



LORENA RIOS-MENDOZA

Chemist Dr. Lorena Rios Mendoza is searching for answers to one of the biggest questions surrounding plastic pollution—the role it plays conveying toxins into the food web. From her lab at University of Wisconsin Superior, she works to identify the chemicals that build up on the surface of microplastics and pinpoint how photo-degradation may alter the way they react to one another.

How did you become interested in microplastic pollution in the Great Lakes?

Overall, my research interests are mainly associated with environmental chemistry pollution, both in marine and freshwater systems. So I actually started my work with plastics in California working with samples from the North Pacific Gyre, which is also known as the Eastern Garbage Patch. In 2010, I moved to Superior, WI and started surveying the beaches and shorelines around Lake Superior in Wisconsin and Minnesota. Then, in 2012, I participated in the first plastic debris collection in the Great Lakes in collaboration with 5 Gyres Institute and State University of New York at Fredonia. The most impactful result from that effort, in my opinion, was the microscopic sizes of the plastic particles we found, particularly in Lake Erie.

What was your role in that study, and what did you find?

My main interest with these plastic samples was the study of persistent organic pollutants (POPs) adsorbed on the surface of the microplastic particles. My lab analyzed the samples from Lake Erie for PCBs [polychlorinated biphenyls], organochlorine pesticides, and PAHs [polycyclic aromatic hydrocarbons]. I found that the concentration of the sum of PAHs was about 800 nanograms of toxic compounds per each gram of microplastics. The PCB concentration was about 400 nanograms per gram. That is higher than has been reported in the Atlantic Ocean, but it is important to remember that the ocean is much larger and deeper. Lake Erie is actually the shallowest of the Great Lakes, so there is not as much dilution happening. I am still working with the identification and concentrations of the pesticides.

Can you tell us more about these POPs and why they are a concern?

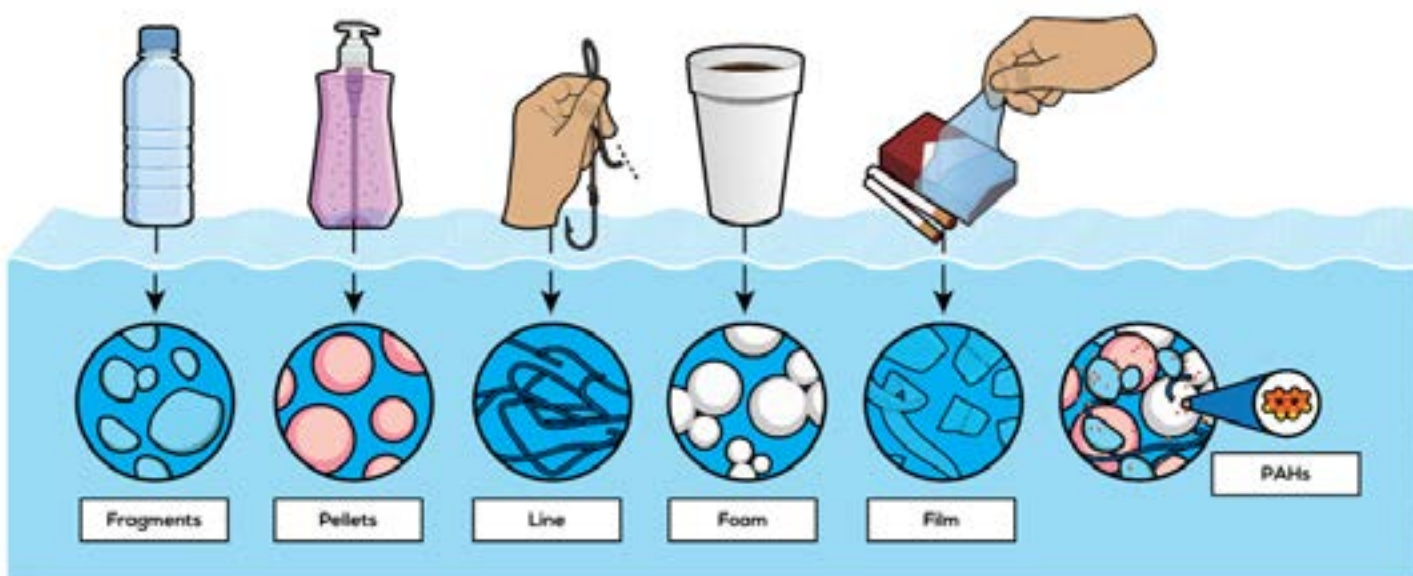
Broadly speaking, POPs include a range of very stable synthetic compounds. They are typically lipid soluble and hydrophobic, so they can easily accumulate in the fatty tissues of organisms. This makes it easy for them to bioaccumulate in the food chain. They are considered among the most persistent anthropogenic organic compounds introduced into the environment. Some of them are highly toxic and have a wide range of chronic effects, including endocrine disruption, mutagenicity, and carcinogenicity.

