Knowledge Gained under the 2014 Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health

Prepared by Environment and Climate Change Canada and
Ontario Ministry of the Environment, Conservation and Parks

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Acronym list

AFFF	Aqueous Film Forming Foam
ALDFG	Abandoned Lost and Discarded Fishing Gear
AOC	Areas of Concern
AOPs	Adverse Outcome Pathways
AVSR	Additional Volatile Solids Reduction
B[a]P	Benzo[a]pyrene
BCFs	Bioconcentration Factors
BFRs	Brominated Flame Retardants
BSAFs	Biota-Sediment Accumulation Factors
CCME	Canadian Council of Ministers of the Environment
CMCs	Chemicals of Mutual Concern
COA	Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health
COCs	Chemicals of Concern
CPs	Chlorinated Paraffins
CWN	Canadian Water Network
DDE	Dichlorodiphenyldichloroe-thylene
DDT	Dichlorodiphenyltrichloroe-thane
DNA	Deoxyribonucleic Acid
DP	Dechlorane Plus
E.coli	*Escherichia coli*
ECAs	Environmental Compliance Approvals
ECCC	Environment and Climate Change Canada
EduTOX	A youth engagement campaign developed by Pollution Probe Foundation
FEQG	Federal Environmental Quality Guideline
GLB	Great Lakes Basin
GLWQA	Great Lakes Water Quality Agreement
GOC	Government of Canada
HBCD	Hexabromocyclododecane
HOCs	Halogenated Organic Contaminants
LC-PFCAs	Long-Chain Perfluoro-carboxylic Acids
MCCPs	Medium-Chain Chlorinated Paraffins
MECP	Ministry of the Environment, Conservation and Parks
MeHg	Methylmercury
NaClO	Sodium Hypochlorite
NASM	Non-Agricultural Source Materials
NNIs	Neonicotinoid Insecticides
OPEs	Organophosphate Esters
PAA	Peracetic acid
PACs	Polycyclic Aromatic Compounds
PAHs	Polycyclic Aromatic Hydrocarbons
PBDEs	Polybrominated Diphenyl Ethers
PCBs	Polychlorinated Biphenyls
PCNs	Polychlorinated Naphthalenes
PFAAs	Perfluoroalkyl Acids
PFAS	Per- and Polyfluoroalkyl Substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
QMRA	Quantitative Microbial Risk Assessment
RAIDAR	Risk Assessment, Identification, And Ranking
REF	Reference Sites Upstream
RNA	Ribonucleic Acid
SCCPs	Short-Chain Chlorinated Paraffins
SOGL	State of the Great Lakes Report
SOUR	Specific Oxygen Update Rate
SSD	Species Sensitivity Distribution
TEK	Traditional Ecological Knowledge
TEQ	Toxic Equivalence Concentration
THg	Total Mercury
U.S.	United States
UV	Ultraviolet

WLF	Water Level Fluctuations
WSER	Wastewater Systems Effluent Regulations
WWF	World Wildlife Fund
WWTP	Wastewater Treatment Plants
YAS	Yeast Androgen Screen
YES	Yeast Estrogen Screen

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Executive summary

The Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health (COA) is an agreement between the governments of Canada and Ontario to promote a healthy, prosperous, and sustainable Great Lakes Basin (GLB) ecosystem for current and future generations. The COA has contributed to improvements in the environmental quality of the Basin and to meeting Canada's commitments under the Canada–United States Great Lakes Water Quality Agreement (GLWQA). The GLWQA identifies shared priorities and coordinates actions to restore and protect the chemical, physical, and biological integrity of the waters of the Great Lakes.

As a part of the COA, the governments of Canada and Ontario agreed to implement Annexes that focus on priority issues that would benefit from cooperative and coordinated action. This COA report serves as a summary of the knowledge gained from a selection of projects under the Harmful Pollutants Annex (Annex 2) and the actions taken while the 2014 COA was in effect (2014-2019 and projects that continued under the 2014 agreement, while the 2021 was being finalized). These projects complement ongoing initiatives, like the binational Great Lakes strategies under the GLWQA, and government monitoring programs.

Under the 2014 COA, ten Chemicals of Concern (COCs) were identified to be potentially harmful to humans and/or the environment under the Harmful Pollutants Annex. Those COCs include: (Hexabromocyclododecane (HBCD), Long-Chain Perfluorocarboxylic Acids (LC-PFCAs), Mercury (Hg), Perfluorooctanoic Acid (PFOA), Perfluorooctane Sulfonate (PFOS), Polybrominated Diphenyl Ethers (PBDEs), Polychlorinated Biphenyls (PCBs), Short-Chain Chlorinated Paraffins (SCCPs), Polycyclic Aromatic Hydrocarbons (PAHs) and Lead. Cooperative research, monitoring, surveillance, and risk management actions were taken to address these COCs and additional harmful pollutants.

Despite years of risk management actions, the legacy pollutants PCBs and Hg continue to be a concern in the GLB as they are the major contaminants driving fish consumption advisories. Though environmental concentrations have been reduced, PCBs and Hg remain a concern as a result of historical use, remobilization from sediments and continued international use. Concentrations of flame retardants (PBDEs and HBCD) have been reduced in select matrices (fish and sediment); however, newer substitution flame retardants are increasing in the Great Lakes environment. Consumer and personal care products continue to be an ongoing and key source of PAHs, per- and polyfluoroalkyl substances (PFAS; PFOS, PFOA and LC-PFCAs) and SCCPs to the environment through either land disposal or wastewater treatment plants.

Scientific research and project results suggest that many of the harmful pollutants that continue to impact nearshore waters are in stormwater and wastewater. Pollution is often associated with urbanization and stormwater runoff during rainfall events. Extreme weather conditions related to climate change are increasing as is urbanization. These factors may result in increases in pollution and contaminant runoff which can include chloride, nutrients, plastics, pathogens, and tire wear residues (TWRs). The new Wastewater and Stormwater Annex under the 2021 COA outlines commitments that will help address gaps in science and policy to reduce impacts to receiving waters.

Novel monitoring and analysis, referred to as non-target analysis, provides the opportunity to identify additional contaminants in the GLB that may be present in levels considered to be harmful. Early use of this approach identified the TWR chemical Hexamethoxymethyl-melamine (HMMM) and a suite of pharmaceuticals (anti-viral drug and antibiotics). Annex 2 also supported the testing of numerous innovative technologies to better understand the impacts that individual pollutants and chemical mixtures may have on organisms in surface waters, wastewaters, and sediments. Select bioassays were reviewed as a complement to chemical analysis for water quality monitoring as they indicate the presence and toxicity of all contaminants in a matrix through biological activity (e.g., impacts on growth or reproduction, endocrine disruption). The use of the estrogen receptor CALUX® assay was able to detect estrogenic activity more effectively and efficiently than standard chemical analysis. The use of omics-based analysis was also investigated as a technique to screen environmental samples for potential biological impacts. However, results indicated that there were no clear direct results to correlate to acute (death) and chronic end points (growth, reproduction) using these different omic profiles and approaches.

Knowledge gaps still exist for several COCs in various environmental matrices such as soil, water, air, biosolids and tissue. Ongoing science needs can be addressed by targeting and/or increasing monitoring for COCs and other harmful pollutants including pesticides (soil and water), current use flame retardants (sediment and tissues), lead, chlorinated paraffins (wastewater and biosolids), PFAS, plastics and their associated chemicals and additives. Monitoring can also be supplemented through modern technologies such as Risk Assessment, Identification, And Ranking (RAIDAR) and modelling. Monitoring and surveillance will continue to help identify pollutant releases and pathways related to anthropogenic and/or industrial activities. Specific areas of interest include wastewater treatment technologies to reduce contaminants, the management of litter and other sources of plastic pollution, and the effects of climate change on sources of contaminants, in particular stormwater management ponds.

Priority chemicals currently in commerce as well as new substances entering the Canadian market are subject to risk assessment; however, improvements could be made in terms of how these assessments are conducted. Including additional considerations in these evaluations, such as cumulative effects and assessment of the chemicals that may be used as alternatives and/or replacements could address certain knowledge gaps (*Healthy Environment, Healthy Canadians, Healthy Economy: Strengthening the Canadian Environmental Protection Act, 1999*). For example, Federal Risk Management Measures have been successful at reducing select COCs (PBDEs, HBCD, PFOS and PFOA) in the environment as levels are generally below the Federal Environmental Quality Guidelines.

However, alternative and replacement flame retardants, like organophosphate esters and shorter chain PFAS, are increasing in the GLB.

The governments of Canada and Ontario have various initiatives in place aimed at reducing the risks posed by chemical substances. Additional risk management actions for select COCs; end-of-life management practices for consumer products (e.g., municipal landfills); cumulative effects information, especially in the context of mixture effects from wastewater treatment plant (WWTP) effluents; and toxicity guidelines for chemicals, such as alkylated PAHs and chloride, would be beneficial. Developing frameworks and screening approaches to better detect chemicals, transformation products and potential chemical substitutions could further mitigate risks.

The governments of Canada and Ontario are also working collaboratively, through the Canadian Council of Ministers of the Environment to implement the Canada-wide Strategy on Zero Plastic Waste and Action Plan and advance additional complementary initiatives within their jurisdictions. Initial studies indicate that key sources of plastics and microplastics in the GLB include: breakdown of litter; intentional and unintentional loss of debris during waste management activities; manufacturing sources; losses from transport and industrial/commercial activities as well as abandoned lost or discarded fishing gear and microfibers from washing machines.

Working with industries to prevent discharges (e.g., plastics) into the GLB will support minimizing or avoiding the creation of harmful pollutants and waste in the Great Lakes. Actions to reduce risks and impacts from pollutants and waste that can have an adverse effect on human and ecological health, such as plastic waste (industrial, commercial and institutional waste and recycling) and chloride, are a new focus of commitments in the Harmful Pollutants Annex in the 2021 COA.

Actions continue to be taken by the governments of Canada, Ontario, and their partners to conduct risk assessment, risk management, research, monitoring and surveillance programs. These actions have been critical to reducing concentrations of chemicals in the Basin. These programs and projects have advanced the science to improve understanding of sources such as select consumer products, funeral homes, hospitals, and pharmaceutical manufacturers, and the impacts of chemicals to the environment. Actions to address these concerns have been identified, where warranted. Many accomplishments have been made; however, more work is needed to understand the potential sources of chemicals (e.g., industrial and municipal wastewater effluents, landfills and personal and consumer products) and to further manage risks these chemicals pose to the environment and/or human health.

Results from these projects led to an improved understanding of pollution sources and releases, and technological advances for enhanced monitoring and analysis of harmful pollutants. This knowledge gained report will be an important resource to assist with, and improve, ongoing program implementation and to meet the commitments identified in the 2021 COA.

Introduction

For more than 50 years, Canada and Ontario have been working together to reduce or eliminate the release of harmful pollutants into the Great Lakes Basin (GLB). The Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health (COA) is an agreement between the governments of Canada and Ontario to promote a healthy, prosperous, and sustainable GLB ecosystem for current and future generations. Since 1971, the COA has contributed to improvements in the environmental quality of the Basin and to meeting Canada's commitments under the Canada–United States Great Lakes Water Quality Agreement (GLWQA). The GLWQA identifies shared priorities and coordinates actions to restore and protect the chemical, physical, and biological integrity of the waters of the Great Lakes.

As a Party to the GLWQA, Canada is responsible for implementing programs and reporting on progress towards restoring and protecting the Great Lakes. Environment and Climate Change Canada leads implementation of the GLWQA, working in collaboration with a number of departments, agencies, and organizations on both sides of the border including various levels of government, Indigenous peoples, watershed management agencies, and other local public agencies. The COA outlines how the governments of Canada and Ontario will cooperate and coordinate their efforts to restore, protect, and conserve the GLB ecosystem. It is the means by which the seven Canadian federal departments interact with the three Ontario provincial ministries to support implementation and meet obligations under the GLWQA, and provincial commitments under Ontario's Great Lakes Strategy and the *Great Lakes Protection Act, 2015*.

Seven federal departments and three provincial ministries are signatories to the 2021 COA:

Federal Departments:

1. Environment and Climate Change
2. Agriculture and Agri-Food
3. Fisheries and Oceans
4. Health
5. Natural Resources
6. Transport
7. Parks

Provincial Ministries:

1. Environment, Conservation and Parks
2. Natural Resources and Forestry
3. Agriculture, Food and Rural Affairs

Science-based management is a guiding principle of the COA. Priorities, programs, and policies are established and adapted based on the best available science, research, and knowledge, including Traditional Ecological Knowledge (TEK). The Harmful Pollutants

Annex (Annex 2) under the COA addresses both legacy and ongoing sources of harmful pollutants in the GLB.

The last update on the status of harmful pollutants was reported in the 2016 "Status of Tier 1 and Tier 2 chemicals in the Great Lakes Basin under the Canada-Ontario Agreement". This report provided an update on the use, release, and concentrations of Tier 1 and Tier 2 chemicals in ambient air, surface water, sediment, fish, and Herring Gull eggs. Originally designated in the 1994 COA, Tier 1 substances were persistent, bioaccumulative, and toxic substances of immediate concern in the GLB. Tier 2 substances had the potential for causing widespread impacts or had already caused local adverse impacts. A summary of current and past risk management actions, research, monitoring, and surveillance activities for these chemicals was also included in the 2016 report.

Under the 2014 COA, ten individual or groups of Chemicals of Concern (COCs) were identified as priority pollutants that generally originate from anthropogenic (human) sources and were potentially harmful to human health or the environment. The COCs were designated based on the chemicals that were identified as Chemicals of Mutual Concern (CMCs) under the GLWQA, and the results of the 2016 status updates on the Tier 1 and Tier 2 chemicals.

COA Annex 2 contains commitments to cooperate on specific research, monitoring, surveillance, and risk management actions for these COCs. In addition, Annex 2 focusses on actions to reduce risks and impacts from additional harmful pollutants that can have an adverse effect on human and ecological health including pesticides, plastics, pharmaceuticals, and chloride.

A. Chemicals of Concern as designated under the COA

1. Hexabromocyclododecane (HBCD)
2. Long-Chain Perfluorocarboxylic Acids (LC-PFCAs)
3. Mercury
4. Perfluorooctanoic Acid (PFOA)
5. Perfluorooctane Sulfonate (PFOS)
6. Polybrominated Diphenyl Ethers (PBDEs)
7. Polychlorinated Biphenyls (PCBs)
8. Short-Chain Chlorinated Paraffins (SCCPs)
9. Polycyclic Aromatic Hydrocarbons (PAHs)
10. Lead

B. Chemicals of Mutual Concerns designated under the GLWQA

1. Hexabromocyclododecane (HBCD)
2. Long-Chain Perfluorocarboxylic Acids (LC-PFCAs)
3. Mercury
4. Perfluorooctanoic Acid (PFOA)
5. Perfluorooctane Sulfonate (PFOS)
6. Polybrominated Diphenyl Ethers (PBDEs)
7. Polychlorinated Biphenyls (PCBs)
8. Short-Chain Chlorinated Paraffins (SCCPs)

The eight designated CMCs have Great Lakes strategies for risk management in place. The strategies include actions to address threats to the Great Lakes by reducing releases and impacts of CMCs. Implementation of actions identified in the strategies by Environment and Climate Change Canada (ECCC), Ministry of the Environment, Conservation and Parks (MECP), and many partners and stakeholders, contributes to improvements in the health of the Great Lakes ecosystem.

Canada and the United States (U.S.) foster coordination and collaboration of scientific efforts including utilizing comprehensive, ongoing, science-based ecosystem indicators to assess the state of the Great Lakes, to anticipate emerging threats, and to measure progress. Every three years, the governments of Canada and the United States, together with their many GLWQA partners, issue a State of the Great Lakes Report (SOGL). To create the SOGL reports, many government and non-government Great Lakes scientists and other experts analyze available data and reach consensus on the assessments of each indicator in relation to both current status and trends. A number of indicators in the suite assess the status and trends of CMCs, COCs, and other emerging chemicals, including toxic chemicals, fish consumption, and groundwater indicators. Indicator assessments also help governments evaluate the effectiveness of environmental programs and policies in place to address challenges and identify priorities for action.

In addition to ongoing science and monitoring activities that are routinely carried out in the Great Lakes by the provincial and federal governments, Annex 2 supported more than 120 scientific research projects from 2014 to 2021. The projects focussed on addressing priorities related to the release of harmful pollutants, including COCs, from industrial, agricultural, and point source processes that discharge directly or indirectly into rivers, tributaries, and lakes in the GLB.

This report serves as a summary of the knowledge gained under the Harmful Pollutants Annex of the 2014 COA while it was in effect (2014-2019 and up until the new COA was finalized in June 2021). This knowledge informed setting of commitments in the 2021 COA and will be used to inform future programming and decision making specific to the Harmful Pollutants Annex and the Wastewater and Stormwater Annex. The report is organized under five themes: Harmful Pollutants; Education and Outreach on Harmful Pollutants; Wastewater Pollutants; Stormwater Pollutants; and Sampling and Analytical Tools, Methods, and Techniques.

1.0 Harmful Pollutants: occurrences, sources, loadings, transport, and impacts to the Great Lakes Basin (GLB)

The GLB has seen some dramatic changes over the past century. The area has experienced marked changes in land use, accelerated population and industrial growth, and a vast array of contaminants and anthropogenic stressors that have changed in composition and relative importance over time.

"Harmful pollutants" refers to chemicals or pathogens that have an adverse effect on human or ecological health including, but not restricted to, COCs or substances of emerging concern.

Harmful pollutants can be released from many sources into Ontario's lakes, rivers, and streams. Chemical pollution can harm aquatic ecosystems and negatively impact habitats and biodiversity throughout the Great Lakes. COCs are generally human-made, persistent, and can bioaccumulate in the food web, potentially exposing humans through fish consumption, air, and drinking water.

A key priority of Annex 2 is to monitor, manage, and support the reduction of the release of harmful pollutants into the Great Lakes. Studies under Annex 2 considered: occurrence, sources, and impacts of COCs, legacy contaminants (including Tier 1 and Tier 2 chemicals), and new and emerging harmful pollutants. A selection of project results is included in the sections that follow.

1.1 Contaminants of Concern (COCs)

1.1.1 Mercury

The documented impacts of mercury exposure to fish and wildlife in the GLB are significant. Elevated levels have been detected in biota throughout the food web. Mercury was identified as a Tier 1 chemical under the 1994 COA. There have been significant international, national, and regional efforts to reduce mercury emissions to the environment since the 1980s. Much of the point-source mercury has been controlled, allowing partial recovery of the Great Lakes, as shown by lower mercury concentrations in lake sediments in the lower Great Lakes and in declines of mercury in fish since the years of higher emissions. However, mercury is still detected at elevated concentrations in soils, sediment, water, and biota.

