almost 5 million, to approximately 18.5 million in 2040 [2].

2 Urban Land Cover in Southern Ontario

Urban land is classified through the Southern Ontario Land Resource Information System (SOLRIS; [3]) as "pervious," "impervious," and "transportation," and together these three categories of urban land cover 8.4% of southern Ontario (Table 1). Recent population increases in Ontario have been accompanied by expansions in urban land cover, although the rate of urban expansion has outpaced that of population growth due to what is commonly referred to as "urban sprawl." Construction of relatively low-density residential subdivisions became the conventional pattern of development in Canada in the 1950s and 1960s, and these often independent, single-family homes were built on agricultural and/or pristine forest or open space lands [5, 6]. Concerns over urban sprawl have generated substantial discussion and a variety of planning regulations and policies purported to direct growth and better protect natural environments and agricultural land from conversion and degradation. For example, Ontario's Places to Grow Plan was finalized in 2006 to address urban sprawl and establish a permanent greenbelt that would protect greenspace, farmland, wetlands, and natural areas in the Golden Horseshoe area, which includes Toronto [6]. Nevertheless, expansion at the boundaries of urban

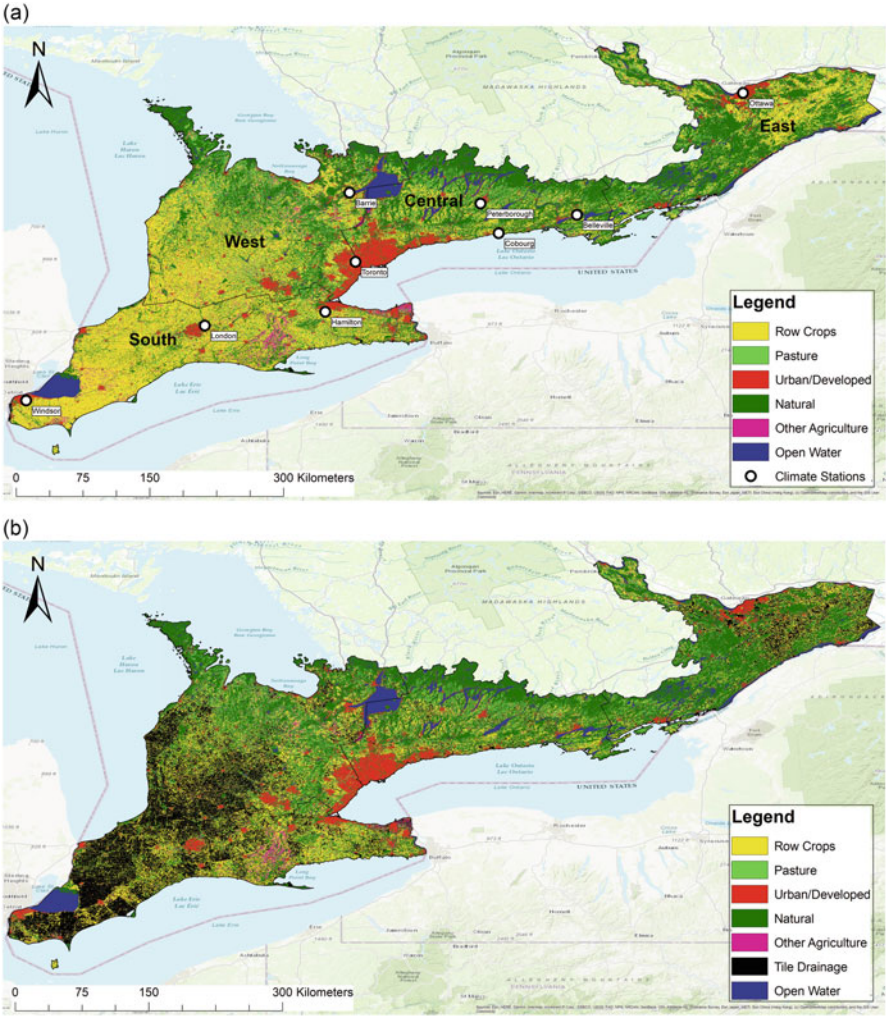

Fig. 1 (**a**) Land cover in southern Ontario. Data are from SOLRIS (version 2.0) and Agriculture and Agri-Food Canada (AAFC)'s Annual Crop Inventory (2018 data). Also shown are locations of climate stations. (**b**) Locations of recorded tile drainage in southern Ontario. Data are from OMAFRA (record updated through 2018)

areas continues, and reported population increases in the Greater Toronto CMA between 2011 and 2016, for example, were entirely due to growth in its "peripheral" census subdivisions including Mississauga, Brampton, and Markham, as numbers within the "central" census subdivision of the city of Toronto itself actually declined over the same time period [1].

Table 1 Land cover in southern Ontario

	Total area (km^2) ($83,905\ km^2$)	% of southern Ontario
Forest (includes coniferous, deciduous, and mixed)	11,300	13
Wetland (includes swamp, bog, and marsh)	11,171	13
Built-up impervious	3,345	4.0
Transportation	2,838	3.3
Built-up pervious	915	1.1
Pasture and forages	14,720	18
Corn, soybean, and cereals	24,830	30
Total agriculture (includes the two categories above plus nursery, sod, vegetables, vineyards, and specialty crops)	44,450	53

Urban and natural land cover areas were assessed using SOLRIS (version 2.0; dated 2009–2011), which is based on the Ontario Ministry of Natural Resources and Forestry (MNRF)'s ecological land classification system [4]. Agricultural land cover is only crudely classified in SOLRIS as "tilled," and so Agriculture and Agri-Food Canada (AAFC)'s Annual Crop Inventory (2018 data) was used to quantify areas and types of agricultural land

2.1 *Effects of Urban Land Use on Water Resources*

Urban development has serious consequences for water resources in the Great Lakes basin. Development alters the local hydrologic cycle by removing vegetation that intercepts and transpires precipitation inputs as well as natural depressions that temporarily store water. Native soils are compacted or covered with impervious surfaces including roads, parking lots, sidewalks, and buildings. Impervious surfaces decrease the amount of water that infiltrates into the ground, increasing the volume and rate of stormwater runoff into recipient waterways. Eimers and McDonald [7] found that annual and seasonal runoff totals were similar between rural and urban tributaries draining into Lake Ontario and were relatively insensitive to urban cover. Instead, urban streams had significantly greater high flow frequency and flow variability and more quickflow and lower baseflow compared with rural streams. Furthermore, differences in high flow frequency between urban and rural stream groups were largest in the summer and fall and less extreme in the winter and spring, perhaps because of the homogenizing effect of winter snow cover, frozen ground, and spring melt on surface imperviousness. The enhancement of extreme flow regimes during the growing season in urban streams may have more severe consequences for aquatic ecosystems and stream habitat.

Habitat within urban-impacted streams is also affected by rapid conveyance of runoff and increases in peak flows, which accelerate erosion and destabilize stream banks [8]. Impervious surfaces augment the transfer of nutrients (e.g., phosphorus and nitrogen) and contaminants from urban areas to waterways including pesticides, road salts, and other chemicals associated with urban areas. Higher nutrient and contaminant exports in urban watersheds are attributed not only to anthropogenic changes to the land surface and subsurface drainage network that promote rapid drainage but also to the relatively large inputs these watersheds receive from external sources, including atmospheric deposition, fertilizer, and pet wastes [9–11].

