Mercury in the St. Louis River Watershed

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Introduction

The St. Louis River in Minnesota is not among America's best-known waterways. It is not widely reflected in folklore or song, like "Shenandoah" or "Old Man River." Yet it is the largest U.S. river flowing into the largest of the Great Lakes, with its watershed covering more than 3,500 square miles. It meanders through an area described by American Rivers as "a land of timber wolves, moose … sturgeon, walleye, northern pike, bass, bluegill ... and 163 species of breeding birds, savoring lush wetlands and wild rice lakes" that long ago led the Anishinaabe to settle along its banks.

Today, Anishinaabe still live, and thrive, within the river's watershed, and at its mouth at Lake Superior, the city of Duluth has emerged as the busiest United States port on the Great Lakes. Along with commerce, it is an area of unparalleled natural beauty, consistently named by Outside Magazine one of the top ten outdoors destinations in the country.

Yet the St. Louis has also been labeled one of America's Most Endangered Rivers, making its way on the ignominious list in 2015, 40 years after being designated an Area of Concern by the U.S. Environmental Protection Agency. The designations followed more than a century of pollution from mining, coal-burning power plants and other heavy industrial activity. One of those pollutants is mercury.

Mercury

Why the focus on mercury? Though toxic, mercury has been used for millennia. Mercury thermometers are probably the best known. It is also a staple in dentistry as an amalgam to fill teeth, in fluorescent lights and batteries. While many of these uses are being curtailed, there are trade-offs, says Environmental Health Sciences Professor Niladri Basu of McGill University: "Mercury is found in a number of items that have great benefit for society and for health, (yet) it causes challenges for us." (Basu, N., personal interview, 09 Jan., 2019).

It also can make us crazy: Mercury was long used in hat-making to process beaver or rabbit fur into felt. The resultant mercury poisoning led to the phrase "mad as a hatter."

Some commercial uses persist, notably in gold mining, in which mercury's ability to amalgamate with other metals is exploited. Though no longer practiced in U.S. mines, that process continues in other countries, including Canada and in South America, where mercury is used to separate gold from rock, then burnt off and sent into the atmosphere. It then can travel thousands of miles, including to Minnesota and other far northern hemispheric regions.

The primary anthropogenic (or human-caused) source in the United States is emissions from coal-fired power plants. (EPA, 2015.) Mercury associates strongly with carbon, including coal, and rapidly volatilizes during combustion and is carried up smokestacks into the atmosphere. Other leading contributors in the U.S. are oil combustion, mining (including taconite), metal smelting, cement production, chemical manufacturing, and waste disposal. Globally, the leading source is artisanal and small-scale gold mining, followed by coal combustion, mining and processing of non-ferrous metals, and cement production — all anthropogenic sources.

EPA-mandated standards targeting mercury released by coal-fired power plants, as well as a reduction in the use of mercury in many products and processes, have been successful in reducing mercury emissions in the US, and particularly in Minnesota. While these regulations have been rolled back by the current administration in Washington, emissions are expected to continue falling (though not as quickly) as a result of reduced dependence on coal.

However, researchers are finding that even with reductions in mercury deposition, there is still excessive mercury in the tissues of fish in the St. Louis River. This is caused primarily by the mining activities that release sulfates, compounds that help liberate legacy mercury stored in wetland sediments.

Sulfate's role in methylmercury production and bioavailability

According to the Centers for Disease Control, the vast majority of human exposure to mercury occurs from *methylmercury* (MeHg), a neurotoxic form created by sulfur-metabolizing bacteria. These bacteria thrive in oxygen-free sediment layers in bogs and wetlands, with adequate levels of their fuel — sulfate. It is the presence of methylmercury in the St. Louis River watershed (SLRW) that is of particular local concern. And sulfate, which has been added to the SLRW environment as a result of mining, boosts levels of methylmercury.

Mining operations — both taconite and sulfur-ore mining — disgorge sulfur compounds from the earth and expose them to conditions that create sulfate. In the past, the compounds leached directly into the watershed; more modern operations seek to sequester sulfur, with varying levels of success. Many environmental groups question whether even the most effective operations can assure sequestration for decades or centuries, when the companies themselves may no longer exist.

