

Citizen Science in the Great Lakes

A Tool for Engagement on Pharmaceuticals and Other Emerging Issues

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Prepared for Environment and Climate Change Canada



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CLEAN AIR. CLEAN WATER.

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ABOUT POLLUTION PROBE



Pollution Probe is a Canadian charitable environmental organization (established in 1969) that is a leading agent of change at the intersection of communities, health and environment. Its approach is to define environmental problems through research, to promote understanding through education and to press for practical solutions through advocacy. Pollution Probe seeks to improve the health and well-being of Canadians by advancing policy that achieves positive, tangible environmental change.

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Pollution Probe is solely liable and responsible for the contents of this report. Inclusion of the names of individuals is for acknowledgement purposes only and does not constitute an endorsement of the material.



ABOUT THIS REPORT

In 2018, Pollution Probe and the Clean Water Foundation undertook a significant meta-analysis examining the sources and impacts of pharmaceuticals found in the Great Lakes in an effort to advance public knowledge and inform policy related to the health of the lakes' ecosystems and communities. The resulting report, [Reducing the Impact of Pharmaceuticals on the Great Lakes](#), provides an overview of measures and actions taken in Canada, the U.S. and elsewhere internationally, to address this emerging environmental issue. The report noted that pharmaceuticals, including painkillers, antibiotics, endocrine disrupting compounds (EDCs) — substances that interfere with the hormonal communications between cells — and antidepressants, have been measured throughout the lakes and across all aquatic media (e.g., the water column, sediment and biota).

Pollution Probe's study found that the presence of pharmaceuticals varied by lake and location, and that primary sources or pathways included municipal wastewater (from homes, hospitals and healthcare facilities, landfill leachate and pharmaceutical manufacturers), agriculture and aquaculture. The continuous use and discharge of many pharmaceuticals into the Great Lakes has also contributed to their being considered pseudo-persistent — chemicals whose supply is continually replenished in the aquatic environment — even if they degrade easily. The study pointed to a lack of systemic sampling, reporting and publicly accessible information on the presence and impacts of pharmaceuticals in the Great Lakes, coupled with knowledge and data gaps related to the specific sources and quantities of those found.

Citizen science initiatives have the potential to amplify current knowledge and contribute to filling gaps in existing science and research programs. They also encourage the public to get outside while undertaking meaningful activities to monitor and improve the environment. Citizen science programs have been shown to be one of the most effective

means of increasing environmental awareness and support for conservation efforts because they build goodwill and provide opportunities for participants to feel like an important part of the solution, share their experiences and advocate for the cause. This approach is important as it acknowledges that everyone has a role to play in the creation of knowledge and protection of the environment, including the Great Lakes, while at the same time providing a means of producing more locally-relevant data.

The Government of Canada has recognized that the public plays an important role in restoring and protecting Great Lakes water quality and ecosystem health. In 2019, Pollution Probe was commissioned by Environment and Climate Change Canada (ECCC) to undertake a study to explore the use of citizen science as a tool for engagement and a means of better understanding pharmaceuticals. The study examined the potential for citizen science to contribute to increased public engagement and the development of a more complete dataset on their presence in the Great Lakes.

This report is the result of an extensive literature review and consultation with a wide range of stakeholders working on issues related to pharmaceuticals, toxicology, water quality and citizen science. It provides an overview of the types of processes and methods that should be considered by those looking to develop a citizen science program related to potential emerging contaminants in the Great Lakes, in an effort to ensure scientifically meaningful and consistent results. In addition to providing high-level guidance, the report uses a focus on pharmaceuticals as a means of providing examples of how these methods can be applied to a specific issue.

OBJECTIVES AND METHODOLOGY

This study sought to answer the following broad questions, key to guiding the use of citizen science as a means of complementing existing research and monitoring efforts on emerging issues, including pharmaceuticals, in the Great Lakes:

- Is there an existing indicator or marker for the presence of pharmaceuticals in the Great Lakes? If not, could one be developed?
- Which pharmaceuticals could be initially targeted for sampling and analysis in the Great Lakes?
- What types of methods and processes should be followed to help ensure that sampling conducted by citizen scientists in different locations yields results that are scientifically meaningful and consistent?

This report explores the development of a citizen science program and the methods and protocols required for a program specific to pharmaceuticals. Based on a number of considerations for pharmaceutical monitoring, it outlines a two-step process to address potential barriers to the use of citizen science: use of an indicator and testing for a target list of pharmaceuticals. A number of potential indicators that could be successfully used to identify the presence of pharmaceuticals in the Great Lakes are introduced, along with considerations for developing a target list of pharmaceuticals for sampling and analysis based on the objectives of a monitoring program. The report also outlines a practical example of how this two-step approach could be applied.

The outcomes of this study will contribute to providing guidance on important strategies for the monitoring of pharmaceuticals that can be adopted by those looking to utilize citizen science as a tool for engagement and awareness-building in the Great Lakes. Providing opportunities for citizen scientists to monitor in their own communities helps to acknowledge the connection and concerns they have for their waters and can lead to increased and active engagement related to pharmaceuticals and other environmental challenges. Participation in citizen science programs will engage the community as active participants in positive change, armed with a better understanding of how to contribute to the preservation and sustainability of the lakes.

Research and Data Collection

The methodology for this study combined an in-depth review of available literature with a series of interviews with key subject-matter experts and stakeholders involved in research and monitoring related to pharmaceuticals, toxicology, water quality or citizen science programs. The literature review included an investigation of national and international scholarly and professional resources such as peer-reviewed articles, research reports, policy documents and discussion papers, and collected information related to the following:

- Effective methods for utilizing citizen science as a tool for increased public engagement and awareness-building
- Past and existing programs and initiatives that aim to engage citizen scientists in contributing to monitoring and data collection undertaken by governments, academia and other researchers
- Pharmaceuticals and their detection in wastewater, drinking water, sediment and biota
- Possible indicators of pharmaceutical presence or criteria for a target set of pharmaceuticals for sampling and analysis

Telephone interviews with key stakeholders and subject-matter experts were also conducted with the aim of filling any information or data gaps in the existing literature. The study employed a purposive sampling strategy, which allowed for the collection of a greater depth of information from a small number of carefully selected participants. Interviewees were chosen based on their expertise and comprehensive knowledge of the subject-matter, their ability to provide an informed perspective related to pharmaceuticals or citizen science and their willingness to participate. A standardized questionnaire and interview format were developed to ensure consistency across interviews and credibility around the findings. However, where appropriate, questions were modified to account for the specific background or expertise of an interviewee.

A total of 14 interviews were conducted with 18 individuals (some interviews involved more than one individual) between November 26, 2019 and January 6, 2020. Each interview lasted approximately 45 minutes to an hour. Input from these interviews appears herein as it has been understood by those conducting the study and as such, sole responsibility for the accuracy of the content lies with Pollution Probe.

In addition, this study benefited immensely from the insights and perspective of an expert advisory group whose members provided guidance on the direction of background research, potential interviewees and interview questions, and who reviewed a draft of this report. While the group provided input on the course and scope of the project based on their experience and expertise, all final decisions related to the literature review, interviews and development of this report were made by Pollution Probe.

REPORT OUTLINE

Section One of this report outlines some of the key benefits associated with the use of citizen science as a means of educating on issues related to the contamination of water and in contributing to existing scientific research and monitoring programs. This section also outlines the types of processes that should be considered when designing a citizen science monitoring program.

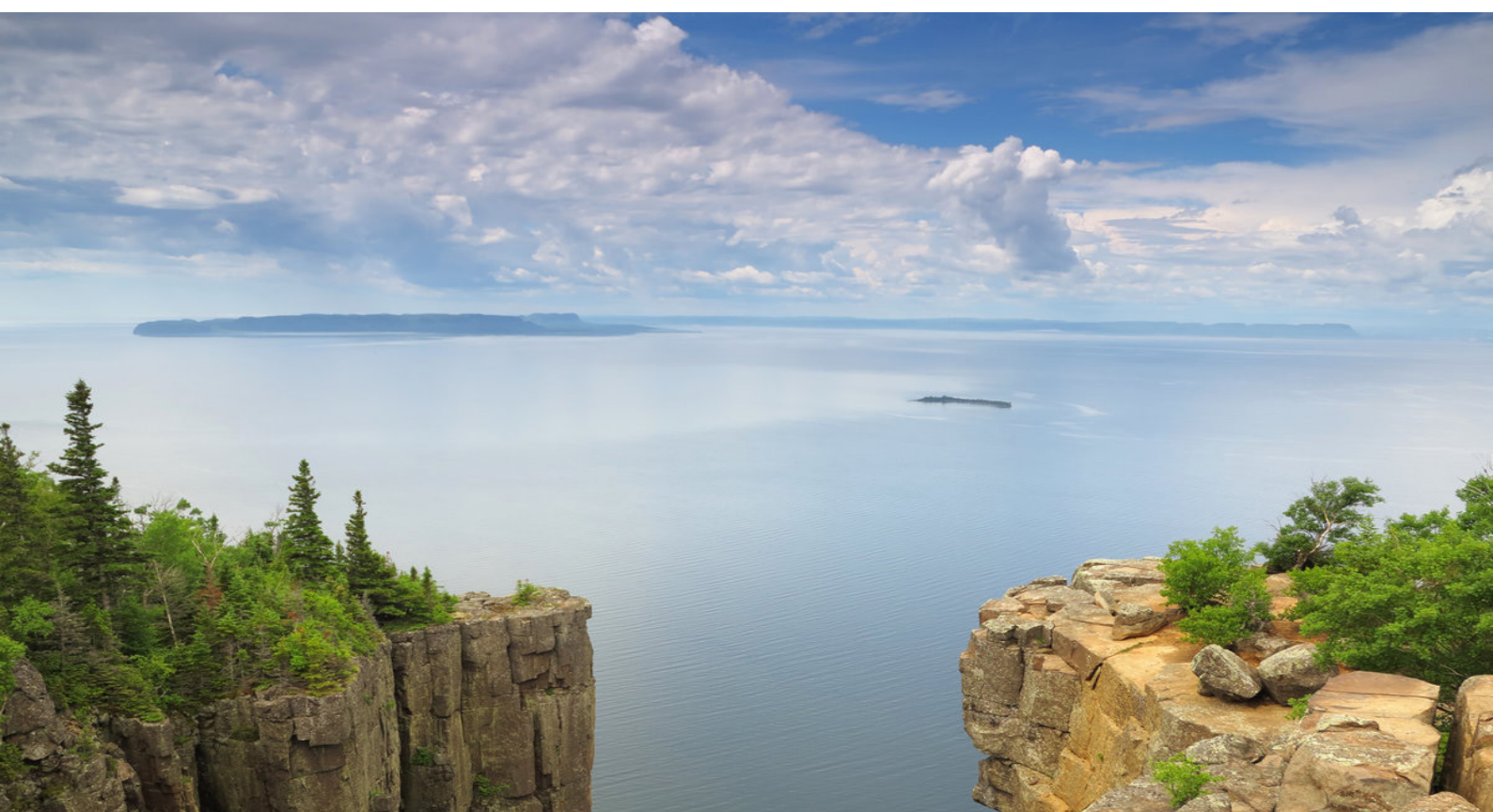
Section Two provides a brief overview of pharmaceuticals in the context of the Great Lakes and describes some of the methods and processes that should be considered when using citizen science to monitor pharmaceuticals and other potential contaminants in the Great Lakes.

Section Three of this report examines the potential for the use of an indicator or marker for determining pharmaceutical presence and identifies a number of considerations for developing a target set of pharmaceuticals for initial monitoring.

Section Four outlines the application of the processes and methods explored in this report as a “proof of concept” based on a separate project undertaken by Pollution Probe, in partnership with Swim Drink Fish and Dr. Chris Metcalfe at Trent University.

Appendix A provides a list of selected resources that can be used to further guide the development of citizen science programs or better understand pharmaceuticals in the Great Lakes.

Appendix B and **Appendix C** include further information about data quality indicators, quality control measures, field equipment cleaning and decontamination protocols.



CONTENTS

About Pollution probe	3
Acknowledgements	3
About This Report	4
Objectives and Methodology	5
Research and Data Collection	6
Report Outline	7
Section One: Designing a Citizen Science Program	10
What is Citizen Science?	11
Citizen Science & Water Quality Monitoring in the Great Lakes	12
Considerations In Designing a Citizen Science Program	14
Program Objectives	14
Quality Assurance and Quality Controls	16
Financial Considerations	19
Program Management and Administration	20
Summary	22
Section Two: The Role of Citizen Science in Better Understanding Pharmaceuticals in the Great Lakes	23
Context	24
Main Sources & Pathways	25
Methods & Processes for Citizen Science Monitoring Specific to Pharmaceuticals	27
Sampling	28
Sampling Design	28
Sampling Methods	32
Shipment and Storage	37
Chain of Custody	38
Analysis	38
Program Evaluation	39
Opportunities for Education	39
Summary	40

Section Three: Determining an Indicator of Pharmaceutical Presence	42
Potential Indicators of Pharmaceutical Presence in the Great Lakes	45
Escherichia Coli	45
Caffeine	46
Sucralose and other Artificial Sweeteners	46
Nitrate	47
Carbamazepine	47
Combination of Indicators	47
Developing a Target List of Pharmaceutical Compounds	47
Summary	52
Section Four: Case Study on Sampling & Analysis of Pharmaceutical Presence in the Great Lakes	53
Swim Drink Fish’s Citizen Science Water Monitoring Hubs	54
Quality Assurance and Quality Control	57
Field Protocols	57
Analysis Using an Indicator for Pharmaceutical Presence	58
Target Compounds for Chemical Analysis	58
Analysis of Chemical Indicators	60
Conclusion	63
Appendix A: Selected Resources & Guidance	66
Great Lakes	66
Citizen Science	66
Water Quality and Water Sampling	67
Pharmaceuticals	67
Appendix B: Common Data Quality Indicators and Quality Control Measures	68
Appendix C: Field Equipment Cleaning and Decontamination Protocols	70
Prior to the Field	70
At the Sampling Site	70
References	72

SECTION ONE

Designing a Citizen Science Program



WHAT IS CITIZEN SCIENCE?

Citizen science — public participation in the science process including helping to address real-world problems by formulating research questions, conducting scientific experiments, collecting and analyzing data, and interpreting results — is not a new concept.¹ Its origins date back thousands of years, with some of the earliest examples organized around the monitoring and recording of insect, bird and animal sightings.² Citizen science in its more modern form emerged around the same time that science became a profession, and has evolved from an initial focus on large groups of participants contributing data or analysing large datasets (often referred to as crowdsourced citizen science), to also include “co-created” research involving smaller groups of volunteers and experts who are involved in almost every aspect of the project.³

Over the past several years, interest in the use of citizen science has grown significantly, with thousands of programs and efforts worldwide aimed at engaging members of the public in research, and empowering communities to contribute in a meaningful way to science and the development of policy. The term citizen science has come to describe an ever-broadening range of activities and approaches including public science, crowdmapping, community citizen science, participatory sensing, popular epidemiology and participation in scientific research.

The advancement of technology has played a major role in opening up new opportunities for deeper interaction and participation. Environmental monitoring technologies and tools for sharing information allow citizen scientists to engage in the collection of data in new and innovative ways, and provide improved means for environmental agencies to use the data generated. Common to each of these approaches is an interest in furthering openness in science, and the engagement of a more diverse range of individuals and communities.⁴

While the sheer number of possible approaches to citizen science can be overwhelming, when planned and implemented effectively, it has the potential to increase scientific knowledge, raise awareness about the environment and allow like-minded people to share knowledge.⁵ One of the most powerful aspects of this tool is its ability to provide unique opportunities for individuals and communities to generate their own questions, collect their own data and advocate for the change they wish to see. It allows for those involved to gain a deeper understanding of their natural surroundings, and contributes to building an informed public that can advocate more successfully for the protection of human health and the environment. It can also be an important way for governments and other social institutions to interact directly with the general public, often across traditional boundaries, while promoting open collaboration in science, research and policy-making.

Pictures from the early days (left) and a recent session (right) of the Audubon Society's annual Christmas Bird Count – the world's longest-running contributory citizen science project.



CITIZEN SCIENCE & WATER QUALITY MONITORING IN THE GREAT LAKES

Water quality is a broad term used to encompass how the physical, chemical and biological characteristics of a water sample measure up to a set of standards. Water quality can be evaluated through a number of different tests for colour, odor, temperature, acidity, and bacterial content. Water quality monitoring provides an opportunity to observe trends over time which can help to avoid major issues by identifying them when they do occur and making informed decisions about their management.⁶

Traditionally, monitoring has been used to verify whether observed water quality is suitable for its intended uses. Over time however, it has evolved to include determining trends in the quality of the aquatic environment and how ecosystems may be affected by human activities. Water quality monitoring programs also play a role in better understanding whether regulatory processes are effective in protecting water bodies from excessive nutrients, metals, pesticides and other potential contaminants.

Water quality in the Great Lakes is monitored by governments, researchers, academic institutions and environmental and citizen science groups. For example, water quality and ecosystem health data are collected by ECCC to support the *Great Lakes Water Quality Agreement (GLWQA)* using a risk-based monitoring approach. The regular monitoring of the physical, chemical and biological conditions in the Great Lakes allows ECCC to measure any natural changes to the conditions of water quality, determine the presence of contaminants, support the development of science-based guidelines for water, fish and sediment and identify emerging issues and threats. The results from the monitoring program are communicated in an Open Source environment to further contribute to resource management in the lakes.⁷

The Government of Canada is also committed to supporting the use of citizen science as a tool for engaging the public, including through maintenance of the Citizen Science Portal which showcases science projects and experiments that individuals can participate in.⁸ The Government of Canada announced an investment of \$44.84 million in 2017 for the Great Lakes Protection Initiative aimed at protecting and restoring the Great Lakes, including through science projects that contribute to enhancing Canadians' knowledge and engagement in addressing water quality issues and ecosystem health.⁹



CITIZEN SCIENCE PORTAL

The Government of Canada's Citizen Science Portal showcases citizen science initiatives from across the country, allowing visitors to identify projects in their communities to participate in. Participants are encouraged to share their experiences using the the social media hashtag #ScienceAroundMe.