Since the 1990s, stormwater management has been required in southern Ontario, and Ontario is considered one of the more "environmentally progressive" provinces with respect to urban storm water management [12]. Stormwater ponds are the most common best management practice in urban areas and are a common feature in new residential developments where they are intended to slow runoff movement into streams and allow sediment (and associated nutrient/contaminant) retention. Because storm water ponds only became standard after the 1990s in southern Ontario, "new"/post-1990s urban areas may respond differently to hydrologic inputs and extreme events compared with older urban centers that were established before urban stormwater management became conventional. As such, the sensitivity of stream flow and nutrient and contaminant transfer may be different in newly urbanized areas, such as those that are currently expanding around the periphery of existing high-density urban areas.

2.2 Urban Contributions to Nutrient Losses

Land use is an important determinant of nutrient export from land to waterways, and urban runoff is recognized as an important source of nutrient inputs to the lower Great Lakes (e.g., [13]). Urban areas are consistently associated with higher total phosphorus (TP) exports compared with natural watersheds, but differences in TP export from urban vs. agricultural landscapes are more varied, with some studies reporting higher TP export at urban compared with agricultural dominated catchments and others reporting the opposite (e.g., [14]). Variability in export rates both among and within land covers is likely due to the very large range of agricultural types (e.g., cash cropping, livestock, horticulture) and practices (e.g., tillage, tile drainage, fertilizer application) as well as form (suburban, high density urban) and phase (construction, established) of urban development and associated use of best management practices. For example, Duan et al. [15] found that P exports were higher from catchments dominated by higher density urban land compared with lower density residential developments along an urban-to-rural gradient in Maryland, United States. Despite expansions in urban cover across southern Ontario since the 1970s, significant declines in TP concentration were observed at almost 70% of the streams studied by both Raney and Eimers ([16]; $n = 114$ streams) and Stammler et al. ([17]; $n = 56$ streams) over a 30-year period, and the highest TP concentrations and the largest TP declines occurred in mixed land use watersheds that encompassed both urban and agricultural land cover [17]. Declines in offshore TP concentrations in the lower Great Lakes over the same time period have been largely attributed to improved P removal from point sources including wastewater treatment plants (WWTPs) [18]. However, Raney and Eimers [16] reported that declines in stream TP occurred at sites both with and without upstream WWTPs and concluded that improved P removal from treated wastewater could not be the sole driver. While the cause(s) of observed TP declines in southern Ontario streams remain unresolved, it is conceivable that land use change may play a role. For example, TP export from “new urban” developments may be lower than expected as a result of BMPs like stormwater management ponds and newer low-impact design (LID) strategies, and therefore increases in urban cover at the expense of agricultural land may be associated with lower P exports if the replacement urban land involves effective stormwater and erosion management. Studies conducted through the Stormwater Assessment Monitoring and Performance (SWAMP) Program in Ontario found that stormwater ponds and retention basins that slow runoff and allow sedimentation generally reduce P losses in runoff [19].

3 Agricultural Land Cover in Southern Ontario

Expansions in urban land have been associated with agricultural loss [20], and total agricultural land in Ontario declined from a peak around 1920 to its current coverage of just over half of total land area by 2011 ([21]; Table 1). Total agricultural land continues to decline, albeit at a slower pace, and currently 1/3 of all urban land in Canada is located in Ontario [22]. Expansions of urban area at the expense of agricultural soils are of particular concern in a country such as Canada, where agricultural land is a scarce resource and only 5% of total land area is considered free from severe constraints to crop production [20]. Indeed, Ontario is home to the best agricultural land in Canada, and over 50% of the nation’s entire endowment of “Class 1” agricultural land (defined as free from any soil or climatic constraints) is found in southern Ontario [20]. Ontario has more farms than any other province (~49,000 in 2016), ranks fourth in Canada for total area and accounts for 1/5 of national farm income [1].

3.1 Changes in Southern Ontario Agriculture

While agriculture remains the most common land cover in southern Ontario (53% of total land area), less well recognized is that while total farmland declined in Ontario, the total area under crop production held relatively constant, and so the proportional area of row crops (also commonly referred to as “cash crops”) actually increased between 1976 and 2011 [21]. Increases in row crop area were largely at the expense of land previously under pasture and forage (e.g., hay), which declined substantially over the same time period. Forest and wetland area also declined [21]. Decreases in pasture and forage area are attributed to a major reduction in cattle and dairy cow numbers in Ontario between 1976 and 2011 (45% and 52%, respectively) which may be partly attributed to an east-to-west shift in cattle production within Canada [21]. Pasture and forage together currently represent approximately 1/3 of total agricultural area in southern Ontario (Table 1).

Two cash crops in particular – grain corn and soybean – currently dominate agriculture in Ontario (Table 1), and Ontario accounts for 60% and 50% of national grain corn and soybean area, respectively [1]. Smith [21] describes increases in soybean production in Ontario (+552%) and grain corn (+29%) between 1976 and 2011 as "meteoric," and similar increases in soybean and grain corn production have occurred in the United States portion of the Western Lake Erie Basin [23]. Dramatic increases in soybean and corn production in Ontario have been attributed to a variety of factors, including the emergence of cold-hardy, short-season soybean cultivars, increased demand from the Chinese market, as well as greater reliance on corn-derived ethanol (e.g., [24]). Much of the cropland in Ontario is concentrated in the extreme southern and western portions of southern Ontario, which drain into Lake Erie and Lake Huron, respectively, whereas agricultural land north of Lake Ontario (central and eastern regions; see Fig. 1) is more mixed, with both cropland and pasture/forage common. Nevertheless, shifts from mixed livestock farming toward increased cash cropping have occurred in the central and eastern portions of southern Ontario as well [25].

3.2 Changes in Agricultural Practices: Impacts on Water Quantity and Quality

In addition to major shifts in the type of agriculture practiced in southern Ontario, there have been substantial changes to agricultural procedures in the region, including tillage methods, type of fertilizer application, and the extent of tile drainage. These shifts may have consequences for both soil and runoff water quality in southern Ontario and the downstream Great Lakes. Soil conservation concerns in the 1980s led to the widespread promotion of reduced tillage as a means of increasing soil organic matter storage and limiting erosion. Current reported levels of no-till or reduced till in Ontario (63% of cropland in 2011) suggest this practice is far more common than conventional tillage, where most of the crop residue is incorporated into the soil (37% in 2011) [21]. While employing methods of reduced tillage encourages organic matter storage in soil, which is generally associated with improved soil structure and lower erosional losses, it also has been speculated to be associated with recent increases in soluble reactive phosphorus (SRP) in Lake Erie and its major tributaries in New York (e.g., [26]). The relationship between tillage practices and runoff water quality is not straightforward and may depend on soil texture and other management methods including whether fertilizer is applied to the soil surface or injected. For example, surface broadcast P fertilizer in combination with no-till practices in a fine textured soil that is prone to cracking and macropore drainage could lead to higher P losses compared with a soil that is coarse textured or where P additions are homogenized through the soil rooting zone via conventional tillage [27]. More frequent extreme rainfall events may exacerbate nutrient losses

Table 2 Tile drainage area and date of installation in the four subregions of southern Ontario

Area (km^2)	South	West	Central	East	Total
Total recorded tiled area	8,279	5,975	452	2,082	16,789
Recorded tiled area with date	1,224	1,322	142	664	3,352
Total urban area	1,965	2,163	1,861	1,110	7,098

Tile drainage areas are from OMAFRA (2018); urban areas (sum of pervious, impervious, and transportation) are from SOLRIS version 2.0. Subregions of southern Ontario are the same as shown in Fig. 1a

through enhanced erosion and associated export of particulate-associated P, especially in areas dominated by fine-textured soils like southwestern Ontario [27].