Mercury levels in Great Lakes fish filets have generally declined by half over the last four decades. Despite the declining trends of mercury in fish, consumption advisories are in effect for all five Great Lakes (SOGL 2022). The declining trend in mercury concentrations is more pronounced in top predator fish, whereas benthivorous (bottom-feeding) fish species show weaker evidence of long-term declining trends. Historically contaminated regions, designated as Areas of Concern (AOC), and bays receiving riverine inputs, still show elevated mercury concentrations across all fish species (Visha et al., 2015).

Recent Lake Superior fish monitoring data have shown inconsistent and conflicting trends. In an effort to better understand sources and trends in the Lake Superior Basin, Annex 2 supported a project to examine levels of mercury in precipitation, surface waters, sediment, and fish. The analysis pointed to an overall decreased loading of mercury in recent decades in all media examined. Given that fish age can influence mercury concentrations, when this study normalized fish concentrations to fish age, a decreasing trend was observed. The resulting data synthesis has improved the understanding and communication of mercury trends in the Lake Superior ecosystem (personal communication).

The Canadian Mercury Science Assessment (the Assessment), published in 2016, was the first comprehensive scientific evaluation and synthesis of information on mercury in the Canadian environment (Environment and Climate Change Canada, 2016). The Assessment included a review of environmental monitoring from the GLB, which found no water samples exceeded the Canadian Water Quality Guidelines for the Protection of Aquatic Life for inorganic and methylmercury (MeHg). Compared to the other Canadian locations studied, the Great Lakes region has shown the largest and most frequent declines in MeHg levels in individual populations (40% of fish and seabird populations reported) (ECCC, 2020). However, recent data illustrate that some populations are now showing increasing trends. Water level fluctuation (WLF) is thought to be a contributing factor (Figure 1). To better understand these increases, Annex 2 supported a study to investigate the impact of WLF on MeHg concentrations in water, sediment, and fish using a set of controlled microcosm experiments emulating the drawdown/refill dynamics in hydropower reservoirs (Ni et al., 2021). The study supports emerging evidence that longer duration and more frequent WLF creates a larger surface area of sediment exposed to air leading to conditions conducive to higher MeHg concentrations in sediments and water.

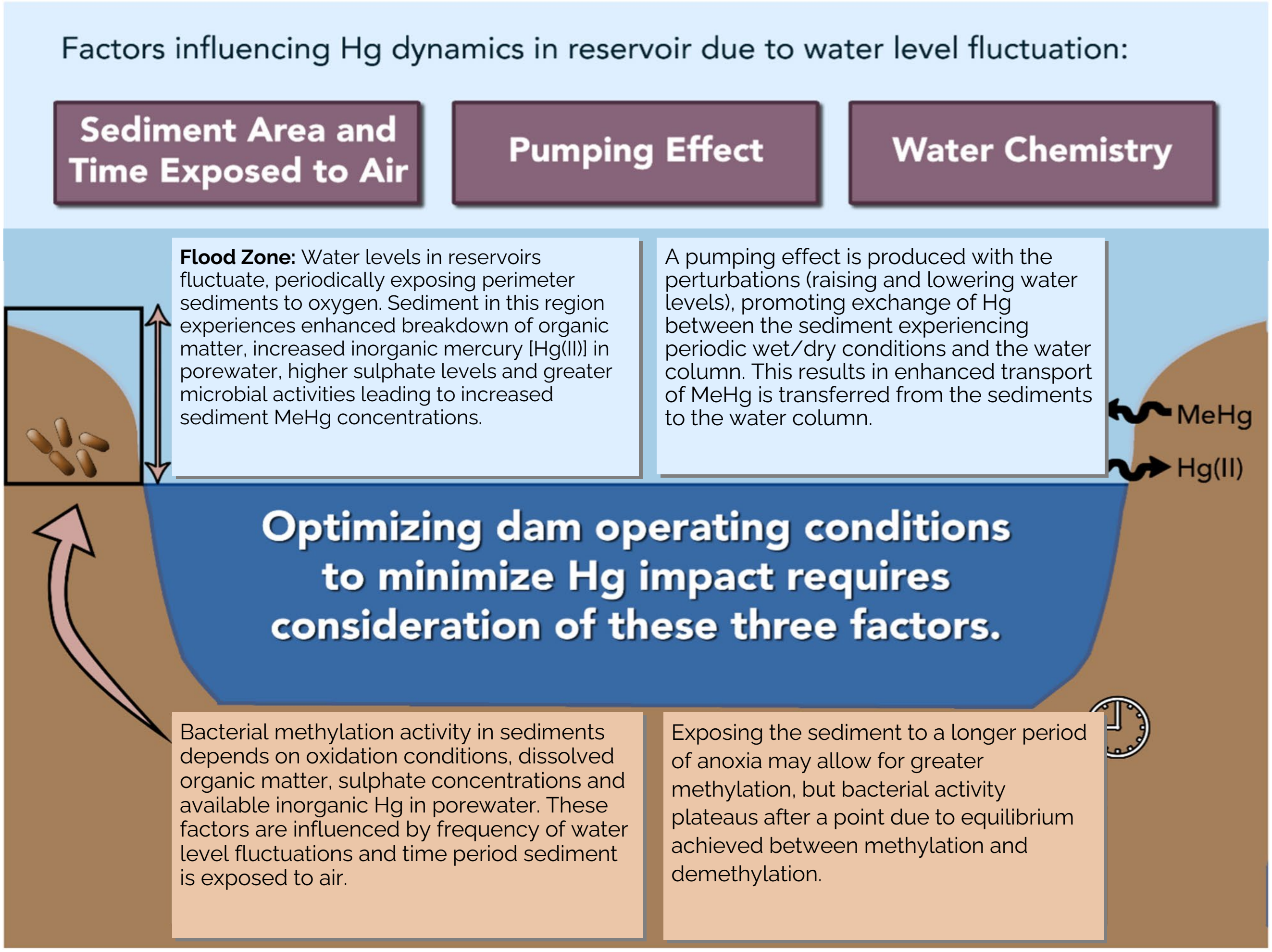


Figure 1. Factors influencing mercury dynamics in reservoirs due to water level fluctuations (Adapted - Ni et al., 2021).

The Government of Canada (GOC) assessed whether current risk management actions are meeting the objective to reduce exposures to mercury. The results were summarized in the Evaluation of the Effectiveness of Risk Management Measures for Mercury which concluded that risk management actions had contributed to reducing mercury concentrations in the environment. However, further efforts were needed to understand mercury levels in some hotspots and areas where increasing trends of mercury were observed in environmental media, including the GLB. Despite effective risk management actions in Canada, long-range transport resulting from the continual global use of mercury accounts for up to 97% of the atmospheric deposition in Canada (Environment and Climate Change Canada, 2021).

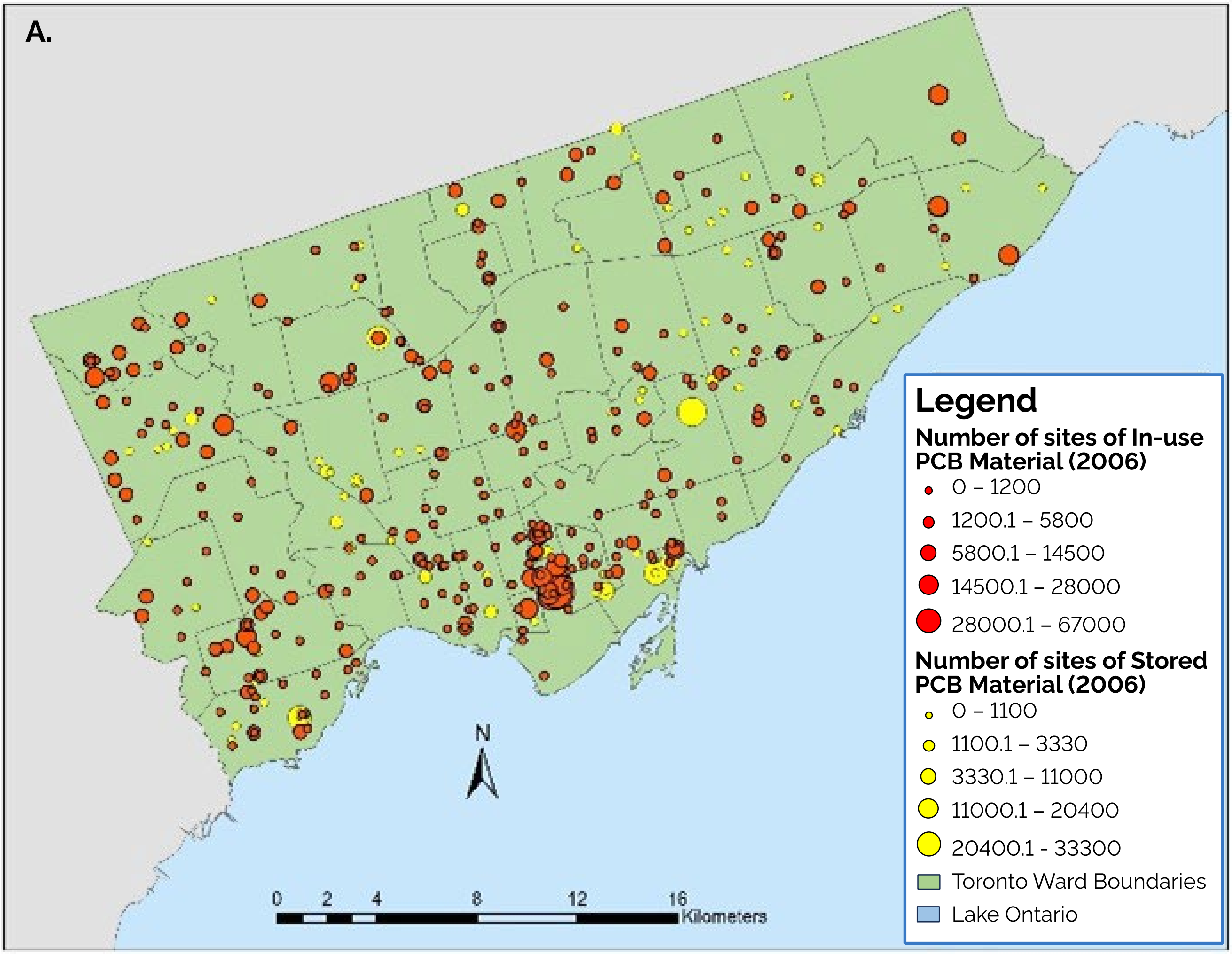
The Minamata Convention on Mercury is a global treaty that addresses all aspects of the life cycle of mercury, including requiring controls and reductions across a range of products, processes, and industries. Due to the adverse impacts of global mercury pollution on Canadians and their environment, Canada has and continues to play a key role in the work of the treaty.

Other stressors in the Great Lakes that may impact further reductions include climate change, changes in food web structures in top predatory fish, invasive species, and high and low flows causing the re-suspension of mercury from sediments. Ongoing environmental monitoring is important to provide information on changes in trends of mercury levels in the environment.

1.1.2 Polychlorinated biphenyls (PCBs)

PCBs in the environment originate from primary and secondary emission sources. Primary sources include 'in-use', 'in-storage', and waste PCBs awaiting destruction, which contribute to ongoing emissions through accidental and other uncontrolled releases into the environment. Secondary sources include sinks from airborne PCBs such as dust from building materials or remobilized PCBs from contaminated land and water bodies. To address concerns over the concentrations of PCBs in the environment, PCBs were designated as a Tier 1 chemical under the 1994 COA and Canadian PCB Regulations came into force in 2008. The objectives of the regulations were to minimize the risks posed by the use, release, and storage of PCBs, and to accelerate the phasing out and virtual elimination of these substances.

To assess the extent of regulatory compliance, Annex 2 supported the completion of an inventory of in-use, in-storage, and waste PCBs in Ontario, Canada and U.S. states surrounding the Great Lakes. This updated PCB inventory, using Toronto as a case study, was compared to an inventory created prior to the 2008 PCB Regulations. This comparison revealed that the number of PCB sites in Toronto decreased from 411 to 4 and that the mass of pure PCBs, in-use and in-storage, decreased from 424 tonnes to 0.8 tonnes over a 10-year period (2006-2016) (Melymuk et al., 2022). This updated inventory determined there were 3 tonnes of pure PCBs remaining in Ontario, with Toronto accounting for 6.8% of the total stock. Most PCB sites in Ontario are widely distributed across the heavily populated shores of lakes Ontario and Erie. Figures 2A and 2B visually demonstrate the decreased number of in-use and storage sites. These data indicate that the regulations were successful in phasing out the majority of PCBs in Toronto; however, continued efforts are needed to address the remaining 3 tonnes.


A.
Legend
Number of sites of In-use PCB Material (2006)
0 – 1200
1200.1 – 5800
5800.1 – 14500
14500.1 – 28000
28000.1 – 67000
Number of sites of Stored PCB Material (2006)
0 – 1100
1100.1 – 3330
3330.1 – 11000
11000.1 – 20400
20400.1 - 33300
Toronto Ward Boundaries
Lake Ontario
N
0 2 4 8 12 16 Kilometers

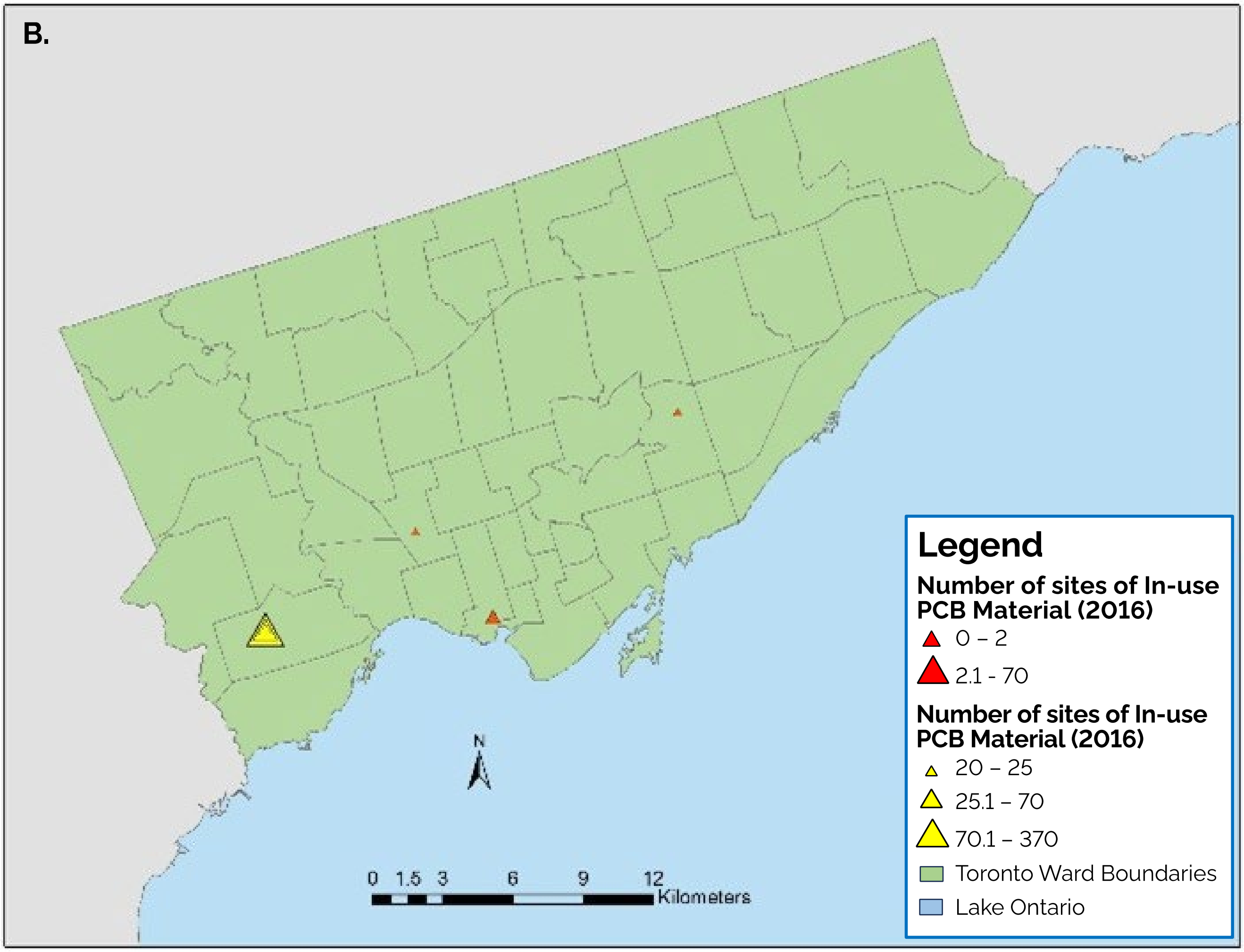


Figure 2. A) PCB sites in Toronto in 2006 and **B)** PCB sites in Toronto in 2016 (Melymuk et al., 2022).

Measurable advancements have been made in limiting PCB releases and remediating previous local PCB contamination. However, PCBs (along with mercury) drive most fish consumption advisories in the Great Lakes due to their past use, persistence in the environment, and resuspension of vast repositories in sediments from historical sources. Lake Ontario and Lake Michigan had historically had the most severe PCB fish contamination, but the differences with the other Great Lakes have diminished more recently due to substantial improvements (Visha et al., 2015, SOGL 2022). To assist in the prediction of concentrations of PCBs and mercury in walleye (*Sander vitreus*) and lake trout (*Salvelinus namaycush*) in Lake Ontario, statistical methods and modelling were reviewed as a potential substitute for annual fish collection from different areas of the lake. Walleye and lake trout are good indicator species as they are top predator fish that bioaccumulate and biomagnify these contaminants as well as being popular fish for human consumption. This study successfully predicted these chemicals in walleye and lake trout, indicating that this is a valuable tool that can account for environmental variabilities and can be useful in reducing the number of fish collected and monitored to support fish consumption advice (Visha et al., 2015).

Continued efforts are needed to minimize the potential risks that PCBs pose to human health and the environment. It is also important to recognize that consuming Great Lakes fish can present both benefits and risks. Future work may consider both elements when issuing fish advisories.

1.1.3 Flame retardants (Polybrominated Diphenyl Ethers (PBDEs) and Hexabromocyclododecane (HBCD))

Flame retardants are chemicals that are applied to materials to prevent the start or slow the spread of fire. They have been used in many consumer and industrial products since the 1970s, to decrease the ability of materials to ignite. Despite risk management actions, PBDEs and HBCD continue to persist in the environment. PBDEs comprise a class of substances consisting of 209 possible congeners (compounds within a homologue series having the same base structure as well as the identical number and type of atoms and differing only in the position of the bromine atoms in the molecule) that can be organized into PBDE homologues (compounds which have the same base structure but which differ from each other by the number of bromine atoms in the molecule) such as: tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE, nonaBDE, and decaBDE.