Once bacteria produce methylmercury, it is readily ingested by small, filter-feeding organisms, which absorb mercury at rates greater than they get rid of it. This process is called *bioaccumulation*. These organisms are then eaten in large quantities by larger invertebrates and fish, which are themselves ingested by larger fish, birds, reptiles and mammals. At each stage in this food chain, mercury levels in the animal tissues increase by a factor of five to ten in the predator over the prey. This phenomenon is called *biomagnification*. As a result, mercury toxicity is of greatest concern in animals highest in the food chain, especially the longest-lived animals. Among freshwater fish, these include smallmouth bass, pike, muskellunge and walleye — the latter one of the most popular species in Minnesota. In birds, herons, eagles, osprey and loons are of concern. Finally, humans — especially populations that consume the most fish and shellfish — are at risk.

Environmental Effects of Mercury Contamination

Methylmercury adversely affects wildlife and ecosystems health in ways that are only gradually becoming clear. (Evers, D. et al, 2018) Studies have shown that birds (ducks, loons, egrets and others) lay fewer eggs in the presence of even low concentrations of mercury in their tissues, and exhibit impaired ability to nest and care for their young. (Whitney, MC and Cristol, DA, 2018 and Evers, D. et al. 2011). Fish reproductive success also declines, along with the ability to form schools and evade predators. (Crump, KL and Trudeau, VL, 2009).

McGill University's Basu describes more specific physical effects, such as, "some subtle changes, for example, in animals' IQ, or motor function, or even ability to reproduce. These things have profound consequences when you look at [an affected] species, its ability to survive in a rapidly changing and hostile environment, its overall ability to compete, to find food, and so forth." (Basu, N., personal interview, 09 Jan. 2019).

Researchers have also found that insect-eating songbirds ingest dragonflies and other insects that accumulated methylmercury while developing as aquatic larvae. (Jackson, AK et al, 2014). Many birds eat sufficient quantities of these prey and accumulate high levels of mercury, lowering their reproductive success and their ability to migrate successfully (Seewagen, CL et al, 2019).

Other emerging research indicates that microplastics — small beads of plastic derived from the general plastic wastestream, now ubiquitous in aquatic systems — can absorb and/or bind to methylmercury, concentrating the toxin in a form that makes it more bioavailable to organisms (Barboza, LGA et al, 2018). Since microplastics and other nanoparticles comprise a new and rapidly growing category of environmental contaminants, the work highlights a potential new route via which methylmercury can be maintained and concentrated in food webs.

It should be noted that even relatively small health effects in wildlife can be significant when added to other threats to wildlife populations, such as habitat loss, climate change, invasive organisms, emerging pathogens and other environmental threats.

Public Health Effects

While elemental mercury used in small scale mining is a major health concern in developing countries, it is methylmercury that causes most toxicity in people living in developed countries, including the U.S. (Driscoll, C. et al. 2013.) Methylmercury poisoning is also known as Minamata Disease, named for the methylmercury deaths of 900 people in Minamata, Japan, first documented in the 1950s after tons of mercury compounds were dumped into the bay next to the fishing town. Along with the fatalities, the contamination severely impacted children born to mothers with high levels of exposure, because the placenta removes mercury from the mother's tissue and concentrates it in the blood of the fetus. The result was infants born with brain lesions and symptoms similar to cerebral palsy.

In another mass disaster in 1971-72, wheat treated with organomercury as a fungicide was imported to Iraq from Mexico, designated for planting. The product was labeled with warnings in Spanish. Some was diverted to a farmer who used it to make bread, however, causing more than 450 deaths and 6,000 to fall ill.

Researchers have found that moderate levels of methylmercury exposure, far lower than those seen in Minamata, also lead to medical issues, including childhood deficits in memory, attention, language skills, and visual-motor skills, and both cardiovascular and immune function disease in adults.

Health effects related to low-level methylmercury exposure are less clear cut. A synthesis of studies conducted on low-level exposure indicated that some research showed that low-level exposure in infants led to reduced birth weight, neurocognitive deficits, and reduced motor function in young children. But other studies have not shown any correlation. (Karagas, M. et al. 2012) In adults, some studies have shown neurocognitive deficits associated with low-level mercury exposure, while others have not. Similarly, heart disease is also evident in some studies, while inconclusive in others, and similar mixed results are seen for increased blood pressure and immunologic dysfunction. (Ibid.) Overall, there are few studies of low-level exposure, and not enough to draw clear conclusions.