Tile drainage is another management practice that may alter both water quality and quantity in the Great Lakes basin. Tile drainage is generally encouraged by the provincial ministry of agriculture (Ontario Ministry of Agriculture, Food and Rural Affairs; OMAFRA) due to its proven agronomic benefits including improved crop production and longer and more reliable access to fields. Drainage is considered almost essential in no-till or reduced-till agriculture, since soil drying is one of the benefits of conventional tillage. Tile drainage installations in Ontario do not require prior consideration of impact on groundwater or offsite water quality or quantity, and the Tile Loan Program, authorized by the *Tile Drainage Act*, provides loans to agricultural property owners to help them finance these tile drainage projects [28, 29]. The sheer magnitude of tile drainage in Ontario and its pace of expansion suggest that this form of agricultural water management may have cumulative impacts on downstream environments. Tile drainage currently underlies over 16,700 km^2 of southern Ontario (see Fig. 1b; Table 2), although this area is widely acknowledged to be an underestimation given the very advanced age of many installations that pre-date modern record keeping, as well as private installations that do not require site plan submission. For example, of the 16,789 km^2 of recorded tile drainage, only 20% is associated with a date of installation (Table 2).

Nevertheless, even this incomplete record indicates that a substantial proportion of agriculture in southern Ontario is currently underlain by tile drainage. Furthermore, the recent rate of tile drainage expansion in southern Ontario appears to outpace that of urban expansion over the past two decades, particularly in the southwestern extreme of the province (Fig. 2).

While tile drainage is an important agronomic tool that boosts agricultural production, it also affects water quality and quantity. Subsurface drainage facilitates export of both P (e.g., [30]) and nitrate (NO_3-N) to waterways by improving drainage beneath the rooting zone and expediting transfer to downstream surface waters [31, 32]. Increases in corn and soybean production in Ontario are of particular concern with respect to NO_3-N, which tends to be higher in surface water and groundwater within agricultural watersheds compared with watersheds dominated by suburban or urban land cover [33]. Corn is known to have a high N-demand but low N-use efficiency, and thus NO_3-N leaching rates from corn fields tend to be much higher than for other common row crops [34]. Studies in Iowa, which is part of

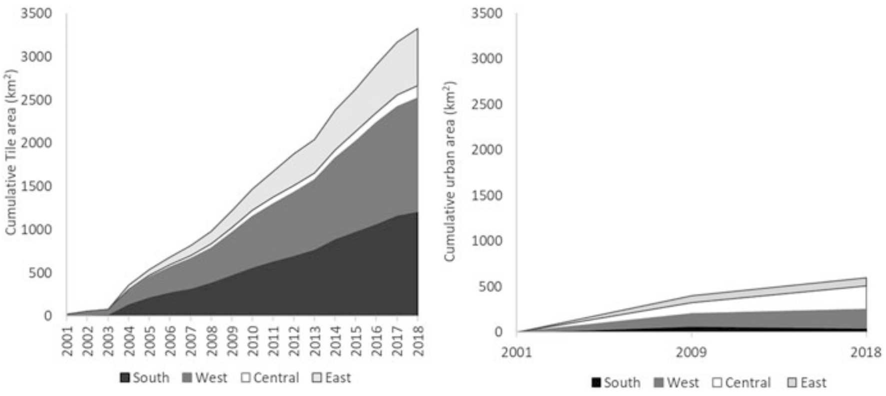

Fig. 2 Cumulative expansions in tile drainage area (left panel) and urban area (right panel) in the four subregions of southern Ontario between 2001 and 2018; analysis is limited to 2001 onward as the area of tile installed prior to this period is unknown

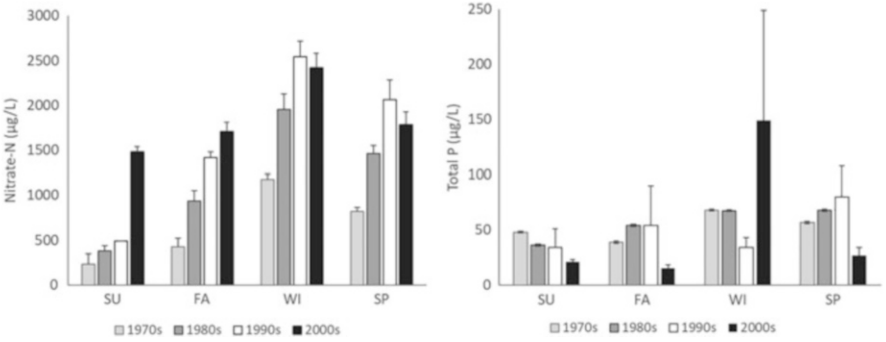

Fig. 3 Decadal averages of seasonal (*SU* Summer, *FA* Fall, *WI* Winter, *SP* Spring) concentrations of stream nitrate-N (left panel) and total P (right panel) at Gages Creek, a 46.6 km^2 agricultural watershed in the central subregion that drains directly to Lake Ontario [25, 37]

the Corn Belt in the Midwestern United States have shown a positive relationship between land under row crop (particularly corn) and surface water NO_3-N concentrations [35, 36]. Soybeans, in contrast, are legumes that fix atmospheric N and are known to augment the soil N pool and may facilitate greater NO_3-N losses from the following corn crop if residual soil-N is not adequately accounted for in fertilizer applications.

Significant increases in stream NO_3-N concentrations occurred at agriculturally dominated watersheds that drain into Lake Ontario between 1971 and 2010 (see Fig. 1b), with the largest and most significant increases occurring in watersheds where row crop cover also increased [25, 37]. Nitrate concentrations increased significantly over time in every season at Gages Creek, for example (Fig. 3), whereas TP trends were more variable. Total urban area increased in Gages Creek between 1971 and 2011 from 2% to 9%, while total agricultural area declined from 91% to

71%. However, the proportion of agricultural land under row crops (primarily corn and soybean) increased over the same period from 42% to 61%, and this may have particular relevance for nitrate export via tributaries [25]. Increases in corn and soybean area at the expense of pasture and forage have undoubtedly altered the N budget of agricultural watersheds in southern Ontario and may even contribute to observed increases in NO_3-N in the lower Great Lakes [18, 21].

The effects of tile drainage on total runoff quantity are more complex and may be influenced by site-specific conditions, but a recent review by Gramlich et al. [27] suggests that stormflow is augmented by tile drainage in areas with a naturally low water table, whereas stormflow may decline following drainage in areas with a typically high water table. The overall water budget may be also affected by increases in tile-drained row crops through replacement of perennial vegetation (i.e., hay, pasture) with annual plants (corn and soybean) that typically have smaller transpiration losses and less evaporation from standing water/saturated surface soils due to improved drainage. Drainage may also cause more rapid conveyance of water from fields to recipient streams, and ditching and straightening of channels that often accompany agricultural production may further contribute to rapid transit times [27]. The few Ontario studies that have examined the effects of drainage on watershed-scale hydrology have been generally inconclusive (e.g., [38]) although the authors acknowledged that the history of drainage preceded the instrumental record of streamflow in much of southern Ontario, which precludes a before-and-after comparison. While this is certainly the case in the south and west subregions of Ontario, where installations date back to 1906 [39] and there is little remaining untiled cropland (see Fig. 1b), the central region of southern Ontario may be a ripe area for research, since it has the lowest amount of currently recorded tile drainage (Table 1) and therefore the greatest potential for expansion. The effects of drainage and vegetation shifts in agricultural headwaters should be considered when evaluating flood potential in downstream urban areas. Indeed, Wiskow and Van der Ploeg [40] argue that agricultural drainage has contributed to increased flood incidence in Germany. The potential for tile drainage to contribute to downstream flood incidence in southern Ontario urban areas has not been evaluated but should be considered particularly in the context of a changing climate.

