How Does Mercury Get into Fish?

A WHOI scientist tackles the mercury cycle

Most everyone has heard by now that we should limit our consumption of certain fish because they accumulate high levels of toxic mercury. But nobody—not even scientists—knows how that toxic mercury gets into the ocean in the first place.

Here's the mystery: Most of the mercury that enters the ocean from sources on land or air is just the element mercury, a form that poses little danger because living things can get rid of it quickly. The kind of mercury that accumulates to toxic levels in fish is called monomethylmercury, or simply methylmercury, because it has a methyl group, CH_3, attached to the mercury atom.

The problem is that we don't know where methylmercury comes from. Not nearly enough of it enters the ocean to account for the amounts we find in fish. Somewhere, somehow, something in the ocean itself is converting relatively harmless mercury into the much more dangerous methylated form.

That's the puzzle Carl Lamborg, a biogeochemist at Woods Hole Oceanographic Institution (WHOI), is trying to solve. Lamborg got hooked on mercury as a master's degree student at the University of Michigan and then pursued his Ph.D. degree at the University of Connecticut with Bill Fitzgerald, one of the foremost experts on mercury in the ocean. Fitzgerald, who was the third student to graduate from the MIT/WHOI Joint Program and the first in chemical oceanography, devoted his career to mercury after seeing photographs in the 1970s of people poisoned by methylmercury dumped from a chemical plant into Minamata Bay, Japan. In one famous picture, originally published in *Life* magazine, a woman cradles her teenage daughter, who had been deformed by prenatal exposure to methylmercury. (The photographer, W. Eugene Smith, later withdrew this and other searing photos from public display at the request of the subjects and their families.)

Minamata Bay was one of the worst cases ever of methylmercury poisoning, but sadly, it was not unique.

"There was a lot of mercury dumped back in the day when folks were not sensitive to what was going on," said Lamborg. "The buzzword that people use for that is 'legacy mercury.' Coastal sediments tend to be really elevated in mercury that was dumped there 30, 40, 50, 100 years ago as a result of some industry. And that might still be in play, because there's worms and shellfish and things living in the mud, and they're always sort of stirring it up."

The big question

At Minamata Bay, the source of the methylmercury was clear. We also know the source of most of the elemental mercury in the ocean. Some comes from natural sources such as volcanic eruptions. About two-thirds comes from human activities. The biggest single source is the burning of fossil fuels, especially coal, which releases 160 tons of mercury a year into the air in the United States alone. From there, rainfall washes the mercury into the ocean.

We also discharge mercury-laden industrial effluents directly into rivers or the ocean. This is not just a scourge of modern life; Lamborg said a mercury mine in Slovenia has been dumping its wastewater into the Gulf of Trieste since Roman times.

But even large discharges such as that wouldn't pose a major threat to human health if the mercury were not converted to methylmercury, which diffuses into phytoplankton and then passes up the food chain in ever-accumulating quantities. Large predator fish such as tuna, for example, contain about 100 million times as much methylmercury as the water around them.

"Something like a shellfish, which is a filter feeder, that's very close to the bottom of the food chain, is generally not as high in methylmercury as something like a tuna or a mackerel or swordfish or striped bass—all the fish, actually, that we really like to eat," Lamborg said.

So where and how does the conversion of mercury to methylmercury take place? Lamborg said the process is probably biotic —done by living things. Beyond that, our knowledge is sketchy. We know that fish don't methylate mercury, and phytoplankton and zooplankton probably don't either.

However, some species of bacteria do produce methylmercury, as a byproduct of their respiration. This has been observed in bacteria living in seafloor sediments along coasts and on continental shelves. It might also occur in deep-ocean sediments, but no one has looked there yet.

In lieu of oxygen

A few centimeters down into the sediment, there's so little oxygen that microbes living there must use anaerobic respiration. One common means is a chemical reaction called sulfate reduction, in which they use sulfate (SO_4^{-2}) in surrounding seawater for respiration and excrete sulfide (S^{-2}) into the water as a waste product. If seawater in porous spaces within the sediment also contains a lot of mercury, the stage is set for the production of methylmercury.

That's because sulfide helps mercury get into cells. Most forms of mercury can't pass through a cell membrane because they are bound to large molecules or because they carry a charge. But when positively charged mercury ions (Hg^{+2}), the most common form of mercury in the ocean, meet negatively charged sulfide, the two bond. The resulting compound, HgS, is small and uncharged—just right to be able to pass into microbial cells.