PCBs are a common industrial POP. Before they were banned in 1975, PCBs were used in transformers, capacitors, and hydraulic fluids and as plasticizers in plastics and paints. The current sources of PCBs are destruction and disposal of old electrical equipment and emissions from incineration and power generation.

Organochlorine pesticides, such as DDT and its metabolites, are synthetic compounds that are chemically stable and hydrophobic. These pesticides were used heavily in agriculture and for fly and mosquito control in cities. Their use was restricted in 1970s, and they are now banned for general use in the U.S. and Canada.

PAHs are actually not considered POPs because they are not man-made compounds. Instead, PAHs are primarily a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil, gas, garbage, or organic substances like tobacco or charbroiled meat. However, a few are synthesized for use in medicines, dyes, plastics, and pesticides. Many PAHs are toxic and tend to bioaccumulate in aquatic organisms. Eighteen of these PAH compounds are

A LIFE AQUATIC PHOTODEGRADATION AND ADSORPTION



PCBs, PAHs, and other hydrophobic toxins bind to the surface of plastics broken down into microscopic pieces by waves and sunlight.

classified by the U.S. EPA as priority pollutants based on their toxicity to humans.

Why do these POPs and other chemicals accumulate on plastics?

POPs are hydrophobic molecules, which means that they don't like water and quickly attach to other substances—natural or man-made. They attach to the plastic particles particularly easily because plastics are organic molecules and have a high carbon content.

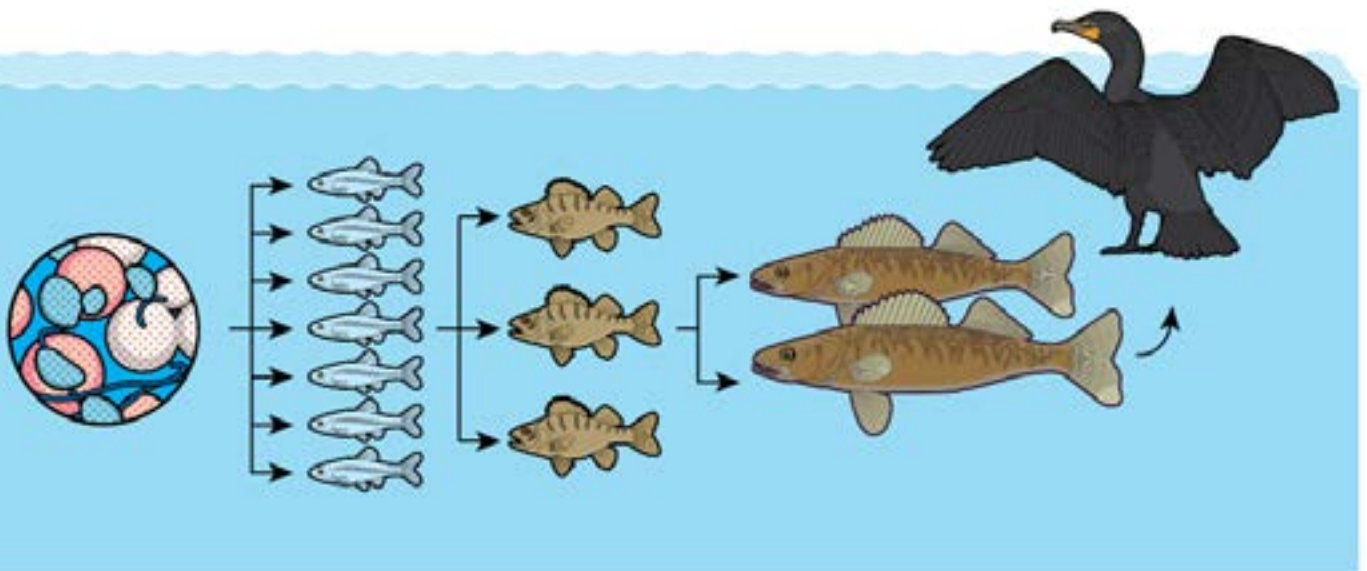
Do the concentrations of POPs tell us anything about how old the plastic is?