3.3 The Interaction Between Water Resources, Land Use, and Climate Change

Water resources are closely connected to the climate elements of air and water temperature, precipitation, evaporation, and snow and ice cover, and so changes in these parameters may have considerable impacts on water resource management. Climate model projections for Ontario over the next century indicate higher air and water temperatures, more precipitation (with high regional and seasonal variability), shorter winters, less ice and snow coverage, a longer growing season, higher rates of evaporation and transpiration, and increased potential for extreme weather events [41]. While differences in annual average (1981–2010) temperature and precipitation across the region of southern Ontario shown in Fig. 1 are relatively small (see Table 3), ranges in extreme conditions are more considerable. For example, Windsor, in the extreme southwest of the province, routinely experiences the greatest number of extreme hot days ($T_{\max} > 30°C$) with an average of 24 days per year exceeding this threshold between 1980 and 2010, compared with Cobourg, where extreme hot days numbered less than 5 per year over the same time period (Table 3). Extremes in precipitation are of greater direct relevance to water resources but are less variable across sites, with much of southern Ontario receiving an average of 8–9 rainfall events per year that exceed the 90th percentile (Table 3). The majority of these large rainfall events occur in the summer and fall, when differences in runoff extremes between urban and rural streams are greatest [7]. Notably, all sites receive at least 1–2 large rainfall events per year during the winter and spring months. Extreme rainfall events during the non-growing season have a high potential to generate flooding due to generally frozen or snow-covered ground that limits infiltration as well as minimal evapotranspiration losses during the period of senescence. A recent national analysis of floods and flood regimes found that 38% of reference rivers in southeastern Canada showed significant ($p < 0.05$) increases in the frequency of extreme runoff events (>90th percentile) between 1961 and 2010 and no sites showed declining trends [42]. Furthermore, 14% of these watersheds showed an advancement in the timing of extreme runoff events, which is consistent with a reduction in snowmelt events and an increased importance of pluvial contributions to flooding [42]. Warmer winter temperatures and/or more regular temperature excursions above 0°C could produce more frequent winter thaw events that result in extreme runoff. While there is limited capacity for older urban areas to adjust to augmented winter flow, newer urban developments that incorporate stormwater ponds have some storage capacity to absorb extreme runoff events, even during the winter. Seasonal comparisons of pond efficiency in southern Ontario, for example, have shown that flow extremes are similarly muted in summer and winter-spring; however, nutrient removal rates are often less in the dormant season likely due to lower biological activity (e.g., [43]). In contrast, tile drains consistently respond to both rainfall and melt inputs during the nongrowing season and very rarely generate discharge during the summer [44]. As a result, winter rainfall and temperature extremes may produce a larger runoff response in tile-drained agricultural systems. As tile-drained agriculture ubiquitously surrounds urban centers in southern Ontario, there is the potential for tile-drained agriculture to amplify the hydrologic response of downstream urban watersheds to extremes in winter rainfall and temperature-driven melt events.

Table 3 Long-term average temperature and precipitation within the southern Ontario study region

1981–2010 averages	Ottawa	Belleville	Peterborough	Cobourg	Toronto	Barrie	London	Hamilton	Windsor
Annual avg (°C)	6.6	8.1	6.2	7.5	8.2	6.9	7.9	7.9	9.9
Jan avg (°C)	−10.2	−6.7	−8.5	−5.6	−5.5	−7.7	−5.6	−5.5	−3.8
Jul avg (°C)	21.2	21.8	19.6	19.9	21.5	20.8	20.8	20.9	23
# days with max $T \leq 0°C$	74	54	62	50	53	67	57	56	44
# days with max $T > 30°C$	12	8	9	1	16	10	10	11	24
Degree days > 5°C	2,182	2,330	1,916	2,015	2,290	2,107	2,211	2,212	2,688
Annual precipitation (mm)	920	912	855	890	786	933	1,012	930	935
%Snow	18	15	17	11	13	24	16	15	12
Annual rainfall; R (mm)	756	772	712	794	682	710	846	792	822
% Summer (JJA)	35	28	32	27	33	35	30	33	30
% Fall (SON)	32	34	32	33	30	33	31	29	29
% Winter (DJF)	10	14	11	15	12	8	13	13	14
% Spring (MAM)	24	25	24	25	25	24	25	24	26
90th percentile of daily R (mm)	19.3	19	19	19	18.4	17	19.6	19.7	21.2
# days daily $R > 90$th									
Annual	8.9	8.7	8.7	8.8	8.1	8.8	7.9	8.8	8.6
Summer	3.8	2.7	3.4	2.7	3	4	2.5	3.6	2.8
Fall	2.5	3	3	2.9	2.4	2.8	2.7	2.9	2.9
Winter	0.7	1.1	0.8	1.2	0.6	0.4	1.1	0.8	1
Spring	1.8	2	1.6	2	2	1.6	1.7	1.5	1.8

Seasons include summer (Jun, Jul, Aug); fall (Sep, Oct, Nov); winter (Dec, Jan, Feb); and spring (Mar, Apr, May)

4 Where Do We Go From Here?

Southern Ontario is a mosaic of urban and agricultural lands with natural cover mainly located in the northern parts of the region (Fig. 1). The intersection between prime agricultural land and a growing urban population poses particular challenges for soil and water resource management in the region. Nitrate levels in the lower Great Lakes have been increasing over the past few decades, whereas total P concentrations have declined [18]. Similar trends in nutrient concentrations in agricultural tributaries draining to Lake Ontario suggest that shifts in watershed land use may be a contributing factor [25, 37]. The area of southern Ontario described in this chapter drains to Lake Ontario, Lake Erie, and Lake Huron, which together supply drinking water for millions of Canadians and Americans in the Great Lakes basin. While there is currently strong interest in sustainable urban development and low impact design strategies are becoming more common in new urban areas, agricultural practices are becoming more intensive. There is significant scope for further increases in tile-drained row crop area within southern Ontario, particularly in the central and eastern regions, if demand for cash crops like corn and soybean remains strong. Understanding the cumulative effects of both agricultural and urban land cover change, as well as possible mitigation strategies, is important for the protection of water quality and flood prevention in the lower Great Lakes basin, particularly under a changing climate.

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Enhanced Transboundary Governance Capacity Needed to Achieve Policy Goals for Harmful Algal Blooms

Irena F. Creed and Kathryn Bryk Friedman

Contents

Abstract The Great Lakes-St. Lawrence River Basin is at risk from environmental contaminants, with the western basin of Lake Erie plagued by harmful algal blooms (HABs). Although science and technology are essential to inform policy, we contend that effective governance is required to achieve policy goals. We analyze the binational management framework for addressing HABs in the western basin using a transboundary governance capacity (TGC) lens and, specifically, the attribute of institutional capacity, to assess its effectiveness. Although the management framework has some level of legitimacy and, in the case of the Great Lakes Water Quality Agreement, resiliency, there are little compliance and functional intensity in place. This is remarkable, given the importance of effective governance to solving urgent Great Lakes water quality issues such as HABs. A comprehensive binational approach at the federal level is not likely; therefore,

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we urge officials in both Canada and the United States to strengthen TGC as it relates to HABs at the sub-federal level through a compact or other binational mechanism.

Keywords Harmful algal blooms, Institutions, Lake Erie, Phosphorus, Transboundary governance

1 Introduction

The Great Lakes-St. Lawrence River Basin is at risk from environmental contaminants including nutrients, metals, organics, and plastics [1, 2]. Science and technology are essential to inform policies and practices designed to ensure the future sustainability of the Great Lakes, but science and technology alone will not be enough. As Dr. John P. Holdren at Harvard's Kennedy School of Government said, "I'm a great believer in science and technology, but the notion that science and technology will ride to the rescue is a pernicious one" [3]. Here we consider the governance structures in place, if they are adequate, to effectively translate science into action. We focus on one ecological impact of environmental contaminants – harmful algal blooms (HABs) – as a case study. But the framework used can be applied to study governance challenges of other environmental contaminants impacting the Great Lakes.