In 2015, the Ontario Legislature passed the *Great Lakes Protection Act*. The act recognizes the diverse issues facing the Great Lakes and provides tools to better tackle them.¹⁰ It commits the province to ensuring monitoring and reporting programs are established and maintained and that more opportunities are created for Ontarians to become involved in the protection and restoration of the ecological health of the Great Lakes.¹¹ Ontario also shares the responsibility of meeting commitments under the GLWQA through the *Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health (COA)*. This includes monitoring the physical, chemical and biological conditions of the lakes.¹²

The Ontario Ministry of the Environment, Conservation and Parks (MECP) and Ontario's Conservation Authorities maintain the Provincial Water Quality Monitoring Network (PWQMN) to measure surface water quality in rivers and streams across the province. The PWQMN involves the collection of monthly surface water samples from April through November for chemical analysis. The samples are analyzed by the province's laboratory for temperature, pH, conductivity, suspended solids, metals, nutrients, turbidity and temperature.¹³

In Ontario, the Lake Partner Program is a volunteer-based, water-quality monitoring program coordinated by the MECP, in collaboration with the Federation of Ontario Cottagers' Association (FOCA). The program boasts approximately 700 volunteers who sample primarily to determine total phosphorus concentrations, but also the presence of chloride from road salt. Volunteers collect water samples and monitor water quality in approximately 550 inland lakes at over 800 sampling locations. The resulting data is analyzed by the province at the Dorset Environmental Science Centre (DESC) and then used by the government, academic researchers, partner agencies, private consultants and members of the public to assess water quality in lakes across Ontario.¹⁴

Stakeholders consulted for this report noted that a key strength of the Lake Partner Program has been its partnership with FOCA, which is responsible for outreach and educating communities on the benefits of citizen science and lake stewardship. With a membership of over 50,000 individuals, FOCA has significant reach, which has contributed to the program being fully subscribed. The Lake Partner Program's low participant turnover rate also speaks volumes to the importance volunteers see in the program.

Despite the success of government programs, stakeholders consulted for this study noted that there are not always sufficient resources available to thoroughly monitor for every potential environmental issue throughout the entire Great Lakes watershed. The sheer size of the region and the number of rivers and lakes within it make it challenging to monitor consistently and comprehensively. Research and monitoring programs were also noted to be some of the first to face budget restrictions in challenging economic times. This points to a potential role for citizen science in contributing additional support for existing water quality monitoring programs, including those related to pharmaceuticals, by collecting the types of data that would be useful to governments or other researchers. It is important to note however, that no citizen science monitoring program should be developed without first critically analyzing the need for the data collected.

CONSIDERATIONS IN DESIGNING A CITIZEN SCIENCE PROGRAM

While citizen science can be used to better understand a range of different environmental media (e.g., air, water, biota, etc.), it is not feasible for any citizen science program to sample or monitor for every possible issue.¹⁵ While this report provides an overview of some of the standard monitoring processes or methods for citizen scientists, it is beyond its scope to address every conceivable approach. There are a number of other methods that may be appropriate and even preferable to meet the needs of a specific program, as well as additional protocols that may be required.

In order to determine the appropriate approach to designing a citizen science program and focusing sampling efforts, it is important to first determine the specific condition it would seek to address. This report uses water quality from the perspective of potential contaminants and more specifically, sampling for pharmaceuticals, as a means of organizing content, providing examples that lend clarity to descriptions and explanations. The following section provides high-level guidance on considerations related to the initial development of a citizen science program, followed by an exploration of how these steps would apply to a pharmaceutical-related program in the Great Lakes.

Program Objectives

In order to determine whether citizen science can play a role in helping meet a program's overall objectives, it is important to understand the purpose of its use. There are an overwhelming number of planning decisions and ways to begin thinking about how to effectively design a program to meet desired outcomes. For example, the U.S. Environmental Protection Agency (EPA) suggests using three high-level project purposes as a starting point for shaping the design process and any associated quality assurance requirements. Citizen science programs may evolve through the following levels over time or incorporate aspects of each one:¹⁶

- **Increasing Public Understanding:** Programs with a primary objective of increasing public understanding tend to focus on environmental issues in order to engage communities and educate citizens. These programs may be less scientifically rigorous and look to collect primarily qualitative data such as general descriptions of phenomena or the presence or absence of a specific contaminant.
- **Scientific Studies and Research:** These programs include those that look to provide scientifically relevant baseline data, or to complement existing monitoring following approved methods. Programs in this category may contribute to evaluating the efficacy of existing environmental protections, such as the effectiveness of wastewater treatment plants (WWTPs) in removing certain compounds. Approved protocols must always be followed if the objective is to contribute to environmental risk or health assessments.
- **Legal and Policy Action:** The most rigorous level of citizen science programs are those that aim to affect legal and policy-related action. Such programs require the highest level of quality assurance and are required to follow approved methodologies where the intent is to affect regulatory decisions.¹⁷

A good starting point is for program organizers to determine the target audience and overall goals of the program. Is the intention to provide credible information on water quality conditions to governments or academia? Or is the main goal to educate the public, including through opportunities for experiential learning? While a number of goals can be pursued, it is important to determine which is of primary importance in order to tailor a citizen science program appropriately and to clearly communicate its objectives to participants. For example, where the primary goal is engagement and education, the program's success or failure will not necessarily be based solely on the quality of the data collected. Instead, the program could provide the justification for trained scientists and researchers to follow-up with more rigorous testing in the same location.

The *UK Environmental Observation Framework's Guide to Citizen Science* outlines the following three types of participant engagement as a means of identifying who should be involved in organizing the design of a citizen science program and their specific role:

- **Contributory programs:** These programs are designed entirely by trained scientists and the citizen participation component is primarily confined to the collection or analysis of data.
- **Collaborative programs:** These programs are also designed by scientists however, citizen participants are involved in more than one stage of the process. This could include contributing data and communicating findings.
- **Co-created programs:** These programs are designed by scientists in collaboration with citizen participants and citizens are involved in most, if not every step of the scientific process.¹⁸

Determining how data that has been collected will be used, and by whom, is also an important consideration early on in the planning process. There is the potential for data to contribute to establishing baseline conditions, determining trends in water quality, or identifying current and emerging issues.¹⁹ If the goal is to incorporate data collected by citizen scientists into an existing monitoring program or to make it available to governments, researchers, scientists or academics, these individuals or organizations should be involved early on to determine what data they would find useful and in what form they may need to receive it.

Additional questions to be answered during the program planning phase to help establish strategic priorities were identified through the literature review and by those consulted for this study. These include the following:

- How and where will samples and other information be gathered?
- What training is required of participants?
- What procedures should be followed for sampling?
- How will potential errors in the field, laboratory or during data analysis be controlled for?
- Who will be analyzing the samples collected?
- How will data be reviewed to determine if it is scientifically relevant, consistent and useful?²⁰

In addition to exploring these questions while planning, they should be revisited intermittently once a citizen science program is underway to help evaluate progress and to inform a change of course, if required.

It should also be noted that citizen science may not always be an appropriate approach to answering a specific research question or need. Consideration must be given to how those involved as participants will benefit, the complexity of the data gathering process and any associated costs. While citizen science is often considered to be more cost-effective than some other methods of data collection, analysis or ongoing monitoring, it is not necessarily an inexpensive option. It is important to examine the geographic and temporal scale a project hopes to address, the type, quantity and complexity of data to be gathered and analysed, and the feasibility of securing volunteer participants to collect it.

Most programs require ongoing engagement to ensure their success, which can be challenging to maintain over time. The contributions of participants should be recognized and valued, their time used appropriately, and something provided for their benefit in return (e.g., training, feedback of results, etc.)²¹. Providing opportunities to embed citizen science within existing research and monitoring programs was noted as a means of ensuring their longevity and ultimately, their ability to contribute in a meaningful way to policy development and the building of more comprehensive datasets. Clearly understanding what motivates citizen scientists and what they are looking to take away from their participation is critical to its long-term success. Even a well-designed program may not result in successful engagement if it fails to connect and align with the needs or interests of citizen scientists.

Where the intent of a program is primarily education and engagement, ensuring program elements highlight participant contributions to better understanding and addressing the specific environmental issue are paramount. There is often a trade-off between the number of participants in a program and the complexity of the protocol. Consideration will need to be given to whether the intent is to attract a large number of participants using a relatively simple set of protocols, or whether a smaller number of individuals will be sought to collect large volumes of data through a more complex protocol.

Citizen science programs will also need to determine how to approach the level of scientific complexity of a program and how to communicate protocols and potential findings to participants. Highly scientific language may not be engaging to some participants and a degree of knowledge translation may be required. Excessive processes or bureaucracy may also introduce barriers to participation and will need to be considered.

Quality Assurance and Quality Controls

As previously noted, the use of citizen science as an engagement and awareness-building tool can help complement and augment existing research and monitoring programs. Governments, not-for-profit organizations and academic institutions around the world are making use of citizen science as a critical component of their routine work, providing excellent examples of how this engagement tool can contribute to the generation of high-quality data and analysis. However, despite citizen science's many supporters, there remain those who are skeptical about the quality and reliability of the information collected or reported on by members of the public, as well as its usefulness in research.

A number of stakeholders consulted in the development of this report noted that while understanding about citizen science has increased substantially over the past several years, there are still some potential data users who believe that only professional scientists and researchers can conduct sampling and generate reliable data. It has been shown that given

proper training and supervision, citizen scientists can conduct monitoring activities that yield high quality results and that they are capable of much more than often given credit for. For example, a study by Millar et al. (2018) sought to determine whether water samples collected and processed by citizen scientists were able to produce data of the same quality and usability as that produced by scientists.²² The study found that participants in the MECP Lake Partner Program produced data that were not statistically different from that of the Ministry, suggesting that there is the potential for citizen scientists to play a supportive role in existing research and monitoring programs, including those within the Great Lakes Basin.

As with any science-based initiative, citizen science programs should use specific strategies aimed at improving the credibility of data. Quality assurance is a system of activities designed to ensure that the data meet defined standards of quality. It pertains to the overall management of the program, and includes planning, documentation, training, consistency in the collection and handling of samples, analyses, validation and reporting. An important part of quality assurance is quality control which is the technical activities used to reduce errors throughout sampling, transport and analysis. These activities measure the performance of a process against defined standards to verify that the data meet the expected quality. Wherever possible, quality control should include both internal (i.e., undertaken by the participants or program staff) and external measures (i.e., undertaken by laboratories or others outside of the program team).²³

Stakeholders consulted for this study argued that further systematizing available research and agreeing to common methodologies or quality assurance and quality control (QA/QC) measures can contribute to overcoming some of the perceptions associated with data usability. A number of resources have been developed in recent years to contribute to improving QA/QC in citizen science programs by providing guidance on how to successfully organize, or for data users on how to effectively integrate the data into their work.²⁴

In general, the highest level of quality assurance and documentation should be pursued in order to meet the program's intended purpose. The development of a Quality Assurance Project Plan should also be considered as it helps to lay out exactly how citizen science groups will ensure they are using appropriate QA/QC measures and that the data they collect can be used for its intended purpose. These types of plans also provide those who use the data with a better understanding of its overall quality.²⁵ There was broad consensus among stakeholders consulted for this study that putting strict QA/QC measures in place is one of the most important factors contributing to the success of a citizen science program, particularly when the intent is to contribute to the development of a more complete dataset on pharmaceutical presence in the Great Lakes.

Data Quality Objectives & Data Quality Indicators

Determining the appropriate level of QA/QC measures requires the development of data quality objectives. These objectives are typically defined by those who will be using the data and set out the performance and acceptance criteria that help to clarify the type, quantity and quality of data required to support the goals of the program. In general, quantitative programs will require a higher level of quality assurance than those with a qualitative focus. Programs aimed at engaging the public might therefore focus more heavily on collecting qualitative information or addressing the presence or absence of a specific contaminant. In contrast, programs that provide information for the purposes of measuring exposure, or to

provide guidance for regulatory decision-making, are more likely to require a quantitative estimation of an important condition indicator.

Data quality indicators (DQI) can help to determine the reliability of any measurements taken, adding further credibility to the quality of data collected, including that undertaken by citizen scientists. The DQIs can be used to flag or qualify data or to help re-examine field or laboratory protocols. The most critical DQI's to support the program's data quality objectives should be identified during program planning, along with a determination of which are quantitative and which are qualitative. Commonly used DQIs include accuracy, bias, comparability, completeness, precision, sensitivity and representativeness. How a program plans to assess DQIs should also be described. For quantitative terms, this will involve outlining the quality control (QC) methods used to assess each DQI whereas for qualitative terms, any processes that are put in place or procedures followed to ensure data quality should be indicated.²⁶



Further information about these DQIs can be found in **Appendix B**.

Quality Controls

A QC is a protocol put in place to ensure that potential errors during sampling, transport or analysis are mitigated to the greatest extent possible. Sound QC practices can help to provide a clearer understanding of the source of any potential errors in the data.²⁷ An accredited analytical laboratory will have a QC system in place to fulfill the requirements for the analytical portion however, it is equally important to use procedures in the field.

The appropriate type and number of QC samples will be dependent on the specific QA/QC needs of a program. Prior to conducting any sampling, consideration should be given to potential sources of error and the variability of the data collected. Where appropriate, field observations should also be made during the sampling process to aid with data interpretation. This may include collecting information about sediment or water colour, texture, odours, wind direction and speed, barometric pressure, air temperature or surface current direction.

Common QC measures include the use of field blanks, trip blanks, temperature blanks, control samples, replicate samples and split samples. Further information about these QC measures can be found in **Appendix B**.

Different organizations or laboratories may have specific requirements for QA/QC and as such, should be consulted prior to determining which methods to use. A number of resources that provide more detailed guidance on sampling requirements for field level QC samples can be found in **Appendix A**.

Financial Considerations

Available budget will also help to determine the scope of a citizen science program. The use of more sophisticated analysis to ensure precision and accuracy is often associated with greater costs due to the types of equipment, procedures, necessary expertise, laboratory fees and time required. Program design must take into account these cost components when determining program goals and objectives.²⁸

Stakeholders consulted for this study noted that financial considerations are of particular relevance when designing a citizen science program aimed at monitoring pharmaceuticals. A number of studies have found these compounds to be present in extremely low concentrations which requires more complex analytical methods, sensitive equipment and highly trained professionals to detect. The required level of complexity for detection introduces an additional economic consideration that other types of citizen science monitoring programs may not have to contend with.

While the cost of analysis is a consideration, stakeholders indicated that there may also be ways of finding savings, particularly for citizen science programs whose objectives are more aligned with engagement and education. For example, this could include analyzing numerous pharmaceuticals together as a group of compounds based on their chemical characteristics or using an indicator for pharmaceutical presence as an initial step. Developing a partnership with a local academic institution with their own laboratory may be another possible option. Citizen science groups could collect the types of data that align with an academic institution's needs or interests and in return, samples could be analyzed at their laboratory at a reduced rate when compared to a commercial laboratory.

As previously noted, another possible option for finding cost efficiencies is for citizen science groups to partner or complement existing monitoring programs. This has the potential to cut down on the upfront costs associated with getting a program up and running by providing access to existing resources, infrastructure and participants. It also provides an opportunity to gain insight from those already undertaking important citizen science efforts. Section Four of this report explores one such example, where additional samples were collected by an existing monitoring program focused on recreational water quality to be analyzed for a separate set of compounds.

Program Management and Administration

Designing a citizen science program also involves consideration for the organizational and administrative structures required to ensure its successful implementation and ongoing delivery. This includes the development of an organizational chart demonstrating lines of communication and roles and responsibilities, particularly with regards to maintaining data quality. Potential roles may include project leader, project coordinator, volunteer trainers, monitoring leaders or volunteer recruiters. Citizen scientists should have access to program staff in order to ask questions or gain clarity on procedures.

Training

Training participants is an essential component of a successful citizen science program and is crucial for assuring data quality. Well-trained volunteers can contribute to accuracy and consistency in sampling and may be better able to identify potential errors and recommend reasonable measures to address them. An important step in designing a citizen science program is the development of a set of training protocols that can be tested and implemented. These protocols should clearly communicate the importance of consistency while collecting and documenting data.

Trainings could involve the provision of information regarding effective field methods, QA/QCs, how to record environmental observations, appropriate documentation and the overall goals of the monitoring program. A number of stakeholders consulted for this study mentioned different approaches to training and providing the information required for program participants to feel meaningfully engaged. Some programs may require in-person training sessions, while others provide YouTube videos and written instructions. Group sessions may be most appropriate for some programs, while the complexity of collection or analysis for others will necessitate one-on-one guidance.

Students practice water quality sampling techniques at a site affected by an algal bloom



Training should be comprehensive enough for the tasks to be completed effectively but also outline the reasons why certain actions are being taken or avoided. Time and resources should be budgeted up front to plan, present and evaluate volunteer training (both at the start of the program and at periodic follow-ups), and as a means of continuing to educate participants. Citizen science training programs play an important role in improving the scientific literacy of participants so that they themselves can inform and train new volunteers, or help educate members of their communities. The opportunity to educate through training can be an important means of enhancing experiential learning and engaging communities beyond the provision of materials alone.

