# Big wildfires mobilize mercury. What are the risks to surface water?

**Megan Sever,** *Science Writer*

The landscape was still smoldering in October 2020 as Jeff Prancevic and Charles Alpers, part of a multidisciplinary team of US Geological Survey (USGS) researchers, drove into the scorched hills above Lake Berryessa in California. Masked and traveling separately because of the pandemic, the team met up at EcoCamp Berryessa, a site that had recently hosted firefighters as they battled the LNU Lightning Complex fires in Northern California. The USGS team was there to sample soils and ash amidst the devastation.

On hands and knees—and sometimes bellies—the team measured water infiltration rates in burned and unburned soils and collected samples of charred and unburned vegetation and related ash deposits. The goal, says Prancevic, a geomorphologist at USGS, is to better understand the risks of post-wildfire runoff, a project "kicked into high gear last year because of all the fires." One of those risks is an infamous toxin: mercury.

Although previous observations have shown an increase in a troublesome form of mercury, known as methylmercury, downstream of recent fires, researchers didn't know why or how much. More thorough study has offered up some rather nuanced answers: Mercury concentrations in stream sediments are often lower because so much mercury is volatilized, but total amounts of mercury downstream are often higher because of increased sedimentation. The details, however, remain as hazy as the smoldering forest. Any uptick in methylmercury is worrisome; bioaccumulation could affect multiple species in a given ecosystem, including humans via the consumption of fish.

Thus far, there's no indication that mercury mobilized by big fires poses a major threat to people's water supplies. But researchers are far from understanding all the downstream implications, for both human and ecological health.

## Mercury Cycling

Spurred in part by climate change, conditions across the West are warmer and drier than they used to be. The 2020 wildfire season broke records in California, Colorado, Oregon, and Washington; fires are bigger, hotter, and more frequent (see News Feature: Foreseeing Fires, https://www.pnas.org/content/117/36/21834).

**USGS scientists Jeff Prancevic and Corina Cerovski-Darriau measure the infiltration capacity of burnt soils in October 2020, just after the LNU Lightning Complex fire scorched Pope Canyon, which drains into Lake Berryessa in California. Image credit: US Geological Survey/Jonathan Stock.**

And decades of forestry policies have increased the amount of highly flammable material strewn across forest floors.

That material contains, among other things, a lot of mercury. In fact, soils, leaf litter, and debris contain up to 91% of the toxic element sequestered in US forests (1). Wildfires mobilize that mercury when they sweep through a forest. Some studies based on lab and airborne measurements after wildfires have shown that fire can volatilize as much as 99% of the mercury held in vegetation and soils (2, 3). But researchers are still trying to trace mercury's path and ultimate destination.

When shrubs, trees, and soils burn, mercury becomes airborne either as a gas or by attaching to particulate matter—thus dictating how far the toxin travels, says Jackson Webster, an environmental engineer at California State University, Chico. Gaseous mercury can remain aloft for years in the atmosphere and move around the planet, whereas mercury-bearing particulates—often produced in fires—fall to Earth's surface closer to their source, increasing the chances that


Published June 30, 2021.

**The 2012 High Park fire burned the Cache La Poudre River watershed in northern Colorado. Rain later washed a lot of sediment through the watershed, which includes drinking water sources for the cities of Fort Collins and Greeley. Image credit: Jackson Webster.**

mercury affects local watersheds. There, microbes can transform the mercury into methylmercury, a potent neurotoxin that then enters the food chain. Parsing the percentage of gaseous versus particulate mercury released is therefore a key to determining how mercury will affect watersheds and ecosystems (4).

## Mercury Release

The type of foliage, landscape hydrology, location of fire within a watershed, soil properties, historical mercury levels (e.g., owing to natural sources and mining), and the individual fire's own properties, such as burn severity and intensity, all have an impact on mercury release. (Burn intensity refers to temperature; burn severity includes both temperature and duration.)

When it comes to the impact of burn severity, recent fires in the Cache Creek watershed in California and in Shenandoah National Park in Virginia present an intriguing point of comparison. The California fires were high-severity and the Shenandoah fire low-severity; the mercury measurements showed clear differences.

Shortly after the 2015 Rocky and Jerusalem fires burned the Cache Creek watershed, which already had high mercury levels attributable to past mining, Alpers, a research chemist at USGS, and his colleagues scooped up samples of fire-affected soils ranging in color from black to red, as well as unaffected brown soils. His team also collected sediments suspended in streams to measure mercury levels. The team had a rare opportunity to compare conditions over time: The USGS had been collecting samples in the watershed before the fires as part of a long-term mercury monitoring effort.

The first rainstorms in December 2015 and early January 2016 were small, causing little runoff; mercury levels in the stream's suspended sediments decreased significantly, Alpers says. It appears that the extreme heat from the high-severity fires had led to loads of mercury being volatilized and carried away through the atmosphere, leaving less in soils and streams.

That's the opposite of what Ami Riscassi, a hydrologist at the University of Virginia in Charlottesville, and her colleagues found after the lower-severity Shenandoah fire: Their measurements suggested that stream-suspended sediments carried an order of magnitude higher amount of particulate-bound mercury than before the fires, she says. The findings suggest that the heat of the fire mobilized mercury in the soils, but most was not volatilized, as Riscassi and her team reported in a 2017 study in *Environmental Science: Processes & Impacts* (1).

Thus, it seems that, at least based on studies of these three fires, higher-severity fires may volatilize more mercury. One might expect, then, to see higher mercury levels in streams after lower-severity fires and lower mercury levels after higher-severity fires.