HABs are a significant threat to the Great Lakes-St. Lawrence River Basin ecosystem and to citizen health. Nowhere is this more prevalent than the western basin of Lake Erie. Although largely absent from this basin throughout the 1980s and 1990s, HABs have grown in frequency and intensity over the past several years [4]. Phosphorus is the main driver of HABs in the western basin, deriving, for the most part, from agricultural management practices. These impacts affect stakeholders in the Canadian province of Ontario and the US states of Michigan, Indiana, and Ohio, and, to a lesser extent, Pennsylvania and New York. Many policy instruments and management regimes have been implemented to address this challenge [5]. Two binational policy instruments are in place to address HABs in the western basin: the Great Lakes Water Quality Agreement (GLWQA) and its subsequent amendments, and the western basin of Lake Erie Collaborative Agreement ("2015 Collaborative Agreement"). The 2015 Collaborative Agreement was signed by the Premier of the Province of Ontario, the Governor of the State of Michigan, and the Governor of the State of Ohio.

This binational framework is examined through a transboundary governance lens to gain insights into its effectiveness in tackling the HABs challenge. Section 2 sets forth the context of the western basin, with focus on the nature of the problem. Section 3 discusses the concept of "transboundary governance capacity" (TGC) and the importance of institutions to achieving effective TGC. Section 4 details the binational policy instruments that are in place to address

HABs. Section 5 analyzes these instruments through the institutional lens of TGC. Section 6 concludes with insights and recommendations to stakeholders in both Canada and the US for next steps.

2 The Context

There are hundreds of species of algae in Lake Erie, many of which are beneficial to the lake ecosystem. Nonetheless, one species of algae – cyanobacteria – has emerged as a significant threat to the lake's ecosystem and human health. The causes of HABs are complex, but generally cyanobacteria thrive in conditions with high levels of phosphorus or nitrogen, which promote excessive algal growth, hypoxia (or "dead zones"), and cyanotoxins [6].

In the 1970s, most of the phosphorus runoff into the Great Lakes derived from point sources, i.e., identifiable sources of pollution from which pollutants are discharged, such as sewage treatment plants and factories. Most experts agree that programs implemented in both countries were successful in treating point source phosphorus runoff. However, beginning in the 1990s, Lake Erie, as the warmest and shallowest of the Great Lakes, experienced a resurgence of HABs, hypoxia, and cyanotoxins driven by non-point source pollution. Non-point source pollution is defined as any source of water pollution that does not meet the definition of a point source. In the western basin of Lake Erie, non-point source pollution in both Canada and the US is derived mostly from a combination of a changing climate and agricultural management practices [7].

According to the Government of Canada, the majority (an average of 94% of total inflow measured between 2011 and 2013) of total surface water inflow to the western basin of Lake Erie's western basin comes from the Detroit River, which is the connecting channel that carries the combined outflows from Lakes Superior, Michigan, Huron, and St. Clair (which includes discharge from Ontario's Thames River) into Lake Erie [8]. Additionally, 4% of flow enters the lake from the Maumee River in Ohio, with the remaining 2% contributed by smaller tributaries [8]. Binationally, the US contributes a majority (80%) of the phosphorous loadings to the western basin (Table 1), a majority of which are discharged directly to the western basin. Of the western basin load from Canadian sources, more than 99% are discharged to the Huron-Erie corridor [8].

Table 1 Annual binational phosphorous loading in Lake Erie

	Phosphorus (tons)	Percentage
Canada	647	12
US	4,407	80
Others[a]	438	8
Total	5,492	100

Source: Government of Canada [8]

[a] Remaining phosphorous loadings derive from the atmosphere and Lake Huron

The increased number of HABs outbreaks has resulted in significant economic, social, and ecological impacts. Degraded water quality reduces the value of lakefront properties [9]. HABs also threaten drinking water quality (more than 10 million people rely on the lake for clean drinking water) and Lake Erie's $12.9 billion tourism industry and world-class fishery. There are human health concerns as well; microcystin can cause skin rashes, gastrointestinal problems, and nervous system, kidney, and liver damage [10].

3 Transboundary Governance Capacity: The Importance of Institutions

HABs management in the western basin of Lake Erie is a complex, multi-scalar transboundary governance challenge that cannot be addressed by a "go-it-alone" approach either sectorally or jurisdictionally [5, 11]. The western basin and its draining river systems span two countries, one province (Ontario), three states (portions of Michigan, Ohio, and Indiana), First Nations territories, and scores of municipalities. It is home to nearly 1.2 million people and plays a significant role in the economic viability of the Great Lakes region [12]. In terms of land mass, it covers approximately 7 million acres, with 75% of the land in agricultural production.

Innovative strategies for evaluating how well HABs in the binational Great Lakes system are managed include the International Organization for Standardization Risk Management Standard (ISO 31000) and bow-tie analysis [5]. The ISO 31000 combined with a bow-tie analysis facilitates the analysis of human activities that drive the causal pathways of ecosystem pressures-effects-impacts and of the links between these causal pathways and the performance of management measures operating within the Great Lakes [5]. This work revealed the potential strengths and weaknesses in the system that manages HABs risk in Lakes Erie and Ontario (see Fig. 1). This work was further refined by combining a bow-tie analysis of farming best practice measures implemented to reduce phosphorus in the Grand River watershed of Lake Erie with a Bayesian belief network to quantify the effectiveness of these measures used in the daily operations of industry sectors to predict the residual pressure that is delivered to the ecosystem [13]. These applications, although innovative, are incomplete because of the focus on government effectiveness rather than governance effectiveness.

Another innovative way to examine HABs management is through a governance capacity lens. The governance of the Great Lakes Basin has been written about extensively in previous papers, beginning over 100 years ago with the ratification of the 1909 Boundary Waters Treaty (BWT) and the establishment of the International Joint Commission (IJC) to manage binational water disputes [5, 14]. The IJC identifies governance as a key issue in the basin and notes "that while collaboration has improved in recent years, there is a critical need to modify existing governance to strengthen