Unfortunately no. It just tells us about the exposure of these compounds. The concentration of POPs lining a piece of plastic does tell us whether that plastic has been photodegraded, however. Degradation is directly proportional with the concentration of toxic compounds. The higher the chemical concentration, the more ultra-violet degradation has taken place.

Your early ocean research found higher POP concentrations in some locations than others. Is there a pattern there?

No, but the higher concentrations of these toxic compounds correspond to the highest concentration of plastic debris. This is mainly because of the higher probability of finding more plastic particles closest to the accumulation center of the north Pacific Ocean gyre. PCB and PAH concentrations were related to atmospheric sources, and the pesticides were degradation products coming from agricultural use on land. Plastic particles in the ocean travel long distances from their original source, so it is difficult, if not impossible, to determine the sources of plastic debris and the toxic compounds adsorbed onto their surfaces.

CHEMICALS IN THE FOOD WEB BIOACCUMULATION



Aquatic animals that inadvertently consume microplastics also ingest the toxins bound to them. The chemicals build up in organ tissues and are passed further up the food chain when those animals become meals themselves.

Is there a concern that those chemicals are leaching out?

That is a concern because we know that plastic debris can adsorb and desorb toxic chemicals. Actually, we did some tests on water from plastic bottles, and we detected phthalates. These are plasticizers added to plastic products to make them soft. The chemicals are considered endocrine disrupters.

You were also involved with Great Lakes sampling projects in the summers of 2013 and 2014. Were the results of that work different from what you found in the 2012 samples?

The results are still to come on the 2014 work. Melissa Duhaime and her students from University of Michigan collected samples from Lake Erie, Lake St. Claire, and the Detroit and Cuyahoga rivers. I've already extracted the POPs and done analysis on the GCMS [gas chromatography-mass spectrometry]. GCMS is one of the best analytical instruments to analyze POPs. Gas chromatography can separate the compounds in the mixture, and the mass spec can do a positive identification of each compound in it. I am currently working with the calculations of their concentrations.

In 2013, I also collected samples from lakes Michigan and Huron and from Lake St. Claire in collaboration with Pangea Exploration aboard the *Sea Dragon* vessel. Unfortunately, the microplastics we collected were so small that I could not do any chemical analysis. But, again, I was astonished with the number and sizes found in the water samples. And these samples revealed plastic fibers, which is a pretty new area of analysis in the oceans and Great Lakes.

You have been involved with other projects that have identified microfibers. Can you tell us more about those?

