Case Study: Determining an Indicator of Pharmaceutical Presence in the Great Lakes

Context

In 2019, **Pollution Probe** partnered with **Swim Drink Fish** and **Dr. Chris Metcalfe and his research group** at Trent University to conduct a proof-of-concept case study to determine whether there is an effective indicator for pharmaceutical presence in the Great Lakes. The study also benefitted from the guidance of a project advisory group comprised of subject-matter experts who provided oversight on overall direction and contributed important resources and data. Study methods and design were aligned with recommendations from Pollution Probe's *Citizen Science in the Great Lakes: A Tool for Engagement on Pharmaceuticals and Other Emerging Issues* report. The study looked to understand whether an appropriate indicator can be used to identify locations where pharmaceuticals are likely to be found, allowing for a more targeted analysis of these sites.

Pharmaceuticals represent a broad range of compounds with a variety of characteristics that enter natural systems sporadically and at differing concentrations, exhibiting varying levels of persistence.

An effective indicator can address some of these challenges by reducing the costs associated with analysis by identifying those locations, situations, or circumstances where more complex testing should occur.

What is an Indicator?

An indicator can be any physical (e.g., fouling), chemical (e.g., caffeine), or biological measure (e.g., *E. coli*) whose presence suggests that another compound or contaminant may also be present. 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 a tool for assessing the extent to which water bodies and other natural systems have been impacted by human activity.

Use of an Indicator can Provide Several Advantages:

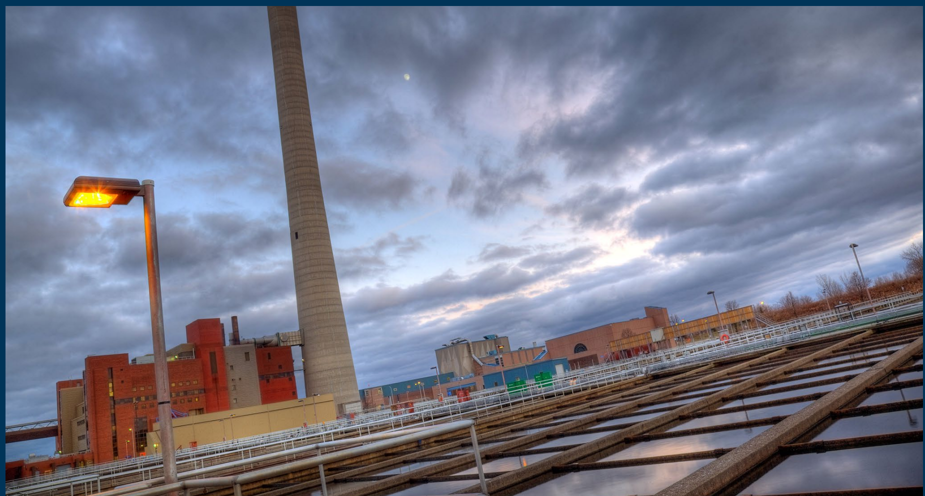
- Establishing a general picture of an aquatic environment, including information about the state of water quality and any changes over time.
- Allowing for an initial snapshot, which can inform whether future action, intervention or policy development are required.
- Acting as an important tool for assessing the extent to which water bodies have been impacted by human activity.
- Reducing costs associated with analysis by focusing on a smaller number of samples.[1]

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:

1. Determine the presence of a specific indicator, or combination of indicators;
2. Prepare samples for analysis of specific pharmaceutical compounds only when the indicator is found.[2]

Characteristics of an Ideal Indicator[3]

Absent from Source Water	Is the indicator found naturally in source water in any reliable concentration? 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).
Persistent	An indicator that is persistent (i.e., one that does not easily degrade) in the aquatic environment can ensure that it will be detected during sampling and analysis.
Found in High Enough Concentration	The indicator should be found consistently in high enough concentrations to be analytically detectable.[4]
Affordable and Easy to Test For	An ideal indicator is one that requires less complex analytical methods or is one that citizen scientists could test for on their own (e.g., E. coli).
Toxicity	Consideration for toxicity is also a factor in determining an effective indicator of pharmaceutical presence in the Great Lakes. Substances that are known to be toxic may need to be prioritized over those with no known impacts to human or ecosystem health.
Does not Partition to Sediment or is not Taken up by Biota	Indicators should remain measurable in surface water samples and not bind to sediment or biota.
Existing Data	Existing data related to an indicator would allow for a baseline against which to measure and better understand any subsequent data.