A study of newborns on the North Shore of Lake Superior in Minnesota unveiled some disturbing indicators of the presence of mercury even in those who did not ingest it themselves. Between 2008 to 2010, 1,465 blood samples were examined from newborns in the area — 1,130 from Minnesota, 200 from Michigan and 140 from Wisconsin (McCann, P, 2011).

Researchers found roughly 8 percent of newborns enrolled in the study had levels of mercury in their blood sufficient to impair health and developmental outcomes. The study detected no differences for exposure of urban versus rural residences, although the results did suggest a pattern of seasonal exposure with the highest concentration of blood mercury levels detected in summer births. This seasonal pattern suggested that consumption of local fish was the primary exposure pathway.

One approach by the Minnesota Department of Health to lessen exposure to mercury is to focus on fish consumption by women of childbearing age, pregnant and breastfeeding women, and young children, and to recommend eating fish lower in mercury, and limiting consumption to two or three servings per week.

How well is that message communicated? The state's Health Department publishes the above guidelines and other advisory material in a variety of media, some targeted to particular audiences. The effectiveness of that messaging is less clear; Youtube videos in Hmong warning that community of the hazards of some consumption have been produced, but with very little traffic (the most-watched of them tallied 83 views more than a year after it was first posted in 2017; others counted less than half as many views during a similar time period).

A Duluth News Tribune article published days before the flood of June 2012 told of as many as 100 Hmong anglers fishing at the Fond du Lac Hydro Station near Jay Cooke State Park, one of the highest-risks areas of the river, as confirmed by the University of Minnesota Duluth's Nathan Johnson. The article indicated the fishing — including catfish and walleye — was for food, not just sport, quoting a DNR officer as saying, "they find it, they catch it, they eat it." Significantly, the article also said most of those on the then-annual outing were from the Twin Cities, suggesting they may not have been familiar with St. Louis River contamination.

Cher Vang, a Hmong elder from Duluth who was among the group that day, says the activity continues, though by smaller groups and less organized since the flood. (Vang, C., personal interview, February 2019).

Nancy Schuldt, the water protection coordinator for the Fond du Lac Band of Lake Superior Chippewa, says the advisories from the Health Department working with the band has been more effective among tribal members, for whom there are both very strong cultural and health reasons for eating fish.

"It's about messaging. The last thing we want to do is stop people from eating fish," she says. "It all started with a band member coming into my office in 1999 with a great, big northern pike that he caught through the ice. He said, 'I want to know if it's safe for me to feed this to my family.'" (Schuldt, N., personal interview, 31 Jan. 2019).

How Much Mercury?