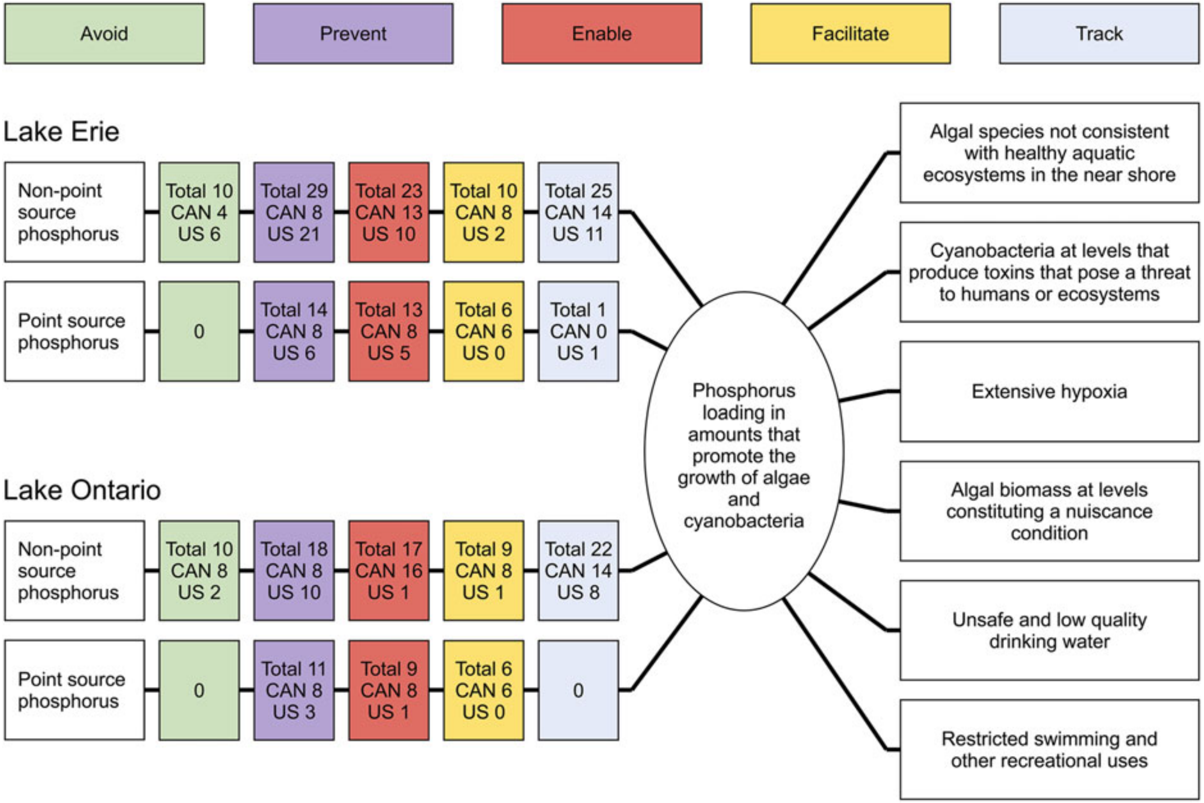

Fig. 1 The pressures, effects, and impacts of phosphorus-loading risk within the Lake Erie and Lake Ontario basins mapped onto a bow-tie analysis framework along with the number of management measures (total, and for Canada and the US) intended to prevent the pressures from causing the risk event (Source: Creed et al. [5])

coordination across jurisdictional lines to address ecological challenges" [15]. This view has been reinforced by scholars [16, 17] and international organizations such as the Organization for Economic Cooperation and Development, which concluded that managing and securing access to water are not simply a question of monetary resources but equally a matter of effective governance [18]. Nonetheless, what does this mean? How is governance defined? How would you recognize effective governance if you saw it? How do we go about strengthening the effectiveness of governance in a way that addresses the HABs challenge and ensures that the western basin remains a sustainable water resource?

There are many different terms in the literature to describe governance, including "water governance," "experimentalism," "modular regulation," "collaborative governance," "network governance," and "regional collaboration," among others [19]. Here, the conceptualization and framework set forth in VanNijnatten et al. [20] are adopted. These scholars set out to identify a deeper understanding of the conditions that promote effective governance in the transboundary context so that the appropriate means to tackle issues such as HABs could be identified. According to these scholars, "'governance' is best understood as the ability to wield and coordinate resources from public and private actors, generally in a more informal manner than 'government' and with the participation of a broader range of actors" [20]. Governance encompasses formal, top-down modes of interaction and informal, nonhierarchical, and/or bottom arrangements, which create new forums of interaction for actors from the public, private, academic, and nongovernmental sectors [21]. Governance therefore reflects formal mechanisms coexisting with participatory and collaborative processes that involve a wide range of interests [20]. Governance represents an integrated way of managing water resources.

Conceptualized in this manner, governance is profoundly boundary-spanning in nature, connecting actors across sectors, levels, and scales [22]. "Boundary" organizations provide a forum for the interaction of these different kinds of knowledge and the coordination of other tasks that enable cooperation and build trust, which is critical to collective action [23]. These organizations play a particularly important role in knowledge generation and co-learning [24, 25], which is increasingly viewed as a crucial component of water governance [16, 24].

With this conceptualization in mind, VanNijnatten et al. [20] identify a matrix of five major attributes of transboundary governance capacity (TGC): (1) high levels of leadership; (2) necessary and sufficient participation; (3) shared discourse and mutual understanding; (4) sustainable resources; and (5) strong institutional basis [20]. Accordingly, Great Lakes policy regimes which exhibit high levels of leadership, necessary and sufficient participation, shared discourse and mutual understanding, sustainable resources, and a strong institutional basis are more likely to exhibit high TGC and achieve the intended results.

For these scholars, a strong institutional basis is a "foundational" attribute for TGC. That is, institutions are crucial in shaping the nature and extent of TGC (see Fig. 2). VanNijnatten et al. [20] constructed four indicators to measure institutional effectiveness: (1) the nature of compliance (to what degree are rules and practices binding? What enforcement mechanisms are in place?), (2) functional intensity (do actors collaborate, cooperate, or have harmonized practice?), (3) resilience (do institutions endure in changing contexts? Do institutions offer learning opportunities or best practices?), and (4) degree of legitimacy (are there mechanisms for participatory governance, accountability, and transparency?) (see Table 2). With these four indicators in mind, Sect. 4 outlines the binational management regime related to HABs in the western basin of Lake Erie, and Sect. 5 applies the indicators of institutional effectiveness to gain insight into the TGC of this binational management regime.

4 History of the Binational Management Regime for Addressing HABs

Management of the western basin of Lake Erie takes place in a complicated environment that dates back more than 100 years to the signing of the 1909 BWT. A complex policy regime is in place to address HABs, which include binational, federal, state, and provincial laws, protocols, regulations, and programs [5, 26]. In addition, hundreds of best management practices (BMPs) are on the books in Great Lakes states and Ontario [5]. Here, only binational mechanisms in place to address HABs are considered.

A brief history of the GLWQA is required in order to properly assess institutional effectiveness in the context of HABs. Pursuant to the BWT – itself an innovative model of transboundary water governance [27] – the GLWQA was executed by Canada and the US ("the Parties") in 1972. It operated under a binational framework for action on water quality issues with joint interests superseding national interests [14]. It set the elimination of point source pollution from industrial sources and sewage treatment plants as a priority. The GLWQA generally is viewed as a success in a number of areas, including its binational nature (as reflected in its parity in structure and obligations and joint fact-finding and research), focus on community participation; accountability and openness in information exchange, and flexibility and adaptability to changing circumstances [28]. It is also viewed as successful in addressing the point source pollution that was the major contributor to HABs at this time.

In 1978, the Parties amended the GLWQA by introducing the concept of "ecosystem management" for the virtual elimination of toxic contaminants and recognizing human health as a concern [14]. Although "ecosystem management" recognized the integrated nature of air, water, land, and living organisms, it was difficult to operationalize [14]. In 1983, the GLWQA was supplemented to further limit phosphorus discharges; Canada and the US also committed to prepare and implement plans for reducing phosphorus.