In the summer of 2013, we worked with the Great Lakes Indian Fish and Wildlife Commission to collect microplastic samples. In addition to finding high numbers of fragments and microbeads, we also discovered lots of small plastic fibers. We've already analyzed more than 1,000 fish stomachs, and we've found fibers in 25-35 percent of the samples. I know colleagues from the University of Michigan have been analyzing fish stomachs too, and they have found fibers as well.

When we first started finding these fibers in fish stomachs, I decided to check the lab for possible contamination from our clothes, hoods, and other lab sources. This is one of the first things you do when you find higher concentrations than you expect—take a closer look at your sampling and testing methods to make sure you haven't inadvertently introduced more of the chemical or material you are testing for. When we did this, we discovered that there were plastic fibers everywhere. So we had to implement some quality control checks by doing things like wearing cotton lab coats when we opened up the fish and examined the stomachs.

Could we also be breathing in these microfibers?

There is a big possibility that this is happening. U.S. EPA has said that if the fibers are long enough—bigger than 10 micrometers—our lungs can expel them. So particles bigger than this are not regulated. Our preliminary results from 77 samples of fibers in the air show a size range of 6-7,550 micrometers and an average of 300 micrometers. So most were much larger than the 10 micrometers.

Another interesting pattern we saw was that the most common fiber color was blue, although we did also find white, red, and brown fibers.

You and other researchers have recommended that plastics be classified as hazardous waste. Why?

If we want to protect humans and wildlife, plastic debris should be classified as a hazardous pollutant. The production of plastic items includes the addition of flame retardants, nonylphenols, phthalates, anti-bacterials, and other compounds that help make the plastic items more resistant and durable. Many of these additives are toxic to organisms, and they can leach out after the plastics are discarded. Another important aspect is their enormous capacity to adsorb persistent organic compounds and heavy metals from the water.

It's important to remember that plastics are non-biodegradable. They are photodegradable, meaning all the plastic particles that enter the environment are just fragmented into smaller and smaller particles that fish and other wildlife can confuse for food. The sizes can get down to microlevels—small enough to be eaten by microplankton. When organisms ingest these particles, it can cause physical damage. This damage has been documented, and research on the direct and indirect effects of ingestion and POP adsorption is increasing.

Recent actions at the local and international level to address this emerging pollution problem highlights its importance. For example, in Wisconsin and Minnesota, legislators recently passed a bill banning microplastics in cosmetic products. European Union countries are also being required by the European Parliament to take steps to limit the use of lightweight plastic bags.

Isn't it sufficient to recycle plastic products when we are done with them?

We do need to reuse the plastic items that we already have at home as much as possible and use plastics responsibly—just when they are necessary. Researchers are also working on new technologies to return plastic products to oil again, but that work is in early phases. But reuse and recycling may not do enough to help us limit plastic debris.

What are the next steps in your research? What questions are you looking to answer?

I'd like to know more about how the dominant chemicals in plastic—polyethylene and polypropylene—adsorb POPs. Do they adsorb them at the same rate? And how does photodegradation affect the adsorption of these compounds? I'm also interested in how molecular weight can change with photodegradation and in bioplastics, which are derived from natural resources. I would like to know what byproducts occur when bioplastics degrade.

I have been working with undergraduate and middle school students to show them that chemistry can help us solve environmental problems and find solutions. Overall, I emphasize that we need young people to study chemistry and come up with new ideas to solve our present problems.

I frequently invite undergraduate students to come to my lab and talk with students that are already part of my research team. While they're there, I explain what we are doing and the chemistry behind each step of the chemical analysis. I ask them to suggest topics, questions, or ideas for research that they would like to develop. I also remind them that internships are a great way to learn and gain experience in commercial labs or industry.

You've mentored many students over the years. What advice do you give high school or undergraduate students considering a career in science?

Most of my undergraduate research students attend conferences while working with me. Several have gone onto graduate school, while others are now working in labs. They have told me how thankful they are for the opportunity to learn first-hand in a lab and gain the skills they need to help them feel confident in their work now.