Once inside, the mercury gets methylated. Scientists haven't yet discovered the chemical reactions involved in this conversion, but soon after HgS enters bacterial cells, the cells release methylmercury. Some of the methylmercury diffuses out of the sediments into the open water. There, it is taken up by phytoplankton to begin its journey up the food chain.

But how much of the methylmercury made by bacteria in sediments finds its way into the water above? Is that the only source of the methylmercury that turns fish toxic?

Lamborg is skeptical of that idea. He thinks there has to be another source of methylmercury adding to the oceanic total.

"What I've been chewing on is the possibility that a lot of methylmercury is actually coming from within the water itself," he said.

Tyler Goepfert, WHOI

WHOI scientist Carl Lamborg (right) helps deploy sediment traps to catch particles drifting down through the water. Lamborg later analyzed the captured material for the presence of mercury.

A mercury-rich layer of the ocean

Lamborg has found that there's a layer of water in the ocean, between 100 and 400 meters thick, that contains high levels of methylmercury. It occurs at midwater depths—from 100 to 1,000 meters below the surface, depending on the specific location in the ocean. He's seen the high methylmercury layer in the relatively isolated Black Sea, the open ocean near the western coast of Africa, and the waters near Bermuda. What's especially intriguing is that peak levels of methylmercury occur at depths where the amount of oxygen in the water drops sharply.

"This drop in oxygen is caused by all the plankton that are growing closer to the surface," he said. "When they die, or when they're eaten by other plankton, those dead cells or the poops of the other plankton sink down and rot. That rotting consumes oxygen."

It's possible that, like bacteria in sediments, any bacteria living in low-oxygen areas of the ocean also rely on sulfate for respiration and could be generating methylmercury in midwater low-oxygen zones.

Lamborg is pursuing that hypothesis, but first he tested another possibility: whether methylmercury in low-oxygen zones came from higher up in the water. Scientists studying phytoplankton have found that 20 to 40 percent of the mercury inside them is methylated. Lamborg wondered: As the phytoplankton or zooplankton that eat them die, sink, and get degraded, does any of that methylmercury get released back into the water and accumulate in midwater depths?

Catch a falling particle

To find out, Lamborg collected tiny particles that were sinking through the water and tested them for the presence of mercury and methylmercury. He caught the particles in sediment traps—polycarbonate tubes about 3 inches across and 2 feet long, that were suspended from a cable at 60 meters, 150 meters, and 500 meters below the surface.

Before deploying the traps, Lamborg filled each one with particle-free seawater. Then he added extra-salty brine, which is denser than seawater. It forms a distinct layer at the bottom of the tube, which trapped the particles.

He left the traps in place for four days, then hauled them up and ran the brine through flat, round filters slightly bigger than a quarter. There's no doubt when a trap is successful at gathering material, said Lamborg; the fine brown residue left on the filters has an air of rotting fish. "They smell pretty bad," he said. "It's not like poop, but it's definitely 'eww!' "

Lamborg collected sinking particles at several locations during a research cruise across the Atlantic from Natal, Brazil, to the coast of Namibia in 2007, and brought them back to his lab at WHOI for analysis.

Panning for mercury

To find out how much methylmercury fell into a trap, Lamborg converted all the mercury on the filter to elemental mercury. He then passed the sample over grains of sand that had been coated with gold. Only mercury stuck to the gold; other chemicals didn't. Then Lamborg heated the gold-mercury amalgam to vaporize the mercury.

"This is the same process that people doing gold mining used to use," Lamborg said. "You know panning for gold? You would squeeze some mercury in your pan and sluice it around, dump off the sediment, and then you would heat it up and burn off the mercury and leave the gold behind."

In Lamborg's version of the process, the gaseous mercury is the valuable product. It gets drawn into wiry Teflon tubes that take it to an atomic fluorescence spectrometer that determines how much mercury was in the sample. On a nearby table, mercury from a parallel sample is run through a gas chromatograph to determine what proportion of it was methylated.

"These are some of the most challenging samples to analyze that I've come across, because the samples are very small," Lamborg said. "There's very little material. The techniques we're using can detect methylmercury in the femtomolar range." One femtomole of methylmercury would be 0.000000000000215 grams per liter of seawater.

The samples contained elemental mercury, but so far, no samples from any of the three depths have shown substantial levels of methylmercury. It was present, but at lower levels than are found in phytoplankton—far too little to explain the levels of methylmercury seen in the midwater zone.