In 1987, the Parties substantially revised the GLWQA by adopting a protocol that, among other items, introduced the development and implementation of Lakewide Action Management Plans (LAMPs) and the development and implementation of Remedial Action Plans (RAPS). Although these were steps in the right direction in

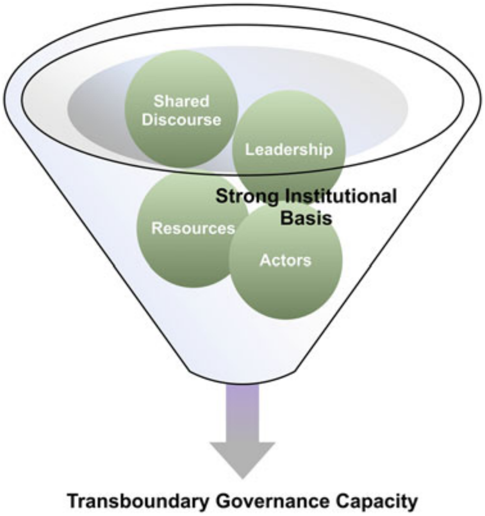

Fig. 2 The role of institutions in TGC (Source: VanNijnatten et al. [20])

Table 2 Institutional indicators of TGC

Institutional indicator	Measure
Nature of compliance	Characterization of compliance mechanisms on spectrum of voluntary to non-voluntary [what is range of possible in terms of “hard” and “soft” mechanisms? are there binding mechanisms to provide “harder” support for compliance regime?]
Functional intensity	Characterization of mandate and activities on spectrum from less intense to more intense collaboration [how intense?]
Resilience	Determination of longevity [how long has institution been in place despite changing conditions?] Characterization of learning opportunities [is there sharing of “best practices”?] Coordination across multiple institutions/networks operating on same issue
Degree of legitimacy	Determination of the degree to which institutions/networks are “widely regarded as legitimate” [is accountability given to elected officials or the public? does the institution have internal vs. external legitimacy?]

terms of community participation, the 1987 GLWQA Protocol also created a Binational Executive Committee (BEC) that allowed for Environment Canada and the US Environmental Protection Agency to consult directly and semiannually without involvement of the IJC. The BEC also took over reporting on the state of the lakes. This reorientation away from the IJC as the binational mechanism for governing water quality issues in the Great Lakes was a significant governance game changer, as the IJCs’ leadership role and budget were severely restricted [29]. In essence, a binational approach to the Great Lakes disintegrated. The BEC was viewed as entrenched in administrative institutions with no authority or accountability, serving merely as an information exchange forum with no ability to set binational programs [29].

Given changing ecosystem conditions – including the increased presence of HABs in the Great Lakes Basin – on June 13, 2009, the Canadian foreign minister and the US secretary of state announced that negotiations would begin on the review of the 1987 GLWQA Protocol. Three years later, the 2012 GLWQA Protocol was signed on September 7, 2012, and, following an exchange of diplomatic notes, entered into force on February 12, 2014.

The 2012 GLWQA Protocol reaffirmed the Parties' commitment to, among other things, not pollute boundary waters. It outlined no less than 16 governing principles, including accountability (i.e., "establishing clear objectives, regular reporting made available to the Public on progress, and transparently evaluating the effectiveness of work undertaken to achieve the objectives of this Agreement"), adaptive management (i.e., "implementing a systematic process by which the Parties assess effectiveness of actions and adjust future actions to achieve the objectives of this Agreement, as outcomes and ecosystem processes become better understood"), coordination (i.e., "developing and implementing coordinated planning processes and best management practices by the Parties, as well as among State and Provincial Governments, Tribal Governments, First Nations, Métis, Municipal Governments, watershed management agencies, and local public agencies"), and adherence to an ecosystem approach (i.e., taking management actions that integrate the interacting components of air, land, water, and living organisms, including humans). The BEC morphed into a Great Lakes Executive Committee (GLEC) under the 2012 GLWQA Protocol. In keeping with the more siloed approach of the BEC versus the binational mechanism of the IJC, the GLEC was to help coordinate and implement the programs undertaken to achieve the purpose of the GLWQA. GLEC membership, however, was more broad-based. It comprises senior-level representatives from Canadian and US federal entities responsible for implementation of the GLWQA, as well as state and provincial governments, tribal governments, municipal governments, indigenous communities, watershed management agencies, and other local public agencies. In addition, representatives from the Great Lakes Commission, IJC, and the Great Lakes Fishery Commission are represented. These new commitments to science and governance would ideally help the Parties achieve their water quality goals.

Specifically with regard to nutrients, the 2012 GLWQA Protocol listed as one of its main objectives that the waters of the Great Lakes should "[b]e free from nutrients that directly or indirectly enter the water as a result of human activity, in amounts that promote growth of algae and cyanobacteria that interfere with aquatic ecosystem health, or human use of the ecosystem" (2012 GLWQA Protocol). The Parties committed to update phosphorus-loading targets and develop strategies and domestic action plans (DAPs) to achieve specific ecosystem objectives – starting with Lake Erie [8]. Pursuant to this protocol, strategies and DAPs are developed in cooperation and consultation with state and provincial governments, indigenous communities, conservation authorities, municipalities, key stakeholder sectors, and the public.

Through the 2012 Protocol Annex 4 (Nutrients), binational phosphorus reduction targets were adopted for the western and central basins of Lake Erie to address HABs and hypoxia. The new targets included a 40% reduction (from 2008 levels) in spring loads of total phosphorus and soluble reactive phosphorus for the Maumee River to minimize harmful algal blooms in the western basin; a 40% reduction (from 2008 levels) in phosphorus loadings to the central basin, with a new binational loading target of 6,000 tons per year of total phosphorus; and a 40% reduction (from 2008 levels) in spring loads of total phosphorus and soluble reactive phosphorus for priority tributaries to minimize harmful algal blooms in the nearshore areas [8]. Progress on Annex 4 objectives is reported every 6 months at the GLEC meetings. Accomplishments are described in the Progress Report of the Parties every 3 years.

In addition to the federal governments, states and provinces play a role in mitigating HABs in the western basin of Lake Erie. Most significant in the transboundary context, on June 13, 2015, at the Quebec City Conference of Great Lakes and St. Lawrence Governors and Premiers, the Governors of the States of Michigan and Ohio and the Premier of the Province of Ontario (the "State-Provincial Parties") signed the Western Basin of Lake Erie Collaborative Agreement ("2015 Collaborative Agreement"). The 2015 Collaborative Agreement is intended to meet the nutrient reduction targets proposed by the Nutrient Annex of the 2012 Protocol. The State-Provincial Parties collectively pledged to work to achieve a recommended 40% total load reduction in the amount of total and dissolved reactive phosphorus entering Lake Erie's western basin by the year 2025 through an adaptive management process. They included an aspirational interim goal of a 20% reduction by 2020. Similar to the 2012 Protocol, the agreement further stated that the State-Provincial Parties would use phosphorus-loading data from 2008 to the western Lake Erie basin as the basis from which progress would be measured. The 2015 Collaborative Agreement focuses on the western basin watersheds of the Maumee, Portage, and Toussaint rivers and the Sandusky River [30].

Three points are important to note with respect to the 2015 Collaborative Agreement and institutional capacity. First, Michigan, Ohio, and Ontario reaffirmed that the restoration of the western basin could "not be achieved solely by the Parties in isolation, but rather, it is dependent upon the collaboration between the Parties to address the water quality of the western basin of Lake Erie." Second, the State-Provincial Parties concluded that the "best means" to improve the water quality of Lake Erie is "through a collaborative initiative between the Parties that has a defined goal, establishes specific implementation plans with timetables and is measured against expected results." Third, the agreement stated that, with respect to implementation, "each state and province commits to developing, in collaboration with stakeholder involvement, a plan outlining their proposed actions and timelines toward achieving the phosphorus reduction goal."

The states and province have taken steps to reach the 2025 reduction goal. In February 2017, Ohio published its *Western Lake Erie Basin Collaborative Basin Framework*. The framework was developed with the adaptive management process at the forefront with input through meetings and conversations with stakeholders and state agencies. No less than 15 state agencies and domestic partners are listed in the framework, with three leading the pack: the Ohio Department of Agriculture is responsible for agricultural non-point source pollution; the Ohio EPA is responsible for point source and water quality monitoring; and the Ohio Department of Health is responsible for monitoring household and small flow sewage treatment systems. Additionally, the framework mentions that "there is involvement and coordination from time-to-time on specific issues, such as monitoring and research by ... international agencies, such as Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change and Ontario Ministry of Agriculture-Agri-Food."