HBCD has 16 possible isomers (same chemical formula with different structures) that were used as part of 3 main commercial mixtures: alpha-HBCD, beta-HBCD and gamma-HBCD. As the use of these brominated flame retardants (BFRs) were discontinued or banned nationally and internationally, newer, replacement and/or other substituted organohalogen flame retardants (e.g., Dechlorane Plus (DP) and decabromodiphenyl ethane (DBDPE)) and Organophosphate Esters (OPEs) were introduced and are now detected in the GLB.

To better understand current levels of PBDEs and HBCD in surface water, Annex 2 supported a study that deployed passive samplers in urban-influenced nearshore freshwaters of Lake Ontario. Passive samplers were analyzed for a broad range of both legacy halogenated organic contaminants (HOCs) including PBDEs and HBCD. The sum of PBDEs ranged from 14–960 pg/L, well below the Federal Environmental Quality Guideline (FEQG) for PBDEs in water. Concentrations of HBCD (sum of 3 isomers; alpha, beta and gamma) ranged between 1–21 pg/L (Zhang et al., 2020). Figure 3 provides the concentration distribution (pg/L) for key PBDE congeners and isomers of HBCD. For most of the HOCs measured, concentrations were greatest in the industrialized Hamilton Harbour and at sites that had stronger influences of wastewater effluent discharges and stormwater runoff through rivers and creeks.

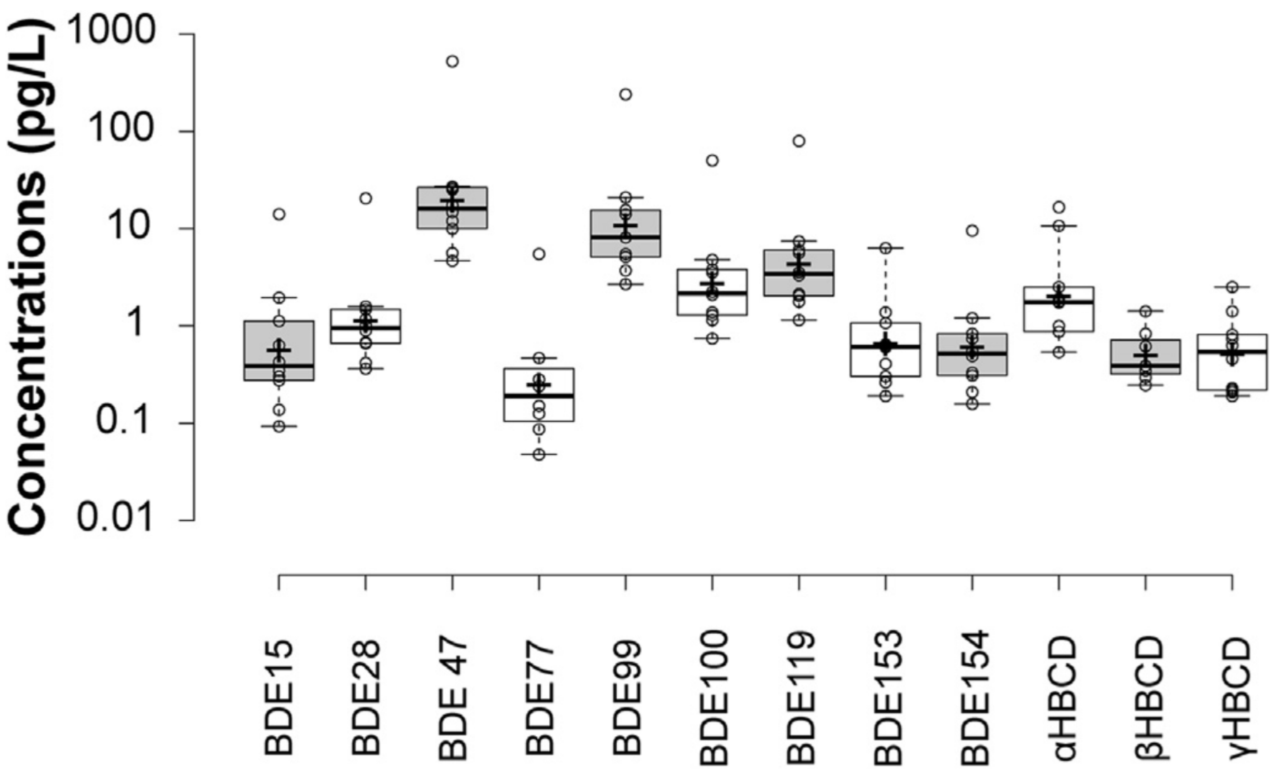


Figure 3. Concentration ranges and distributions of the major individual PBDE and HBCD congeners measured in nearshore waters of northwest Lake Ontario (Zhang et al., 2020).

Legend

Acronym	**Chemical name**	**Chemical Abstract Number**
BDE 15	4,4'-Dibromodiphenyl ether	2050-47-7
BDE 28	2,4,4'-Tribromodiphenyl ether	41318-75-6
BDE 47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1
BDE 77	3,3',4,4'-Tetrabromodiphenyl ether	93703-48-1
BDE 99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9
BDE 100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8
BDE 119	2,3',4,4',6-Pentabromodiphenyl ether	189084-66-0
BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2
BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4
α-HBCD	α-Hexabromocyclododecane	134237-50-6
β-HBCD	β-Hexabromocyclododecane	134237-51-7
γ-HBCD	γ-Hexabromocyclododecane	134237-52-8

These monitoring results are consistent with the recent 2020 evaluation conducted by the GOC on whether current risk management actions were effective in meeting the objective to reduce exposures to PBDEs. The results are summarized in "Evaluation of the Effectiveness of Risk Management Measures for Polybrominated Diphenyl Ethers". The evaluation report indicated that domestic risk management measures have contributed to reductions of the majority of PBDEs being imported, sold, and used in Canada, and environmental monitoring results have shown decreases in levels of PBDEs in air, sediment, and fish. However, environmental levels of pentaBDE and decaBDE were found above their respective FEQGs at some sites across the GLB.

Select HOCs, including PBDEs and Polychlorinated Naphthalenes (PCNs), tend to accumulate in sediments and fish tissues rather than surface waters. To better understand their potential risk to human consumers, Annex 2 supported a comprehensive review of PBDEs and PCNs in a variety of fish species (fillets) from the Canadian waters of the Great Lakes. Concentrations of PCNs spatially varied in the order of the Detroit River > Lake Erie > Lake Ontario > Lake Huron > Lake Superior. PCN-66/67 was the dominating congener contributing to the toxic equivalence concentration (TEQ) for human consumption concerns. TEQ weighs the toxicity of the less toxic compounds as fractions of the toxicity of the most toxic compounds. However, when PCNs were compared to other similar HOCs that are of concern to human health (dioxins, furans, dioxin-like PCBs) they contributed <15% of the total toxicity, and thus are not the main chemical of concern for fish consumption. The study also indicated that there has been a slow decline of PCN-66/67 between 2006 and 2012 (Gewurtz et al., 2018).

Unlike PCNs, concentrations of PBDEs in fish species vary dramatically across the GLB (Gandhi et al., 2017). The highest levels are detected in benthic species (carp and white sucker) from Lake Ontario followed by Lake Erie. Lower concentrations were seen in lakes Huron and Superior (Lake Ontario > Lake Erie > Lake Huron > Lake Superior). These measured levels of PBDEs resulted in one previous consumption advisory for the common carp from the Toronto waterfront, but none were issued in the most recent fish consumption advisories. DecaBDE (BDE-209) was the major congener in panfish, while a component of pentaBDE (BDE-47) was the major congener in top predator fish (Gandhi et al., 2017). Based on these updated monitoring studies, routine monitoring for PBDEs in fish can be reduced (pending no new toxicological data) as levels do not result in consumption advisories. New targeted focus and surveillance should be given to other in-use flame retardants, like OPEs.

OPEs have been used for decades and are now widely used in various products as flame-retardants, plasticizers, and performance additives in engine oil. OPEs as flame-retardants became popular as a substitution for highly regulated BFRs. Due to the increased use of OPEs in products, indoor air concentrations were studied to understand this potential route of exposure to humans (Choi et al., 2022). Results indicated that the concentration of OPEs in indoor air represents the key exposure route for impacts to human health. Since product use continues to expand, it can be assumed that concentrations in wastewater may also be increasing, thus increasing the load and exposure to aquatic organisms. To better understand the concentrations and distribution of OPEs in the Ontario environment, a multi-media study was conducted to determine loadings and factors influencing concentrations. Using Toronto as a case study, streams in the nearshore known to be impacted by stormwater and wastewater, including Etobicoke Creek, Don River, and Highland Creek, were monitored. The total OPE (Σ6OPE) concentrations were higher during high flow scenarios with maximum levels reported as 8.1, 7.8 and 5.3 µg/L respectively (Rodgers et al., 2018). Estimated mass loadings showed that wastewater treatment plant (WWTP) discharges contributed significantly to the mass of OPEs entering into nearshore waters of Lake Ontario; however, streams and rain could contribute equal or higher loadings during wet periods. These results suggested two major pathways to Lake Ontario, direct discharge from WWTPs, atmospheric deposition, and wash-off into streams.

In a complementary study, the fillets of lake trout across Lake Ontario were analyzed for 22 OPEs. Twelve of the 22 OPEs were detected in >50% of the fish. Based on these results, it was determined that the intake of OPEs via human consumption of lake trout is approximately 1–2 orders of magnitude lower than exposures via indoor air and dust (Choi et al., 2022).

Municipal landfills receive waste from residential and industrial sources. Annex 2 supported an investigation into the presence of 24 different OPEs (Table A, Appendix) in landfill leachate impacted groundwater samples. OPEs were frequently detected, particularly in historic landfills (closed in the 1960s and later). The presence of OPEs indicate their broad use in products and not just as a substitute flame retardant. The maximum total OPE (Σ24 OPE) concentration for leachate impacted study samples was 81.4 µg/L. The general persistence of OPEs within the landfills over this time may reflect reduced susceptibility to degradation under anaerobic (absence of oxygen) conditions, typical in a landfill environment. The predominant substances were TBOEP (tris(2-butoxyethyl) phosphate), TnBP (tributylphosphate), and TEP (triethylphosphate). These three compounds typically comprised >70% of the Σ24 OPE concentration in this study (Propp et al., 2021).

The flame retardants described above (BFRs and OPEs) make their way to the GLB via the use and disposal of personal and commercial products containing these retardants. However, one family of chlorine-based flame retardants (Mirex, also known as Dechlorane) were manufactured at a facility along the Niagara River, upstream of Lake Ontario in New York State, which led to direct impacts to the GLB. Mirex (Tier 1 chemical) was also used as an insecticide but was never registered for use in Canada and is now banned. Some of the Dechlorane flame retardants (Dechlorane Plus (DP), and Dechloranes (Dec) 602, 603, and 604) remain in use today. In 2011, Shen et al., first reported biota-sediment accumulation factors (BSAFs) for Mirex (BSAF 7.4, high) and Dec602 (BSAF 0.27, low). A higher BSAF means the chemical is more likely to accumulate in sediment and fish. In an updated 2014 study, Shen et al., 2014, reported that when select Dechlorane products were exposed to ultraviolet-light, they underwent photodebromination giving rise to new analogues with higher BSAFs than the parent products. These results highlight the gap in chemical assessments that may not consider impurities, metabolites, and degradation products in the environment.

Risk-based models can be used to complement environmental monitoring and to estimate concentrations and the potential for impacts to the Great Lakes ecosystems and humans.

The Great Lakes Binational Strategy for PBDEs Risk Management identified a need to continue to evaluate and assess risks associated with alternatives to PBDEs. In order to explore the use of models in the context of the GLB, Annex 2 supported a pilot project that examined the Risk Assessment, Identification, And Ranking (RAIDAR) model. For this project, the RAIDAR model was refined to incorporate regional-specific environmental parameters (i.e., flow rates), and monitoring data in Canada and the United States to take a "whole-watershed" approach to describe the fate and effects of PBDEs in the Great Lakes region. This model proved to be successful in predicting BDE levels in the absence of monitoring data in different environmental media. The project demonstrated that models can be utilized in the presence or absence of monitoring data. The ability to substitute models for select monitoring data for certain chemicals provides the opportunity to re-focus targeted monitoring needs to fill data gaps moving forward.

As supported by recent government assessments and studies under Annex 2, continued targeted environmental monitoring for PBDEs and HBCD in select media is still required in lakes Erie and Ontario. Environmental monitoring will also help determine whether current and proposed Regulations to further restrict the import, sale, and use these two substances contribute to further reductions in the environment.

In addition, it has been identified that there is an ongoing need to evaluate the risks of alternative and substitute organohalogen flame retardants, such as DP, DBDPE and OPEs.

1.1.4 Short-chain chlorinated paraffins (SCCPs)

SCCPs are manufactured for use as lubricants, coolants, plasticizers, and flame retardants. Binational efforts addressing the manufacture and import of SCCPs have reduced new sources, but limited monitoring information suggests that environmental concentrations resulting from historical releases remain a concern in the GLB.

Great Lakes environmental monitoring data for SCCPs was identified as a data gap in the Great Lakes Binational Strategy for SCCP Risk Management. To address this gap, Annex 2 supported a screening study using passive samplers deployed in Hamilton Harbour, Toronto Harbour, Humber Bay, and in select rivers and creeks. Additional samplers were deployed in the effluent of three WWTPs discharging to Lake Ontario. Neither SCCPs nor medium-chained chlorinated paraffins (MCCPs) were detected in wastewater samples. Conversely, SCCPs were detected at several of the monitoring locations; two locations in Lake Ontario; in open waters of Hamilton Harbour (~30,000 ng/g per sampler), nearshore at the west end of Cootes Paradise (~2000 ng/g per sampler) and in urban-impacted Etobicoke (4,000 ng/g per sampler) and Mimico creeks (~2000 ng/g per sampler). MCCPs were only detected in Etobicoke Creek at approximately 7,000 ng/g per sampler (MECP, unpublished data). This initial screening suggests that SCCPs and MCCPs have site-specific distributions across Lake Ontario and concentrations are highest in areas impacted from nearshore runoff.

The Binational Strategy for SCCP identifies the need to develop cost-effective and standardized means of collecting and analyzing SCCP concentrations from a variety of sources including in environmental samples. Annex 2 supported a project that combined analytical "fingerprinting" with source-receptor modelling to identify likely sources of SCCPs to the Great Lakes. This novel sensitive methodology allowed for the detection of hundreds of congeners of chlorinated paraffins (CPs) not previously distinguishable in earlier methods. This methodology was used to screen different environmental samples including: indoor house dust, sewage sludge from Ontario WWTPs, and surface waters, to investigate the transport of chlorinated paraffins from the indoor environment to the GLB. SCCPs, MCCPs, and long-chain chlorinated paraffins (LCCPs) were detected in all house dust samples, indicating these occur ubiquitously in a wide range of in-use products (Kutarna et al., 2023). CPs were also detected in all sewage sludge samples, but at concentrations approximately 100 times lower than those in house dust. MCCPs were the dominant CPs for house dust, sewage sludge, and surface water samples, possibly caused by an increase in use as replacements for SCCPs, which have been regulated since 2019. A simple mass flow model demonstrated that indoor dusts, via laundry water, could be the primary source for CPs to enter WWTPs. The study had difficulty detecting SCCPs in surface water samples due to extremely low concentrations.

Based on the differing results of concentrations of SCCPs and MCCPs in wastewaters from the above two studies, additional efforts across the GLB, inclusive of other lakes and urbanized areas, are needed to continue to identify sources and further refine the detection of CPs from environmental samples.

1.1.5 Perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), long-chain perfluorocarboxylic acids (PFCAs)

Per- and polyfluoroalkyl substances (PFAS) are a group of almost 4,700 human-made substances (OECD, 2018) that are used as surfactants, lubricants, and repellents (for dirt, water, and grease). They are found in a wide variety of products, including certain firefighting foams (used at airports and other locations), textiles (including carpets, furniture, and clothing), cosmetics, and in food packaging materials. Some of these chemicals make their way into storm water and wastewater during product use and from product disposal in landfills and in landfill leachate.

Adverse environmental and health effects have been observed for well-studied PFAS (PFOS, PFOA, and LC-PFCAs and their salts and precursors) and they have been shown to pose a risk to the Canadian environment. In Canada, PFOS, PFOA, and LC-PFCAs (and their salts and precursors) are prohibited through regulations; however, scientific evidence to date indicates the PFAS used to replace regulated PFOS, PFOA, and LC-PFCAs may be associated with environmental and/or human health effects (GOC, 2021). The overall concentration of PFOS, PFOA, and LC-PFCAs in the environment has decreased since the early 2000s (Gewurtz et al., 2019 and Kleywegt et al., 2020); however, concentrations of these persistent compounds remain in soils, water, air, biota tissues, wastes, and certain in-use products throughout the GLB and globally.

Canada's Great Lakes Strategy for PFOS, PFOA, and LC-PFCAs Risk Management identifies the need for additional comprehensive Great Lakes data to inform future management actions to reduce concentrations in the Great Lakes environment. The Government of Canada is also working to develop an approach to address PFAS as a class of chemicals and amend regulations to further restrict PFOS, PFOA and LC-PFCAs.

To understand the current concentrations and potential impacts of PFAS (including PFOS, PFOA and LC-PFCAs) in waters and biota (crayfish and snails), Annex 2 supported a study to collect samples upstream and downstream of WWTPs and airports across the GLB (see Figures 4 and 5). Concentrations of PFAS were lower upstream of airports (Hamilton, London, and Toronto) and higher downstream. Similar results were observed for WWTPs, where higher concentrations were detected in effluent, crayfish, and snails downstream compared to upstream samples. Body burdens of perfluoroalkyl acids (PFAAs) in crayfish were generally proportional to levels in water. Bioconcentration factors (BCFs) were low for short-chain PFAS (regardless of whether they were carboxylic acids or sulfonates) but increased with longer chain PFAS (carbon chain length of C8 – C11, e.g., PFOS and PFOA).