While most citizen science programs will not have to worry about legal concerns, there may be laws that limit the ability to gather information. Prior to beginning sample collection, citizen science programs should be sure they have knowledge of any legal issues that might be relevant to the design of a monitoring or sampling strategy. For example, verifying property ownership will avoid issues like trespass. Citizen scientists should also be provided with training on safety protocols to ensure they are followed closely, including while in the field.



Volunteers at a citizen science training day

Documentation and Records

It is important that citizen science programs provide participants with clear instructions, descriptions of procedures and checklists to be used when performing tasks. This contributes to the consistency of results from all those involved and can assist with any data analysis and reporting. Thorough documentation of the data collected and stored ensures it can be used with confidence in future. This is of particular importance when the intent is to contribute to existing programs where there may be a need to compare two datasets. Programs should also consider whether there is existing data that can be sourced to help provide context for the work that is to be undertaken.

Summary

Prior to building out a program, it is important to determine whether citizen science can play a role in helping meet its identified objectives. Where pharmaceuticals are concerned, a number of different overall objectives may be relevant depending on needs or priorities. A collaborative approach to a citizen science monitoring program for pharmaceuticals would be appropriate as there are many contributions individuals can make in addition to collecting samples, including helping communicate messages within their communities. The complexities of analysis however, may preclude their involvement in a co-created program.

There is clearly a role for citizen science where the program goal is to increase public understanding about pharmaceuticals in the Great Lakes given its ability to provide opportunities for acknowledging the connection between concern about the environment and active community engagement. Citizen science training programs can also play an important role in improving the scientific literacy of participants related to pharmaceuticals, arming them with important information that can be brought back to their families and communities.

There is also a potential role for citizen science in a program with an objective of contributing to scientific studies and research on pharmaceuticals. The main barrier to this option is the level of complexity of detecting many of these compounds and the associated financial considerations. However, cost efficiencies could be found by partnering or complementing existing monitoring programs. Providing opportunities to embed citizen science within existing programs can also help ensure the longevity of the program and contribute to building more comprehensive datasets. Analyzing numerous pharmaceuticals together as a group of compounds based on their chemical characteristics or using an indicator for pharmaceutical presence to help narrow testing to a limited number of locations are other methods for reducing costs.

In an ideal scenario where a sustainable budget exists, it is recommended that a citizen science program related to pharmaceuticals combine these approaches with particular emphasis on educational and science literacy opportunities and encouraging stewardship in the Great Lakes. Spending time at locations around the Great Lakes, interacting with the natural surroundings, will foster a deeper understanding of their importance and the need to better protect them from improperly disposed of pharmaceuticals.

Section One has described the important steps for establishing a citizen science program, noting where considerations apply to pharmaceuticals. **Section Two** will outline protocols and best practices required for a citizen science sampling program that focuses specifically on pharmaceuticals.

SECTION TWO

The Role of Citizen Science in Better Understanding Pharmaceuticals in the Great Lakes



CONTEXT

Pharmaceuticals play an important role in the treatment of disease and are widely used to improve quality of life for humans and animals. However, they have also been identified as substances of emerging concern based on evidence that a wide variety of compounds are finding their way into water bodies, including the Great Lakes.²⁹ Pharmaceuticals include an enormous group of compounds which are challenging to detect and understand because they are not homogenous and do not necessarily possess the same physical, chemical, structural or biological properties.³⁰ Commonly used pharmaceutical groups include pain killers (e.g., acetaminophen and ibuprofen), birth control pills containing synthetic hormones, antidepressant medications and antimicrobial drugs.

Advancements in understanding emerging contaminants is due in large part to the development of highly sensitive and powerful analytical instrumentation capable of identifying trace quantities in complex environmental matrices.³¹ The detection of pharmaceuticals, even in extremely low concentrations, has the potential to spark public concern about risks to human health and the environment. This is often due to the perception that people are being unknowingly medicated, or concerns that WWTPs are in some way ineffective. Many are also worried about the potential human health impacts from exposure to pharmaceuticals. These concerns point to a need to better educate and engage the public around pharmaceuticals in an effort to replace misinformation with facts and provide context based on science.

Pharmaceuticals have been found in all of the Great Lakes, primarily in effluent or surface water downstream from WWTPs however, compounds have also been detected in open waters, fish tissues and drinking water treatment plants.³² Concentrations of pharmaceuticals vary greatly between sites, likely due in part to a greater degree of dilution the further away compounds are found from discharge sources.³³ Surface water concentrations of pharmaceuticals are often correlated with human population density in the drainage area, volume of the receiving water body and the technologies used in local WWTPs.³⁴ Some of the most frequently detected pharmaceuticals include antidepressants, anti-inflammatories, hormones, antibiotics, anti-diabetics and beta-blockers since these are widely prescribed across the basin.



MAIN SOURCES & PATHWAYS

Pharmaceuticals can end up in the aquatic environment through agricultural runoff, discharges from pharmaceutical plants and via wastewater effluents from human excretion and improper disposal of unused or expired medications.³⁵ A number of studies have identified WWTPs as a primary pathway for human pharmaceutical compounds to enter the aquatic environment, including the Great Lakes.³⁶ Conventional processes at WWTPs may remove some pharmaceuticals however, they were designed primarily to remove compounds with high biological degradation, hydrophobic properties and low polarity such as carbon, nitrogen and phosphorus. In contrast, active pharmaceutical ingredients may have specific biological activity at low concentrations, are stable and hydrophilic.³⁷

As previously noted, metabolism of pharmaceuticals may not fully occur when consumed, meaning that metabolized forms and free forms of the drug are excreted with urine. In addition, pharmaceuticals that are past their expiration date or no longer required are often flushed down toilets and discharged from homes with wastewater.³⁸ The level of removal of pharmaceuticals by WWTPs varies widely depending on the specific compounds and usage patterns, operating conditions, flow of the waste stream and type of treatment technologies.³⁹ While WWTPs are well-equipped to effectively remove oxygen demand, suspended solids, nutrients, foreign materials, and microorganisms from the water, the removal rate or breaking down of the various compounds found in pharmaceuticals depends on the physical and chemical properties of a specific drug.⁴⁰ Pharmaceutical residues can make their way to surface water along with treated effluent and some pharmaceutical conjugates have been shown to be excreted at levels rivalling those of their parent compounds.⁴¹

Recent evidence has pointed to urban centres that are home to pharmaceutical manufacturers also having elevated concentrations of some active pharmaceutical compounds in their receiving water bodies.⁴² A study by Kleywegt et al. (2019) showed that discharges from pharmaceutical manufacturers represented a key source of pharmaceutical pollution in municipal wastewater. The study found that some facilities may be discharging as much as several kilograms of lost product directly to sewers each day.⁴³ Similar studies have examined other sources and pathways for pharmaceuticals with some of the highest pharmaceutical loads detected in wastewater from hospitals and health care centres. Veterinary offices and animal husbandry also contribute to pharmaceuticals finding their way into the environment. Antibiotics may be added to animal feed within approved maximum levels and are present in manure applied for soil fertilization, leading to the drugs ending up in groundwater.⁴⁴ This points to a potential for greater concentrations of pharmaceuticals in water bodies located in close proximity to these sources.

Environmental and Human Health Impacts

The Great Lakes Basin has been a focus of concern in recent decades because it acts as a repository for a number of pollutants, including pharmaceuticals, from direct and indirect sources. The water in the lakes replenishes slowly, and persistent substances are not readily flushed from the system. The exposure of living organisms to pharmaceuticals is determined by the fate and distribution of these substances once they enter the ecosystem. Some pharmaceuticals may not always be present in the water column as they can be absorbed by other media, including suspended particles, organic matter and biological organisms.⁴⁵ Others may be available initially, but rapidly transform or degrade into other substances.

These transformed substances may be more or less harmful than the original form and more or less available for uptake by the surrounding environment.

It is important to note that while many pharmaceutical compounds have been detected in aquatic environments, the majority are at very low concentrations, typically in the microgram to nanogram per litre range. While questions remain related to the impact of these levels of pharmaceuticals on human health, studies have shown impacts on the environment, even at these microgram or nanogram per litre concentrations.⁴⁶ A study by Uslu et al. (2013) found concentrations of many active pharmaceutical ingredients discharged into the Great Lakes were below environmentally relevant levels.⁴⁷ However, there is limited information on the potential cumulative impacts of even low concentrations of pharmaceuticals on aquatic ecosystems.

While an individual exposure to a specific pharmaceutical may not be serious in itself, cumulative exposure over a long period of time can lead to potentially harmful effects. In addition, studies have pointed to some pharmaceuticals having the potential to bioaccumulate. Bioaccumulation occurs when living organisms take up a chemical substance more rapidly than they can eliminate it, so that the contaminant accumulates in their bodies. As a result of the bioaccumulation process, exposure to small, continuous doses can become a serious issue and in some cases, internal concentrations can become greater than that in the surrounding water. For example, anti-depressants have been shown to bioaccumulate within fish brains and cause changes in behavior such as mating, aggression, and predator avoidance.⁴⁸

Research on pharmaceuticals has tended to focus on demonstrating the effects of individual compounds on various aquatic organisms, often under laboratory conditions. In reality, pharmaceuticals are found in the environment in complex multi-compound mixtures, rather than in isolation, resulting in highly dynamic patterns of exposure for aquatic organisms.⁴⁹ A number of stakeholders consulted in the development of this report noted that how the results from assessment of individual compounds translate to a complexity of mixtures and environmental conditions is not well-studied. The literature also points to potential mixture effects as a major source of uncertainty when determining management strategies for pharmaceuticals.⁵⁰

Bioaccumulation of antidepressants has been recorded in several Great Lakes species, including the largemouth bass (*Micropterus salmoides*), a game fish species popular with anglers



In addition, whether, or how pharmaceuticals may alter wildlife behaviour remains poorly studied. Effects on the behaviour of aquatic and terrestrial wildlife are of ecological importance given that they are linked to individual and population survival. In addition, studies have shown that the behavioural effects of pharmaceuticals can differ between species and that prey consumption may be an important exposure route.⁵¹

Stakeholders consulted for this study also noted the potential for the release of some antibiotics to contribute to the development or spread of antibiotic resistance within the environment.⁵² This subject is also explored in the literature, including one study that found that decaying and free-floating *Cladophora* sampled near a WWTP had the highest bacterial densities on antibiotic-treated plates, indicating that some level of antibiotic resistance was present. It was not clear however, whether this was a direct result of exposure to WWTP effluent.

Pharmaceuticals have a target population and their use is restricted so that those who do not require them do not come into contact. While there may not be clear evidence of short-term human health effects, some studies have pointed to a need to better understand the impact of certain types of molecules over the long-term and the effects of chronic exposures. For example, a report from the BIO Intelligence Service (2013) noted that antibiotics, anti-cancer or anti-parasitics are groups that are especially intended to kill target organisms or target cells.⁵³ If these were to find their way into the environment in any measurable level, there may be a need to be protective of more vulnerable or sensitive populations (e.g., children or elderly populations). However, the same report noted that “For a range of other pharmaceuticals, environmental risks can be rather negligible, due to low environmental persistence and ecotoxicity of the compounds.”⁵⁴ Some of these concerns may be limited to a specific set of circumstances.

Methods & Processes for Citizen Science Monitoring Specific to Pharmaceuticals

Citizen science can play an important role in helping individuals and communities better understand the nature of potential risks associated with the detection of pharmaceuticals in the Great Lakes through opportunities for first-hand, experiential learning, which can be a direct way to sort fact from fiction. At the same time, there is a need for additional research to better understand the presence and impacts of pharmaceutical pollution in multiple media, and to monitor and report on concentration changes and the effects of potential chronic exposure over the long-term. A targeted citizen science monitoring program could help to provide a more complete picture of the extent of pharmaceutical presence and impacts in the Great Lakes, while helping to support a coordinated approach to research, analysis and action on pharmaceutical pollution.

Stakeholders consulted in the development of this report pointed to there being great potential for a citizen science program related to pharmaceuticals, particularly from the perspective of its ability to further educate the public about their environment. Communities are passionate and protective of local water quality and there is a long history of community involvement related to similar environmental challenges. It was noted by many, that while issues related to potential pollution tend to galvanize public interest, a citizen science program

could play a key role in increasing understanding on-the-ground about the complexities of pharmaceuticals while reinforcing the message that detection does not always mean there is a risk to human health. At the same time, it is important that programs are not developed solely for the purpose of addressing a small group of individuals that show concern related to a specific issue. The degree of public interest should also be factored in, and where pharmaceuticals are concerned, there has been considerable interest in recent months.⁵⁵

A range of considerations specific to the development and implementation of a citizen science pharmaceutical monitoring program in the Great Lakes are outlined below. The processes and methods described relate to the collection and transport of water samples, and to a lesser extent, any related analysis. The purpose of introducing these methods is to provide high-level guidance and in no way should this information act as a substitute for following approved standards and protocols for the specific processes required to meet a program's objectives.

SAMPLING

Prior to commencing with any sampling, it is important to establish standard methods for the field and for laboratory analyses. Depending on the determined objectives, (see **Section One**), programs may collect water or substrate samples, or various types of aquatic biota. Samples may be collected manually or with an automated sampler, as discrete or combined with others. Each of these methods should follow a set of procedures that may vary by parameter analyzed or medium sampled. Many citizen science programs produce standard operating procedures that can be referenced by staff or volunteer participants.

A number of protocols should be followed related to field equipment cleaning and decontamination both prior to, and once located in the field. Further information about these protocols is found in **Appendix C**.

Sampling Design

Once program objectives have been established a sampling regime should be designed that specifies who will collect what data, where, when and how. Sampling designs will differ dramatically based on the goals of the program and the types of questions that will be answered. Any details about the sampling design should be documented so that others wishing to duplicate the project can generate similar results.⁵⁶

While effluent and surface waters have been the most studied for pharmaceutical presence, certain compounds have also been detected in open water, drinking water, fish tissue and sediment.⁵⁷ A range of interrelated factors can play a role in the concentration of pharmaceuticals found in water and should be considered when determining how to design a sampling program. The following factors should be taken into consideration when looking to better understand if, where and to what extent pharmaceuticals may be present in the Great Lakes, as identified in the literature and by stakeholders consulted for this study.

Sampling Location

The decision of where to sample should be determined based on the program's overall objectives, the indicators or substances selected to be analyzed and the type of medium (e.g., surface water, ground water, sediment, etc.). The following are potential approaches to choosing a site location for sampling:

Probabilistic	A probabilistic approach to sampling involves selecting locations at random from a set of possible sites, and can be used to statistically characterize water quality in a given watershed. This approach avoids potential bias that could occur when sampling only those sites where contamination is expected to be greater.
Targeted	A targeted approach selects critical locations (e.g., upstream or downstream of a known discharge) to characterize specific impacts or to obtain data on a specific water body. It is important when using this approach to ensure data is not portrayed as an average. For example, when choosing locations where there is known contamination, data should be presented as a potential worst case scenario rather than representative of an entire lake.
Rotating	A rotating approach monitors sites on a rotating cycle (e.g., every three years) with each location being monitored for a specific length of time before sampling moves on to the next. This approach can be helpful in situations where changes do not occur rapidly over time as it avoids capturing a lot of unnecessary variability.
Fixed Station	A fixed station approach is when samples are collected at a regular site on a continuous basis. This approach is typically used for small-scale sampling programs or longer-term research studies. ⁵⁸

Any of these approaches could be applied to sampling for pharmaceuticals depending on the specific objectives of the program. If for example, the goal is to determine whether pharmaceuticals are found in wastewater effluent or in close proximity to WWTPs, a targeted approach could be employed with collection occurring near sewage outflows.⁵⁹ If the program objective is to understand the levels of pharmaceuticals across an entire lake, a more probabilistic approach could be applied that would include sampling in nearshore areas, harbours and tributaries, in order to build a picture of how specific compounds may move, where they are more likely to be found, and in what concentrations.

Given the size of the Great Lakes, dilution from the source is likely to play a key role in the occurrence and detection of pharmaceuticals. Stakeholders consulted in the development of this report noted that there have been a limited number of studies related to pharmaceuticals conducted on large bodies of water, likely due to expected low concentrations from dilution and other complex hydrodynamics. A 2010 study by Li et al. found that Hamilton Harbour had the highest concentration of every pharmaceutical measured when compared to other study areas throughout Lake Ontario.⁶⁰ It is believed that this may have been due in part to the fact that the harbour is separated from Lake Ontario by a sandbar. This separation could contribute to contaminants concentrating given they are less likely to flow into the lake where they would become more diluted.⁶¹

The literature and stakeholders consulted for this study note that citizen science monitoring programs may tend to focus on sampling in a way that can lead to spatial bias (e.g., sampling in those locations that are easiest to access or closest to a point source).⁶² A study by Millar et al. (2018) found that participants in citizen science monitoring programs were more likely to sample accessible locations associated with recreation or summer home ownership. The study noted that while professional monitoring programs are not immune from spatial bias, citizen scientists may be more influenced by factors including natural and demographic biases related to the size and attractiveness of a lake and accessibility when determining where to sample.⁶³ This may be of less concern if the purpose of the program is related to building awareness and educating than when looking to produce a more complete dataset for pharmaceuticals in the Great Lakes.