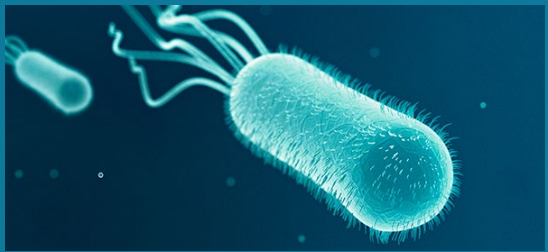


Wastewater treatment plants (WWTPs) are the primary pathway for human pharmaceutical compounds to enter the aquatic environment. Treatment processes may remove some, but WWTPs were not designed to remove most synthetic compounds, including some pharmaceuticals.[5] An ideal indicator would point to the presence of wastewater.

Potential Indicators of Pharmaceutical Presence in the Great Lakes

For the most part, the indicators listed below point to the presence of wastewater based on the idea that some pharmaceuticals may also be present in wastewater effluent. Indicators that meet several, or all, of the criteria in the preceding table are listed here.[6]

E. Coli



E. coli is often used as an indicator for potential sewage or fecal contamination in a waterbody. It is found in greater concentrations than other pathogenic organisms while also being substantially more economical to test for.

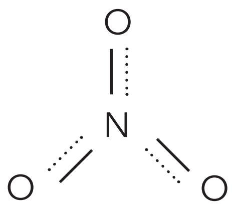
Caffeine

Caffeine has been shown to be an effective indicator of human excretion given its prevalence in society. It is often found in sufficiently detectable concentrations in water bodies, even when diluted.

Sucralose and other Artificial Sweeteners

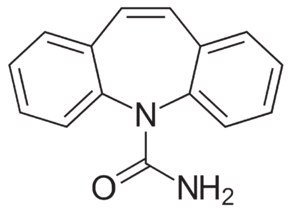
Artificial sugar substitutes or sweeteners have also been identified as potential indicators of wastewater, primarily due to the fact that they are excreted mostly unchanged and degradation at WWTPs has been shown to be minimal.

Nitrate



Nitrate is a potential biomarker for wastewater effluent. Human waste contains ammonium which can contribute to adverse environmental effects. Some WWTPs conduct a nitrification process whereby bacteria oxidize the ammonia to form nitrate, which is less harmful. Nitrate is an effective indicator only where nitrification processes occur.

Carbamazepine



Carbamazepine is a commonly prescribed anti-convulsant that has been used in numerous studies as an indicator of wastewater based on its persistence in the environment. It is frequently detected in WWTPs and does not easily degrade.[7]

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 concentration and distribution at a given sample location.

Developing a Target List of Pharmaceutical Compounds

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 endocrine disrupting compounds 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.[8]

A number of general approaches 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 include:

- Public Interest[9]
- Pharmaceutical family
- Degree of metabolises
- Concentration
- Cost and ease of analysis

Method

1. Samples were collected from three of Swim Drink Fish's citizen science monitoring hubs.

Sites were selected based on three main criteria: (1) The site is currently unmonitored by local health departments, (2) The site has potential for contamination, and (3) The site is used regularly by members of the community:

Swim Drink Fish is a Canadian charity working for a swimmable, drinkable, fishable future. Swim Drink Fish inspires people to know and safeguard their local waters using citizen science and communications technology.

Toronto Hub

Monitors three sites located in Toronto's inner harbour, historically a heavily developed area that has transformed into a residential neighbourhood and recreational destination.