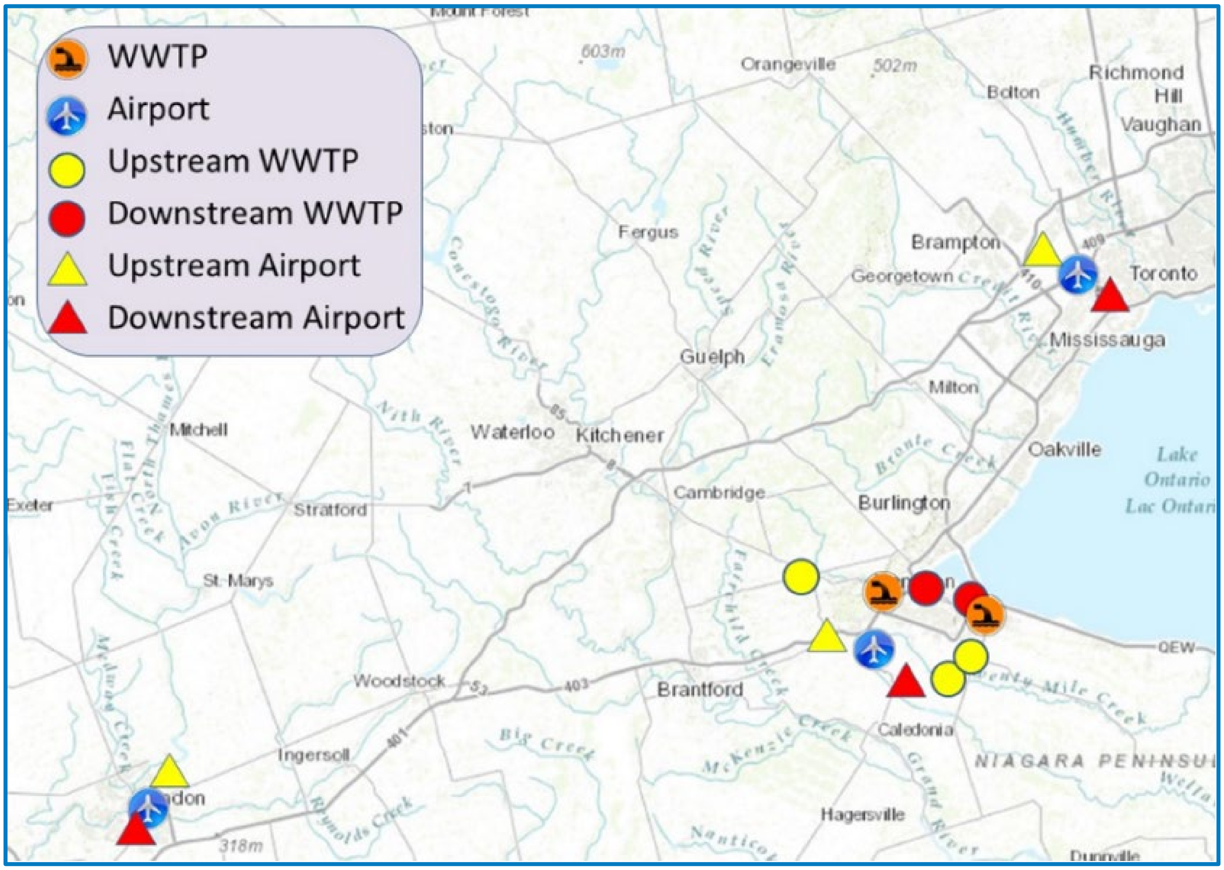
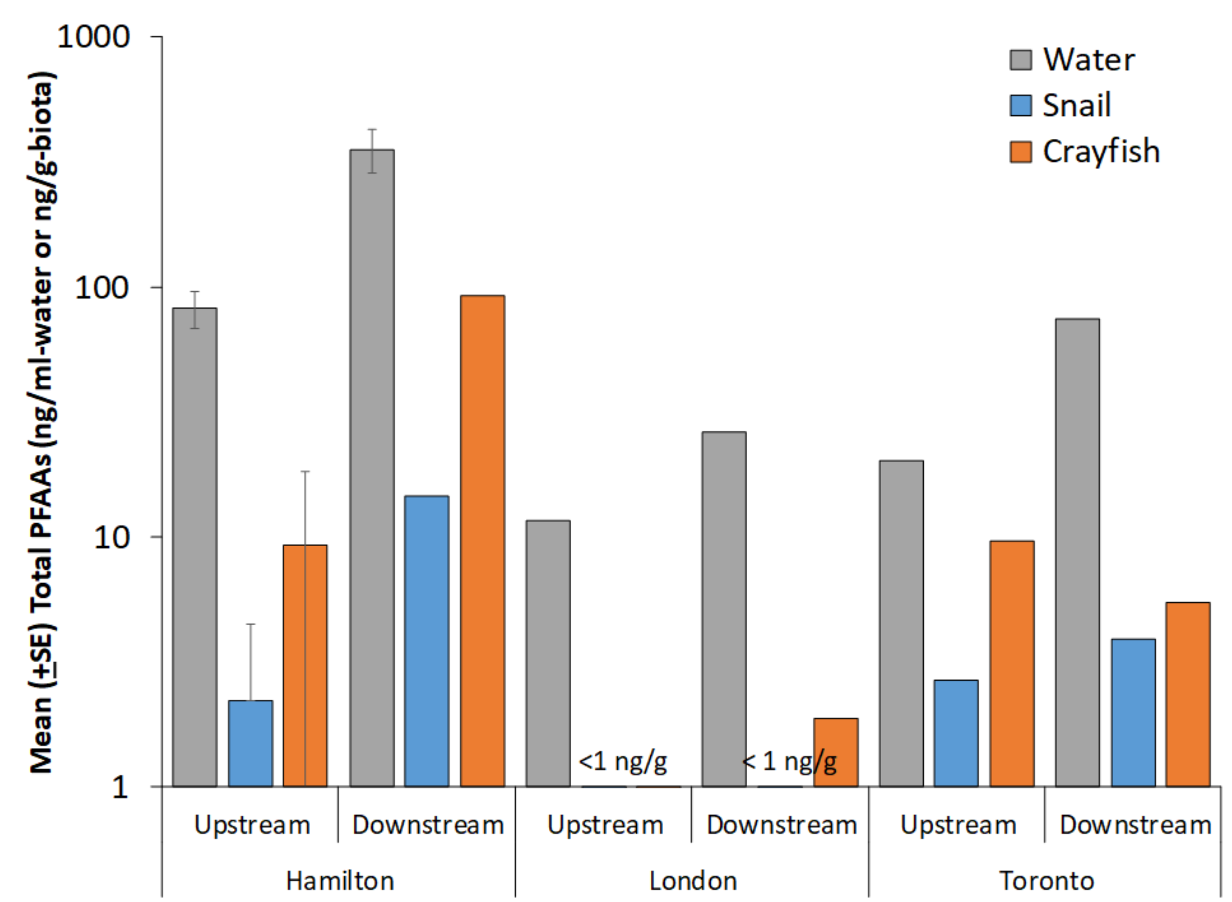


Figure 4. Sample locations for perfluoroalkyl acids (PFAAs) near airports and WWTPs (ECCC unpublished results)



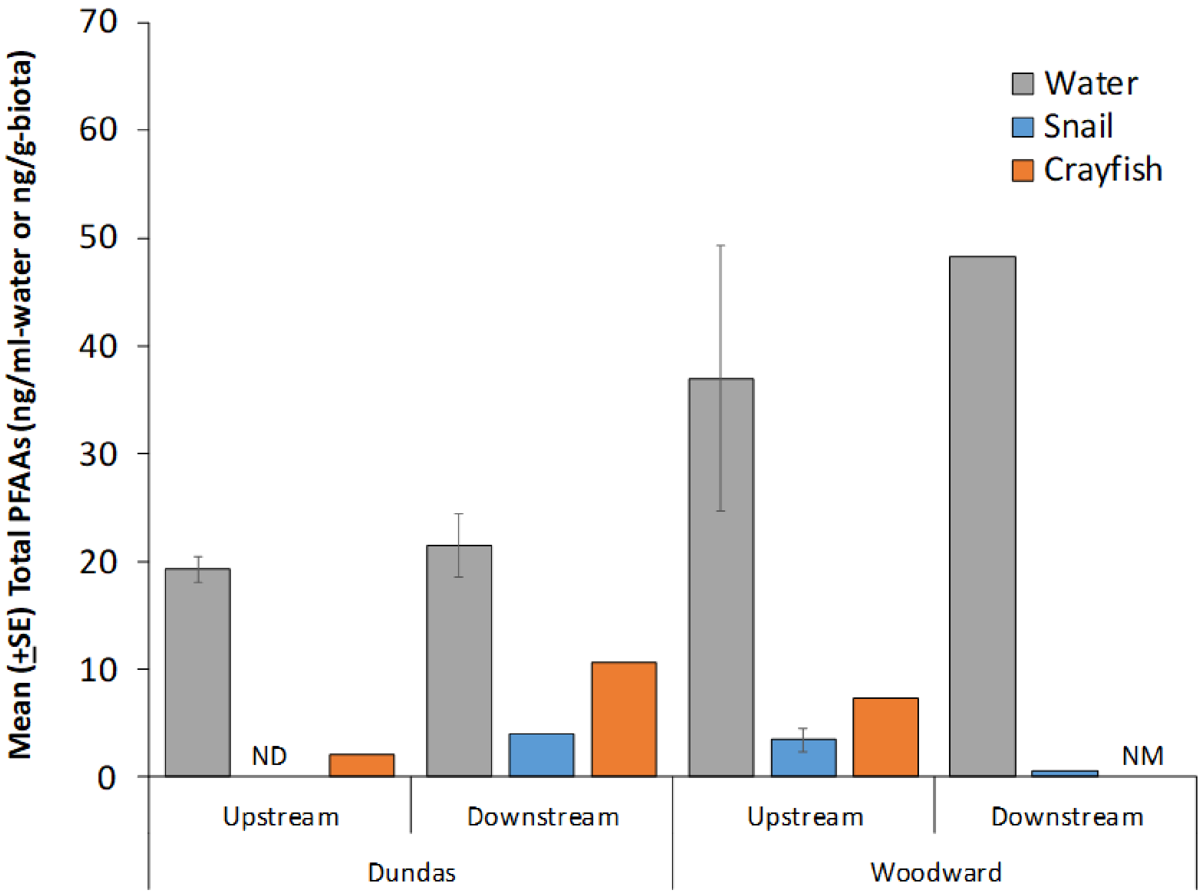


Figure 5. Concentrations of perfluoroalkyl acids (PFAAs) in waters, snails and crayfish upstream and downstream of airports and WWTPs (ECCC unpublished results).

In another study, focusing on fish, PFAS partitioning was not directly related to chain length as observed in crayfish and snails above. This study was conducted on the edible portion of 32 different fish species from across the GLB and PFAS was detected in all fish. PFOS was the dominant substance detected (99%), while the longer chain PFAS (generally C8-C12) were detected in greater than 50% of the samples. As expected, the highest levels of PFAS in fish were detected in highly urbanized areas in the lower Great Lakes (lakes Erie and Ontario).

Twenty percent (20%) of the fish monitored in the Great Lakes exceed Ontario's current PFAS benchmark for unrestricted consumption of 18 ng/g. This study demonstrated that PFAS are accumulating in Great Lakes fish. A key observation from the studies to date is that there does not seem to be a direct correlation between the size and type of fish and the levels of PFAS in fish (as has been demonstrated with other COCs like the flame retardants, i.e., the level of COC increases as the size of the fish increases). Characterization of human health risk from exposure to PFAS via consumption of Great Lakes fish would benefit from widespread fish PFAS monitoring to account for variability observed in levels within and among fish.

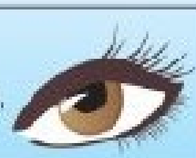
Canada's Great Lakes Strategy for PFOS, PFOA and LC-PFCAs identifies the need to better characterize sources, and the need to develop innovative, cost-effective tools and approaches for monitoring, measuring, and reducing releases from various sources. Annex 2 supported several projects to identify consumer products containing fluorinated compounds and estimate the potential for entry into waste streams (WWTPs or landfill leachate) from the use or disposal of these products. Food contact materials, cosmetics, and children's products marketed as water and/or stain resistant were the categories investigated. Total fluorine was screened using particle-induced gamma ray emission spectroscopy. Products with elevated levels of total fluorine were then subjected to speciation analysis for individual substance identification. PFAS, including PFOS, PFOA and LC-PFCAs, were found in all product categories. Results of these projects are described below.

Fast food contact materials (e.g., disposable wrappers and containers) tended to have higher measured total fluorine concentrations than food contact materials purchased at grocery stores (e.g., boxes or pouches used to hold foods), with the highest amounts measured in molded plant-based compostable bowls. The study found that each year between 2018 and 2020, an estimated 9,000 (range 1,100 – 25,000) and 940 (range 120-2,600) tonnes/year of polymeric PFAS were used in ~2% of food packaging in the U.S. and Canada, respectively (Minet et al., 2022). Eleven tonnes/year of non-polymeric PFAS also moved through the food packaging lifecycle. Approximately 6,100 (range 690–13,000) and 700 (range 70–1,600) tonnes/year of these PFAS were landfilled or entered composting facilities in the U.S. and Canada, respectively, with a potential to contaminate the environment (Minet et al., 2022). The results show that the use of PFAS in food packaging contaminates the entire waste stream. PFAS and PFOS, PFOA, and LC-PFCAs in food packaging can enter the GLB from littered food packaging, landfill leachate, runoff from biosolids, and other types of discharges (Minet et al., 2022).

PFAS in cosmetics can enter the environment directly when washed down the drain or into the solid waste stream when removed with cosmetic cleaning pads. Unused cosmetics can also enter the solid waste stream when disposed of by the consumer. Approximately half of the tested cosmetics marketed as being "water-proof", "long-lasting", or "wear resistant" (which can be indicative of PFAS) contained elevated levels of total fluorine (Figure 6) with further analysis confirming the presence of select PFAS (Whitehead et al., 2021).

Unfortunately, this study could not estimate the amount of PFAS entering waste streams from these products.

Figure 6. Categories and number of different cosmetics tested for fluorine content (Adapted – Whitehead et al., 2021).

Product Category or Sub-Category	Number of Products Tested	Percentage of Products with High Fluorine
All Lip Products (lipsticks, glosses, shadows, liners, shimmers, balms)	60	55%
Liquid Lipstick	42	62%
Foundations (liquids, creams)	43	63%
Concealers	11	36%
Other Face Products (powders, blush, bronzers, highlighters, primers, sprays) 	30	40%
All Mascara	32	47%
Waterproof Mascara	11	82%
Other Eye Products (shadows, liners, creams, primers, pencils) 	43	58%
All cosmetics tested	231	52%

While children's products that were tested contained low amounts of detected PFAS, these substances have the potential to be released from the garments through wear and laundering with the potential to enter surface waters via WWTP effluents. Further, PFAS can enter the environment when these garments are discarded in landfills. PFAAs precursors were abundant in school uniforms. The estimated median potential children's exposure to PFAS via dermal exposure through school uniforms was 1.03 ng/kg body weight/day (Xia C. et al., 2022).

As noted above, since many products and packaging are disposed of in landfills, a separate study was undertaken to evaluate the concentrations of PFAS in landfill leachate. Landfills represents a potential exposure route for PFAS to humans (groundwater to drinking water wells) and a potential risk to aquatic ecosystems. PFAS was monitored in the leachate and surface waters of 20 Ontario landfills. Maximum concentrations of PFAS in the leachate ranged from 1–10 µg/L (1,000–10,000 ng/L) in the older landfills (1950s) which is lower than aqueous film forming foam (AFFF)-impacted sites and fire-training areas previously reported. Lower concentrations were observed in newer landfills (Propp et al., 2021). The results indicate that landfills (predominantly historic sites) can be an ongoing, long-term source of PFAS to groundwater wells, surface waters, and WWTPs if they are receiving leachate collected from these landfills.

To identify other potential ongoing sources of PFAS to the environment, a study was conducted to review additional sources and sectors where PFAS may have been or are currently being used in Ontario. The individual sectors and number of sites included: pulp and paper mills (47 sites), metal plating (146 sites), waste disposal sites (2406 sites), WWTPs (499 sites), automotive manufacturing (128 sites), and fuel storage and distribution sites (24 sites). In an effort to reduce the risk of contamination, the location data for these industrial sites are being compared to sensitive hydrogeological areas in the province in an effort to prioritize sampling sites, particularly those in close proximity to private drinking water wells.

The results from the projects above will inform additional actions to reduce the risks of PFOS, PFOA, and LC-PFCAs in the Great Lakes. These efforts could include further use restrictions, researching and ensuring safe end-of-life management practices for products containing PFOS, PFOA and LC-PFCAs, prioritization of environmental monitoring including industrial effluents, and the establishment of inventories of known or possible sources.

1.1.6 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are largely produced through the combustion of materials either naturally or through human activity. They are present in the environment in complex mixtures that are difficult to characterize and measure. Benzo[a]pyrene (B[a]P) and a list of 17 PAHs were originally targeted as Tier 1 and Tier 2 chemicals respectively (Table B, in Appendix), and a number of regulatory and non-regulatory actions have been taken to reduce PAH concentration levels in the Great Lakes. Most PAHs were found to be decreasing in air in the GLB between 1997 and 2017 (Li et al., 2021). The 2016 Status of Tier 1 and Tier 2 Chemicals in the Great Lakes Basin report found that PAHs continue to be present at concentrations of concern in water and sediment in the GLB. As a result, PAHs (Tier 1 and Tier 2 chemicals and coal tars and their distillates) were designated as a COC under the 2014 COA and nominated by Canada as a CMC under the GLWQA in 2017. PAHs were recognized as a candidate CMC in December 2022 and a second level review and screening of PAHs is underway with a decision anticipated by June 2024.

As science and analytical methods develop, the understanding of the types and associated potential toxicity of additional PAHs has expanded (e.g., alkylated PAHs and substituted PAHs (sulphur, nitrogen, oxygen)), which are now collectively referred to as polycyclic aromatic compounds (PACs).