A number of stakeholders consulted for this study felt that initially sampling in populated areas or near urban centres may be appropriate due to the fact that pharmaceuticals are likely to be found in higher concentrations where there is greater population density. In addition, these areas may also be home to industry, another potential source of pharmaceuticals in the Great Lakes. Demographics may also play a role in determining appropriate sampling locations for specific pharmaceuticals. For example, municipalities with a substantial elderly population may have higher than average usage of some heart medications, while urban centres may have an increased incidence of antidepressants or birth control pills.⁶⁴ As previously noted, any data from these samples would need to be carefully contextualized in order to paint an accurate picture of what these concentrations represent.

When looking to select sampling locations, citizen science programs should consider which geographic areas are already monitored to avoid duplicate efforts. For example, stakeholders consulted for this report noted that where there are index stations monitoring a certain distance from shore there may be value in a citizen science program sampling in nearshore areas to contribute to a better understanding of the concentration gradient.

Where possible, the exact position that a sample is collected should be obtained using GPS or a smartphone application. Samples should be collected at the same depth, height and temperature, where appropriate. This information will be particularly helpful during data review, where a reported value appears to be a potential outlier. With specific details about location, it may be possible to resample the same point where the initial sample was collected.⁶⁵



Monitoring can be conducted at regular sites on a continuous basis, at selected sites on an as needed basis, infrequently on an emergency basis or on a temporary or seasonal basis. The following are some of the factors that should be considered when determining the frequency of sampling:

<p>Season or Time of Year</p>	<p>The use of specific types of pharmaceuticals may vary dramatically by season or time of year (e.g., cold and flu remedies in winter or antihistamines in spring and summer). Water body flow rates also contribute to the fate and concentration of pharmaceuticals found in the lakes. For example, higher water levels in early spring may contribute to greater dilution, while water levels have usually dropped by fall, resulting in greater concentrations of detected compounds.</p>
<p>Water Temperature</p>	<p>Water temperature may also be a factor to consider when sampling and where possible, collection should take place at different times of the year to capture any differences based on temperature. In addition, more wildlife is present in the warmer months meaning that better understanding pharmaceutical levels during the spring and summer seasons could prove valuable in providing further context related to potential impacts.</p>
<p>Wet or Dry Conditions</p>	<p>Variation of concentrations in dry and wet weather conditions are also important to consider given the contribution of combined sewer overflows — a system designed to collect rainwater runoff and domestic sewage in the same pipe — to contaminant levels in the lakes during storm events. The capacity of WWTPs and storm drains may not be adequate to deal with heavy precipitation in certain areas, resulting in releases of untreated stormwater and sewage into the Great Lakes.</p>

Programs pursuing long-term monitoring may require a greater number of samples to provide enough information to compare over time, whereas those hoping to explore a worst-case scenario may only require sampling based on specific conditions (e.g., at regular intervals during a storm event). The majority of citizen science programs maintain a regular sampling schedule from spring through early fall, typically collecting samples once or twice a week. Stakeholders consulted for this study noted that this would be an appropriate approach for a program aimed at better understanding pharmaceutical levels, particularly in its first season so as to develop a baseline. Given the need to better understand changes over time, a continuous sampling method would be ideal for long-term monitoring of pharmaceuticals.



Sampling Methods

A successful citizen science program will rely on a consistent protocol for the collection of samples. Participants should be trained in these methods so that data collection is feasible and repeatable. Water samples can be taken from shore, by wading into the water, from a boat in open water or through the ice during colder months. Depending on the program, samples may be analyzed while in the field or transported to a laboratory for analysis at a later date.⁶⁶

From a citizen science perspective, the sampling method employed needs to balance a number of considerations including ease of use, cost of testing and analysis, and the representativeness of the sampling being conducted. It is beyond the scope of this document to explore all recommended sample collection methods or technologies. The following are those noted by stakeholders consulted in the development of this report that could feasibly be used by citizen scientists looking to better understand pharmaceuticals in the Great Lakes.

Further resources related to general sampling methods or those specific to water quality can be found in **Appendix A**.

Grab Samples

Grab samples are considered to be one of the simplest, most cost effective and therefore most commonly used, sampling methods for citizen science programs monitoring water quality. These samples are collected at one location and at one point in time, representing a “snapshot” of information. Given this specificity, grab samples may not always be representative since episodic events (e.g., storm events or effluent discharges) may be missed. However, they can still be a useful method for determining whether contaminants may be present.

Stakeholders consulted for this study noted the dynamic nature of water and the fact that it is constantly changing due to various natural processes such as currents, wind flow, temperature or length of time since the previous rainfall. The information presented by a grab sample must therefore, be carefully contextualized so as not to misrepresent the nature of any contamination. Pharmaceuticals may enter the Great Lakes periodically, or at different levels of concentration, meaning that findings from a single sample at a single location are likely to vary greatly from one day to the next. In other words, the presence of pharmaceuticals in a single grab sample should not be interpreted to mean that the same concentrations would be found throughout the lake being sampled, or even that these same concentrations would be found on a different day.

Grab samples can be formalized to achieve desirable data usability through good sampling program design. There should be enough samples collected at appropriate locations and depths to meet the physical analysis or statistical evaluation needed to achieve the objectives of the program.⁶⁷ It is best practice to rinse the sample bottle three times with the water being sampled before collecting the actual sample. When collecting a grab sample near the surface, the bottle is submerged in the water until covered with the flow direction moving towards the bottle. If possible, the lid should be screwed back on at the testing depth to avoid contamination from surface scum or film. The sample volume depends on the type

and number of analyses to be performed.⁶⁸ A particular order should also be followed when collecting grab samples.

The first samples to be taken should be any blanks that are needed, followed by the samples for which field measurements are measured. The final samples would be any replicates.⁶⁹

Grab Sampling from Shore

Sampling from shore can be desirable given that it requires minimal equipment, however, safety considerations should be taken into account. It is important to wear a personal flotation device, especially when shore sampling from a stream or river with considerable current. Tethering oneself to a tree or similarly stable object can also help with ensuring secure footing. Such sampling should be done with a spotter. A sampling rod can be used to extend reach further into the water body.

Grab Sampling when Wading

Grab samples taken while wading can increase access to the water column but require additional equipment such as rubber boots and hip or chest waders. As with sampling from the shore, a personal flotation device should be worn. A wading rod can also be used to help determine potential depth changes and to ensure safe footing. Bodies of water with swift currents should be avoided when possible however, if necessary, ensure that the participant is tethered to the shore and done with another team members.

Grab Sampling from a Personal Watercraft or on Ice

Grab samples may also be taken further out from shore in a personal watercraft (e.g., kayak, canoe or motorboat) or through the ice in winter. These approaches may be less attractive for pharmaceuticals based on the assumption that dilution may be a factor in detection and the likelihood of citizen scientists volunteering to collect samples in winter. However, this approach could prove useful where the intent is to better understand to what extent pharmaceuticals are found throughout the lakes or over the full course of a year.



Composite Sampling

Composite samples consist of multiple individual samples taken over a period of time (often 24 hours), or at different depths to provide a control for how placement in the water column may affect results. The samples are collected in a common container representing an average over the collection period.⁷⁰ A composite sample reduces potential variation based on its being representative of an average and thus adds the benefit of being more statistically reliable than a single sample.

There are two methods of collecting composite samples: manually by hand (i.e., grab samples) or using an automated sampling device. Automated sampling can be a more effective way to produce uniform, representative samples and are ideal for situations where there is a need for a continuous sample or to collect samples at frequent intervals. These samplers also reduce the potential for contamination associated with handling.

Composite sampling can be useful when looking at emerging contaminants such as pharmaceuticals as they may be found in trace amounts in a single grab and their presence varies greatly based on a number of conditions (e.g., time of day, weather conditions, etc.). By increasing the total volume of the sample through a composite, a given concentration may reach a greater threshold of detection.

A stakeholder consulted for this study noted that composite samples can also be used to provide a better understanding of water quality at a specific location, such as a bay or beach. A number of samples would be collected from different points and pooled together (also called composite integrated sampling or area integrated). This sampling type would account for spatial heterogeneity and provides an estimate of average water quality. The composite sample would then act as a representation of the general condition of the water quality at the beach or bay at the given time and day.

Manual composite sampling would follow a similar process to grab sampling however, once a sample is collected, it would be poured into a composite sample bucket which has been pre-cleaned as per laboratory instructions.⁷¹ If there is a reason to pause between dumping samples, the bucket lid should be firmly placed. Water samples would continue to be collected until sufficient composite volume has been collected. When sampling at the same location at different times, the grab bottle should be submerged at the same GPS location at the same depth each time.⁷²

Collecting and analyzing composite samples can be a more expensive and time-consuming option than grab sampling due to the need for automated equipment or the collection of multiple samples manually over a period of time. For these reasons, it may not be considered the most appropriate option for citizen science programs operating on a more limited budget.⁷³

Passive Sampling

Passive sampling involves the use of a collecting medium, such as a man-made device, to accumulate chemical pollutants in the environment over time. With passive sampling, average chemical concentrations are calculated over the time a device is deployed which avoids the need to sample a site multiple times. Passive samplers have been developed and deployed to detect a range of contaminants found in water including heavy metals,

pesticides, polychlorinated biphenyls (PCBs), pharmaceuticals and other organic compounds. They are often used for compounds typically found in low concentrations in a grab sample but which may exist in detectable concentrations when sampled over a longer period of time. Stakeholders consulted for this study spoke to how passive samplers can be deployed from between two to six weeks and up to a year, depending on the type of sampler and the degradation rate of the compounds being investigated.

There are a number of examples of passive samplers being used successfully by citizen scientists to sample air, water and personal exposures, pointing to the potential for this approach to be used for pharmaceuticals. Low density polyethylene (LDPE) passive samplers are a well-documented, relatively low-cost, and easy-to-use method where a similar process is employed to that for grab sampling.⁷⁴ In other words, samplers could be prepared prior to shipping to citizen scientists who would deploy and then collect them again after a specified period of time to send back to researchers or program organizers.

Stakeholders consulted for this study noted that passive samplers could also be deployed through a citizen science program together with other sampling methods or to complement existing monitoring programs. For example, passive samplers could be used in locations that require less frequent monitoring or which are less accessible, while grab samples are collected in those areas that can be easily reached. Taken together, these methods would provide a clearer picture across the water body.

POCIS (Polar Organic Chemical Integrative Sampler) disks mounted in a stainless steel holder for passive sampling



Citizen Science Sampling for Pharmaceuticals

Stakeholders consulted for this study noted that while grab sampling is the easiest and least expensive method to implement, it is also the least representative and has the potential to present numerous false positives or negatives. In contrast, passive sampling is considered the most representative sample. Composite sampling is a balance between the two as it is relatively easy to do with minimal equipment and is fairly representative of a given metric (time, space, depth, etc.). However, composite sampling using an automated sampling device is an expensive option.

There was general agreement that despite its potential disadvantages (e.g., required manpower, transport, etc.), and the value other sampling types would provide specific to pharmaceuticals, the use of grab samples is likely to be the most feasible option for citizen scientists. However, the objectives for the program should drive the sampling approach, while balancing the capabilities of the citizen science group and any budget considerations. Where additional budget exists, a combination of sampling methods would be preferable as they would provide a more detailed overall picture.

The most appropriate method of sampling also depends on the overall objective of the program. When education and engagement are the purpose of a citizen science program, comprehensive sampling and detailed analysis may not be necessary whereas, a goal of developing a more complete dataset for pharmaceuticals in the Great Lakes would likely benefit from incorporating more than one sampling method.

Biota or Sediments

The idea of encouraging citizen scientists to collect biota or sediments while in the field was also explored through this study. Stakeholders had differing opinions on the feasibility of adding a more complex element to the sampling process. Some felt that this could be an important way to determine whether bioaccumulation is of concern for certain species (e.g., fish), or to better understand whether pharmaceuticals (particularly those that are lipophilic) found in sediments could be re-suspended from contact with water. However, others felt that the majority of pharmaceuticals are hydrophilic and that given the lack of data even for this medium, water quality sampling should be the primary focus in the short-term.

Stakeholders discussed opportunities to explore the option of also collecting biota in the longer-term, possibly through a partnership with anglers or fishing derbys like the Great Ontario Salmon Derby. Mussels and other filter-feeders were also mentioned as potential candidates for collection given that they process the water around them and have been shown to be sensitive to different contaminants.



SHIPMENT AND STORAGE

Proper handling and the transport of samples from the field site to the laboratory are integral to ensuring data validity and reliability. A number of questions specific to shipment should be considered when designing the sampling program, including the following: :

- Does the sample need to be analyzed within a certain timeframe?
- What modes of transport are necessary or available?
- Will the sample's integrity be affected by outside influences (e.g., temperature, pressure, humidity)?

It is important that samples are cooled as quickly as possible once they have been collected to reduce any chemical or biological activity. A number of pharmaceuticals or indicators may have short half-lives meaning they can degrade if not properly cooled or if shipment is significantly delayed, resulting in misleading findings. While in the field, coolers should be kept in the shade.⁷⁵ If immediate transport is not possible, samples should be kept in a refrigerator or freezer until which time they can be shipped. Most samples should be cooled to between 4°C and 10°C during transit to a laboratory. Where possible, this is accomplished through the use of ice packs rather than loose or bagged ice given the potential to contaminate the sample.

Coolers should be handled and packed while wearing clean gloves that were not used during sampling and kept clear of any areas where there may be smoke or other emissions (e.g., tailpipe emissions). Ideally, samples should be processed within seven days of collection however, stakeholders consulted for this study noted that if they are frozen, analysis can be conducted at a much later date.

Samples should be delivered to the laboratory using a transport container (e.g., cooler, shipping box) for protection from breakage or contamination. Many citizen science programs provide bubble wrap or an alternative protective material to enclose each sample prior to shipment and minimize direct impact on the bottles. When shipping samples by courier, they should be sent express whenever possible and with appropriate tracking numbers and signage to indicate "FRAGILE", "HEAVY", and "THIS SIDE UP". Only professional and reliable services should be used and tracking numbers made available.⁷⁶

Corresponding field notes and observations, including proper cataloging and descriptions of any potential abnormalities in the sampling process, should accompany any shipment for reference by the laboratory. All paperwork should be provided in sealable, waterproof plastic pouches to prevent damage from leaking fluids or condensation. It may also be necessary to plan sample collections around when it is most feasible and inexpensive to ship containers, which is likely to vary by region. When an individual will be available to receive the shipment at the laboratory should also be taken into account to ensure samples do not remain unsigned for, thus increasing the time between collection and analysis.⁷⁷

Chain of Custody

A chain of custody form, sometimes referred to as a sample submission form, is critical to the validity and soundness of a program and ensures that samples have not been tampered with.⁷⁸ The chain of custody form is a traceable record used to track the handling of samples through all stages of storage, including processing and analysis at the laboratory, and the form should accompany the samples at all times. The chain of custody allows the laboratory to have confidence that the samples are a true representation of what the sampling methods outline and that they have not been altered.

Some chain of custody documents are laboratory specific but in general, they should indicate each person who has handled a sample, who they received the item from and when, as well as whom they delivered it to and at what time.⁷⁹ This helps to clarify when and where potential issues may have occurred and helps to mitigate similar issues in future. The chain of custody ensures that only authorized members of the citizen science monitoring team have handled samples and that appropriate field sampling techniques have been used. Proper documentation is essential for external auditors or when attempting to integrate the data into another project. For citizen science programs, it can also provide greater credibility and validity when releasing data.⁸⁰

ANALYSIS

A reputable laboratory should be consulted for the analysis of samples related to pharmaceutical and other emerging contaminant compounds. As previously noted, the process of testing for the presence of what are primarily trace amounts of pharmaceutical compounds, is analytically complex, requiring highly trained professionals using precise instruments and exact settings. Not all laboratories specialize in trace analyses of environmental matrices, and the quality of the analysis, particularly related to pharmaceuticals, is a critical component in ensuring the resulting data is credible and scientifically relevant. Stakeholders consulted in the development of this report noted that the cost for analysis of a sample for pharmaceuticals could run in the range of \$300 to \$500 per sample while a full suite of 120 compounds could cost between \$2,200 and \$2,400.

Some laboratories may be unable to detect compounds at such low concentrations and where it is possible, the level of complexity understandably equates to greater costs. There are only a handful of commercial laboratories in Canada that test for pharmaceutical compounds meaning that samples may also need to be transported long distances at additional cost. In addition, stakeholders consulted in the development of this report noted that some laboratories may require additional information before accepting samples collected by those who have not had extensive training or expertise to ensure data quality, an important consideration where citizen scientists are involved.

It is beyond the capabilities of a citizen science program to conduct analysis on pharmaceuticals. For this reason, it is beyond the scope of this report to explore the complexities of analysis specific to pharmaceuticals. However, liquid chromatography and mass spectrometry (LC-MS/MS) are often the method of choice for detecting contaminants found in trace concentrations in environmental samples, including pharmaceuticals.⁸¹ Commercial laboratories refer to U.S. EPA Method 1694: *Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS* when analysing pharmaceuticals. This method “determines

pharmaceuticals and personal care products (PPCPs) in environmental samples by high performance liquid chromatography combined with tandem mass spectrometry (HPLC/MS/MS) using isotope dilution and internal standard quantitation techniques.”⁸² It is restricted to use by or under the supervision of analysts who have experience with HPLC/MS/MS.

PROGRAM EVALUATION

It is important that citizen science programs undertake continuous tracking and reviewing of progress and performance over time to determine what is working well and what processes or methods may need to be updated. The following are a few of the potential questions that could be asked to determine whether the program’s outputs align with its intended purpose or stated goals:

- Were the right types of data collected?
- Are data being collected from the most appropriate locations?
- Can the results be compared statistically?
- Did all datasets meet the QC criteria and if not, what is the impact on the study or program?

