



## Tracking Fish Contamination in the Great Lakes

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Pollution has become the hallmark of an industrialized society, despite the best efforts of governments and environmental groups. Even when the addition of new pollutants has been reduced or eliminated, chemicals tend to stick around for a while, and in many cases, they tend to accumulate in the animals that humans value for recreational fishing and hunting.

The directive of the Great Lakes Fish Monitoring Surveillance Program (GLFMSP) is to look for toxic chemicals in top predator fish of the Great Lakes, such as lake trout and walleye, which play an important role in Lake Erie's multi-million-dollar sport fishing industry. These chemicals tend to bioaccumulate up the food chain and are generally most concentrated in large predator fish, so sampling those fish yearly is the most effective way to detect potentially problematic chemicals that may be affecting the Great Lakes.

The program's scientists monitor changes in the accumulation of toxic chemicals in the food web as a result of changing regulations on, for example, cancer-causing compounds like polychlorinated biphenyls (PCBs). PCB concentrations have been decreasing since the late 1970s, when their production was banned in the United States. The monitoring program has mapped this trend and laid the groundwork for many other toxin monitoring programs in the U.S.

In 2010, the researchers were also tasked with looking for new toxic chemicals that aren't on the radar of many monitoring agencies yet, in addition to known contaminants like PCBs. But how do they identify

contaminants when they're not even sure the chemicals are there yet?

It's an analytical chemistry problem at which the scientists have come to excel. The fish they've received from their partners at the New York State Department of Environmental Conservation and the Ohio Department of Natural Resources are homogenized (basically ground up to a paté-like consistency) before the researchers remove all biological molecules from the mix. Biological macromolecules like proteins, lipids and other organic components are much larger than the molecules that make up most contaminants, so techniques based on size and molecular weight allow for an initial separation of potentially interesting puzzle pieces.



The remaining molecules – thousands of them, even after that first separation process – are then run through a gas chromatograph (GC) connected to a mass spectrometer (MS). The GC separates the mixture into individual molecules and the MS breaks down those individual molecules into smaller components, which provide a "fingerprint" to help identify the molecule. Once the scientists have a better idea of what's out there in the lake, it's much easier to determine which chemicals' concentrations are changing and which are most likely to cause problems in the future.

With the help of CSMI, the researchers were also able to incorporate a third type of assessment into the monitoring program: a more intensive look at the lake of interest during a given year. This facet of the program gives them a chance to study the food web in more detail, to see which types of source contribute the contaminants they find in top predator fish and how they're distributed in the environment.

That means extensive sampling of water, sediment, plankton, benthic invertebrates like mussels and worms, as well as small forage fish and top predator fish that are collected by state partners. The samples are analyzed for things like stable isotopes of carbon and nitrogen (additional neutrons in these atoms make them heavier) that can be traced from one step of the food chain to another, and for particular fatty acids that accumulate in fish based on what they've been eating (much like eggs are enriched with omega-3 fatty acids by feeding chickens flax seed high in omega-3s).

From that information, scientists can learn about how both energy and contamination flows through the food web, who eats what, and how the introduction of invasive species can alter that flow because it adds or eliminates a step in a particular food chain.

In Lake Erie, findings often show a difference between the eastern and western basin, both in contamination levels – eastern basin fish often have higher levels of mercury than fish from the western basin – and in the isotope data that indicates energy flow. One possible explanation for both is that the eastern basin has a greater diversity of prey fish, which makes for more steps in the food chain and more opportunities for toxins to bioaccumulate upwards towards those top predator fishes like walleye and lake trout. Water and the contaminants contained in it also spend less time

in the western basin, so fewer organisms are likely to be exposed to pollutants before they move into the eastern basin, where they can stick around for a while. Having all of that information, instead of just data on top predator fishes, helps the monitoring program put results into context – a change in the fish one year may just be an interesting blip on the radar, but when combined with the CSMI data collected every five years may provide important insight into the changing health of an ecosystem.

Of course, comparing data over time requires comparable samples, otherwise observed changes may well be due to something out of the researchers' control. For the open lake sampling of walleye and lake trout, one of the important variables to keep track of is the age of the sampled fish, as older fish have had more time to accumulate toxins and are naturally going to show higher concentrations when analyzed. Historically, scientists used the size of the fish as a way to approximate its age, but recently, they found that sampled fish were actually older than expected, despite being within a size range that would indicate younger fish.

To adjust for this discrepancy, the program modified how the samples are processed before arriving at the lab. Instead of randomly combining their 50 fish into ten processed samples, they first remove the maxillary bone from the upper jaw of each fish and cut it in half, allowing them to "read" the bone just like one would read rings on a tree. It's a relatively simple addition to their protocol that makes it easier to combine fish that are closest in age for each of the ten composite samples, which in turn helps them more accurately assess to health of a lake's fish population and overall ecosystem.