Using Lake Ontario sediment samples, diagnostic fingerprinting was used in an attempt to differentiate different PACs from a variety of petrogenic (rock) and pyrogenic (incomplete combustion) sources including coal tar sealants, asphalt-based sealcoat products, diesel particulate matter, diesel fuel, used motor oil, and roofing shingles. These source results reduced data gaps and improved accuracy and understanding of the sources and potential toxicity of PACs entering the Great Lakes from coal tar-based materials (Figures 7 Bowman et al., 2019)

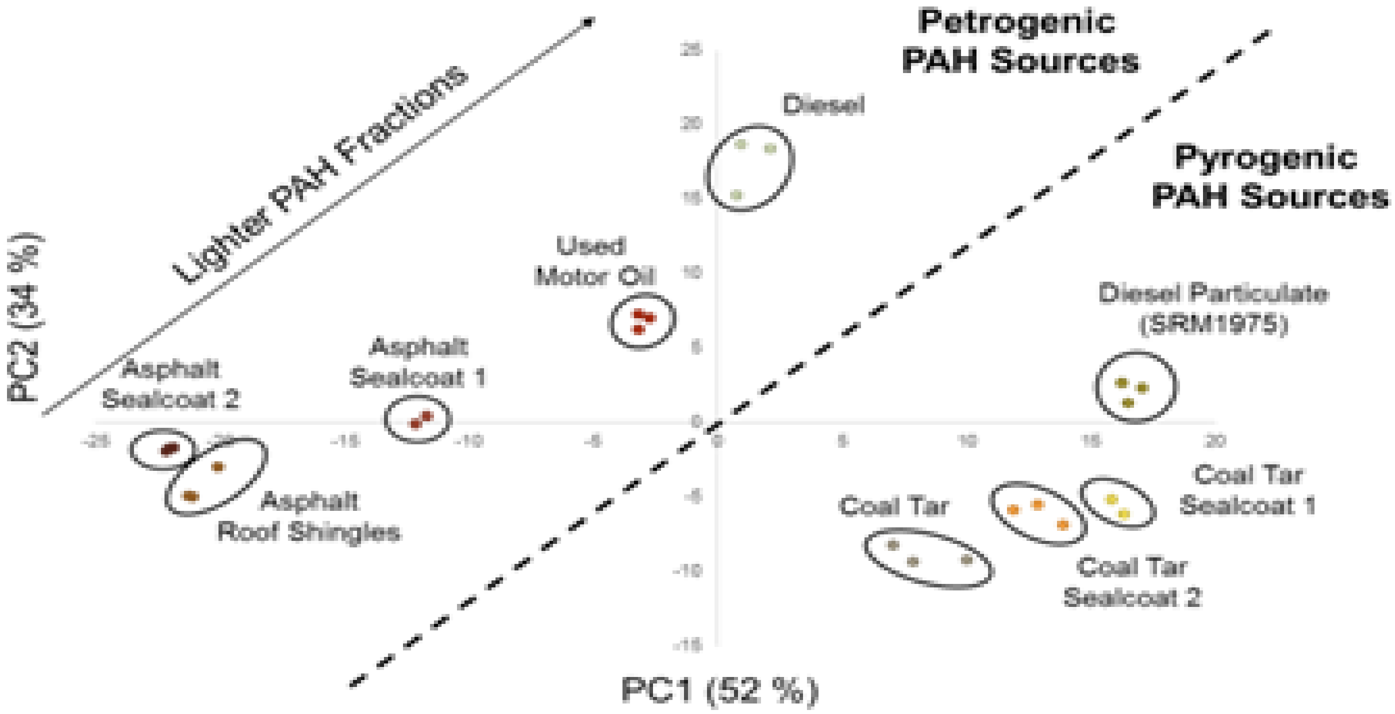


Figure 7. Diagnostic fingerprinting to differentiate different PACs from a variety of petrogenic and pyrogenic sources including coal tar sealants, asphalt-based sealcoat products, diesel particulate matter, diesel fuel, used motor oil, and roofing shingles (Bowman et al., 2019).

A particular PAC (benzo[b]carbazole) identified by Bowman et al., 2019, shows promise as an indicator to track source contributions from coal tar-based products and PACs, which could support management and remedial actions in select regions in Lake Ontario (Hamilton Harbour and Toronto Harbour). This work further supported the GOC's risk assessments, resulting in the published final screening assessment report on Coal Tars and their Distillates. In August 2022, the GOC published a consultation document outlining its proposal to prohibit the manufacture, import, and sale of coal tar-based sealant products (at levels of 1,000 ppm or more) in Canada. The GOC expects to propose regulations in the summer of 2023 for public comment, with the final Regulations to be published in fall 2024.

A current study is underway to analyze sediment, sediment cores, and biota samples for distinct PAC finger printing characteristics identified from petrogenic and pyrogenic source materials (Table B. List of PACS to be targeted, in Appendix). This information will be critical to support the toxicity review and development of a new guideline for PAHs based on predominant PACs in environmental media in the GLB.

Initial surveillance of alkylated and sulphur substituted PAHs was undertaken utilizing passive samplers located across Lake Ontario, focussing on Hamilton Harbour, Humber Bay, and Toronto Harbour. In general, concentrations varied from 1,300–6,000 ng/g per sampler for a sum of 46 alkylated PACs. Concentrations were highest in the Windermere Basin arm of Hamilton Harbour, compared to other index stations in the harbour. Concentrations in Humber Bay and Toronto Harbour were similar (1,500 ng/g per sampler). Effluent concentrations from two WWTPs were approximately 2,000 ng/g. Monitoring data from rivers and creeks in the western Basin of Lake Ontario were significantly higher than concentrations in the harbours, with concentrations of up to 8,000 ng/L in Etobicoke and Mimico creeks. Concentrations in the Don River were around half of this value. Overall, alkylated PAHs were two times higher than PAHs (MECP, unpublished results). Since alkylated PACs have been associated with asphalt and coal tar sources, sources of elevated concentrations in Etobicoke and Mimico creeks could be the result of urban runoff and stormwater from paved surfaces. Sulphur substituted PAHs (N=6) concentrations were more consistent across the western Basin of Lake Ontario and were at least an order of magnitude lower than the alkylated PAHs.

1.1.7 Lead

Lead is a naturally occurring metal found in the Earth's crust and can be released during natural processes, such as rock and soil erosion. Lead is also released directly to the environment from sources such as metal production and processing, aviation fuel, and indirectly through wastewater treatment facilities. Lead found in wastewater effluents usually comes from industrial discharges to sewers and the use of lead pipes/solder. Lead emitted to air can be deposited on land or water surfaces and then builds up in soils, sediments, humans and wildlife. Lead in air in the GLB has been declining from 2005 to 2017 (Li et al., 2020). Significant lead releases to water and land also come from fishing tackle (lead sinkers and jigs) and ammunition respectively. The popularity of shooting sports has grown over the past 5 years and the trend is expected to continue. Increased uses and releases of lead via ammunition are expected with annual lead releases to the environment increasing from ~5,000 tonnes in 2016 to ~5,800 tonnes in 2025 (ECCC, 2018).

Alkyl-lead, originally identified as a Tier 1 chemical under the 1994 COA, was used as an additive in automotive gasoline, contributing significant amounts of lead to the environment. Governments of Canada and the U.S. banned the use of alkyl-lead additives in automotive gasoline in the 1990s, significantly reducing concentrations of lead in the ambient environment.

In 2020, the Government of Canada conducted an evaluation of whether risk management actions were effective to reduce exposures to lead, and summarized the results in a publication of the "Evaluation of the Effectiveness of Risk Management Measures for Lead". The results indicate that progress has been made in reducing releases of lead to the environment from human activities; concentrations in the environment have declined over time, but that additional risk management actions, ongoing performance measurement, and monitoring activities are important to further protect the environment against the harmful effects of lead.

The report notes there are no tissue guidelines to provide context for lead levels in fish, making it difficult to draw conclusions on how lead concentrations in fish tissue affect the long-term fish health and survival. Some unknowns exist regarding how lead concentrations in fish tissue relate to concentrations of dissolved lead found in the surrounding environment. Long-term monitoring is needed to better understand trends in lead levels observed in the environment, particularly to identify current/ongoing releases that may be associated human and/or industrial activities.

Source tracking of Tier 1 and Tier 2 chemicals, COCs and other harmful pollutants

Investigating specific sectors is one way to identify sources of COCs and other harmful pollutants requiring further management. For example, funeral homes and crematoria were identified as potential point sources of harmful pollutants to receiving municipal WWTPs.

A monitoring study was undertaken to identify chemicals including Tier 1 chemicals (aldrin/dieldrin, chlordane, DDT, Mirex, Benzo[a]pyrene, mercury and PCBs), Tier 2 chemicals (anthracene, cadmium hexachlorocyclohexane and PAHs), pharmaceuticals and other personal care products, and other contaminants discharged from funeral homes to municipal sewer systems.

More than 30 samples were collected and analyzed for over 200 chemicals from eight different facilities. Many of the Tier 1 and Tier 2 chemicals were not detected in any of the samples except PCBs (detected in 53% of samples), DDE (metabolite of DDT; in 82% of samples) and select PAHs. Two main constituents of embalming fluids, formaldehyde and triclosan, were detected at maximum concentrations of 561,000 mg/L and 505 mg/L respectively, which may pose a risk to receiving sewersheds due to their antimicrobial activities (Kleywegt et al., 2019b). Lead was not detected in any of the sampling effluents, confirming funeral homes are not a significant source of lead to the environment.

1.2 Harmful Pollutants

1.2.1 Pesticides

In Ontario, pesticides are used in a number of ways, including in the agriculture and forestry industries, that may result in their release to the Great Lakes. Pesticide residues can be transported from land to streams through runoff, stormwater catchments, tile drain systems, and leaching through soil. Annex 2 supported the monitoring and assessment of several classes of pesticides including biocides, herbicides, fungicides, and select insecticides, such as neonicotinoid insecticides (NNIs).

Annex 2 supported one of the most comprehensive studies of NNI toxicity to aquatic invertebrates. Invertebrates were the focus of this study as they are known to be significantly more sensitive to NNIs than fish or amphibians. Data from this study is being used to support the development of Canadian Council of Ministers of the Environment (CCME) Canadian Water Quality Guidelines for the Protection of Aquatic Life for NNIs, including an updated Guideline for imidacloprid. The study generated toxicity data for six neonicotinoids (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid, thiamethoxam) for ≥20 aquatic invertebrate species under different exposure scenarios: short-term, acute (2- to 4-day), pulsed (24-hour exposure followed by long-term recovery in reference/non-exposure conditions), and long-term, chronic (7- to 56-day) ((Raby et al., 2018 a, b, c, d; et al., Raby et al., 2019). These comprehensive toxicity endpoints provided the data necessary to derive a species sensitivity distribution (SSD), a common tool to estimate the concentration below which adverse effects are unlikely to occur. This information was also used to conduct a hazard assessment of NNIs to aquatic invertebrates in a southern Ontario context. The Ontario hazard assessment showed a moderate acute hazard to aquatic invertebrates for imidacloprid. For other neonicotinoids, no or low hazard was concluded. The chronic hazard assessment concluded a moderate hazard to aquatic invertebrates for clothianidin and a high hazard for imidacloprid. Results have identified which NNIs may require additional risk management actions to protect aquatic organisms.

To assess the potential impact of select NNIs to human health in high intensity agriculture regions in southern Ontario, source and finished drinking waters were collected from six drinking water systems using both passive samplers and grab samples (Sultana et al., 2018). Thiamethoxam, clothianidin, and imidacloprid were detected in both passive and grab samples in source waters, which is consistent with monitoring results across the GLB watersheds, noted above. The frequency of detection of NNIs was much lower in treated drinking water, with some compounds detected at estimated concentrations in the low ng/L range. Overall, the concentrations detected were orders of magnitude lower than the 2017 interim Water Quality Guidelines for Drinking Water established by Health Canada for clothianidin, imidacloprid and thiamethoxam of 400, 600 and 40 μg/L, respectively.

To better understand the current concentrations of pesticides in the GLB, passive samplers were deployed across 18 watersheds (Metcalfe et al., 2019). The NNIs thiamethoxam, clothianidin, and imidacloprid were detected in several watersheds, where levels of imidaclopid exceeded the interim Canadian Water Quality Guideline for imidacloprid of 0.23 μg/L. Newer generation insecticides, flonicamid and flupyradifurone, were also detected in some watersheds, which is the first report of these pesticides in peer-reviewed literature. Atrazine, 2,4-D, dicamba, carbendazim, thiophanate methyl, and several azole-based fungicides were also widely detected. The lack of water quality guidelines and aquatic information made it difficult to assess the impacts of the presence of certain fungicides. The use of statistical tools indicated that the presence of select pesticides correlated not only with the type of crops to which it was applied but also the density of the crops. This type of analysis will be beneficial in predicting potential impacts of other pesticides uses in the future.

Annex 2 also supported a project to investigate the concentrations, cumulative use, and impact of agricultural operations, including pesticides, on water resources, wetlands, wildlife, vegetation, and consumption of traditional foods of the Walpole Island First Nation community. The project followed up on two previous studies, in 2001 and 2005. There were no detections of pesticides in any of the sediment or water samples in this study.

Although some work has been completed to derive SSDs to determine concentrations related to adverse effect, a key scientific gap is a lack of understanding of the correlation between the presence of select pesticides and their potential impacts to non-target organisms. This is particularly important where water bodies (and aquatic organisms) may be exposed to multiple stressors and chemicals (e.g., industrial emissions, WWTPs, alternating flow levels, climate change) with the need to understand whether impacts may be targeted, independent, or cumulative.

1.2.2 Plastic pollution

Plastics are among the most universally used materials in modern society; however, the improper management of plastic waste has led to plastics and microplastics becoming ubiquitous in all major compartments of the environment. This represents a widespread pollution issue as well as a lost economic opportunity. Plastic that is discarded, disposed of, or abandoned in the environment outside of a managed waste stream is considered plastic pollution. In Canada, it is estimated that 48,000 tonnes, or 1% of plastic waste was released into the environment as pollution in 2018, while only 8% of plastic waste was recycled. These values are anticipated to continue to increase over time if no action is taken. There are growing concerns that plastic pollution adversely impacts the health of the environment and potentially humans (PSPC, 2022).

In 2021, the Government of Canada stated that plastic manufactured items meet the ecological criterion for a toxic substance as set out in the *Canadian Environmental Protection Act, 1999*. By adding "plastic manufactured items" to Schedule 1 of CEPA, the ministers can propose risk management measures on certain plastic manufactured items to manage the potential ecological risks associated with those items becoming plastic pollution.

To understand the extent of contamination, sources, fate, and effects of plastic pollution, Annex 2 supported a systemic review to synthesize the current state of the science for macro- and microplastics in the Great Lakes. It is estimated that approximately 10,000 tonnes of plastic waste enters the Great Lakes annually from Canada and the United States, accumulating in some areas to levels comparable to those found in the ocean's "garbage patches" (Hoffman and Hintinger, 2017). Available data reports high levels of contamination across the sediments of lakes Ontario and Erie and the beaches of lakes

Huron and Erie. Community-based science data from shoreline clean-ups reported that more than three million pieces of plastic litter has been collected over a two-year span across the shorelines of the five Great Lakes (Earn et al., 2021).

Annex 2 also supported several studies which included analyzing more than 500 samples (surface water, fish and sediment) to better understand: the sources and pathways that contribute to plastic pollution into the Great Lakes, including the patterns, trends, and abundance of plastic and microplastic pollution and the effects on wildlife.

Initial studies in the GLB focussed on characterizing the types and shapes of microplastics, i.e., plastic particles less than 5 millimeters, to understand the potential point and non-point sources. The sources included: breakdown of litter; intentional and unintentional loss of debris during waste management activities; the release of microbeads from personal care products; manufacturing sources; losses from transport and industrial/commercial activities as well as separate studies on abandoned fishing gear and microfibers from washing machines.

The highest abundances of plastics measured in Great Lakes waters were in the Toronto waterfront (Humber Bay and Toronto Harbour area) where particles and scrap from commercial plastic processes such as flash and trimmings (e.g., excess materials from molded or casted products) contributed significant proportions of plastics found in sediment and water (Ballent et al., 2016; Helm, 2017). A recent survey of more than 60 beaches across the Great Lakes found the areas with the highest number of plastic pellets, accounting for most of the pellets found across the Basin, occurred in Sarnia and western Lake Ontario, where large quantities of pellets are manufactured or used for plastic applications (Zbyszewski et al., 2014, Ballent et al., 2016; Dean et al., 2018). High numbers were also found in Lake Superior near a rail car derailment that spilled pellets a decade ago (Corcoran et al., 2020). Further monitoring documented higher proportions of plastic particles from commercial and industrial activities, such as trimmings, flash, and pellets from watersheds and sewersheds where plastics industries are located. Identifying and understanding sources facilitates the implementation of risk management actions, including capture and treatment technologies.

To examine the potential impacts of microplastics on fish, both laboratory exposure/feeding studies and collection of wild fish at different life stages was conducted. Initial laboratory studies focussed on determining whether microplastic particles ingested accumulate within the fish. Results indicate that most particles passed through the digestive tracts of fish but may accumulate on occasion and may cause blockages. Lifecycle testing of fish exposed to microplastics in water (from virgin plastics and from plastic found in the environment) showed inconclusive results on the impacts to the fish. It could not be determined whether some of the effects observed in fish were from plastic particles themselves, or from other contaminants present on or in the plastic particles collected from the environment (Bucci et al., 2022). These results are consistent with the previous findings (Bucci et al., 2020).

Wild fish collected from lakes Ontario and Superior contained microplastics in their digestive tracts, with the highest amount reported in fish from Lake Ontario near Toronto (Munno et al., 2022). Lake Ontario fish also had greater complexity in the types of plastic particles present, reflecting inputs from a wide variety of sources. Some plastics have been found in fillets of sportfish (e.g., from Lake Simcoe, Ontario); however, preliminary estimates suggest that human exposure to plastics via fish consumption is lower than from other sources such as indoor air (McIlwraithe et al., 2021). At this time, it seems that the predominant impacts to aquatic organisms from microplastics are related to food dilution (ingestion of plastics replacing food), internal and external physical impairments (blockages, entanglement), and oxidative stress (de Ruijter et al., 2020).

Sources of plastics to the Great Lakes

Abandoned Lost and Discarded Fishing Gear (ALDFG) can be a major source of plastic to the oceans. To determine its potential in the Great Lakes, existing information on ALDFG in the Canadian portion of Lake Erie was compiled to develop a predictive model to identify probable locations of lost fishing gear, locations where lost fishing gear is accumulating, and the potential negative impacts on species and habitats.

Lake Erie was selected because it has the largest commercial fishing effort of any of the Great Lakes, and the fishery uses gillnets, a fishing gear rated as high risk for impacts from ALDFG. Three probable hot spot areas for fishing gear loss and accumulation on the Canadian side of Lake Erie were identified.

Data from 2019 showed that ALDFG does contribute to plastic pollution in the Great Lakes but was significantly lower in quantity compared to other categories of plastics found. This data represents what is washed up on shores and does not account for gillnets and other fishing debris that remains floating in the lake or at the lake bottom.