Whether overall program objectives are being met should also be evaluated, along with whether data are usable. Incorrect assumptions may have been made in the planning or sampling design phases that should be addressed moving forward.⁸³ Any data that does not meet acceptance criteria should also be discussed and explained in any reporting of findings.

A number of stakeholders consulted for this study mentioned how data from a citizen science program for pharmaceuticals could be used by different organizations. It was noted that it could contribute to prioritizing risk assessments by the federal government because it would provide a clearer picture of whether pharmaceuticals are present in the environment. This would help with determining the extent to which they may be a risk to human health or the environment.

A number of citizen science organizations also make use of a participant survey following their time in the field. This survey may include questions about environmental conditions, or may look for insight into how fulfilling the experience has been and where there may be room for improvement. This can be an important way of not only gathering further data, but also keeping the lines of communication open between those leading the program and participants. Incorporating this feedback into the program’s operations can ensure more active engagement from participants moving forward.

OPPORTUNITIES FOR EDUCATION

While a sampling program provides an excellent opportunity for individuals and communities to get out in the field to experience the Great Lakes firsthand and to better understand how to care for them, it is also a perfect time to provide further educational resources (i.e., beyond experiential). For example, while not specific to pharmaceuticals, Pennsylvania State University’s “Empowering Citizen Scientists to Reduce Sources of Emerging Contaminants in the Susquehanna River Basin” program focuses on using citizen science as an educational tool to better inform about EDCs. In addition to collecting and analyzing water samples

for the presence of EDCs, the program has developed a tool that calculates an individual's EDC footprint based on the types of products (e.g., health and beauty, laundry or cleaning) consumed.⁸⁴ The calculator is similar to existing water and carbon footprint calculators and results are put into perspective in terms of total EDC contributions if the entire U.S. population consumed the same amount.

This approach of combining experiential learning and the provision of further information helps participants make a personal connection to what they see firsthand. It empowers citizen scientists to make changes in their own lives to complement the time spent on sampling and analyses. This is of particular relevance to pharmaceuticals, given that one of the quickest ways to reduce their presence in the environment is for the public to become more informed about their appropriate disposal.⁸⁵

Summary

The protocols and methods outlined in this section are suitable for a citizen science program specific to pharmaceuticals however, determining the most appropriate will be based on alignment with the program's overall objectives. There was broad agreement that where possible, samples for pharmaceuticals should be collected on a regular basis to gain a clear sense of changes in concentrations over time and based on weather or other events. However, this approach requires a budget capable of covering the costs associated with the necessary analysis.

The approaches outlined herein for determining a site location (e.g., probabilistic, targeted, rotating, fixed station) would all be effective for a citizen science program focused on pharmaceuticals. Where the goal is to determine whether pharmaceuticals are present in wastewater effluent, a targeted approach with collection near sewage outflows may be more suitable. If the objective is to provide an understanding of concentrations across an entire lake, a probabilistic approach including samples collected from a number of different locations (e.g., nearshore areas, harbours, etc.), taking into account the need to avoid spatial bias, would provide more information about how specific compounds move and where they are most likely to be found.

Where a citizen science program has a more sustainable budget, a combination of sampling methods were noted as the preferred approach because it would provide a more detailed overall picture of pharmaceutical presence. If the program has budget limitations, grab sampling or passive sampling (where pursued in collaboration with researchers) would be the most feasible options for citizen science programs based on the fact that composite sampling can be time and labour intensive. Where education and engagement are the



EDC footprint calculator is similar to existing water and carbon footprint calculators. The user inserts the amount of household products they own into three categories; health and beauty, laundry, and cleaning.

Humans use a large variety of chemicals in personal care products in their everyday lives that become part of the wastewater stream. Wastewater treatment plants were not designed to remove these chemicals, and therefore these products and their metabolites persist in the effluent.



Pennsylvania State University's online EDC footprint calculator

purpose of a citizen science program, comprehensive sampling and detailed analysis may not be as necessary whereas, a goal of developing a more complete dataset for pharmaceuticals in the Great Lakes would benefit from incorporating more than one sampling method.

A reputable laboratory should be consulted for the analysis of pharmaceutical samples as the process is analytically complex, and requires experienced professionals. Not all laboratories specialize in trace analyses of environmental matrices, and the quality of the analysis, particularly related to pharmaceuticals, is a critical component in ensuring the resulting data is credible and scientifically relevant.

Section Two has explored the methods for sampling, transport and analysis that should be considered by citizen science programs in an effort to ensure that monitoring yields results that are scientifically meaningful and consistent, with a specific focus on those that could be applied to pharmaceuticals. **Section Three** will outline a two-step process for monitoring pharmaceuticals, identify a number of potential indicators and explore the considerations that should be factored into determining a list of compounds to target for analysis.



SECTION THREE

Determining an Indicator of Pharmaceutical Presence

The majority of stakeholders consulted for this study agreed that a potential strategy for mitigating the challenges and costs associated with testing for pharmaceutical presence, while maximizing the impact of a citizen science program, would be to use a two-step approach. The first step involves determining the presence of a specific indicator (or combination of indicators), and only when a compound is found in a significant concentration would samples be prepared for analysis of specific pharmaceutical compounds. The purpose of the two-step process would be to reduce costs associated with analysis by focusing on a smaller number of samples.

The use of an indicator can be an important means of establishing a general picture of an aquatic environment and providing information about the state of water quality and any changes over time. Indicators allow for an initial snapshot which can inform whether future action, intervention, or policy development are required. They can also be an important tool for assessing the extent to which water bodies and other natural systems have been impacted by human activity.

A simple indicator that points to the presence of other compounds or contaminants can be a useful first step to determine whether further monitoring and analysis is required. For example, *Escherichia coli* or *E. coli*, is commonly used as an indicator for the presence of a range of disease-causing bacteria, viruses or protozoans due to the relative ease and cost associated with analysis.

A number of potential challenges associated with monitoring for pharmaceuticals in the Great Lakes have been explored in this report. For example, pharmaceuticals represent a broad range of compounds with varied chemical, structural and biological characteristics, requiring unique responses or mitigation strategies. Pharmaceuticals enter natural systems sporadically and at differing concentrations, and exhibit varying levels of persistence.

Analytical methods also differ based on the compound in question. To address this challenge, this study sought to determine whether there may be an effective indicator for the presence of pharmaceuticals that could be used as an initial screening prior to additional analyses. An indicator approach for pharmaceuticals would help to cut down considerably on the costs associated with analysis by identifying those locations, situations or circumstances where more complex testing should occur.

The literature review and stakeholders consulted for this study pointed to a number of characteristics of an ideal indicator for pharmaceutical presence in the Great Lakes (see Table 1). These criteria would need to be evaluated in the context of a program's stated objectives, timelines and budgets to determine an appropriate indicator.

Table 1: Characteristics of an Ideal Indicator for Pharmaceutical Presence

Criteria	Description
Absent from Source Water	It is important to ensure that when determining an appropriate indicator for pharmaceutical presence, consideration is given to whether it is typically found naturally in source water in any reliable concentration, as this would make it difficult to determine whether it is naturally-occurring or based on contamination. It is also ideal if the indicator has a known source or pathway (e.g., wastewater effluent or agricultural run-off). Given that WWTPs were not designed to remove many synthetic or anthropogenic contaminants, including some pharmaceutical compounds, it has been suggested that an indicator that points to the presence of wastewater effluent may be an effective means of determining their presence. ⁸⁶ Where wastewater effluent is found, it can be reasoned that there is also the potential for pharmaceuticals, albeit in trace amounts. It should be noted however, that many stakeholders consulted for this study pointed to the fact that while there is likely to be trace amounts of pharmaceuticals found in wastewater effluent, an indicator will not identify which ones, at what concentration, or from which sources. An indicator is only able to provide the grounds for further research and analysis, or investment in monitoring or remediation programs. ⁸⁷
Persistence	Some compounds break down easily in the environment, while others may persist or remain long after their use has been discontinued. Many pharmaceutical compounds have a higher degree of degradability, making them difficult to detect during sampling and analysis. Deciding on an appropriate indicator for pharmaceutical presence should in general, involve consideration for persistence to ensure detection during sampling and analysis. However, there may be examples where a compound degrades easily but is so ubiquitous that it can reliably be found despite the fact (e.g., caffeine). A stakeholder consulted for this study noted that previous work they had conducted on pharmaceuticals in the Great Lakes had relied on the Government of Canada's Prescription Drug List – a list of the most prescribed drugs in the country – as one factor in determining which compounds to test for. This approach however, failed to capture some of the compounds least likely to degrade at the WWTP (e.g., carbamazepine), focusing instead on those that are more heavily prescribed but which degrade easily prior to entering the environment.
Concentration	An ideal indicator should also be found consistently in high enough concentrations to be analytically detectable. ⁸⁸ Concentration is often linked to persistence as those compounds that undergo very minimal degradation or transformation at the WWTP tend to be discharged in greater concentrations. ⁸⁹ In addition, the large quantities of some compounds that make their way into the lakes on a continual basis mean that they can become pseudo-persistent pollutants, and found in some reliable concentration. Indicators should also have a sufficiently large discharge to detection level ratio to be able to exceed receiving water dilution factors.
Affordability and Ease of Testing	An ideal indicator is one that requires less complex analytical methods or that citizen scientists could test for on their own (e.g., E.coli). The presence of the indicator in a sample could then precipitate further analysis for specific pharmaceutical compounds.
Toxicity	Consideration for toxicity was also mentioned as a factor in determining an effective indicator of pharmaceutical presence in the Great Lakes however, a number of stakeholders noted that not all pharmaceuticals have comprehensive environmental toxicity data or a good benchmark against which to compare. Carbamazepine is one pharmaceutical for which a CCME guideline exists for the protection of aquatic life however, other guidelines have also been developed both in North America and Europe. ⁹⁰
Partitioning to Sediment or Uptake by Biota	Some compounds or substances remain in water phase while others may sorb or bind to solids like soil, making them more difficult to detect when sampling water. ⁹¹ An ideal indicator for pharmaceutical presence would therefore be one that remains measurable in surface water samples.
Existing Data	The occurrence of existing data is another potential criteria for determining an effective indicator for pharmaceutical presence as it allows for a baseline against which to measure and better understand any subsequent data.

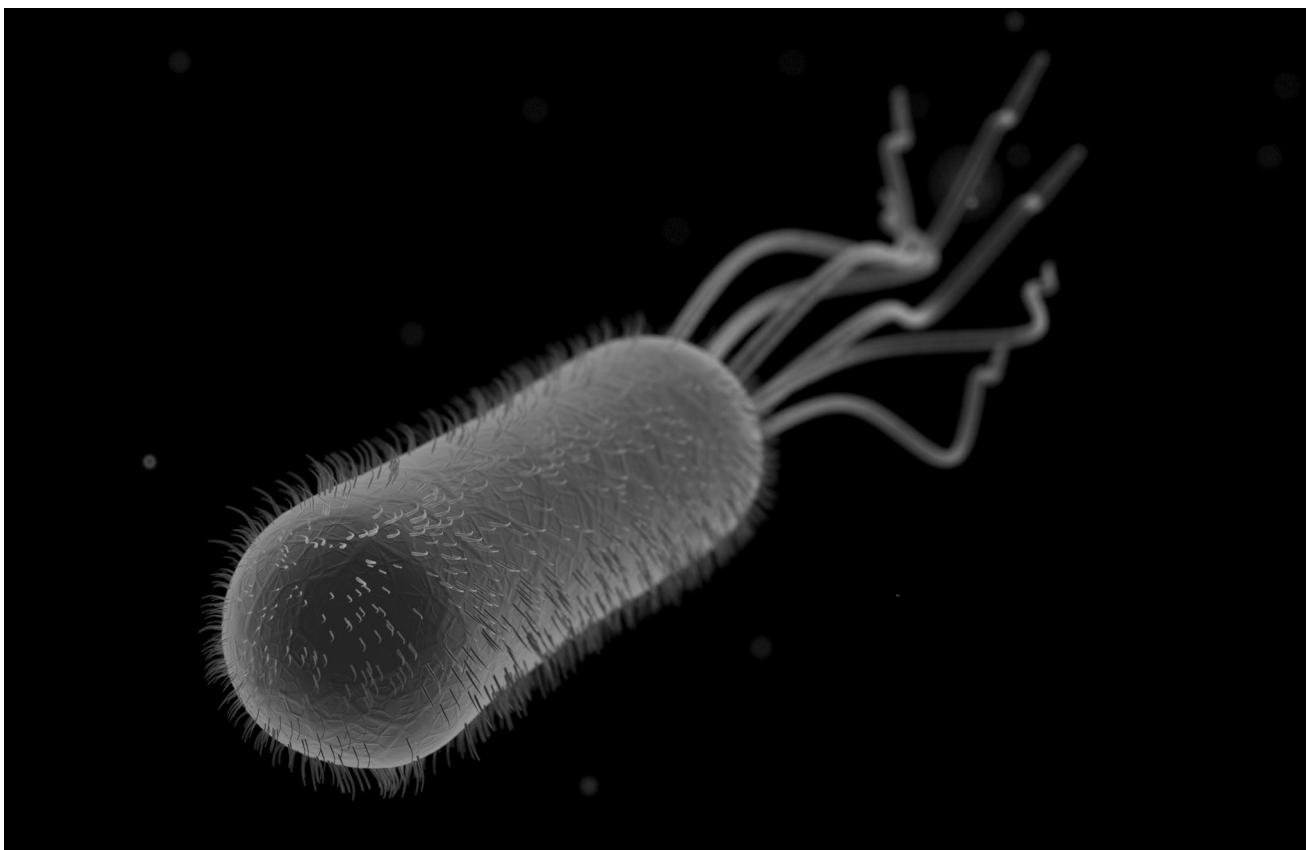
Potential Indicators of Pharmaceutical Presence in the Great Lakes

A number of potential indicators for pharmaceutical presence in the Great Lakes are explored in the literature and were noted by stakeholders consulted for this study. For the most part, these indicators point to the presence of wastewater based on the idea that some pharmaceuticals may be present in effluent. Indicators that meet several, or all, of the criteria outlined in Table 1 are described in greater detail below, including a discussion of potential benefits or challenges associated with their use as it relates to pharmaceuticals.

Escherichia Coli

As previously noted, *E. coli* is often used as an indicator for potential sewage or fecal contamination in a water body. This is due primarily to the fact that it is found in larger concentrations than other pathogenic organisms while also being substantially more economical to test for. Given its successful use as an indicator for the presence of wastewater, it has also been suggested as a potential indicator for pharmaceutical presence.

A stakeholder consulted for this study noted that some laboratories have the ability to discern whether the source of *E. coli* is human, bovine or other (e.g., horses, pigs, pets, wildlife, etc.) based on DNA extraction. This approach would provide a sense of whether the *E. coli* has entered the environment via wastewater, agricultural run-off or another source. It is unclear however, the exact cost or level of effort required to extract and analyze the DNA and there may be a limited number of laboratories capable of conducting the analysis. These factors should be taken into consideration by citizen science programs interested in pursuing this option.



Caffeine

Caffeine has been shown to be an effective indicator of human excretion given its prevalence in society in the form of beverages, foods and therapeutic applications. Its use as a potential indicator for pharmaceutical presence is based primarily on the idea that it is often found in sufficiently detectable concentrations in water bodies, even when diluted. However, caffeine is known to deteriorate easily, with some studies noting as much as 99% degradation in WWTPs.⁹² While the concentration of caffeine found in wastewater influent is likely to be greater than other compounds such as pharmaceuticals, the rate at which it breaks down during sewage treatment processes means that concentrations are significantly reduced in wastewater effluent.⁹³

Given its ubiquitous use in society, it may also be challenging to determine the specific source of caffeine found in water samples. For example, an individual who had been in contact with coffee or tea prior to collecting a sample and using improper techniques or sampling protocols could inadvertently introduce contamination, or a caffeinated beverage could be directly deposited into the lake. In addition, a stakeholder consulted for this report noted that a study they had conducted found pharmaceuticals in samples where caffeine was not detected. It is assumed that this was due to the tendency of caffeine to degrade more rapidly than some pharmaceuticals.

Sucralose and other Artificial Sweeteners

A more recent addition to discussions around potential indicators of wastewater loading to water bodies are artificial sugar substitutes or sweeteners, primarily due to the fact that they are excreted mostly unchanged and degradation at WWTPs has been shown to be minimal. While acesulfame, cyclamate, saccharin and sucralose are some of the most commonly consumed sweeteners, acesulfame and sucralose are mentioned more often in the literature and by stakeholders consulted for this study as effective indicators of wastewater. Because the introduction of artificial sweeteners as an indicator is relatively new, most available data is sourced from research laboratories and there may be few commercial laboratories offering analyses.

Acesulfame was noted by one stakeholder to be the most stable artificial sweetener, both in environmental and in wastewater treatment systems (including septic systems). Recent journal articles have shown that acesulfame can be broken down by microbes, however it typically survives wastewater treatment processes in relatively high concentrations compared to other indicators or tracers. In addition, acesulfame may persist in the environment longer than other artificial sweeteners. Schaidler et al. (2016) showed that it was always present where other organic wastewater compounds were found in septic-impacted groundwater.⁹⁴

Sucralose is also considered to be one of the more appropriate indicators of human excretion due to its persistence in WWTPs and concentrations found in wastewater effluents.⁹⁵ Sucralose is often found in high concentrations, is considered highly water soluble, and does not bind easily to sediment and other solid phases, making it ideal for measurement.⁹⁶ It is also more cost effective to analyze than some other artificial sweeteners. While sucralose may be a highly effective indicator, proper and skilled analytical sensitivity is still required when testing.⁹⁷

Nitrate

Nitrate has also been identified as a potential biomarker for wastewater effluents. Human waste contains ammonium, which must be mitigated in some effluents to prevent adverse effects to aquatic ecosystems. WWTPs that discharge into sensitive areas are required by their provincial regulations to conduct a nitrification process whereby bacteria oxidize ammonia and form nitrate, which is less harmful in the environment. Other WWTPs may conduct nitrification processes in the summer when temperatures are higher, and conditions are favourable for the nitrifying microbes in the treatment process. Therefore, nitrate may be an effective and inexpensive indicator for the presence of wastewater effluents, but only where nitrification has occurred (e.g., in warmer months or in environmentally sensitive areas).