Non-point sources of pollution from urbanization, including stormwater runoff, are a main contributor to poor water quality. Discharges from WWTPs and industrial sources can also contribute to the degradation of water quality at this site.

Zhiibaahaasing First Nation Hub

Monitors recreational waters at three sites located on Manitoulin Island and Cockburn Island. In contrast to the Toronto hub, these sites are not located in close proximity to point source pollution and are surrounded by undisturbed forest. It was not anticipated that any significant pharmaceutical contamination would be found at this site given its location rather, it could be used to compare with the other two sites.

The beach where samples were collected is used by local community members for recreational and ceremonial purposes and community events.

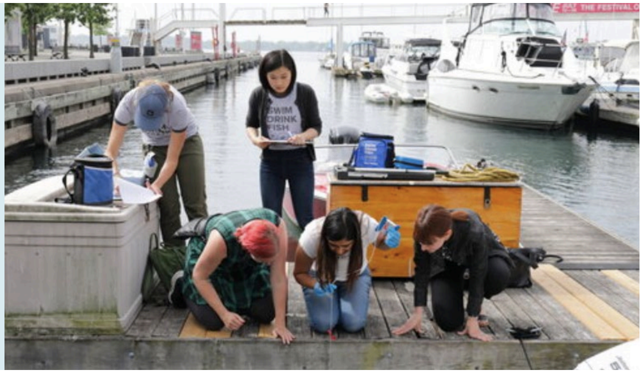
Lake Erie – Niagara Hub

Monitors three sites along the north shore of Lake Erie. Samples were collected from Sugarloaf Marina in Port Colbourne, which is situated in a parkland area and is a popular destination for fishing, boating, and wakeboarding.

Contamination of microorganisms from the local geese population and sewage discharge from boats and nearby drainage ditches contribute to water quality concerns at this site.

2. Quality Assurance & Quality Control.

Swim Drink Fish maintains rigorous quality assurance/quality control (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.



3. 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.

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).

4. Analysis Using an Indicator for Pharmaceutical Presence

Sucralose has been shown to be poorly removed in WWTPs and persistent in the aquatic environment. Caffeine is removed more efficiently (>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. Based on these characteristics, sucralose and caffeine were chosen as indicators of contamination of wastewater origin in the Great Lakes for the purposes of this study. Swim Drink Fish collects *E. coli* data and total coliform numbers from the sampling locations chosen for the study as part of their existing programming. This data was compared to the findings from the analysis of the indicator samples. A combination of indicators was chosen to control for issues unique to each individual indicator. Using a suite of indicators can control for variations in concentrations and distribution at a given sample location.

Preliminary Findings

The analysis of the samples collected by Swim Drink Fish was conducted by Dr. Chris Metcalfe and his research group at Trent University based on their extensive expertise.