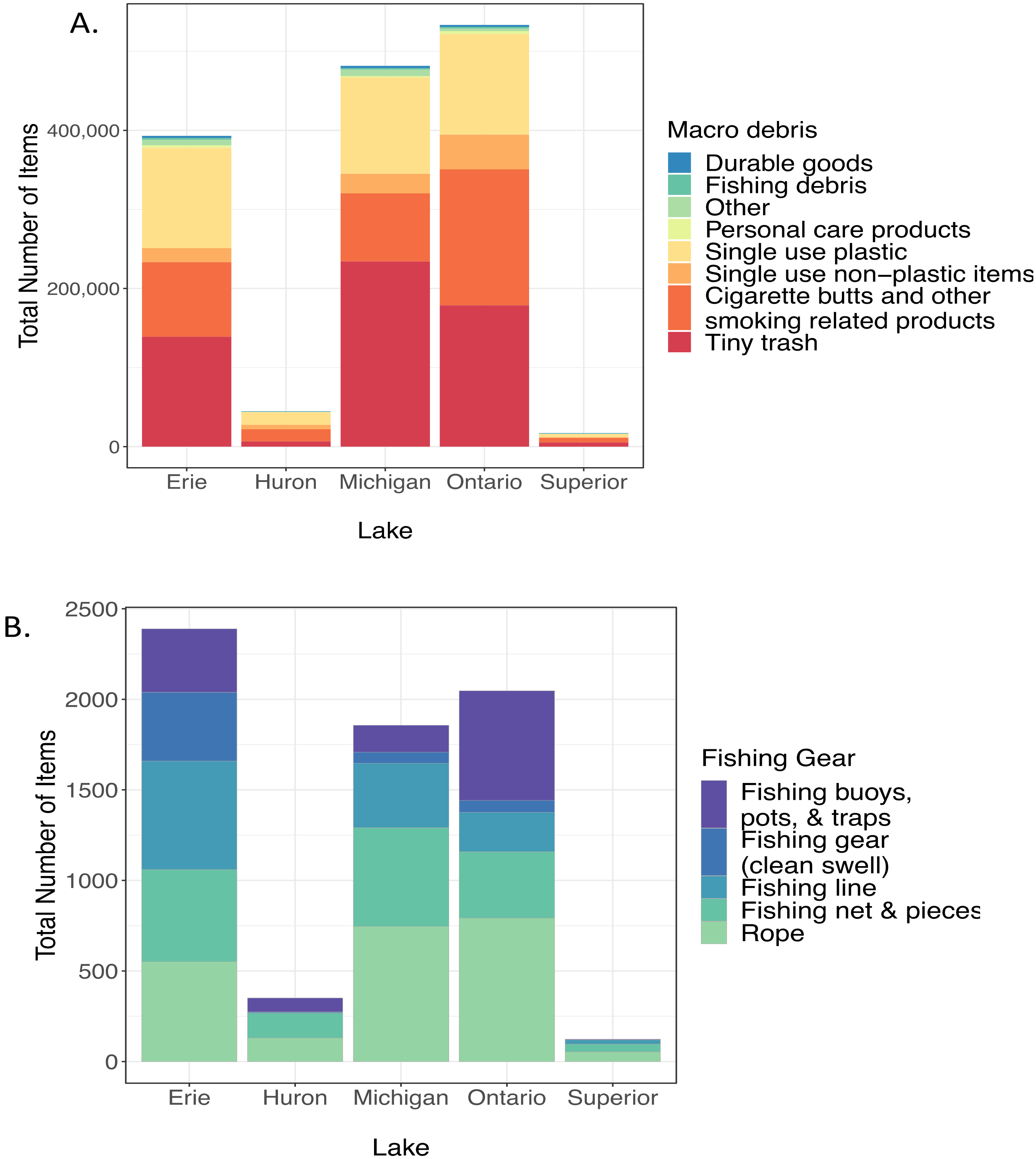


Figure 8. A) Distribution of macro debris and **B)** Fishing Gear in individual Great Lakes.

Microfibers can be released from synthetic fabrics during laundering which make their way to receiving municipal WWTPs. To reduce microplastics loadings to WWTPs and water bodies, the use of home washing machine filters was studied. Filters were installed in 97 homes, representing approximately 10% of households connected to the municipal WWTP. The effluent from the WWTP showed a significant reduction in microfibers after filter installation. Lint samples from the filters revealed average weekly lint capture of 6.4 grams, equivalent to 179,200 – 2,707,200 microfibers. It is estimated that 934 million to 14.1 billion microfibers could be diverted from WWTPs annually just from the households participating in this study. The results from this project informed proposed Ontario legislation requiring new washing machines to be equipped with a filter to remove microplastics (Erdle, et al., 2021).

Figure 9. A) Samples of microfibers removed by washing machine filters. Credit: Georgian Bay Forever. **B)** Cigarette butts in jar collected from shoreline clean up events. Credit: R Moore.

Cigarette butts are one of the most commonly littered items on the planet, and many do not realize that cigarette filters contain plastic. This plastic, known as cellulose acetate, is slow to degrade, and will never fully decompose. Filters are designed to remove toxins from tobacco while the cigarette is smoked, so each filter can contain up to 165 chemicals. Research has shown that these chemicals will leach into the surrounding environment, particularly when wet, reducing soil and water quality. Annex 2 supported the Lake Huron Centre for Coastal Conservation to promote a public awareness campaign on "Butt Free Beaches". Eighteen shoreline cleanup events were completed over the duration of the program, with a total of 1,031 kilograms of garbage collected by 585 volunteers. Of the items collected 50% were smoking-related items, with a total of 11,735 cigarette butts collected through these cleanups.

Work to date under the COA advanced the identification of key sources of plastics to the GLB. The Government of Canada's Science Assessment of Plastic Pollution (2020) recommends action be taken to reduce plastics from entering the environment and additional research, including the expansion and development of consistent monitoring efforts in less characterized environmental compartments. Reducing plastic waste and pollution, such as, working closely with industries to prevent releases and support onsite capture technologies to reduce discharges to storm and sanitary sewers will be key to reducing loading of plastics to the GLB. Next steps will be to address knowledge gaps on the types, release, and impacts of chemicals and additives to plastics (anti-oxidants, flame retardants, plasticizers, UV inhibitors), their mobility in the environment, and an improved understanding of toxicological pathways to the development of exposure thresholds (levels), if warranted.

1.2.3 Pharmaceuticals

The release of pharmaceuticals and their metabolites into the aquatic environment has drawn increasing concern in recent years. Many varieties of pharmaceuticals have been detected throughout the Great Lakes in all aquatic media (water, sediment, and biota), with the main types found including pain killers, hormones, and endocrine disrupting compounds, antibiotics, and psychiatric drugs. The presence of these pharmaceuticals varies by lake and location, with the highest concentrations near WWTPs. It is well known that WWTPs were not originally designed for the reduction and/or removal of pharmaceuticals. Conventional activated sludge processes remove carbon, nitrogen, and phosphorous, including compounds with high biological degradation, hydrophobic properties, and low polarity. In contrast, pharmaceuticals often have specific biological activity at low concentrations (ng/L), are stable, and hydrophilic. The consistent and continuous discharge of pharmaceuticals into the environment implies that some of these products can be considered as pseudo-persistent pollutants. Incidents of alterations to fish reproductive biology, reproductive behaviour, and community behaviour coincide with areas in which environmentally relevant concentrations of pharmaceuticals have been observed.

Annex 2 supported two reconnaissance studies to better understand key sectors that may be contributing to WWTPs with a specific focus on healthcare facilities and pharmaceutical manufacturers. The first study measured the concentrations of over 100 pharmaceuticals, metabolites, or additives to personal care products in effluents from three hospitals and a long-term care facility. As noted above, commonly used substances, including cotinine (nicotine metabolite), caffeine and its metabolite 1,7-dimethylxanthine, ibuprofen and naproxen (analgesics), venlafaxine (antidepressant), and N,N-diethyl-meta-toluamide (insect repellant commonly known as DEET) were detected in all samples at all sites. Cytotoxic drugs (tamoxifen and cyclophosphamide) used in cancer treatments and x-ray contrast media (iopamidol and diatrizoic acid) were infrequently detected in hospital effluents (Kleywegt et al., 2015).

Antibiotics azithromycin, clarithromycin, ciprofloxacin, erythromycin, ofloxacin, and sulfamethoxazole were consistently detected in hospital wastewaters, as was triclosan (antibacterial agent). In this particular study, these facilities accounted for a small contribution to the overall pharmaceutical load when compared with the total concentrations entering the receiving WWTP. This may not be true for other sewersheds where hospitals may represent a greater contribution to the total flow at receiving WWTPs. Since pharmaceuticals were designed to be biologically active at low concentrations, cumulative effects should be considered for large WWTPs discharging to small receivers (rivers and streams), like the Grand River.

The second point source study for pharmaceuticals focussed on pharmaceutical manufacturers. This was the first Canadian study to evaluate the potential impact of this industry to WWTPs. Direct effluent samples were collected from five pharmaceutical manufacturers during manufacturing and processing. Results indicated that 200 grams to approximately 14,000 grams of pharmaceutical products were being directly discharged to the sewers daily during active manufacturing (Kleywegt et al., 2019b). This survey demonstrates that direct point source discharges from pharmaceutical manufacturers represents a key source of pharmaceutical pollution to receiving sewersheds.

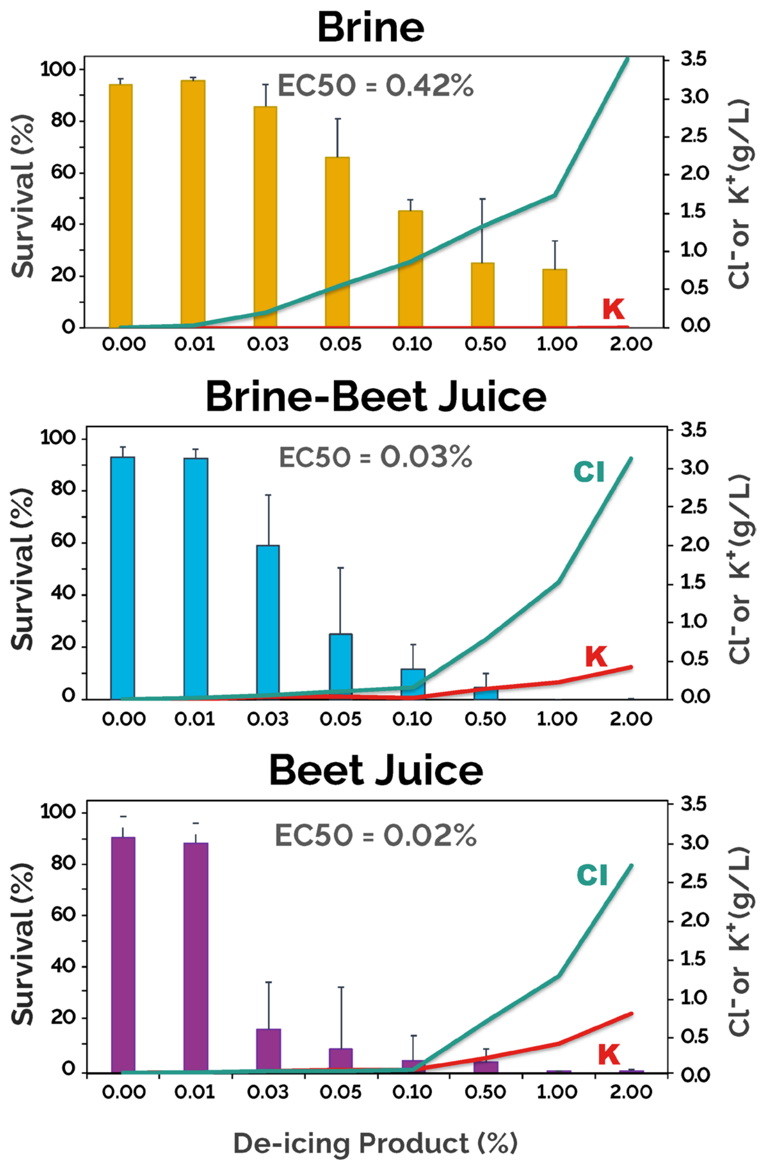
1.2.4 Chloride

Road salt has become the largest anthropogenic contributor of chloride to the environment. As a result, chloride contamination of surface waters and groundwater is a common issue in urban areas. Though overall chloride levels in the Great Lakes are below Canadian Council of Ministers for the Environment (CCME) guidelines for acute and chronic toxicity, indirect effects, such as changing the lake's chemical suitability for aquatic species or impacting the mixing ability of the water column, may be occurring.

In a recent review of chloride monitoring data in Ontario, it was clear that chloride concentrations are highest and are increasing in urbanized and populated areas and those with close proximity to roadways (Sorichetti et al., 2022). The concerns of chloride toxicity to freshwater organisms have led to an interest in "eco-friendly" de-icing products. Annex 2 supported a toxicity study using freshwater mussels to determine whether these chloride alternatives (salt brine, beet juice, and a brine-beet juice product) pose a risk to aquatic organisms compared to current salt use. Results indicated that based on toxicity and application rates, beet juice de-icing products pose more of a hazard to early life stage mussels than traditional de-icing products and could contribute substantial potassium to receiving environments (Gillis et al., 2021).

Annex 2 also supported a project to summarize the state of science regarding chloride contamination in the GLB to better understand knowledge gaps on other sources of chloride other than road maintenance. The study found that it was not feasible to develop a clear understanding of the extent and/or impact of chloride contributions from water softener use in the GLB; however, studies in Ontario, Wisconsin, and Minnesota have demonstrated that residential water softener use is responsible for approximately 50% of the chloride load to receiving WWTPs. The use of potassium chloride fertilizers on agricultural lands was also identified as a potentially significant non-point loading source to the Great Lakes. The project provided a number of recommendations to address research and monitoring gaps and to inform the development of priority actions and best management practices for WWTPs and septic system management.

Acute Toxicity to Glochidia



Legend
Left y-axis = percent survival of test organism (mussel larvae) following exposure to solution (% survival)
Right y-axis = concertation of either chloride (Cl^-) red line or potassium (K^+) green line in grams/litre (g/L)
x-axis = percent of de-icing product tested

Relative Hazard Based on Toxicity and Application Rates

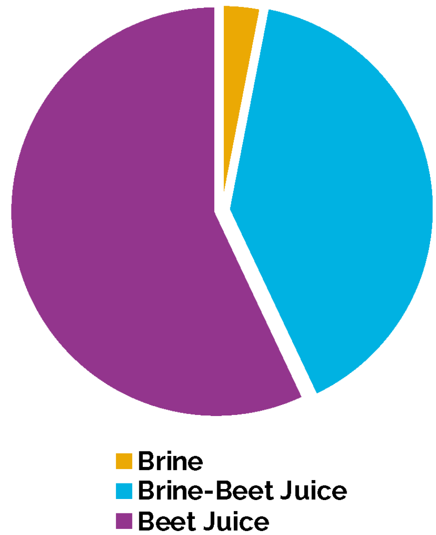


Figure 10. Toxicity of brine, brine-beet juice and beet juice to mussels and relative hazard based on toxicity and application rates (Gillis et al., 2021).

Product	Effective Concentration toxic to 50% of the test organism
Brine (salt solution)	0.42%
Brine with Beet Juice	0.03%
Beet Juice	0.02%

The lower the percent concentration, the more toxic the solution.

1.2.5 Nanosilver

Silver nanoparticles are used in various personal, consumer, and industrial products as an antimicrobial ingredient. To better understand the concentration and loadings to Lake Ontario, Annex 2 supported a research study to investigate if WWTP effluent is a source of silver to the aquatic environment. Two WWTPs in western Lake Ontario were selected and quantification methods to differentiate between silver particles and nanosilver particles were developed. Concentrations of silver in surface water (suspended or dissolved) at sites impacted by the WWTP were below detection limits or were in the low ng/L range, suggesting that silver nanoparticles are efficiently reduced by WWTPs (Metcalfe et al., 2018). However, elevated silver concentrations in sediments and suspended sediments were measured near WWTPS. About 15–25% of silver in these sediments was re-suspended into the water phase and subject to release when agitated. Particles tentatively identified as silver nanoparticles were detected in suspension after agitation of these sediments. These results indicate that more work is needed to assess silver nanoparticles (and nanoparticles in general) in sediments near WWTP discharges, and the potential for resuspension into the water column.

2.0 Education and outreach on Harmful Pollutants

A key commitment of Annex 2 is to share data on research, monitoring, surveillance, and related science activities and information with the Great Lakes community. Information is shared through a variety of mechanisms including public webinars hosted by ECCC, MECP, and other partners; posting of information to websites; and issuing publications and reports. Annex 2 also supported several projects to share information on COCs and other harmful pollutants with Ontarians and GLB residents.

In 2016, Annex 2 collaborated with the Pollution Probe Foundation to develop a youth engagement campaign (EduTox) to increase public awareness about contaminants in consumer products to help reduce exposure, usage, and risks to human health and the environment within the GLB. The EduTOX campaign engaged with Ontario youth (ages 14-22) to develop short videos on contaminants in the GLB. Teams and individuals from three provinces sent forty-five (45) video submissions, including 28 from Ontario. The topics addressed included mercury exposure and the safe consumption of fish, safe drinking water, radon gas exposure, air pollution, and pesticide use. Awards for the EduTOX Video Challenge were presented at the 2016 World's Largest Sandbox in Ottawa, an event attended by several hundred individuals including Parliamentarians and media, non-profit organizations, and industry professionals. Winning EduTOX videos were screened at the event, allowing the educational content to reach a diverse audience. This project contributed to strengthening public understanding of the risks associated with toxic substances encountered in daily life.

Annex 2 also collaborated with Environmental Defence Canada to develop and provide education and outreach materials for the public on select COCs in consumer products that may be affecting human and ecosystem health and/or can be found in the GLB. The objective was to provide easy access for consumers to the types of chemicals that could be in products that they use. Environmental Defence Canada developed and distributed more than 300 wallet cards in various Ontario communities in addition to posting the wallet card on their website. The key COCs targeted included: PAHs (coal tar sealant), lead, mercury, PCBs, flame retardants (clothing, furniture foam and mattresses), and PFAS.

Another initiative investigated the use of citizen science to support the collection of pharmaceutical data. Citizen science initiatives encourage the public to spend time in their natural environment while undertaking meaningful activities to monitor and improve the environment. It has been shown to be one of the most effective means of increasing environmental awareness, education, stewardship, and support for conservation efforts because initiatives build goodwill and provide opportunities for participants to feel like an important part of the solution. For this work, Pollution Probe partnered with Swim Drink Fish and Trent University to produce a report that explored the development of a citizen science program including the methods and protocols required for a program specific to pharmaceuticals. The report concluded that the value in developing a citizen science program would be in its ability to effectively educate the public on the presence and impacts of pharmaceuticals in the Great Lakes. The report also identified a number of challenges associated with the feasibility of citizen scientists undertaking a monitoring program specific to pharmaceuticals.

As previously discussed, plastic pollution is a serious issue in the Great Lakes. Support was given to engage Lake Superior Basin small businesses, schools, Indigenous communities, and other institutions to develop and implement action plans to reduce plastic waste. Actions included waste auditing, options for non-plastic alternatives, and an evaluation plan to determine the local impact of changes. Two shoreline cleanup events were held, ten businesses participated in waste audits to identify opportunities to remove plastic in their operations, several options for alternative products and suppliers were identified, and a Plastic Reduction workshop was delivered to high school students.