Carbamazepine

Carbamazepine is a commonly prescribed anti-convulsant that has been used in numerous studies as an anthropogenic indicator of wastewater based on its persistence in the environment. It is frequently detected in WWTPs and does not easily degrade, even through the use of a combination of tertiary treatment methods including ozonation.^{98,99} While carbamazepine has been shown to be a consistent indicator of municipal wastewater due to its persistence through treatment, the concentrations found are often still low enough to create challenges for some testing devices and can therefore, lead to false negatives depending on dilution levels.¹⁰⁰

Combination of Indicators

A combination of indicators could be applied to control for issues unique to each individual indicator. Using a suite of indicators could control for variations in concentrations as well as distribution at a given sample location. Some studies have used the co-occurrence of different indicators as the confidence threshold to apply to future testing, whereby each indicator alone isn't enough to trigger additional action.¹⁰¹

Developing a Target List of Pharmaceutical Compounds

This study has highlighted a number of challenges associated with determining a specific list of pharmaceuticals for further monitoring and analysis, given the sheer number of compounds, and wide range of uses and potential impacts. Determining which specific compounds to target will depend heavily on the objectives and intent of the study or monitoring program. For example, where looking at risks to aquatic organisms, pharmaceuticals that are known as EDCs might be preferred given their associated health impacts in exposed biota, or those compounds that remain persistent and therefore have greater potential to bioaccumulate. If considering risks to human health, compounds that are reactive at low concentrations may be more appropriate.

Stakeholders consulted in the development of this report noted that another approach would be not to use a list of target pharmaceuticals and to analyse for a standard full suite of compounds to get a sense of which of them are actually present in the Great Lakes instead. In other words, pursuing a more exploratory study. This approach could serve to focus future government risk assessments, based on those compounds actually found in the environment.

The literature and stakeholders consulted for this study noted a number of general approaches that could be considered in determining which pharmaceutical compounds to target for initial monitoring and analysis, once a citizen science program's specific needs and objectives have been determined. These approaches are similar to those discussed for determining a potential indicator and are described in further detail below.

Cost and analytical ease: This approach would involve focusing on those pharmaceuticals that can be tested with the greatest analytical ease, which as previously mentioned, tends to align with lower costs. For example, certain antibiotic compounds were noted to be relatively inexpensive to analyze as compared to other pharmaceutical types. This approach would require consulting with a laboratory to determine specific analytical requirements and associated costs however, it could be particularly useful when designing a program for long-term monitoring where sustainable financial support has not been secured.

Concentration: This approach would likely involve a focus on those pharmaceuticals believed to be found in more significant concentrations in wastewater effluent however, it could also include consideration for those compounds that are most widely used or prescribed in a given area. The use of prescription information or volume of use do not necessarily mean higher concentrations will be found in the environment because this fails to take into account dosage, removal during wastewater treatment or environmental fate.¹⁰² However, understanding presence in influent versus effluent may help with increasing understanding about the extent of any potential environmental risks, particularly if this approach is pursued in combination with others.

A 2014 study by the U.S. EPA used an analytical method to target 63 priority active pharmaceutical compounds (APIs) in 50 very large WWTPs located across the U.S. Hydrochlorothiazide — a diuretic used for the treatment of hypertension — was detected in all of the effluents examined. Metoprolol (antihypertensive), atenolol (antihypertensive) and carbamazepine were detected in more than 90% of effluents examined. Valsartan (antihypertensive) was found in the highest concentration, while ibuprofen, sertraline, propranolol were also measured in greater concentrations than other pharmaceuticals.¹⁰³



In addition, stakeholders consulted in the development of this report noted the following pharmaceuticals being commonly prescribed and found in either very high or moderate concentrations in surface waters:

- Ibuprofen
- Acetaminophen
- Carbamazepine
- Gemfibrozil
- Metformin
- Sulfamethoxazole and Trimethoprim (often prescribed together)
- Estrone
- Androstenedione

Any of these compounds could be included as part of an initial target list of pharmaceuticals for analysis based on being found in greater concentrations than many other compounds.

Degree of metabolises: This approach would determine pharmaceuticals for analysis based on the degree to which they are generally metabolized, or their resistance to metabolization, as this can be indicative of their persistence in the environment. For example, one stakeholder noted that carbamazepine is less frequently prescribed than selective serotonin reuptake inhibitors (SSRIs) — a type of antidepressant — but is found more frequently in the environment. This is believed to be due in part to the stability of the drug which is not designed to metabolize completely within the patient.

In addition, because many pharmaceuticals are introduced to the environment after human or veterinary use, some metabolite concentrations may be more significant than that of the parent compounds. For example, some acetylated metabolites of antibiotics (e.g., N4-acetylfulfapyridine) have been shown to be more toxic than parent compound sulfapyridine in algae.¹⁰⁴ Persistent metabolites require consideration because the effects resulting from exposure to a mix of parent pharmaceuticals and their metabolites is likely to be different than what would be observed based on analysis of a single compound.

Examples of pharmaceuticals that produce metabolites that may exhibit potential ecotoxicity in the environment and could be included in a target list of pharmaceuticals include:

- Acridine (metabolite of carbamazepine)
- Norfluoxetine (metabolite of fluoxetine)
- Norsesertraline (metabolite of sertraline)
- Acetylsulfamethoxazole (metabolite of sulfamethoxazole)¹⁰⁵

Mode of Action: Given that many pharmaceuticals are found in trace amounts, stakeholders suggested the possibility of exploring a family of compounds with the same mode of action (e.g., antibiotics, SSRIs or other antidepressants). Current environmental risk assessments focus on single substances and are unable to account for a number of compounds that have the same mode of action and could potentially have greater impacts when found together.

A study conducted in the Niagara River in 2017 found the antidepressants citalopram, paroxetine, sertraline, venlafaxine and bupropion, and their metabolites norfluoxetine and norsesertraline, concentrated in various fish organs, with norsesertraline exhibiting the highest bioaccumulation factor in the liver of rudd, an invasive species.¹⁰⁶

Stakeholders consulted in the development of this report noted that SSRIs would be an effective initial group of compounds with a similar mode of action based on the fact that they are widely prescribed. The following SSRIs could be included in an initial target list:

- Norfluoxetine
- Fluoxetine
- Norsesertraline
- Sertraline
- Bupropion
- Venlafaxine
- Citalopram
- Cotinine
- Duloxetine
- Paroxetine

Public Interest: The types of pharmaceuticals that are of interest to the general public should also be considered, particularly by citizen science programs where the primary focus is engagement and education. Given the need to ensure the experience is meaningful and resonates with those involved, working with pharmaceuticals that may be associated with misinformation related to potential risks or those that are more familiar to participants, could help create a more impactful program. Antidepressants have received considerable attention in the media based on their ecological effects, including impacts on aquatic species. The same is true of birth control pills containing synthetic hormones, painkillers and antibiotics while antimicrobial drugs are of interest based on their potential contribution to antimicrobial resistance.

As determining the citizen science program's objectives is necessary to develop a specific list of target pharmaceuticals, it is also helpful to understand the types of pharmaceuticals that are most likely to be detected. **Table 2** is adapted from Pollution Probe's previous study on pharmaceuticals and shows those compounds that have been detected in the Great Lakes. The majority of these were also mentioned either in the literature or by subject-matter experts consulted in the development of this report. The most mentioned pharmaceuticals to consider for an initial target list include acetaminophen, sulfamethoxazole, carbamazepine, norfluoxetine, metformin, naproxen, ibuprofen, estrone and gemfibrozil.



Table 2: Pharmaceuticals Identified in the Great Lakes that could be used as an Initial Target List for Analysis*

Group	Type of Pharmaceutical
Analgesic	Acetaminophen
Antibiotics	Erythromycin Sulfamethoxazole Trimethoprim Thiabendazole Azithromycin
Anticoagulant	Warfarin
Anti-Convulsant/Anti-Epileptic	Carbamazepine Dilantin Gabapentin
Anti-Depressant	Norfluoxetine Fluoxetine Norsertaline Sertraline Bupropion Venlafaxine Citalopram Cotinine Duloxetine Paroxetine
Anti-Diabetic	Metformin
Anti-Histamine	Diphenhydramine Dehydronifedipine
Anti-inflammatory	Diclofenac Naproxen Fenoprofen Ketoprofen Ibuprofen
Anti-Microbial	Triclosan
Beta Blocker	Atenolol Metoprolol Propranolol
Hormones	Estrone 17 α -ethynylestradiol Estradiol Androstenedione Testosterone
Lipid Regulators	Gemfibrozil Bezafibrate Atorvastatin

*Adapted from Pollution Probe's [Reducing the Impact of Pharmaceuticals in the Great Lakes](#)

A number of previous studies have targeted compounds using a multi-step selection process that combined a number of considerations noted here (e.g., volume of use, toxicity, public interest, pharmaceutical class and availability of analytical standards). Stakeholders consulted in the development of this study also agreed that taking a number of these factors into consideration in combination would be appropriate to determine a target list of pharmaceuticals for initial analysis. However, the final list of substances would need to align with the program's objectives and should involve some form of scientific assessment. **Section Four** outlines a number of target substances chosen for analysis as part of a separate project underway by Pollution Probe, in partnership with Swim Drink Fish and Trent University.

Summary

Section Three has explored the application of a two-step approach for analysing samples for pharmaceutical presence in an effort to address potential financial constraints associated with the cost of testing. There was broad consensus among stakeholders consulted for this study that an effective means of mitigating these financial challenges, while maximizing the impact of a citizen science program, would involve first determining the presence of a specific indicator (or combination of indicators) and only when found in a pre-determined concentration, would samples be prepared for further analysis for pharmaceutical compounds.

The use of an indicator would provide an important means of establishing a general picture of where pharmaceuticals may be found in greater concentrations in the lake (specific thresholds should be determined based on the program objectives) in order to then target a reduced number of locations where further monitoring and analysis should occur. While indicators may be present throughout the lakes, most of those outlined in this report are likely to be found in greater concentrations close to WWTPs. Any of the indicators outlined in this section are recommended for use in the Great Lakes. Those that will be most effective for a particular program will depend on its overall objectives, budget, timelines and the considerations highlighted herein (e.g., persistence, toxicity, ease of analysis, existing data).

This section also introduced a number of potential pharmaceuticals that could be used to populate an initial target list for analysis as part of the second step of the process. Where appropriate, this section pointed to potential pharmaceuticals based on a number of different approaches. Where funding is available, examining a full suite of 120 compounds to determine which are present in higher concentrations could also be an effective exploratory approach.

Section Three has provided an introduction to a number of potential indicators of pharmaceutical presence and considerations for determining a target list of pharmaceutical compounds for analysis. **Section Four** will outline a related project being conducted by Pollution Probe in partnership with Swim Drink Fish and Dr. Chris Metcalfe at Trent University. While this work is separate from this report, it is included as a means of highlighting a practical application of the concepts explored herein including the use of an indicator and development of a target list of pharmaceuticals.



SECTION FOUR

Case Study on Sampling & Analysis of Pharmaceutical Presence in the Great Lakes

This section outlines a separate project currently underway by Pollution Probe, in partnership with Swim Drink Fish and Dr. Chris Metcalfe and his research group at Trent University. The project involves the collection of samples from the Great Lakes to be analysed for two indicators for pharmaceutical presence and a number of target pharmaceuticals. It is included in this report as a means of highlighting how the high-level processes and methods outlined herein can be applied in a real-life context to determine how to develop an effective citizen science program related to pharmaceuticals in the Great Lakes. This work took guidance from the considerations in this report in partnering with an existing citizen science program, developing objectives and following sampling, shipment and analysis protocols applicable to pharmaceuticals.

Based on findings from the literature review and discussions with stakeholders consulted for this study, the sampling approach involved partnering with Swim Drink Fish, an organization that engages the public in citizen science through recreational water quality monitoring hubs in the Great Lakes, and in Vancouver. The monitoring hubs leverage Swim Drink Fish's expertise, experience, existing infrastructure and excellent QA/QC to help connect people to their local water bodies, collect important recreational water quality information, and share data through their platforms.

The analysis of the samples collected is being conducted by Dr. Chris Metcalfe and his research group at Trent University based on their extensive expertise. The analyses follow the two-step process described herein: first, testing for two indicators of wastewater and pharmaceutical presence (i.e., caffeine and sucralose), and only if these are detected in sufficient concentration, proceeding with further analysis of a targeted list of pharmaceutical compounds.

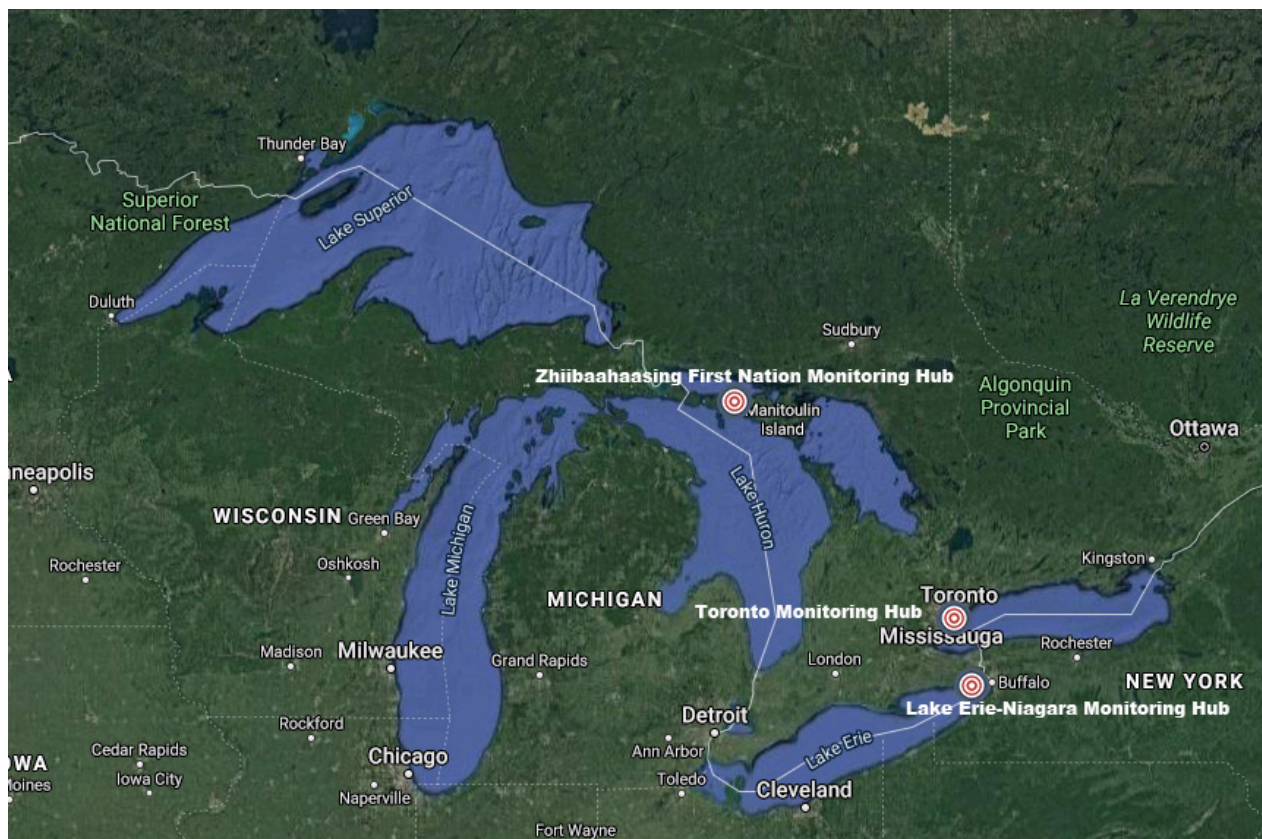
While work on this initiative is still underway, the context, process and findings to-date are described briefly below.

Swim Drink Fish's Citizen Science Water Monitoring Hubs

In 2018, Swim Drink Fish received funding through ECCC's Great Lakes Protection Initiative to establish and support recreational water quality monitoring hubs in six communities along the Great Lakes as part of their citizen science monitoring hubs. To date, Swim Drink Fish has established the following three citizen science monitoring hubs in the Great Lakes region, which were also those where samples were collected for this work.

- 1. Toronto Monitoring Hub:** This hub monitors sites on Lake Ontario along Toronto's shoreline. It was officially established in 2016 by Lake Ontario Waterkeeper, an initiative of Swim Drink Fish, and has been monitored by Swim Drink Fish since its inception.
- 2. Zhiibaahaasing First Nation Monitoring Hub:** This hub monitors Lake Huron beaches in Zhiibaahaasing First Nation on Manitoulin Island and Cockburn Island. It was established in the fall of 2018 and is hosted by Zhiibaahaasing First Nation.
- 3. Lake Erie - Niagara Monitoring Hub:** This hub monitors beaches in the Niagara region on the north shore of Lake Erie. It was established in the spring of 2019 and is hosted by the Niagara Coastal Community Collaborative and Niagara College.