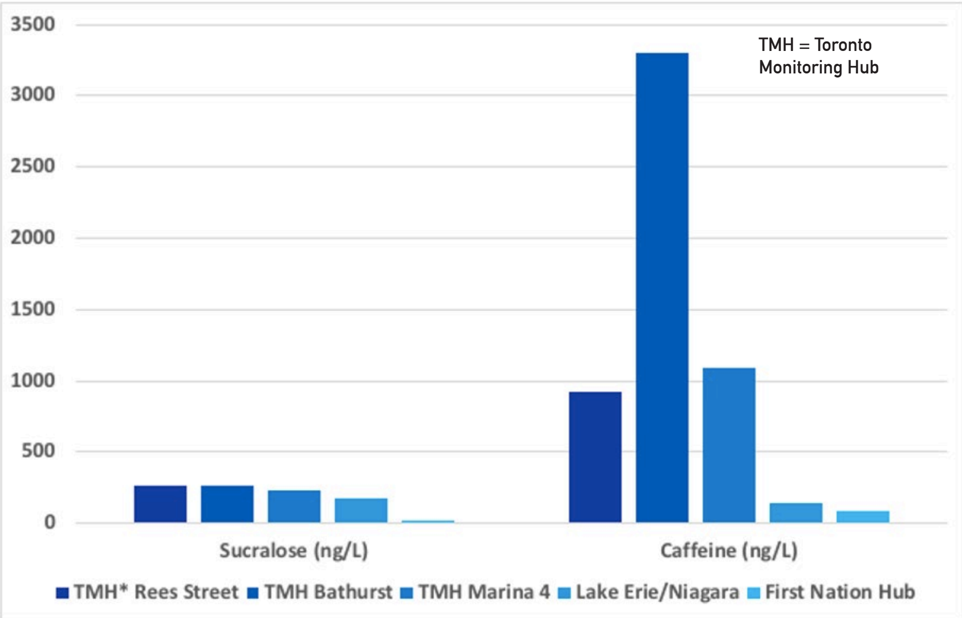


Figure 1. Sucrose and caffeine concentration by sample site

Site/Monitoring Hub	Total Coliform (MPN)	*E. coli* (MPN)
Toronto Rees Street	546	29
Toronto Bathurst Street	21496	2129
Toronto Marina 4	5172	496
Lake Erie/Niagara	2420	35
First Nation	50	1

Table 1. Total coliform and E. coli concentration by sample site

The data on concentrations of sucralose and caffeine (ng/L) (Figure 1) 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.

Comparing the chemical (Figure 1) and biological data (Table 1) for the samples that were analyzed, there is a good correlation between the levels of the indicator compounds and the counts of E. coli. However, the relationship between chemical and biological indicators was less clear for the total coliform data.

- This is likely due to the fact that coliform bacteria can come from a variety of sources, including domestic animals and wildlife, whereas E. coli bacteria 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.

Conclusion

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 is 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.

Images

Lake Ontario Shoreline by Joe deSousa, Flickr

Swim Drink Fish Toronto Hub staff and citizen scientist sampling in the Toronto Harbour by Swim Drink Fish

Kilbear Provincial Park by Fraser Mummery, Flickr

Ashbridges Bay Wastewater Treatment Plant Exterior by Timothy Neesam, Flickr

References

1 Pollution Probe (2019). *Reducing the Impact of Pharmaceuticals in the Great Lakes*. Retrieved from: http://www.pollutionprobe.org/wp-content/uploads/112354-1-PP-PharmGreatLakesReport.pdf

2 Ibid.

3 Ibid.

4 Van Stempvoort, D.R. et al. (2013). An artificial sweetener and pharmaceutical compounds as co-tracers of urban wastewater in groundwater. *Science of the Total Environment*. 461–462, 348-359.

5 Arvai, A. et al. (2014). Protecting our Great Lakes: assessing the effectiveness of wastewater treatments for the removal of chemicals of emerging concern. *Water Quality Research Journal*, 49, 23–31. Retrieved from: https://iwaponline.com/wqrj/article/49/1/23/21557/Protecting-our-Great-Lakes-assessing-the and Kleywegt, S., Payne, M., Ng, F. & Fletcher, T. (2019). Environmental loadings of Active Pharmaceutical Ingredients from manufacturing facilities in Canada. *Sci Total Environ*, 646, 257-264.

6 Pollution Probe (2019). *Reducing the Impact of Pharmaceuticals in the Great Lakes*. Retrieved from: http://www.pollutionprobe.org/wp-content/uploads/112354-1-PP-PharmGreatLakesReport.pdf

7 Uslu, M. O.; Jasim, S.; Arvai, A.; Bewtra, J.; Biswas, N. (2013). A Survey of Occurrence and Risk Assessment of Pharmaceutical Substances in the Great Lakes Basin. *Ozone: Science & Engineering*, 35 (4), 249–262. https://doi.org/10.1080/01919512.2013.793595

8 Pollution Probe (2019). *Reducing the Impact of Pharmaceuticals in the Great Lakes*. Retrieved from: http://www.pollutionprobe.org/wp-content/uploads/112354-1-PP-PharmGreatLakesReport.pdf

9 Ibid.