Mercury in Bay Area fish a legacy of California mining

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Mercury contamination, a worldwide environmental problem, has been called "public enemy No. 1" in California's San Francisco Bay.

Mercury mining and gold recovery in the mid-1800s to late 1900s, combined with present day oil refineries, chemical manufacturing plants and wastewater treatment plants have contributed enough mercury to threaten wildlife and prompt a fish consumption advisory in the Bay Area. With so many possible sources of contamination, environmental scientists and regulatory agencies would like to know which specific sources contribute most to harmful levels of mercury in the aquatic food web.

Teasing out that information was not possible in the past, but with the use of a mercury "fingerprinting" technique, researchers from the University of Michigan, the University of California, Davis, and the San Francisco Estuary Institute, have identified the main sources of mercury in bay floor sediments and shown that small fish near the base of the food web acquire their mercury from those sediments.

"Without a clear answer to what was responsible for mercury in fish in San Francisco Bay, we needed a way to trace its origins," said Joel Blum, who is the John D. MacArthur Professor of Geological Sciences and a professor of ecology at U-M. "This is the first study to track mercury directly from source to sediment to food web."

While this study draws conclusions only for San Francisco Bay, the

fingerprinting technique can be broadly applied, said graduate student Gretchen Gehrke, the paper's lead author. "Mercury contamination is a problem in areas all over the world, and most of those places have multiple possible mercury sources. There's a lot of interest in figuring out which sources are contributing the mercury that most readily gets into the food web and creates environmental and health risks."

The findings appear in two companion papers, one in the Feb. 1 issue of the journal *Geochemica et Cosmochimica Acta* and the other published online Jan. 21 in *Environmental Science & Technology*.

Mercury is a naturally occurring element, but some 2,000 tons of it enter the global environment each year from human-generated sources. Deposited onto land or into water, mercury is picked up by some types of microorganisms, which convert a small portion of it to methylmercury, a highly toxic form that builds up in fish and the animals---and people---that eat them.

The primary way people in the United States are exposed to methylmercury is by eating fish and shellfish. Health effects include damage to the central nervous system, heart and immune system. The developing brains of young and unborn children are especially vulnerable.

In San Francisco Bay, Gehrke, Blum and coworkers suspected small fish such as silverside and topsmelt were acquiring mercury from sediments on the bay floor and then passing it along to larger fish and other fish-eating animals, but it also was possible that mercury from the atmosphere or localized industrial sources was ending up in the fish.

To resolve the question, the research team compared chemical "fingerprints" of mercury in sediments and in fish, much as a detective compares a suspect's fingerprints to those found at a crime scene. The

fingerprints result from a natural phenomenon called isotopic fractionation, in which different isotopes of mercury react to form new compounds at slightly different rates. In one type of isotopic fractionation, mass-dependent fractionation (MDF), the different rates depend on the masses of the isotopes. In mass-independent fractionation (MIF), the behavior of the isotopes depends not on their absolute masses but on whether their masses are odd or even.

The team sampled sediment at 20 sites in the bay and fish at 26 sites. "We used young fish, less than four months old, that have a very small home habitat," said Gehrke. "Because they're restricted to one location, rather than migrating around the bay, any mercury they have is most likely present in that location."

Looking at MDF fingerprints in sediments, the researchers saw that the values were distributed along a gradient from north to south. MDF fingerprints in the fish from different locations mirrored the pattern found in the sediments, suggesting the fish were acquiring mercury directly from the sediments.

Where did the mercury in the sediments come from?

"Our analysis of the sediments showed that it's most likely coming from either two or three dominant sources," Gehrke said. "There's one distinct fingerprint coming from historic mercury mines to the south and a different fingerprint coming from historic gold mines to the north. We see intermediate values in sediments in the middle of the bay, which could represent either mixing of the two or possibly a separate third source, so we can't say for sure whether it's two or three sources. But the fact that we see at least two separate fingerprints and a strong spatial gradient instead of a hodgepodge of many different fingerprints tells us that the mercury is coming from a small number of large sources rather than a lot of localized sources like a power plant here, a refinery there."

The researchers hope the results will help local agencies decide where to focus their efforts to protect wildlife from exposure to mercury.

More information: *Environmental Science & Technology* --- pubs.acs.org/journal/esthag
Geochemica et Cosmochimica Acta -- www.sciencedirect.com/science/journal/00167037

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