Figure 1 provides a visual representation of the location of existing monitoring hubs overseen by Swim Drink Fish.

Figure 1: Location of Current Great Lakes Monitoring Hubs

Each hub monitors three core sites. These sites are selected based on three main criteria:

1. The site is currently unmonitored by local health departments
2. The site has the potential for contamination
3. The site is used regularly by members of the community

The Toronto Monitoring Hub monitors three core sites at Marina 4, Rees St. Slip and Bathurst Quay, located in Toronto's Inner Harbour. Historically a heavily developed area used primarily for industrial purposes, in recent years the Toronto Harbour has transformed into a residential neighbourhood and recreational destination. Although City of Toronto Municipal Code #608 prohibits swimming in much of the area, other recreational activities (e.g., canoeing, kayaking, boating etc.) are very popular at these sites. Non-point sources of pollution from urbanization, including stormwater runoff, are a main contributor to poor water quality conditions with the Toronto area however, discharges from WWTPs and industrial sources can also contribute to the degradation of water quality.¹⁰⁷

In contrast to the Toronto Monitoring Hub, the Zhiibaahaasing First Nation Monitoring Hub monitors recreational waters at three pristine and isolated sites on Manitoulin Island and Cockburn Island (Gaanogwong Apgishmok, Rocky Beach and Sandy Bay). These sites are not located in close proximity to point source pollution and are surrounded by undisturbed forest. Surface water samples for Pollution Probe and Trent University were collected from the Gaanogwong Apgishmok site, a communal beach located in Zhiibaahaasing First Nation on the western-most end of Manitoulin Island. The beach is used by members of the local community for recreational and ceremonial purposes, and for community events.

The Lake Erie - Niagara Monitoring Hub monitors three sites along the north shore of Lake Erie sites (Windmill Point, Waverly Beach and Sugarloaf Marina). Surface water samples were collected from Sugarloaf Marina, in Port Colborne. The site is situated in a parkland area with an adjacent marina and is a popular destination for fishing, boating and wakeboarding during the summer season due to the fact that the recreational water is easily accessed. Contamination of microorganisms from the local geese population and sewage discharge from boats and nearby drainage ditches have contributed to water quality concerns at this site.

Table 3 provides further detail, including general characteristics of the sites at each monitoring hub. Sites sampled as part of the Pollution Probe and Trent University work are noted with an asterisk.

Table 3: General Site Characteristics for Great Lakes Monitoring Hubs

Monitoring Hub	Site Name	General Site Characteristics
Toronto Monitoring Hub (Core Sites)	Marina 4*	Urban, combined sewage overflow outfall, marina
	Reese St. Slip*	Urban, combined sewage overflow outfall, marina
	Bathurst Quay*	Urban, combined sewage overflow outfall, marina
Toronto Monitoring Hub (External Sites)	Wards Island Dock Beach	Toronto Island, residential, parkland, beach
	Algonquin Bridge	Toronto Island, lagoon, residential, parkland, beach
	Snake Island	Toronto Island, lagoon, residential, parkland, waterway (monitored by boat)
	Ontario Place	Parkland, beach
	Humber Bay West	Parkland, beach, adjacent to river mouth
Zhiibaahaasing Monitoring Hub	Gaanogwong Apgishmok*	Rural, forested, relatively undeveloped
	Sandy Bay	Remote, forested, relatively undeveloped
	Rocky Beach	Remote, forested, relatively undeveloped, communal cabin
Lake Erie – Niagara Monitoring Hub	Sugarloaf Marina*	Residential, recreational, marina, parkland
	Windmill Point	Residential, recreational, parkland
	Waverly Beach	Residential, recreational, parkland

* Indicates site chosen for sample collection for Pollution Probe and Trent University

Quality Assurance and Quality Control

Swim Drink Fish maintains rigorous QA/QC measures for its volunteers in order to ensure the quality of the samples collected at its monitoring hubs. All volunteers are required to attend a minimum of two training sessions, each approximately three hours long. Volunteers are trained by hub coordinators on field methods, QA/QCs, environmental observations, how to effectively use field sheets and the overall goals of the monitoring program. During each sampling session in the field, all activities are overseen by Swim Drink Fish hub coordinators.

Field Protocols

Field protocols follow Swim Drink Fish's Standard Operating Procedures (SOPs), which were designed specifically for the establishment and undertaking of citizen science monitoring hubs in the Great Lakes and in Vancouver. Each hub follows the local governmental recreational water quality criteria and applicable protocols for beach monitoring and sample collection (i.e., Health Canada's Guidelines for Canadian Recreational Water Quality.¹⁰⁸ Prior to the collection of samples at a monitored site, a chain of custody document is filled out to provide a record of the handling and transportation of any samples. A range of environmental observations are also recorded at the site (e.g., historical and current weather and precipitation, characteristics of the water, types of litter, human and wildlife usage of the beach and potential discharge sources).

In accordance with Ontario standards, there are a minimum of five sampling locations at each site. Staff and volunteers collect samples of the surface water using sterile 100 mL Whirl-Pak bags at a depth of 0.15 - 0.30 m below the surface.¹⁰⁹ Samples are then kept cold (<10°) until analysis. At sites that are more beach-like with a soft slope towards the water, staff and volunteers waded out to a depth 0.5 - 1.0 m and wait until any disturbed sediment has settled prior to collecting a sample. Temperature and clarity of the water, along with depth, are also recorded for each sampling location.

A total of 10 samples were collected between September 18, 2019 and September 27, 2019, as part of the work being undertaken by Pollution Probe and Trent University (six from the Toronto Monitoring Hub, two from the Zhiibaahaasing First Nation Monitoring Hub and two from the Lake Erie-Niagara Monitoring Hub). At each site, a duplicate set of surface water samples were obtained at a depth of between 0.15 - 0.30 m below the surface in two, one-litre, high-density polyethylene (HDPE) Nalgene® bottles after rinsing three times with the targeted water. Samples were kept cold in the field using ice packs and a cooler, and were frozen as soon as possible after returning.

Temperature indicators were used for every site during each visit and field blanks are prepared for each week of sampling to assess whether there has been any contamination from the field. Field duplicates are produced by Swim Drink Fish for every tenth sample, to assess whether there is any variance in the field methods.

Analysis Using an Indicator for Pharmaceutical Presence

In order to assess whether contaminants of wastewater origin are present in surface waters in the Great Lakes Basin, the 10 samples collected from Swim Drink Fish's monitoring hubs were transported to Trent University for analysis in triplicate of:

- a. Chemical indicators (all samples)
- b. Pharmaceuticals and steroid hormones (selected samples)

Target Compounds for Chemical Analysis

The findings from this report pointed to the applicability of a two-step approach to analyzing samples collected to test for the presence of pharmaceuticals. Pollution Probe and Trent University followed this approach as a "proof of concept". This approach helps to reduce costs associated with analyzing pharmaceuticals by identifying locations where they are most likely to be found through the use of an indicator, allowing for a more targeted analysis of these sites.

More specifically, the approach followed involved:

- 1. Presence of a Chemical Indicator Compound:** The first step involved one of each of the replicate samples being analyzed for chemical indicator compounds. Sucralose and caffeine were used as indicators of contamination of wastewater origin in the near-shore zone at several locations in the Great Lakes. Sucralose has been shown to be poorly removed in WWTPs and persistent in the aquatic environment. Caffeine is removed more efficiently in WWTPs (>80% removal) and is less persistent in the aquatic environment, but is present in such high concentrations in wastewater that it can be used as an effective indicator compound.
- 2. Analysis of Pharmaceuticals and Steroid Hormones:** The remaining replicate samples are prepared for analysis of the target pharmaceuticals and steroid hormones where in discussion with subject-matter experts, the project team decides it is warranted. The specific compounds chosen as an initial target list are based on the previous work and experience of Dr. Chris Metcalfe and a number of the approaches described herein. The list includes a combination of those pharmaceuticals that are commonly used, those that do not degrade easily in WWTPs and those shown to have environmental impacts (e.g., steroid hormones). The specific reason for inclusion of each compound is noted in Table 4 below. This approach to developing a target list of pharmaceuticals is recommended based on an objective of determining if pharmaceuticals are present where the indicators are also found because it captures a range of different compounds likely to be present.

Table 4 shows the chemical indicators and pharmaceuticals identified for analysis as part of this separate project, their source or application and the specific reason for their selection.

Table 4: Target Compounds for Analysis

Classification	Compound	Source or Application	Reason for Selection
Chemical Indicators	Caffeine	Coffee, tea, energy drinks	Commonly used indicator of wastewater contamination; Usually present in very high concentrations in impacted surface waters
	Sucralose	Artificial sweetener	Commonly used indicator of wastewater contamination; Usually present in very high concentrations in impacted surface waters.
Pharmaceuticals and Steroids	Ibuprofen	Non-prescription analgesic (e.g. Advil)	Commonly used non-prescription medication for colds and fever; Extracted using OASIS MAX cartridge; Usually present in relatively high concentrations in surface waters.
	Acetaminophen	Non-prescription analgesic (e.g. Tylenol)	Commonly used non-prescription medication for colds and fever; Extracted using OASIS MAX cartridge; Usually present in relatively high concentrations in surface waters.
	Carbamazepine	Prescription cholesterol-reducer	Very persistent prescription medication commonly used to treat epilepsy, but also for treatment of PTSD and other psychological conditions; Extracted using OASIS MAX cartridge; Usually present in relatively high concentrations in surface waters.
	Gemfibrozil	Antibiotic	Moderately persistent prescription medication used to treat high cholesterol; Extracted using OASIS MAX cartridge; Usually present in moderately high concentrations in surface waters.
	Trimethoprim	Antibiotic	Highly prescribed antibiotic with moderate persistence. Extracted using OASIS MAX cartridge; Usually present in moderately high concentrations in surface waters.
	Sulfamethoxazole	Steroid hormone (estrogen)	Highly prescribed antibiotic with moderate persistence. It is usually prescribed in tandem with trimethoprim. Extracted using OASIS MAX cartridge; Usually present in moderately high concentrations in surface waters.
	Estrone	Steroid hormone (androgen)	Metabolite of the female hormone, 17 β -estradiol that is typically present at higher concentrations in surface waters than the parent compound; Extracted using OASIS MAX cartridge; An indicator of the presence of estrogens of wastewater origin.
	Androstenedione	Prescription anti-epileptic	Metabolite of the male hormone, testosterone that is typically present at higher concentrations in surface waters than the parent compound; Extracted using OASIS MAX cartridge; An indicator of the presence of androgens of wastewater origin.

Analysis of Chemical Indicators

To date, the first step of the process (i.e., determining presence of chemicals indicators) has been completed. Water samples were frozen until prepared for analysis for caffeine. After thawing, aliquots of the water samples were extracted using solid phase extraction (SPE) cartridges. All samples were analyzed in triplicate. The 150 mL subsamples of water were extracted for caffeine using Oasis mixed-mode anion exchange (MAX) cartridges. Water samples were adjusted to pH 8 and then loaded onto cartridges after the addition of an internal standard of caffeine-d₆ stable isotope surrogate. The cartridges were eluted sequentially with 2 ml methanol and then 3 x 3 ml of 2% formic acid in methanol.

Sucralose was extracted from separate 150 mL subsamples using Oasis mixed mode cation exchange (MCX) cartridges. Subsamples were acidified to pH 1.5 prior to spiking with an internal standard, sucralose-d₆. The analytes were eluted from the SPE cartridges with 3 x 3 mL of 5% ammonium hydroxide in methanol. All extracts were evaporated and reconstituted in 0.4 mL methanol for analysis.

Caffeine and sucralose were analyzed separately by liquid chromatography and tandem mass spectrometry with an electrospray ionization source (i.e. LC-ESI-MS/MS) using an Agilent 1100 series HPLC system and an AB Sciex QTrap 5500 tandem mass spectrometer. Analytes were separated chromatographically using a C18 column and guard column. The target compounds were quantified by monitoring in multiple reaction monitoring (MRM) mode. For the determination of caffeine, analysis was in positive ion mode and for analysis of sucralose, analysis was in negative ion mode.

Quantitation of the target analyte in units of ng/L will be conducted using an internal calibration curve, adjusted according to the recoveries of the internal standards. When an analyte was not present at a concentration above the limit of detection, the target analyte was identified as being "not detected". When an analyte was present, but at a concentration below the limit of quantitation, the target analyte was identified as being "present".

Preliminary Findings

Figure 2 below shows the analytical data for the analysis of sucralose and caffeine as potential indicators of pharmaceutical presence. Table 5 contains the sample data and the quantification of total coliforms and E.coli from the same sample sites.

Figure 2: Sucrose and caffeine concentration by sample site

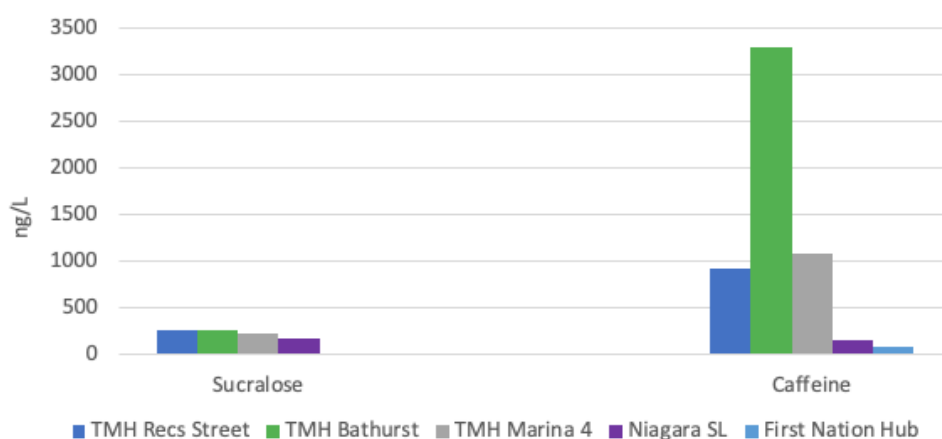


Table 5: Sucralose, Caffeine, Total Coliform & E. Coli Concentration by Sample Site

ID	Sucralose	Caffeine	Total Coliform	E. Coli	Latitude	Longitude
	ng/L	ng/L	MPN	MPN	D.D	D.D
Lab Blank	ND	ND				
TMH Recs Street Rep 1	273	947	547.5	29.4		
TMH Recs Street Rep 2	307	924				
TMH Recs Street Rep 3	208	908				
Mean TMH Recs Street	263	926			43.63835	-79.38726
TMH_Bathurst Rep 1	280	3359	24196	2480.9		
TMH_Bathurst Rep 1	269	3378	24196	1777.1		
TMH_Bathurst Rep 1	235	3162				
Mean TMH Bathurst	261	3300	24196	2129	43.63645	-79.39696
TMH Marina 4 Rep 1	285	1051	5172.1	495.9		
TMH Marina 4 Rep 2	229	1048				
TMH Marina 4 Rep 3	188	1171				
Mean TNH Marina 4	234	1090			43.638809	-79.3843384
Lake Erie/ Niag SL Rep 1	161	151	2419.6	34.5		
Lake Erie/ Niag SL Rep 2	195	160				
Lake Erie/ Niag SL Rep 3	176	126				
Mean Niagara SL	177	145			42.8776938	-79.2559739
First Nation Hub Rep 1	12	86	50.4	1		
First Nation Hub Rep 2	19	96				
First Nation Hub Rep 3	15	88				
Mean First Nation Hub	15	90			45.96003	-82.87693

The data on concentrations of sucralose and caffeine (ng/L) indicate that the near-shore zones at all five sampling locations are contaminated with these compounds of wastewater origin, although the First Nations site is only mildly contaminated relative to the other sampling sites (Table 5). The order of contamination at the sites is: Bathurst > Marina > Rees Street > Niagara SL > First Nation, with the Bathurst location being the most contaminated. This may be due to the fact that the Zhiibaahaasing site is more remote than the other samples locations.

Comparing the chemical and biological data for the samples that were analyzed, there is a good correlation between the levels of the indicator compounds and the counts of *E. coli* (Table 5), with the order of *E. coli* contamination being: Bathurst > Marina > Rees Street - Niagara SL > First Nation. However, the relationship between chemical and biological indicators was less clear for the total coliform data (Table 5). This is likely due to the fact that coliform bacteria can come from a variety of sources, including domestic animals and wildlife (many coliform bacteria are actually beneficial) while *E. coli* contamination is indicative of contamination from fecal matter originating from warm-blooded animals, including humans. Therefore, the data on indicator compounds and *E. coli* counts indicate that the nearshore zone for at least four of the five sites is impacted by discharges of domestic wastewater.

It is probable that analysis of the samples collected at these sites for levels of pharmaceuticals will indicate that there is contamination by a range of prescription and non-prescription drugs. However, based on previous monitoring studies, it is predicted that the concentrations of pharmaceuticals, where detected, will be a factor of 10 or even 100 less than the concentrations of sucralose and caffeine (i.e. 10-100 ng/L).

The results of the analysis show that both caffeine and sucralose are likely to be effective indicators for pharmaceutical presence based on the fact that both are present in wastewater effluents, which is also a key pathway for pharmaceuticals. While further analysis would be required to determine which pharmaceuticals are present, caffeine or sucralose could be used to help narrow the number of locations requiring further analysis for a citizen science program geared towards determining a more complete dataset in the Great Lakes or where the objective is to test for a broad suite of pharmaceuticals to gain a better sense of which are found in the lakes in the highest concentrations. As previously noted, a program based primarily on building awareness and understanding may not need to complete the second analysis of specific target pharmaceuticals and could instead be provided with educational resources to complement the sample collecting and initial analysis.