In February 2018, the Ontario government and the Government of Canada developed a *Canada-Ontario Lake Erie Action Plan* to reduce algal blooms and phosphorus loads in Lake Erie. This plan met Ontario's commitments under a number of agreements, including the Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health, 2014; the Great Lakes Protection Act, 2015; the Great Lakes Commission's Lake Erie Joint Action Plan; and the 2015 Collaborative Agreement. The Canada-Ontario action plan is being led by five federal and provincial government agencies: Environment and Climate Change Canada; Agriculture and Agri-Food Canada; Ontario Ministry of the Environment and Climate Change; Ontario Ministry of Agriculture, Food and Rural Affairs; and Ontario Ministry of Natural Resources and Forestry. The plan has more than 120 actions to help reduce phosphorus loading into Lake Erie.

Also, in February 2018, Michigan adopted its Domestic Action Plan (DAP) a guiding document toward achieving a healthier Lake Erie ecosystem. The Michigan Department of Environment, Great Lakes, and Energy (EGLE); Department of Natural Resources (DNR); and Agriculture and Rural Development (MDARD) are working together on implementing the DAP. The DAP affirms actions toward two objectives: (1) fulfilling commitments under the 2015 Collaborative Agreement; and (2) meeting the targeted phosphorus reductions and nutrient-related ecosystem goals for Lake Erie under Annex 4 of the 2012 GLWQA Protocol. The DAP also outlines strategies for Michigan to reach these objectives in collaboration with local municipalities, nongovernmental organizations, other stakeholders, the states of Ohio, Indiana, Pennsylvania, and New York, and the province of Ontario, and the US and Canada.

Most recently, in an executive order dated June 20, 2019, Michigan Governor Gretchen Whitmer ordered additional steps. Importantly, acting under Sections 1 and 8 of Article 5 of the Michigan Constitution of 1963, she directed that the directors of MDARD, EGLE, and DNR "shall work in collaboration to adopt policies, procedures, and actions as soon as possible to ensure full implementation of the DAP and its objectives, including the objective of reducing the nutrient loadings from certain tributaries and priority watersheds by 40 percent by 2025" [31]. She also ordered that certain state departments disseminate the adopted policies and procedures to other state departments and autonomous agencies. She ordered that the same departments must report to the governor on their progress annually. This report must include, to the greatest extent practicable, quantifiable measures of progress toward the DAP objectives, including nutrient loading reduction targets.

In June 2019, at the meeting of the Great Lakes and St. Lawrence Governors and Premiers, Governor Whitmer, Ohio Governor Mike DeWine, and Ontario's Minister of the Environment, Conservation and Parks Rod Phillips, representing

Ontario's Premier Doug Ford, pledged their commitment to the goals of the 2015 Collaboration Agreement and their intention to reduce phosphorus inputs into the Western Lake Erie Basin by 40% by 2025.

5 Institutional Effectiveness of the Binational Management Regime for Addressing HABs

Using the TGC institutional lens to analyze the history of the GLWQA and the 2015 Collaborative Agreement provides key insights regarding the effectiveness of the binational management regimes for addressing HABs in the western basin of Lake Erie.

First, with respect to compliance, the binational institutional regimes seem to fall somewhere in the middle of the compliance spectrum (Fig. 3). That is, although neither the 2012 GLWQA Protocol nor the 2015 Collaborative Agreement adopts formal compliance or enforcement mechanisms, they equally do not have self-enforcing norms. In fact, the current approach to HABs in the western basin and indeed around the globe is deficient in that most measures are voluntary in nature and hence not effective. With the GLEC mechanism in place to report to each government and Governor Whitmer's order to have Michigan agencies report to her office periodically, it appears that some level of compliance exists. Nonetheless, it is important to note that this compliance is *domestic* in nature. Thus, we contend that this indicator of institutional effectiveness of binational compliance is quite weak.

Second, with respect to functional intensity, the 2012 Protocol has mechanisms in place for information sharing and consultation between the Parties – the least intensive form of cross-border interaction (Fig. 4). Both the 2012 GLWQA Protocol and the implementation plans under the 2015 Collaborative Agreement call for information sharing and research. In addition, under the 2012 GLWQA Protocol, the Parties consult twice a year. Nonetheless, under both the protocol and the agreement, there is no evidence of cooperation; i.e., actions leading to

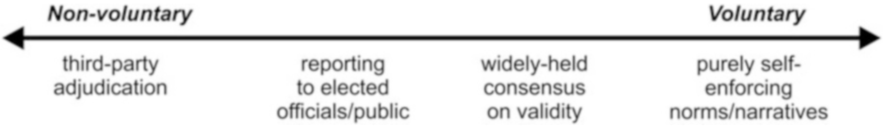

Fig. 3 Spectrum of compliance mechanisms (Source: VanNijnatten et al. [20])

Fig. 4 Spectrum of functional intensity (Source: VanNijnatten et al. [20])

mutual benefits beyond information sharing or soliciting advice. Efforts toward harmonization and integration are nonexistent. Thus, despite pledges to achieve their phosphorus reduction goals by 2025, federal, state, and provincial parties curiously are moving forward in silos in terms of creating their distinctive DAPs and implementation plans. There is no evidence to date of a binational approach based more fully on cooperation, harmonization, or integration.

Third, with respect to resilience as an indicator of institutional effectiveness, we conclude that the GLWQA has withstood the test of time. The GLWQA as a policy regime is quite resilient, as evidenced by the fact that it is almost 50 years old and has been revised substantially at least three times. Thus, it has adapted to changing circumstances – a key attribute of resilience in the literature [23]. The jury is still out on the 2015 Collaborative Agreement, as it is a mere four years old. The degree of coordination, although slightly stronger in the case of the 2012 GLWQA, is weak as well.

Fourth, with respect to the legitimacy indicator, both the protocol and the agreement are legitimate in the transboundary context. As a normative construct [20], both the 2012 GLWQA Protocol and the 2015 Collaborative Agreement allow for activity by myriad nongovernmental actors through participation on the Nutrients Annex Working Group or the plans of each state and province. Both have mechanisms that ensure accountability to public officials, but again, this is domestic legitimacy within each country.

6 Conclusions

Successfully mitigating HABs is not simply the product of government effectiveness. Although tools like the ISO 31000 are useful, analyzing collaborations among government, the private sector, NGOs, academics, and other stakeholders provides key insights. Thus, governance is crucial to success. A TGC lens was used to assess the institutional effectiveness of the GLWQA and its amendments as well as the 2015 Collaborative Agreement. Although these agreements have some level of legitimacy and, in the case of the GLWQA, resiliency, there are little compliance and functional intensity in place in terms of both instruments. This is remarkable, given the importance of effective governance to solving urgent water quality issues such as HABs.

There is little likelihood that the Parties will establish a truly binational mechanism at the federal level; however, there are opportunities to strengthen TGC at the sub-federal level. For example, the 2008 Great Lakes Compact, as the governance regime regulating water "takings" and water levels, provides a relatively strong institutional foundation for managing actors around the basin at the state-provincial level. Enhancing water quality generally and mitigating HABs in the western basin more specifically at the state-provincial level have proven to be more difficult. A compact or other binational mechanism related to HABs that builds upon the foundation of the 2015 Comprehensive Agreement may be in order. Indeed, as a binational, sub-federal instrument, this agreement is a unique governance mechanism and has potential to expand to all states and provinces in the basin to approach HABs in a binational, comprehensive manner. Currently, none of the Parties have suggested establishing a binational mechanism. We believe that this idea should be seriously considered by stakeholders in both Canada and the US in order to strengthen our collective approach to solving the HABs challenge in the western basin of Lake Erie and, indeed, throughout the basin in order to preserve and protect this tremendous resource.

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