But the weather can scramble those expectations. When heavy rainfall follows a high-severity fire, sediment and ash are washed into streams as the system is "flushed out," explains Martin Tsz-Ki Tsui, a biogeochemist at the

University of North Carolina Greensboro who analyzed and led the interpretation of some of the Cache Creek samples (5). Those samples, collected from streams and analyzed shortly after a big storm, showed a huge increase in mercury fluxes—up to 1,000 times higher than normal, Tsui says. The high-severity fires had left less mercury in the watershed's soils, but the huge increase in post-storm sediment runoff increased the total amount of mercury in streams.

## Feeling the Heat

Exactly how mercury is activated in soils is unclear, but some studies pinpoint heat. When fires singe soils, mercury is released. To determine how much is volatilized and carried away in smoke versus mobilized locally—where it can then enter surface water—Webster and his colleagues heated soil samples in a furnace at different temperatures. They then measured the amount of mercury remaining. They found that mercury release starts at about 150 degrees Celsius. By 250 to 300 degrees Celsius, the mercury is completely volatilized; none remains in the soil.

The lab results match what Webster has found in the field in hundreds of 10-cm-deep soil cores he collected from regions in Colorado that burned from 1934 through 2013 and recent massive infernos in California, including the Carr, Mendocino Complex, and Camp fires in 2018 and the North Complex fire in 2020—four of the worst on record. Wildfires volatilize mercury in the topmost, hottest soil and duff layers, leaving little to no mercury behind. Then, mercury levels incrementally rise with soil depth, corresponding to lower temperatures. Lower-severity fires that burn cooler will mobilize but not volatilize mercury in the soils, leaving more available to be transported by runoff during storms.

Plus, drier soils—those baked by drought, for example—transfer heat faster. They also result in more complete combustion and more gaseous mercury emissions, thus leading to lower local mercury levels in ash and lower amounts of subsequent runoff into aquatic systems, Tsui notes.

## Combustion Considerations

Combustion levels, related to fire severity, seem to affect mercury release as well. In any fire, not everything will be completely combusted. Incomplete combustion creates black ash or charred wood; complete combustion generally results in piles of white ash, with little organic material remaining.

Some research suggests that black ash may retain higher mercury levels than white ash because of the black carbon content (5). But both have far higher levels of recalcitrant mercury (i.e., mercury that isn't easily converted into methylmercury) than unburned or even charred vegetation, Tsui says.

Using gas chromatography-mass spectrometry and acid digestion, Tsui and his team, including Alex Chow of Clemson University, SC, found a link between recalcitrant mercury and black carbon levels in black ash from the Rocky fire and the Wragg fire, which burned nearby in 2015 as well.

The findings, Tsui says, suggest that the organic matter in black carbon creates chemical reactions with mercury that make it nonreactive (5). Thus, although mercury-laden sediments may increase in streams after fires, leading to higher mercury levels in streams, it doesn't look like methylmercury levels are likely to increase significantly, Tsui says. The black carbon caused by fires seems to reduce mercury's reactivity and hence its transformation into methylmercury.

How the organic matter left in black ash creates these chemical reactions and affects mercury release and transformation "is a really good and important question," Tsui says. "The short answer is that we don't know."

One possible key player is sulfur (6). Mercury binds strongly to sulfur in organic matter, Webster explains, allowing mercury to accumulate in soils and surface water. When heated, the sulfur in soil organic matter changes its form, as Webster and his adviser Joseph Ryan at the University of Colorado Boulder found during Webster's dissertation work (7). Although much of the sulfur is converted to sulfate, which doesn't bind with mercury, some sulfur is converted to a form that does, Webster says, thus allowing more mercury binding than before the soils were heated. "This is surprising," he says, noting that the researchers thought soil would lose the strong binding ability because of conversion to sulfate. "I think these results help explain some of the environmental behavior of mercury following fire, but not all," adds Webster.

Taken together, the results suggest that even in the case of high-severity fires, methylmercury usually doesn't form in large amounts, except when rains trigger extreme runoff—that is, when the increased organic matter and mercury interact to create methylmercury.

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**—Charles Alpers**

## Historical Contradictions

But the case is far from solved. Indeed, these latest results actually contradict some other studies from the last 20 years suggesting that mercury methylation downstream of wildfires *does* increase. Results from the Everglades to New Mexico revealed large increases in methylmercury in stream sediments after wildfires, creating "methylation hot spots," Webster says. Alpers has also measured increased methylmercury concentrations in streams after fires in California.

The discrepancy, Webster speculates, may be attributable to complex interactions among microbes and the nutrients and organic carbon in the watershed, interactions that are fundamentally changed by fires. For example, burning not only converts a lot of sulfur into sulfate but also liberates sulfate from soil. "Sulfate-reducing bacteria are the main mercury methylators," he explains. So in an area where you

have the right geochemical conditions, and sulfate-reducing bacteria, adding sulfate to the system will cause increased methylation.

How might researchers hope to disentangle this complex web of findings to offer counsel to researchers and policymakers? Alpers and Webster are working on a model with colleagues at the federal Bureau of Reclamation to help land and water resource managers predict whether methylmercury mercury levels in streams will increase or decrease in response to wildfire (8, 9). A well-informed model could help "test hypotheses regarding biogeochemical factors that influence mercury methylation," says Alpers. And that could allow scientists to someday forecast methylmercury levels in surface water.

Of course, models alone can't solve the myriad mysteries surrounding mercury release after wildfires and mercury methylation. "A well-designed data collection effort is needed," Alpers says, "perhaps a combination of field and laboratory observations."

To that end, Prancevic and his USGS team have been back out in the field this winter and spring, again on hands, knees, and bellies, collecting samples of soils and stream sediments and analyzing them, trying to figure out how fires affect the infiltration and runoff of water and sediments, and how long it takes hydrologic systems to recover. As fires increase in frequency and severity, solving such mysteries could have big consequences for ecosystems—and people.


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