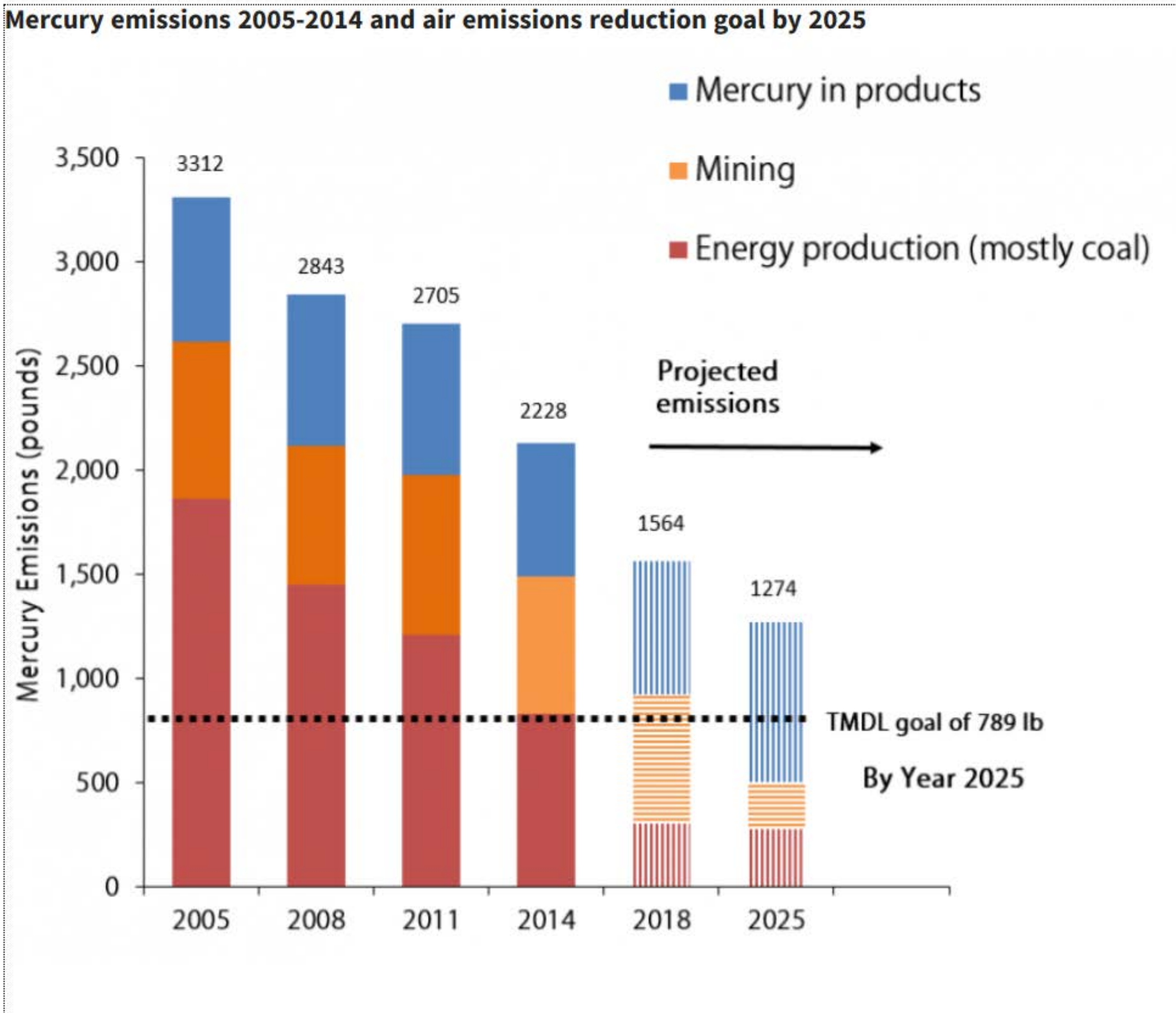
What has Minnesota been doing to control mercury in its waters, especially in the St. Louis River? The first step is figuring out how much there is.

Minnesota has a well-known success story to tell. While mercury is being spread in the atmosphere from multiple sources outside the state, Minnesota has seen dramatic reductions in mercury emissions from inside the state.

In 2008, an EPA analysis of 2001 data showed 56.9 percent of mercury depositions in Minnesota came from within the state, while 40.4 percent could be attributable to sources outside the state, e.g., airborne mercury from as far as thousands of miles away.

More recently, the MPCA has found that annually, greater than 90 percent of mercury depositions originate from out of state. Since 1990, Minnesota has made significant reductions in statewide mercury emissions and is on track toward reaching its mercury reduction goals. In other words, from 1990 to 2016, the amount of mercury emitted in Minnesota that has been deposited back onto Minnesota has dropped by 68 percent.

Since 1990, Minnesota has made significant reductions in statewide mercury emissions and is on track toward reaching its mercury reduction goals. Source: MPCA



Those figures, however, are of current depositions. The state's soil still contains tons of inorganic mercury from legacy emissions such as mining operations and other industrial activities for more than a century. In other words, the problem of primary mercury has been addressed, but methylmercury still persists, as do aquatic impairments due to it.

Sidebar: The Legacy of Mining: Michigan and Minnesota

Lake Superior contains roughly 3 quadrillion gallons of freshwater, or 10 percent of the world's unfrozen fresh water. The lands surrounding it are naturally rich in minerals, including iron, copper, silver and even gold.

One of the best places to understand mining's past is Upper Michigan. At the tip of the Keweenaw Peninsula is Copper Harbor — a name testament of its boom-town origins in the 1840s. Mining there and elsewhere on the U.P. had a 40-year head start on the enterprise in Minnesota, which began with the short-lived Vermilion Lake Gold Rush in 1865. While that quickly fizzled, iron ore was discovered during this time, and was first mined and shipped from Minnesota's Iron Range in 1884.

Charles Kerfoot of the Michigan Technological University in Houghton is well-acquainted with the legacy of Copper Harbor and similar towns in the U.P. where copper and other metals were extracted. He has visited the sites of many current and defunct mining operations and written extensively on mercury deposition globally and around the Lake Superior watershed.

Referring to a state study finding fish in the U.P. with a higher concentration of mercury relative to fish downstate, Kerfoot relates baffled state researchers asking, "What is going on here?"