CONCLUSION

The popularity of citizen science programs has grown rapidly in recent years. Governments and other scientists and researchers have recognized the important role that the public can play in helping to restore and protect their environment, including the Great Lakes. Citizen science initiatives encourage the public to spend time in their natural environment while undertaking meaningful activities to monitor and improve the environment. Perhaps most importantly, citizen science has been shown to be one of the most effective means of increasing environmental awareness, education, stewardship and support for conservation efforts because they build goodwill and provide opportunities for participants to feel like an important part of the solution.

A number of challenges associated with the feasibility of citizen scientists undertaking a monitoring program specific to pharmaceuticals were outlined in this report. Perhaps the most considerable of these, is the fact that complex analytical methods are required to detect pharmaceuticals in what are often trace amounts, which can add considerable time and cost to the program. However, the public has shown concern about the potential risks that these substances may pose for human health and the environment, pointing to a need to better educate and engage around the science in a way that can help to replace fear with facts.

This report examined the potential for a two-step approach aimed at minimizing the costs associated with testing for pharmaceutical presence while maximizing the impact of the program. This involves first determining the presence of an indicator (or combination of indicators) and only where found at a specified concentration, would samples be prepared for further analysis of pharmaceutical compounds. A number of potential indicators are described in the report, all of which have been used successfully as an indicator for wastewater. They are also likely to indicate the presence of pharmaceuticals, given that wastewater effluent has been shown to be a key pathway for their entry into the Great Lakes.

The use of an indicator would provide an important means of establishing a general picture of where pharmaceuticals may be found in greater concentrations in order to take a more targeted approach to further monitoring and analysis. Determining which compounds are present and at what concentrations, particularly over time, could build an important dataset that could be used to better understand the impacts of pharmaceuticals given the current lack of a dedicated, long-term monitoring program. This dataset could also be made public and used by academic institutions, governments and other researchers to complement their own work.

Each of the indicators outlined in this report are recommended for use in the Great Lakes however, those that will be most effective for a particular program will depend on its overall objectives, budget, timelines and priorities in terms of what it is looking to better understand (e.g., persistence, toxicity, ease of analysis, existing data). In the absence of a clear set of objectives, budget and timelines for a citizen science program, this report also used work undertaken as part of a separate project as a proof of concept. To-date, this work has pointed to the effectiveness of using caffeine and sucralose as indicators of wastewater effluent, a key pathway for pharmaceuticals entering the Great Lakes. However, further analysis is required to determine which specific pharmaceuticals may also be present.

There was broad agreement among stakeholders consulted in the development of this report that the given the complexity of the analysis for pharmaceuticals, the greatest value of developing a citizen science program would be in its ability to effectively educate the public about the difference between what they may hear in the media and the reality of pharmaceutical presence and impacts in the Great Lakes. A program focused on education would ideally involve a combination of data collection methods in order to build a more complete picture of pharmaceutical presence in the Great Lakes, and an awareness-building element to improve scientific literacy and understanding. A citizen science program focused on developing a more complete dataset would require a more substantial budget for analysis than one aimed primarily at education.

In an ideal scenario where a sustainable budget exists, it is recommended that a citizen science program related to pharmaceuticals combine a focus on education, with an objective of contributing to scientific research and the development of a more complete dataset for pharmaceutical presence in the Great Lakes. Citizen science provides an opportunity to spend time at locations around the lakes, interacting with the natural surroundings will foster a deeper understanding of their importance and the need to better protect them from for example, improperly disposed of pharmaceuticals, and can also provide opportunities to correct misunderstandings related to potential environmental and human health impacts.

A combination of sampling methods were noted as the preferred approach for pharmaceuticals as this would provide a more detailed overall picture of their presence across the lakes. If the program has financial limitations, there was general agreement among stakeholders consulted in the development of this report that grab sampling or passive sampling (where pursued in collaboration with researchers) would be the most feasible options for citizen science programs based on the fact that composite sampling can be time and labour intensive. Where education and engagement are the purpose of a citizen science program, comprehensive sampling and detailed analysis may not be as necessary whereas, a goal of developing a more complete dataset for pharmaceuticals in the Great Lakes would likely benefit from incorporating more than one sampling method. A citizen science program could also consider collecting biota as a means of determining whether bioaccumulation is a concern for certain species (e.g., fish) or to better understand whether pharmaceuticals found in sediments could be re-suspended from contact with water. This step could be introduced once the program is well-established.

The report highlighted the fact that despite citizen science's many supporters, there remain those who are skeptical about the quality and reliability of the information collected or reported on by members of the public, and its usefulness in research. Ensuring that a citizen science program focused on pharmaceuticals is grounded in strict QA/QC methods can contribute to overcoming some of the perceptions associated with data usability and is an important means of ensuring that citizen science investigations are effective and scientifically meaningful. Consistency of data is of particular importance given that this study also pointed to an opportunity for a citizen science program related to pharmaceuticals to complement existing research and monitoring programs. A number of important efforts are already underway to help protect the Great Lakes, and including an additional level of information or dataset through citizen science could be useful in providing further context for environmental changes over time.

The outcomes of this study will contribute to providing guidance on important considerations for the monitoring of pharmaceuticals that can be explored or adopted by those looking to utilize citizen science as a tool for engagement and awareness-building, particularly in the Great Lakes. Despite the challenges associated with pharmaceuticals, there are ways to make a program more financially viable and citizen science provides an unrivalled opportunity for the public to monitor their own communities and acknowledge the connection and concerns for their waters. Participation in citizen science programs will engage the community as active participants in positive change, armed with a better understanding of how to contribute to the preservation and sustainability of the lakes.

APPENDIX A: SELECTED RESOURCES & GUIDANCE

Great Lakes

Government of Canada. Great Lakes Water Quality Agreement.

<https://www.canada.ca/en/environment-climate-change/services/great-lakes-protection/2012-water-quality-agreement.html>

Government of Canada. The Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem.

<https://www.canada.ca/en/environment-climate-change/services/great-lakes-protection/canada-ontario-agreement-water-quality-ecosystem.html>

Government of Canada. Great Lakes Protection.

<https://www.canada.ca/en/environment-climate-change/services/great-lakes-protection.html>

Province of Ontario. Great Lakes Protection Act, 2015.

<https://www.ontario.ca/laws/statute/15g24>

Province of Ontario. Great Lakes Guardian Community Fund.

<https://www.ontario.ca/page/great-lakes-guardian-community-fund>

Province of Ontario's Great Lakes Strategy.

<https://www.ontario.ca/page/ontarios-great-lakes-strategy>

International Joint Commission.

<http://www.ijc.org/>

United States Environmental Protection Agency.

<http://epa.gov/greatlakes/>

Citizen Science

Citizen Scientists. Homepage.

http://citizenscientists.ca/Citizen_Scientists.html

Dorset Environmental Science Centre. Ontario Lake Partner Program.

<https://desc.ca/programs/LPP>

Government of Canada. Citizen Science Portal.

http://www.science.gc.ca/eic/site/063.nsf/eng/h_97169.html

Ontario Nature. Citizen Science.

<https://ontarionature.org/programs/citizen-science/>

Penn State. Endocrine Disrupting Compounds Calculator.

<https://sites.psu.edu/edccalculator/>

Swim Drink Fish. Citizen Science

<https://www.swimdrinkfish.ca/citizen-science>

United States Environmental Protection Agency. Citizen Science for Environmental Protection.
<https://www.epa.gov/citizen-science>

United States Environmental Protection Agency. Quality Assurance Handbook and Guidance Documents for Citizen Science Projects.
<https://www.epa.gov/citizen-science/quality-assurance-handbook-and-guidance-documents-citizen-science-projects>

UK Environmental Framework. Guide to Citizen Science.
<https://www.nhm.ac.uk/content/dam/nhmwww/take-part/Citizenscience/citizen-science-guide.pdf>

Water Quality and Water Sampling

Canadian Council of Ministers of the Environment. Protocols for Manual Water Sampling in Canada.
https://ccme.ca/files/Resources/water/water_quality/protocols_document_e_final_101.pdf

Government of Canada. Wastewater.
<https://www.canada.ca/en/environment-climate-change/services/wastewater.html>

Health Canada. Guidelines for Canadian Recreational Water Quality.
<https://www.canada.ca/content/dam/canada/health-canada/migration/healthy-canadians/publications/healthy-living-vie-saine/water-recreational-recreative-eau/alt/pdf/water-recreational-recreative-eau-eng.pdf>

Ontario Ministry of Health and Long-Term Care. Operational Approaches for Recreational Water Quality Guideline, 2018.
http://www.health.gov.on.ca/en/pro/programs/publichealth/oph_standards/docs/protocols_guidelines/Operational_Approaches_to_Rec_Water_Guideline_2018_en.pdf

United States Environmental Protection Agency. Environmental Sampling and Analytical Methods (ESAM) Program.
<https://www.epa.gov/esam>

Pharmaceuticals

Canadian Water Quality Guidelines for the Protection of Aquatic Life. Carbamazepine.
<http://ceqg-rcqe.ccme.ca/download/en/358?redir=1583683868>

Pollution Probe. Reducing the Impact of Pharmaceuticals in the Great Lakes.
<http://www.pollutionprobe.org/wp-content/uploads/112354-1-PP-PharmGreatLakesReport.pdf>

Government of Canada. Canadian Environmental Protection Act, 1999.
<http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=126220C5-1>

Government of Canada. The Chemicals Management Plan.
<http://www.chemicalsubstanceschimiques.gc.ca/index-eng.php>

United States Environmental Protection Agency. Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS.
https://www.epa.gov/sites/production/files/2015-10/documents/method_1694_2007.pdf

APPENDIX B: COMMON DATA QUALITY INDICATORS AND QUALITY CONTROL MEASURES

Table 6: Commonly Used Data Quality Indicators

Data Quality Indicator	Description
Accuracy	Accuracy is closeness to a standard or known value. Accuracy can be affected by the equipment or procedures used to measure a sample parameter. A specific compound found at a very high concentration in a water sample but which can never be duplicated, could call into question the accuracy of the results.
Bias	Bias is any influence on a project that has the potential to skew the data in a particular direction. For example, if collection locations for water samples were chosen only from an area where there is a known water quality issue rather than being distributed across a broader geographical area. Sampling bias can include temporal bias (irregular recording effort over time), spatial bias (irregular coverage across a given area), observation bias (irregular or uneven recording per visit) or detection bias (differences in participant ability to detect, leading to selective or incomplete results). Bias in sampling can lead to miscalculations, skewed results or false conclusions. ¹¹⁰
Comparability	Comparability is the extent to which one dataset can be compared to another. Comparability is of importance for citizen science programs looking to augment or contribute to existing research or monitoring programs as it ensures these two datasets can be easily compared to each other.
Completeness	Completeness is a measure of the amount of data or samples collected versus the amount expected to be obtained in order to achieve the objectives of the program. It is often expressed as a percentage (e.g., sampling completed 90 out of 100 times would be 90%).
Precision	Precision refers to the ability of a measurement to be consistently duplicated or reproduced and is usually calculated using replicates or splits. Precision is often measured as the relative percent difference or the relative standard deviation and can be affected by human error in sampling techniques. ¹¹¹
Representativeness	Representativeness is the degree to which the data gathered can represent the condition being measured. The time of day data is collected, along with the season or location, can all play a role in whether it is representative. For example, if the monitoring objective is meant to characterize the presence of human pharmaceutical compounds in the Great Lakes, collecting a sample in a remote area far from human activity may not be representative of the condition of the lakes as a whole.
Sensitivity	Sensitivity is the lowest detection limit of a method, instrument or process. ¹¹² Sensitivity helps determine whether field or laboratory methods are sensitive enough to answer the research question being asked.

Table 7 outlines a few of the more common QC measures used in the field that could be utilized for a citizen science program, including one related to detecting or observing pharmaceuticals.

Table 7: Common Quality Control Measures

Sample Type	Description
<p>Blank Samples: A blank sample is a “clean” sample used to detect or document contamination at any point during sampling, transport or laboratory analysis. Blanks are typically de-ionized water that is exposed to a particular condition which has the potential to cause contamination, thus representing environmental factors that may be present in the sample.¹¹² Blank samples are intended to act as a check-and-balance for potential systemic errors as they identify potential contamination, add valuable background information when assessing the integrity of the data and allow for corrections to the process moving forward.</p>	<p>Field Blanks: A field blank is meant to detect and identify contaminants from the sampling site that are not under investigation.¹¹³ Field blanks are created when de-ionized water or water free from organic debris is taken to the sampling site and poured into the container in the field, exposing it to the environment. Once samples and blanks have been returned to the laboratory, the field blank can be compared to the site samples to test for the degree of influence the site-specific environment or the handling of the sample containers has on the sample.¹¹⁴</p> <p>Trip Blanks: Trip blanks are similar to field blanks except that they are not opened during the sampling process and are therefore, not exposed to the environment. A sample of de-ionized water is taken from the laboratory to the site along with the sampling containers and then returned to the laboratory unopened. The purpose of a trip blank is to detect and identify any contamination caused by conditions during the transport of the sample to and from the laboratory.¹¹⁵</p> <p>Temperature Blanks: A temperature indicator (often referred to as a temperature blank) is a vial or other small sample bottle filled with distilled water and placed into each cooler or container used for transport, along with the samples that have been collected. The temperature of the vial is measured once it arrives at the laboratory to evaluate whether samples were appropriately cooled during shipment of the sample.¹¹⁶</p>
<p>Control Samples</p>	<p>A control sample is used to isolate a source of contamination. This could require the collection of a sample at an upstream location where the medium being studied is unaffected by the site studied, as well as a downstream control which may have been affected by contaminants contributed from the site being studied.¹¹⁷</p>
<p>Replicate Samples</p>	<p>Replicate samples, often referred to as duplicate samples, are two separate samples taken at the same time in a manner that helps to minimize differences (e.g., taken by the same person simultaneously or in quick succession at the same location). The samples are then treated in the same manner throughout the field, transport and laboratory procedures. This provides an opportunity to better understand and document the precision of the sampling process.¹¹⁸</p>
<p>Split Samples</p>	<p>Split samples are a type of replicate sample where water is collected at double the volume of a typical sample and then split in two or more separate containers so that any variability can be evaluated. These containers are often analyzed by different laboratories or using different methods.¹¹⁹ In this way, split samples can help to compare results between laboratories.¹²⁰</p>

APPENDIX C: FIELD EQUIPMENT CLEANING AND DECONTAMINATION PROTOCOLS

Prior to the Field

In order to avoid contamination, it is also advisable to follow a set of protocols for the cleaning of field containers. It is likely that this step would be undertaken by those delivering the citizen science program rather than participants themselves. All sampling bottles should come from the appropriate analytical laboratory and should remain capped before and after actual sampling. A standard sample bottle typically used for water sampling is 500 mL or 1 L and produced from Teflon, glass or stainless steel. However, high-density polyethylene (HDPE) bottles may also be used, particularly when analyzing those compounds or substances that are less likely to interact or be absorbed by the surface of the bottle.

The following outlines a typical process for decontaminating sample bottles prior to heading into the field:

- 1. Wipe the equipment:** The entire decontamination process should be conducted while wearing safety glasses and non-powdered nitrile or latex gloves. It is important that the gloves used have not been worn to perform any other activities.
- 2. Rinse the equipment in water:** Ideally, water for decontamination should be de-ionized — tap water that has been treated by passing through a de-ionizing resin column — or at minimum, should contain no heavy metals or inorganic compounds above analytical detection limits. Alternatively, organic-free water can be used in place of de-ionized water if it has been treated with activated carbon and has no detectable organic contaminants. Citizen scientists may not have access to de-ionized water or organic-free water so may need to purchase pre-cleaned containers.
- 3. Wash the equipment with detergent and water followed by a rinse:** A standard, phosphate-free laboratory-grade detergent should be used to soap wash equipment because they are not as harsh as some other cleaners and are known to consistently remove contaminants while not leaving lasting film or soap grease. While not in use, detergent should be kept in clean containers and only poured directly into the decontamination target.

Once decontaminated, bottles should only be handled by someone wearing clean gloves (i.e., those that have not been used during the decontaminating process) and then stored with lids secured away from any equipment that has not yet been decontaminated, or where other contaminants may be found.

At the Sampling Site

Before heading into the field, participants should ensure that they have all necessary equipment (e.g., bottles, gloves, icepacks, transport container, etc.). Previously unworn disposable nitrile or latex gloves (without powder) should be worn at each sample location and only put on immediately before sampling takes place. A stakeholder consulted for this study however, noted that their personal experience had pointed to citizen scientists wearing gloves being less careful about contamination.

Those collecting samples should avoid the use of personal care products on the day of sampling if possible, as they have the potential to contribute to contamination. Hand sanitizers and other alcohol-based products should also be avoided as they can degrade the integrity of the gloves. If a specific sampling site is likely to have high levels of contamination, sample bottles from that site should be separated from others during transport using new sealable plastic bags. Labeling and categorization systems should be in place and followed after each collection to help limit the chance for human error.

Prior to entering the field, all team members should familiarize themselves with the area in order to anticipate any potential risks. It is imperative that sampling be conducted safely using appropriate equipment including footwear, gloves, personal floatation devices and emergency kits. Ideally, sampling should be done in teams for both safety and the reliability of the samples. A team approach allows for one member to be responsible for collecting the sample, while another ensures safety measures are taken. A third team member records all field notes, location and site identification, and environmental observations. Citizen scientists should be provided with specific forms that outline the types of information that will be collected so that it can be easily and systematically entered into appropriate databases. In addition, comprehensive emergency response plans should be provided and completed for each site visit.

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