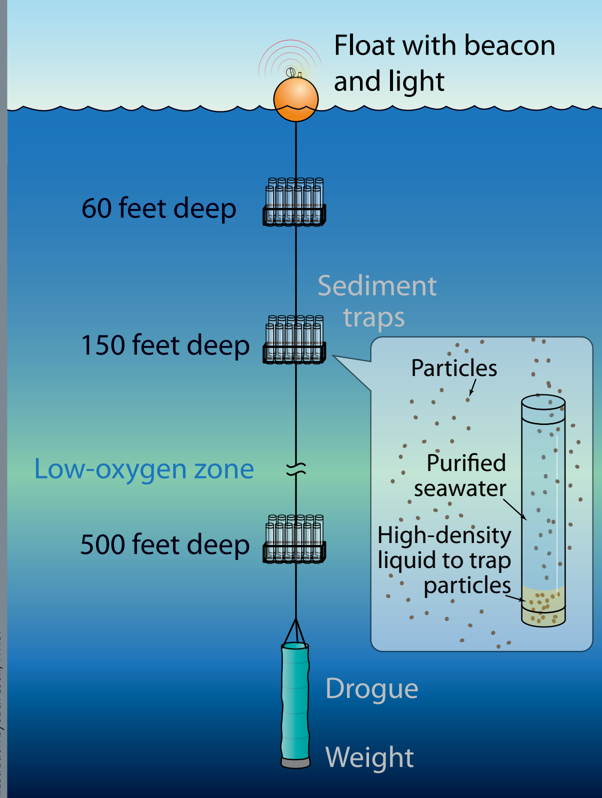

Illustration by Jack Cook, WHOI

Levels of toxic methylmercury spike higher in mid-water depths of the ocean where oxygen levels are lower. To find out why, WHOI scientist Carl Lamborg suspended tube-shaped sediment traps to capture sinking particles above, in, and below the low-oxygen zone.

If organisms in surface waters are not the source of methylmercury in the midwater layer, where does that methylmercury come from? Lamborg said it could be made by bacteria in sediments on the continental shelf and released into the water. Currents could sweep these methylmercury-rich waters off the shelves and into the open ocean at depths about the same as the midwater layer. Other researchers are exploring that possibility.

Lamborg, though, favors the notion that methylmercury found in midwaters is being made there, just as it is in sediments, by microbes that are reducing sulfate. He recently started working with biogeochemist Tracy Mincer to identify the genes that bacteria use to methylate mercury. Their research could identify similar genes to look for in microbes in low-oxygen midwater zones.

And he's still interested in those sinking particles and what role they might play. Methylating microbes can't do their thing unless they have mercury to work with, and Lamborg thinks the particles offer an efficient shuttle service for mercury that enters surface layers of the ocean from the atmosphere, groundwater, or rivers.

"Mercury entering the ocean today is reaching that low-oxygen zone somehow," he said. "These particles are still playing an important role in moving mercury from a part of the ocean where methylation doesn't occur to a part of the ocean where it does."

—*Cherie Winner*

WHY THE HATTER WENT MAD

Mercury poisoning affects many parts of the body, notably the brain, kidneys, lungs, and skin. Symptoms include red cheeks, fingers, and toes; bleeding from the mouth and ears; rapid heartbeat and high blood pressure; intense sweating; loss of hair, teeth, and nails; blindness and loss of hearing; impaired memory; lack of coordination; disturbed speech patterns; and birth defects.

The most dangerous form of mercury is monomethylmercury, which living things such as fish and humans can't easily get rid of, so it accumulates to high, toxic levels in their tissues. However, other forms of mercury also can cause problems, if exposure is prolonged or frequent.

When Lewis Carroll created the Mad Hatter in *Alice in Wonderland*, he drew on a common occurrence of his day, the mid-1800s. Hatmakers often did act loopy, trembling and sputtering and being excessively shy one moment and highly irritable the next. But Carroll might not have known that their "madness" was caused by exposure to mercury, which was part of the mixture they used to felt the furs their hats were made of.

"Mad hatter's syndrome" still occurs today, often in modelmakers or other hobbyists who heat up metals that contain mercury, often in poorly ventilated areas. Fortunately, this form of mercury does not accumulate in the body; if exposure ends before the nervous system suffers permanent damage, the symptoms it causes are completely reversible. Had the Mad Hatter stopped making felt hats, he might eventually have regained his senses—but lost his place in literature.

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