"We start(ed) to put the pieces together. We found a good source of mercury. There is some contribution from coal-burning power plants around the Lake Superior basin. But historically, a large amount of it is coming from mining, very clearly." (Kerfoot, C., personal interview, 01 Jan. 2019).

Copper mining continued much longer, until 1968, at nearby Torch Lake, also on the Keweenaw Peninsula. With few of the environmental controls in force today, it was designated a Superfund site in 1986 and is evidence of the longevity of mercury contamination, says Kerfoot.

Those legacy issues may be more pronounced in Michigan but are not unique to the state, he says.

"Michigan ends up being a really excellent place to talk about this issue of legacy. We have pretty good ideas of what's the amount of mercury being deposited," he says, adding, "In Northern Wisconsin (and) Minnesota, it's very similar."

Minnesota's Mercury Total Maximum Daily Load initiative

So it is a fact that there is excessive mercury in the fish of the St. Louis River. What can be done about it?

The federal Clean Water Act mandates that states, tribes and territories assess and report to the EPA on the quality of water and designate appropriate uses for water bodies. States must publish a list of impaired waters and are required to consider developing a Total Maximum Daily Load (TMDL) plan for water bodies to reduce pollutants and attain appropriate water quality standards.

The TMDL calculates the maximum amount of a single pollutant that a waterbody may receive in order to meet water quality standards. Minnesota began initiating a statewide TMDL for mercury in 1989, with the EPA granting final approval for it in March 2007. In the course of the process, the state was divided into two regional TMDLs: Northeast and Southwest. The regions are vastly different, with the Southwest informed by inland lakes and the Mississippi River system, and the Northeast encapsulating Lake Superior and the entire St. Louis River watershed.

This initial Northeast TMDL established mercury levels and identified waterbodies that failed to meet water quality standards for their designated uses. In October 2009, the MPCA published its Implementation Plan for Minnesota's Statewide Mercury TMDL. This addressed atmospheric point source emissions of mercury and established a permitting process for all emissions released into the Lake Superior basin.

Howard Markus, a retired MPCA water quality research scientist, recounts it this way: "The St. Louis River and several other rivers and lakes in the St. Louis River Watershed remained on the TMDL List of Impaired Waters after the approval of the Statewide Mercury TMDL because the fish tissue concentrations of mercury in those waters remained above the reduction level calculation that would result in mercury fish tissues meeting state water quality standards."

In 2010, the stage was set for a definitive study of the mercury contamination in the St. Louis River. Another TMDL was planned specifically for the St. Louis River watershed, partnered by the Fond du Lac Band, the EPA, the Wisconsin DNR, and the MPCA. But in early 2013, the MPCA pulled out, citing a lack of sufficient analysis of chemical and biological data to understand the processes of mercury loading, mercury methylation, and bioaccumulation of mercury into fish tissue occurring in the area.

According to the MPCA, "aquatic consumption [fishing] impairments span the entire length of the St. Louis River with mercury posing the biggest concern." Of the 47 streams contributing to the St. Louis River, 24 are considered impaired for mercury, as are 21 of the 24 lakes within the watershed from which data has been collected (the area has more than 350 in total). But despite the severity of the problem, MPCA claimed the TMDL study of the watershed should not proceed, because it relied on flawed models that would produce unreliable results.

Markus, the retired water quality research scientist with the agency, took issue with that contention. “What is ‘flawed’ is the mistaken insistence on combining the TMDL analysis in CWA Section 303[d] with the Implementation planning in CWA Section 303[e],” he said.

The remaining partners in the project, and the federal agencies funding it, expressed surprise, if not dismay, at MPCA’s sudden departure. “We were working for nearly three years on a separate St. Louis River TMDL study (when) MPCA pulled the plug,” recounts FDL Water Resources Coordinator Nancy Schuldt. “Six years later, we’re no closer to a mercury TMDL in the St. Louis River watershed.” (Schuldt, N. Personal interview, 31 Jan. 2019).

Explaining her agency’s position, the MPCA’s Catherine Neuschler said, “I don't know if I want to get back into things that happened 5-plus years ago in the process the EPA was working on. We have been very clear throughout that process that we didn’t think the model was correct.”

The St. Louis River Watershed and Sulfates

Shaped by glaciers, the St. Louis River flows southwest from the edge of the Mesabi Range, before turning south at the confluence of the Swan River. The river continues south to Floodwood, where it takes an easterly flight into Lake Superior.