As noted in the Harmful Pollutants section, concentrations of chloride in some urban creeks within the GLB are reaching levels that can negatively impact fish, amphibians, turtles, and other aquatic life. Annex 2 supported a project to reduce excessive winter salt application. World Wildlife Fund (WWF), in collaboration with academia, environment non-government organizations, winter contractors, and property management companies, created a multi-disciplinary project to reduce road salt applications within the GLB. Two university campuses trained and certified staff in the handling of road salt, equipment was upgraded to facilitate a reduction in the use of road salt, and scientific studies demonstrated saving of upwards of 25,000 kg of road salt from entering our waterways. Data and tracking allowed WWF to create interactive tools to communicate the state of our freshwater and how excessive road salt is putting species at risk. These tools garnered national coverage and support from all levels of government. By bridging the communication gap between contractors and property managers, this project facilitated clear winter management plans being put into place, leading to the reduction of more than 1,000,000 kg of road salt in a single season.

New approaches to fish consumption advisories

Fish consumption advisories have been issued for the North American Great Lakes due to elevated levels of contaminants. Fish are typically considered a healthy part of our diet and fish consumption is promoted by nutrition and health experts. A study was conducted to understand the relationship between the benefits of fish consumption (essential fatty acid intake like omega-3) and the potential risks from contaminants (mercury and PCBs) that lead to fish consumption advisories. Fifteen different fish species from Lake Huron and Lake Superior were reviewed for this study. Overall, it was determined that it was more important to focus on the type of fish species than the particular lake to balance the risks-benefits of fish consumption (Strandberg et al., 2020).This initial work will help guide outreach in communicating the benefits of fish consumption, working with Indigenous communities to include not just the chemical but also the nutritional, cultural, and spiritual value in understanding fish use and consumption.

3.0 Wastewater pollutants

Effluents released from wastewater systems can contain contaminants, as even advanced wastewater treatment systems are unable to remove all pollutants and chemicals. Further complicating the situation, some sewer collection and treatment systems are combined with stormwater collection systems that can become overloaded during heavy rainfalls, resulting in the release of partially treated or untreated effluents to the environment. During wastewater and sludge treatment processes, the liquids are separated from the solids and some contaminants may partition to the solid residuals (sludge). Depending on the level of treatment, solid residuals can be landfilled or incinerated, further treated and land applied to recycle nutrients and organic matter or transformed into a registered fertilized product.

Municipal wastewater is the main conduit for which harmful pollutants reach the receiving waters of the GLB. Previous work under the COAs demonstrated the higher the level of wastewater treatment, the higher the reduction and removal efficacy of contaminants. The Federal Wastewater Systems Effluent Regulations (WSER) support national standards for wastewater effluent discharges which are reflected in site-specific Environmental Compliance Approvals (ECAs) for individual treatment plants. Many Ontario WWTPs provide advanced treatment. As of March 2023, there are 500 municipally regulated WWTPs in Ontario (which include mechanical, lagoons and sub-surface systems).

3.1 Pathogens

Municipal wastewater and sludge can contain microbial pathogens such as bacteria, viruses, and protozoa. Due to the lack of information regarding viral pathogens in Ontario wastewater effluents, Annex 2 undertook research to determine the risks of exposure of pathogens from municipal wastewater. Pre- and post-disinfection effluent was collected from five WWTPs, on a monthly basis, for one year. Enteroviruses, noroviruses, coliphages (bacterial viruses), and *Escherichia coli* (*E. coli*) were measured using U.S. EPA methods 1615, 1602, and membrane filtration. Results demonstrated that enteric viruses are abundant in wastewater effluent following routine chlorine or UV disinfection processes. The measurement of coliphages appeared to be a good indicator for evaluating the potential effectiveness of different wastewater disinfection treatments for all enteric viruses (Simhon et al., 2019).

Peracetic acid (PAA) has been used as a wastewater disinfectant in Europe since the early 2000s but has only recently gained interest in North America as an alternative to chlorine (and sodium hypochlorite (NaClO)). PAA has several promising attributes in view of its strong oxidation potential, potentially short contact time requirements, absence of chlorinated disinfection by-products, and bacterial inactivation. Although PAA has been shown to be effective against bacteria in wastewater, there is limited data on its efficacy against enteric viruses and bacteriophages. Annex 2 supported a two-year study of virus disinfection with PAA and chlorine as hypochlorite (NaClO) in a secondary WWTP. A side-stream comparison of PAA and NaClO against enteroviruses and noroviruses, coliphages, and *E. coli* was conducted. PAA fish toxicity testing under flow through conditions was also assessed. Overall, PAA and NaClO did not significantly reduce enteroviruses and noroviruses; however, both performed well at reducing *E. coli*, and NaClO performed better at reducing levels of coliphages. A 96-hour toxicity testing revealed that PAA residual was lethal to rainbow trout only prior to quenching (when the toxic activity was quickly stopped with another chemical). To ensure protection of aquatic life, an interim 0.27 mg/L PAA residual discharge limit was derived (Pileggi et al., 2022).

Water recovery and reuse from sources such as greywater, wastewater, and stormwater can help increase water efficiency and reduce impacts of water shortages. Currently there are about 25 golf courses in Ontario that use reclaimed water for irrigation, where disinfection is verified by testing *E. coli* limits. As presented above, enteric viruses are less susceptible to disinfection than *E. coli* when WWTPs use conventional (secondary or tertiary) treatment and routine (chlorine or UV) disinfection. Annex 2 supported a review of the potential impacts of hypothetical pathogen exposure to human health when using reclaimed water for golf course irrigation. The risks to golfers from handling wet golf balls following irrigation was assessed using the principles of quantitative microbial risk assessment (QMRA). Overall, the study concluded that the presence of noroviruses in reclaimed water used for golf course irrigation does not have a direct risk of infection to golfers (Simhon et al., 2020).

3.2 Sludge stabilization and biosolids

In Ontario, sewage biosolids from WWTPs that have been stabilized through aerobic or anaerobic digestion are characterized as non-agricultural source materials (NASM) for land application under the *Nutrient Management Act*, General Regulation (O. Reg. 267/03).

To assess the potential terrestrial and aquatic impacts of land applied biosolids that may contain harmful pollutants, Annex 2 partnered as a collaborator on a national Canadian Water Network initiative. The project included 18 bioassay responses of terrestrial earthworms (*Eisenia andrei, E. foetida*, *Lumbricus terrestris)* and aquatic organisms (*Ceriodaphnia dubia*, *Daphnia magna)* to three different biosolids, at two different application rates (Canadian Water Network (CWN), 2015). The conditions used simulated a worse-case scenario with excessive biosolids runoff and little dilution, which are unlikely to occur in real-world conditions. Overall, there was little evidence of negative impact to organisms when municipal biosolids were used to amend soil at appropriate application rates. Plants grown in soil amended with biosolids showed similar or improved germination and growth parameters compared to plants grown in reference (laboratory control) soil; chemical analysis showed little evidence of accumulation of different emerging contaminants in plant tissues and terrestrial and aquatic organisms exposed to simulated runoff and tile drainage from biosolids-amended soil were not affected, except for two species. These organisms were negatively impacted by the high levels of ammonia and turbidity in the runoff and drainage samples (Puddephatt et al., 2022a, Puddephatt et al., 2022b).

Biosolids from sewage lagoons are more variable in quality due to a wide range of operating parameters. Ontario currently does not have any direct "stability" standards. To address this knowledge gap, Annex 2 supported a literature review and jurisdictional scan on municipal sewage biosolids and septage, with a focus on lagoon biosolids and the assessment of its quality and stability. The objective was to better understand if there were significant differences in the quality and impact of these different land applied materials (NASM) to soil and aquatic (from potential run-off) organisms. The review included a comparison of standards from different jurisdictions (Ontario, Quebec, British Columbia, Alberta, Nova Scotia, the United States, and Europe) for metals, pathogens, stability, and other pollutants as well as the types of technologies/methods used to assess biosolid stability and quality. The review recommended two methods (additional volatile solids reduction (AVSR) and specific oxygen update rate (SOUR)) by the U.S. EPA for further investigation and potential application for Ontario lagoon biosolids. The review found insufficient evidence to establish a relationship between operating factors and the quality of lagoon biosolids.

3.3 Wastewater treatment technologies

In Canada, chlorination or UV-irradiation are the primary methods used for disinfection of treated wastewater prior to discharge into the aquatic environment. While these disinfection technologies can be effective at reducing the levels of certain pathogenic microorganisms, they do not remove many chemicals. Annex 2 supported a project to evaluate the efficiency and cost-effectiveness of ozonation in the removal of PFAS and BFRs from municipal wastewater. The study showed that the addition of ozonation and chlorination of wastewater prior to discharge, at doses typically applied for disinfection, did not make significant contributions to removal of PFAS or BFRs from the dissolved (liquid) phase of wastewater. This study confirmed that WWTPs can be a significant source of PFAS and BFRs (such as PBDEs and HBCD) to the Great Lakes. Further research into advanced wastewater treatment technologies should be explored.

Tracking technology-based WWTP upgrades and impacts on aquatic life in the Grand River

Municipal WWTP effluent is one of several point sources of contaminants which can lead to adverse responses in aquatic life. The University of Waterloo studied the impacts of WWTP effluent on fish in the Grand River for a decade to track how treatment upgrades to WWTPs can improve overall river ecosystem health.

In 2007, the University first observed up to 80% intersex of rainbow darters (a species of fish), downstream from the Kitchener and Waterloo WWTPs. The researchers also identified significant changes in both gene expression and steroid production in the fish. Fish were not the only aquatic species impacted. The size (length) and frequency (visual search) of freshwater mussels *(Lasmigona costata)* were significantly reduced downstream of the WWTPs compared to upstream sites. In order to reduce these major impacts to fish and mussels, technology-based upgrades were planned and completed over a 10-year period at both the WWTPs.

Upgrades to the Kitchener WWTP in 2013 were associated with an improvement in many of the disruptions previously observed in fish. Upgrades to the Waterloo WWTP came fully on-line in 2017/2018. After the upgrades, all biological end points (intersex, gene expression, steroid production) were no longer statistically different from the upstream reference sites. Although annual variations in water temperature and flow can potentially mask or exacerbate the effects of the WWTP effluent, major capital investments in wastewater treatment targeted at improving effluent quality positively corresponded with the reduction of adverse responses in fish in the receiving environment. These results demonstrate the environmental benefits that can be realized when process upgrades are implemented to improve general effluent quality (Gillis et al., 2017; Hicks et al., 2017a,b; Tetreault et al., 2021).

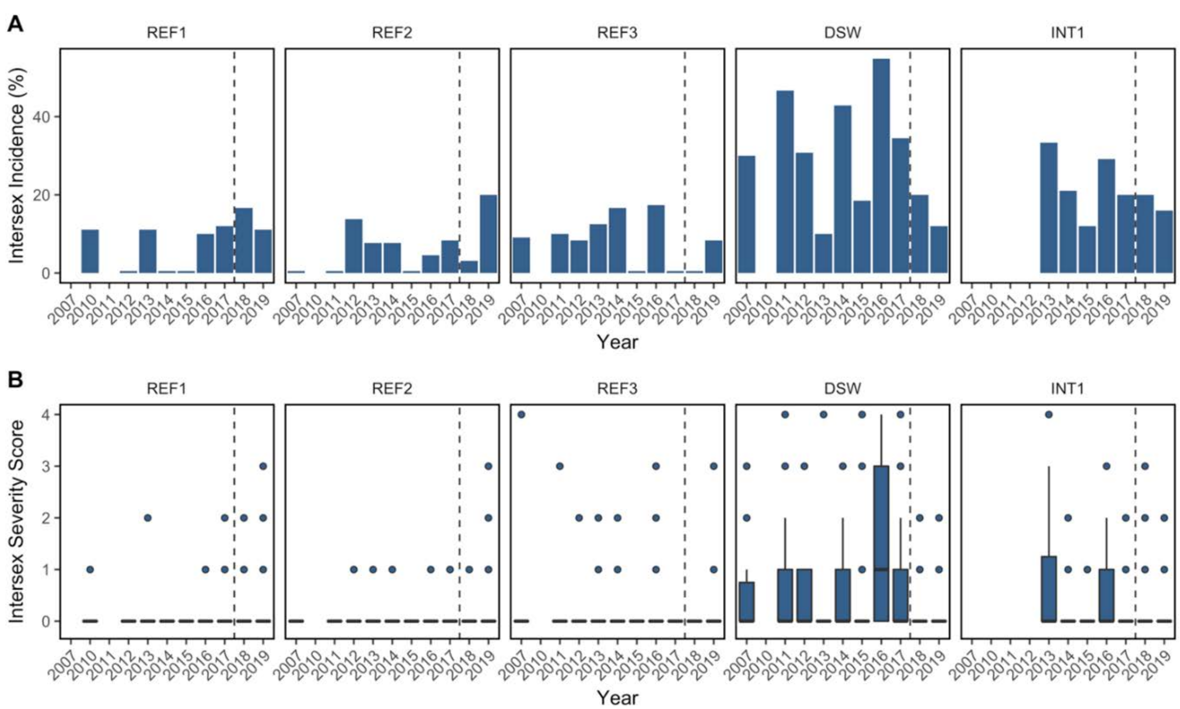


Figure 11. A) Intersex incidence and **B)** severity for fish collected in the fall in 2007 and 2010-2015. (REF = reference sites upstream of WWTPs, DSW=downstream of Waterloo, INT=Intermediate Reference site).

4.0 Stormwater pollutants

Stormwater is water that originates as rain or snow which during storm events or melting leads to run-off to stormwater ponds or combined sewer overflows. In urban areas stormwater ponds are a common best management practice for the treatment of stormwater runoff. They temporarily store runoff to prevent flooding and improve water quality by allowing suspended sediment and sediment-bound contaminants to settle out. This reduces chemical and nutrient concentrations released to downstream water bodies, including the Great Lakes. However, over time, pollutants build up in settled sediment. Annex 2 supported a study to investigate urban stormwater pond sediment as a potential source of harmful pollutants to the Great Lakes.

A literature review concluded that harmful pollutants were detected in all stormwater management pond sediment samples, but with variable detection frequencies. The sediments serve as a sink for many of these pollutants, with little known about their long-term fate or degradation potential. Phosphorus and chloride were identified as key pollutants that become concentrated in stormwater management ponds, especially older ponds. Chloride concentrations are typically above water quality guidelines, which means their discharge could cause elevated local chloride pulses in receiving waters after storm events. Stormwater management ponds, for the most part, trap and retain a suite of stormwater contaminants, including metals and organic pollutants. However, there remains a large gap in data and knowledge pertaining to pollutant and contaminant fate in Ontario stormwater management ponds, as well as their potential impact on receiving waters. Priority data and knowledge gaps include: lack of integrated information on the number of stormwater management ponds; lack of monitoring and performance data; limited information on how climate change will affect design and performance criteria; and lack of data on pollutant and contaminant fate.

5.0 Sampling and analytical tools, methods and techniques

Developing, improving, and validating sampling and analytical tools, methods, and techniques for the measurement of harmful pollutants in the environment and evaluating their potential impacts are key commitments of Annex 2.

Many environmental monitoring programs focus on known, regulated contaminants. These programs are not designed to identify unmeasured or unknown contaminants or include the potential environmental impacts. The collection, analysis, and interpretation of ecosystem health-related data can address this knowledge gap while providing additional lines of evidence to environmental monitoring programs.

5.1 Non-target analysis

The number of "known" chemicals is very small (and regulated chemicals even smaller) relative to the tens of thousands of anthropogenic chemicals and their transformation products that may be present in the Great Lakes. To address the challenge of determining what "unknown" chemicals, breakdown products, or metabolites may be present, novel "non-targeted" analytical methods have been developed to identify "unknown" compounds with advanced chemical analysis and instrumentation. Enormous quantities of data are produced in each analysis, used to identify thousands of compounds present in a single sample.

Annex 2 supported two independent studies that utilized targeted and non-targeted analytical methods (Anaraki et al., 2021; Johannessen et al; 2021) to, respectively, quantify known contaminants of emerging concern (CECs) and to identify previously undetected contaminants. Analysis of samples collected through the use of passive samplers deployed in Lake Ontario allowed for the tentative identification of several compounds that are candidates as novel contaminants of concern, including tire wear compounds (Johannessen et al., 2021) and others not previously detected in the environment (e.g., antiviral and antimicrobial pharmaceuticals).

These studies highlighted how different monitoring approaches and analysis can be used to identify new pollutants in the GLB.

5.2 Methods and techniques as early indicators

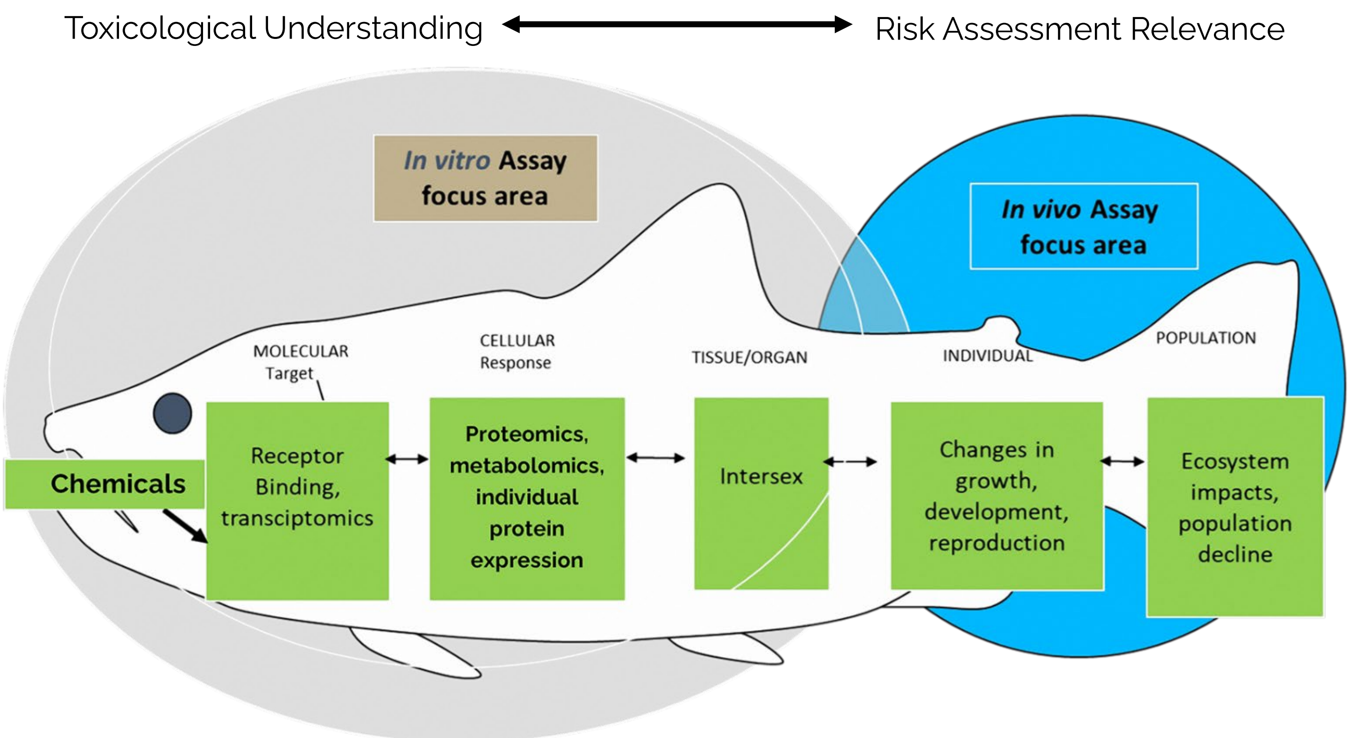


Figure 12. Description of the types of *in vitro* and *in vivo* assays that can test chemical impacts via molecular, cellular, tissue/organs in an organism (adapted from Estrogen Receptor | Research | US EPA).

Toxicity testing to determine the impact of harmful pollutants to aquatic and benthic organisms has primarily focussed on whole organism impacts including acute (short-term, typically lethality) and chronic impacts (survival growth, reproduction). Newer rapid tests have been developed to understand, at the molecular and cellular level (e.g., receptor binding, protein expression, *in-vitro* assays; Figure 12), how harmful pollutants may affect organisms (*in vivo* assays; Figure 12), as well as different end points (e.g., endocrine disruption, intersex and population decline; Figure 12). Annex 2 supported the testing of numerous innovative technologies to better understand the impacts that individual pollutants and chemical mixtures may have on organisms in surface waters, wastewaters, and sediments. These biological impact assays or tests can be classified into categories based on the measured end point. There are several processes or descriptions that have been used to characterize these tests, they include: biological impact assessment, effects-based monitoring, and adverse outcome pathways (AOPs). The following sections will provide an overview of some of the tests assessed and reviewed by Annex 2 and their potential application in the assessment and impacts of harmful pollutants.

5.2.1 Omics

The omics field of research and study has been driven by technological advances that have made cost-efficient, high-throughput analysis of biological and environmental samples possible. The use of omics-based studies and responses in the environment is relatively new. Omics approaches used in toxicology provide a tool to characterize and quantify the molecular and biochemical changes in cells, tissues, and organisms following exposure to chemicals and in different environmental media. Types of omics analysis include: genomics (which genes in organisms are altered at the DNA level), transcriptomics (how DNA is transcribed to RNA), proteomic (proteins produced in cells, tissues, organs), and metabolomics (which metabolites are produced in a cell, tissue, organ) of an organism once it has been exposed to a chemical or environmental samples (Figure 13). The use of omics is a way to determine potential early warning indicators that then can be used or modelled to understand impacts seen at the ecosystem level such as intersex/reproductive impacts, disease or mortality.

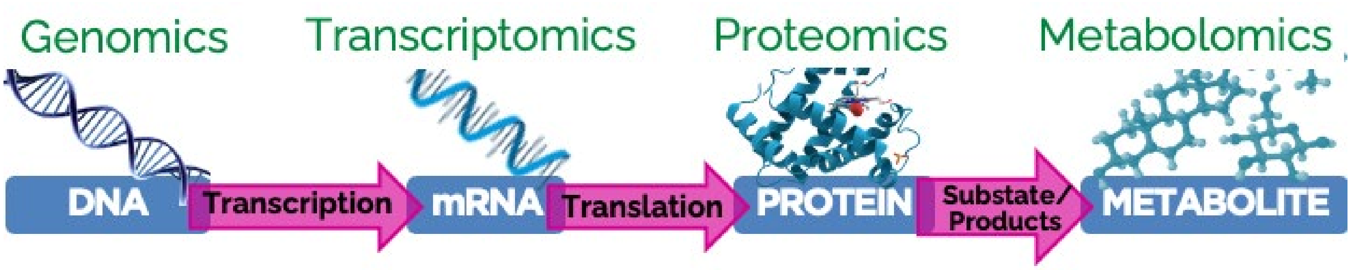


Figure 13. Description of the interconnection between genomics, transcriptomics, proteomics and metabolomics (Adapted from Simmons et al., 2018 International Association for Great Lakes Research [IAGLR]).

In order to explore the use of these tools in the GLB, Annex 2 partnered with several collaborators to initiate a multi-omic approach to the analysis of organism responses to Great Lakes sediment, WWTP effluent, and surface water exposures. The goal of the study was to determine if correlations could be identified for typical acute and/or chronic toxicity end points and chemicals detected in WWTP effluents and surface waters. The project was conducted in partnership with the University of British Columbia (transcriptomics), University of Waterloo (proteomics) and AXYS analytical (metabolomics).

Surface water, sediment, and WWTP effluent samples were collected from two study sites (Hamilton Harbour and Toronto Harbour/Humber Bay) in Lake Ontario between 2014 and 2016. These sites were selected based on their location and proximity to WWTP discharges, direct industrial discharges, and nearshore urbanization impacts (stormwater runoff). Select aquatic organisms, *Hexagenia* (sediment dwelling mayfly) and fish (fathead minnow and rainbow trout) were exposed to water, sediment, and effluent samples to see if, and how the organisms' transcriptome, proteins, and metabolites may be altered/changed. Overall, the results from Hamilton Harbour indicated that proteins and metabolite expressions in *Hexagenia* were significantly different from controls. Wastewater effluent showed the greatest differentiation of stress and impacts compared to controls and the Hamilton Harbour index station. Similarly, there were significant differences in metabolites expressed when comparing exposure *of Hexagenia* to surface water and sediment.

There was no clear direct results to correlate to acute (death) and chronic end points (growth, reproduction) using these different omic profiles and approaches. One of the proposed reasons why is that different organisms (e.g., fish) may be able to modulate or adapt to “pulses” or brief exposures. Continuing to support the review and advancement of different approaches to omics or biomarkers (proteins, metabolites) and their translation to deleterious effects will improve the understanding of cumulative impacts from exposure to complex mixtures.

5.2.2 Bioassays

Bioassays are another tool that can be used to predict biological impairment in aquatic matrices. “Bioassay” means a biological assay, which is a type of test that is used to determine a biological impairment, generally through a particular mode of action (MoA), which can include: binding to membrane receptors (endocrine disruption), inhibiting cellular processes (photosynthesis), or causing cell death (cytotoxicity).

Annex 2 supported an evaluation of five different bioassays using WWTP influent and effluent samples, and surface water samples collected from Lake Ontario. The suite of bioassays evaluated included hormone related (e.g., activation of the estrogen receptor, using ERα CALUX® which can lead to intersex or feminization of fish); oxidative stress (imbalance of oxygen which can lead to cell death or damage, using AREc32); inhibition of photosynthesis for plants (using LuminoTox SPAS I-II and LuminoTox PEC); cytotoxicity (cell damage or death using MTS assay); as well as a qualitative multi-end point test (endocrine / hormone disruption Qiagen 10- pathway receptor assay) (Table 1).

Bioassay	Mode of Action (MoA)	Test Organism	Description
NRF2 Luciferase Luminescence assay AREc32	Reactive	NRF2 Luciferase reporter MCF7 stable cell line	Reporter gene assay which predicts presence of chemicals that induce oxidative stress response pathway
LuminoTox SAPSI&II	Specific	Chlorella vulgaris (SAPSI)	Detects presence of pesticides that inhibit photosynthetic process -phytotoxicity

LuminoTox PEC	Non-specific	Photosynthetic enzyme complex (spinach Thylakoids)	Detects presence of pesticides in addition to diverse toxic chemicals
ERαCALUX	Specific	ErαU2OS Luciferase Biodetection Systems ®	Detects presence of estrogenic compounds
Qiagen Nuclear Receptor (10 pathway assay)		MCF7 cell line	Qualitative assessment with multiple receptors (e.g., estrogen, androgen, progesterone etc)

Table 1. Types of bioassays, mode of action and test organisms assessed using wastewater influent and effluent samples.

The bioassays were conducted in tandem with targeted chemical analysis for a suite of chemicals in hopes of obtaining an indicator chemical or sub-set of chemicals that may be causing the biological effect measured (similar to the use of omics to predict acute and/or chronic end points).

Results of the study indicated that certain assays were more reliable and reproducible than others. For instance, LuminoTox assay (cell toxicity) shows great potential in detecting impacts from pesticides, especially for wastewater quality monitoring. The most complex of the bioassays tested, Qiagen Nuclear Receptor, provided excellent information on the types of biological pathways that could be triggered by the exposure to WWTP influents and effluents (Petosa et al., 2022). The estrogen-based (ERα CALUX® Chemically Activated Luciferase eXpression) and oxidative stress (Nrf2 Luciferase Luminescence) assays found that impacts were lower in effluent samples compared to influent samples indicating that WWTP can reduce estrogenic type chemicals (similar to the results observed on the Grand River). Overall, the study demonstrated that bioassays provide complementary information to chemical analyses; however, no correlations could be established between the results of the chemical analysis and the cellular activity detected in *in vitro* assays (Petosa et al., 2022). This result may be due to the limited number of chemicals that can be measured.

Based on the positive results in identifying a reduction in estrogenic activity from WWTP influents to effluents, Annex 2 supported an additional study to assess the estrogenic and anti-estrogenic quality of WWTP raw sludge and processed biosolids aqueous extracts (to emulate the runoff from sites where biosolids are applied) using the estrogen-based (ERα CALUX®), cell toxicity (LuminoTox) as well as the YES (Yeast Estrogen Screen) and YAS (Yeast Androgen Screen) assays. The study tested raw sludge and biosolids from anaerobic and aerobic digesters from 16 from different municipalities. Results using the estrogen-based (ERα CALUX®) assay indicated that there was estrogenic activity (development of female characteristics) in select samples even though conventional chemical analysis indicated no detections of known estrogenic compounds (e.g., estrone, estradiol). In addition, androgenic activity (development of male characteristics) was observed in samples that had undergone ozonation treatment. These findings further highlight the importance of employing bioassays to complement chemical analyses when assessing efficacy of wastewater treatment or when optimizing treatment conditions.

The last type of bioassays Annex 2 evaluated as a potential screening tool for biological impairment was for genotoxicity and immunotoxicity in the testing of WWTP influent and effluent and their effects on freshwater organisms (fish and mussels). Genotoxicity (DNA strand breaks) was assessed in mussel hemocytes (blood cells) and immunotoxicity was determined by the phagocytic immune response of rainbow trout kidney leukocytes (white blood cells). The results indicated that while some wastewaters induced DNA damage in fish and mussels (Gilroy et al., 2023) others did not. There was no significant immunotoxicity of influent or effluent samples in any of the tested wastewaters.

The complex mixture of chemicals in water means that targeted chemical analysis alone cannot assess the total chemical burden. Bioassays are a good complement to chemical analysis for water quality monitoring, as they may react to all chemicals in a sample, including both known and unknown chemicals (as observed with the ERα CALUX® assay). Bioassays can also account for mixture effects and group chemicals that elicit the same MoA. Effect-based monitoring is often applied as a screening tool, but bioassay results can be used as input for risk-based monitoring programs.

Combining effects-based monitoring with passive sampling may be more comprehensive, informative and cost-effective than individual chemical monitoring alone. Incorporating a screening approach prior to multiple chemical analysis and/or acute or chronic toxicity tests provides a step forward in more comprehensive water assessment. It provides a means to rank and prioritize the degree of pollution of a region, watershed, or treatment system, enabling more traditional assessments to be undertaken in a more efficient, targeted basis where needed.

6.0 Conclusion

Based on the knowledge gained under the 2014 COA, it has become clear that the most concerning pollutants are those that are ubiquitous in our everyday lives (e.g., personal and consumer products), and often are a result of urbanization resulting in greater wastewater discharges and stormwater runoff to streams, rivers and lakes. These pollutants can include chemicals released from personal and consumer products, pesticides, litter, plastic pollution, excess road salt and tire wear residues. Climate change is increasing the frequency of extreme weather events which may drive higher short-term pulses of harmful pollutants into our waterways. A better understanding of the effects of multiple stressors and repeated pulses is needed to better understand the impacts and extent that these pollutants are having on the Great Lakes ecosystem via air, land, and water. As populations in urban centers grow, the impacts on the Basin may be magnified.

Passive sampling coupled with non-target analysis is one comprehensive approach to identifying new contaminants in the GLB. This approach generates massive amounts of data, requiring significant computational and analytical resources. As new information is gained, the presence of previously unknown chemicals can be identified. Incorporating additional environmental media into this approach/tool to identify new contaminants, by-products and metabolites in air, industrial wastewaters and drinking waters would be beneficial.

Canada, Ontario, and their many partners are taking actions to protect the GLB through the implementation of risk management, research, monitoring, and surveillance programs. These actions have been critical to reducing concentrations of chemicals in the Basin. These programs and projects have advanced the science to improve understanding of sources and impacts of chemicals to the environment and have identified actions to address these concerns, where warranted. Many accomplishments have been made; however, more work is needed to understand the potential sources of chemicals and to further manage risks these chemicals pose to the environment and/or human health.

In summary:

1. The 2014 COA addressed several knowledge gaps on the current and on-going sources of COCs to the GLB
2. Knowledge gaps still exist for several COCs in different environmental compartments. Additional monitoring and analysis to address these gaps would be beneficial
3. Many of the harmful pollutants that continue to impact nearshore waters are from stormwater, nearshore, and wastewater influences. Further risk management of chemicals used in products should be explored for additional pollution prevention planning
4. Novel monitoring and analysis referred to as non-target analysis provides the opportunity to identify new harmful pollutants

5. Plastics (primary and secondary) are detected in the GLB. A comprehensive review of the management of litter and sources of plastic pollution in the province would allow for better management of waste and target action
6. Bioassays are a good complement to chemical analysis for water quality monitoring, as they can detect chemicals in an environmental or water sample that are active (e.g., MoA, endocrine disruption), including both known and unknown chemicals
7. A key scientific gap is a lack of understanding of the correlation between the exposure to multiple chemicals and their potential impacts to target and non-target organisms. This is particularly important where water bodies such as the Great Lakes which are exposed to multiple stressors and chemicals (e.g., industrial emissions, WWTPs, alternating flow levels, climate change) with the need to better understand whether impacts may be targeted, independent or cumulative

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Appendix

Table A. List of 24 Organophosphate Esters (OPEs) measured in landfill leachate (Propp et al., 2021).

TEP	Triethylphosphate	**TOTP**	Tritolyl phosphate
TBPO	Tributylphosphine oxide	**IDDPP**	Isodecyl diphenyl phosphate
TPrP	Tripropyl phosphate	**TBOEP**	Tris(2-butoxyethyl) phosphate
TnBP	Tributylphosphate	**TEHP**	Tris(2-ethylhexyl) phosphate
TiBP	Tri-isobutylphosphate	**TBPDPP**	Tert-butylphenyl diphenyl phosphate
TPPO	Triphenylphosphine oxide	**DPIPP**	Diphenyl-3-isopropylphenyl phosphate
TEEDP	Tetraethyl ethylenediphosphonate	**TXP**	Tris-xylenyl phosphate
TCEP	Tris(2-chloroethyl) phosphate	**T35DMPP**	Tris(3,5-dimethylphenyl) phosphate
TCPP	Tris(2-chloroisopropyl) phosphate	**DTBPPP**	Di-tert-butylphenyl phenylphosphate
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate	**T2IPP**	Tris(2-isopropylphenyl) phosphate
TPHP	Triphenylphosphate	**TTBPP**	Tris(p-tert-Butylphenyl) phosphate
EHDPP	2-ethylhexyl diphenyl phosphate	**TDBPP**	Tris(2,3-dibromo propyl) phosphate

Table B. List of PAHs, alkylated-PAHs and sulphur-substituted PAHs to be identified in environmental matrices. Chemicals denoted with an * represent PAHs included as a COC.

PAHs	Alkylated PAHs		Sulphur substituted PAHs
Naphthalene	2-Methylnaphthalene	2,6-Dimethylphenanthrene	Dibenzothiophene
Acenaphthylene	C1-Naphthalenes	1,7-Dimethylphenanthrene	C1-Dibenzothiophenes
Acenaphthene	C2-Naphthalenes	1,8-Dimethylphenanthrene	2/3-Methyldibenzo-thiophenes
Fluorene	1,2-Dimethylnaphthalene	C1 Phenanthrenes/Anthracenes	C2-Dibenzothiophenes
Phenanthrene*	2,6-Dimethylnaphthalene	C2 Phenanthrenes/Anthracenes	2,4-Dimethyldibenzo-thiophene
Anthracene	C3-Naphthalenes	C3-Phenanthrenes/Anthracenes	C3-Dibenzothiophenes
Fluoranthene*	2,3,6-Trimethylnaph-thalene	1,2,6-Trimethylphenanthrene	C4-Dibenzothiophenes
Pyrene*	2,3,5-Trimethylnaph-thalene	C4-Phenanthrenes/Anthracene	
Benz[a]anthracene*	C4-Naphthalenes	C1-Fluoranthenes/Pyrenes	
Chrysene*	1,4,6,7-Tetramethylnaph-thalene	3-Methylfluoranthene/ Benzo[a]fluorene	
Benzo[b]fluoranthene*	C1-Acenaphthenes	C2-Fluoranthenes/Pyrenes	
Benzo[j,k]fluoranthenes*	C1-Fluorenes	C3-Fluoranthenes/Pyrenes	
Benzo[e]pyrene*	2-Methylfluorene	C4-Fluoranthenes/Pyrenes	

PAHs	Alkylated PAHs		Sulphur substituted PAHs
Benzo[a]pyrene*	1,7-Dimethylfluorene	C1-Benzo[a]anthracenes/ Chrysenes	
Perylene*	C2-Fluorenes	5/6-Methylchrysene	
Dibenzo[a,h]anthracene*	C3-Fluorenes	1-Methylchrysene	
Indeno[1,2,3-cd]pyrene*	3-Methylphenanthrene	C2-Benzo[a]anthracenes/ Chrysenes	
Benzo[ghi]perylene*	2-Methylphenanthrene	5,9-Dimethylchrysene	
Retene	2-Methylanthracene	C3-Benzo[a]anthracenes/ Chrysenes	
	9/4-Methylphenanthrene	C4-Benzo[a]anthracenes/ Chrysenes	
	1-Methylphenanthrene	C1-Benzofluoranthenes/ Benzopyrenes	
	3,6-Dimethylphenan-threne	7-Methylbenzo[a]pyrene	
		C2-Benzofluoranthenes/ Benzopyrenes	