The river has powered the industry of northeast Minnesota for more than a century at its hydroelectric generation facilities. Its dams utilize the river's natural drop of 1,067 feet over its course to generate a maximum 92.1 megawatts.

These dams include a series of reservoirs, such as at Island Lake and Boulder Lake, to maintain consistent flow. A 2016 study found mercury concentrations in reservoirs to be 1.5 to 2.6 times higher than concentrations in natural lakes. In some reservoirs, even after a century, the level of mercury has yet to return to pre-reservoir levels. The study suggests that reducing the amount of exposed sediment through raised water levels during spring and summer growing seasons can reduce fish methylmercury concentrations.

In 2007, active monitoring of the St. Louis River watershed began, funded by appropriations from Minnesota's Clean Water Legacy Act. This endeavor incorporates three elements: monitoring of fish tissue, monitoring of water columns, and monitoring of biological elements.

These efforts resulted in two reports to Minnesota DNR on sulfate and mercury chemistry within the St. Louis River. In line with historical data, the majority of river sulfate originates in the iron mining district, and upstream sulfate is diluted downstream with waters originating in wetlands. Sulfate from the Iron Range accumulates slowly over the winter months and is flushed downriver during snowmelt and high precipitation events.

Based on samples, water that is not impacted by mining is assumed to contribute 3mg/L sulfate to the St. Louis River, while waters impacted by mining have measured sulfate levels ranging from 17 to 241 mg/L, correlating linearly with water flow. In other words, where the river drains active mining areas, levels of sulfate are 5 to 80 times higher.

The reports also show that methylmercury is generated in the sediments surrounding streams and wetlands throughout the St. Louis River watershed wherever sulfate levels exceed a single milligram per liter. This methylmercury binds to dissolved organic carbon (DOC) and is then transported downriver into oxygenated waters. High concentrations of methylmercury are found along the river following high precipitation events due to the transportation of DOC to oxidizing portions of the watershed. "The strange thing is the fish upstream from the dams are elevated compared to average Minnesota concentrations, and the [Lake Superior] fish are at or near the average of Minnesota fish concentrations," says Nathan Johnson of the University of Minnesota Duluth. "But right in the middle [of the river's route … methylmercury levels] are about double or triple as either up the river or in Lake Superior. (Johnson, N. Personal interview, 22 Jan. 2019).

"Our research is trying to untangle whether there's something unique about the geochemical characteristics of mixing water from the lake and upstream sulfur from the watershed, to make mercury more bioaccumulative," he continues, "or if it has something to do with the food web — in that up in the river, it's all river-food web characteristics [while] out in the lake, it's all [lake]-food web."

One way to evaluate those differences may be through a Total Maximum Daily Load plan for mercury in the St. Louis River watershed, which the MPCA is no longer actively developing.

Chronology of pollution and cleanup efforts in the St. Louis River Watershed

Year	Event
1953	Construction on first taconite mining facility on Minnesota's Iron Range begins at Erie Mining Site in Hoyt Lakes. Mining begins four years later.
1969	US Steel discovers copper-nickel deposit at the present NorthMet site.
1970	Mercury concentration in atmosphere peaks. Employment at Hoyt Lakes site also peaks.
1971	Comprehensive sampling of fish tissue begins along the St. Louis River.
1972	U.S. and Canada sign Great Lakes Water Quality Agreement (GLWQA). U.S. passes Clean Water Act.
1973	Minnesota establishes standards for sulfate in waterbodies.
1989	Portions of St. Louis River listed as an Area of Concern under GLWQA.
1989-1990	Minnesota begins to establish statewide standards for mercury; initiates study on mercury point source emission and sets goals for reductions by 2010 and 2025
2003	PolyMet begins to look at repurposing an idle mine site.
2015	PolyMet Final Environmental Impact Statement approved by MPCA; comment and review process begins
2016	Partridge and Embarrass rivers listed as too impaired for inclusion in statewide TMDL implementation.
2018	MPCA says the science on mercury in the St. Louis River watershed is not clear enough for a separate mercury TMDL for the watershed.
2018	NorthMet project considered fully permitted by MPCA and MN-DNR, leaving Army Corps of Engineers the only federal or state permit remaining.
Present	MPCA says in filings it has no planned completion for a St. Louis River watershed TMDL.

Source: Minnesota Pollution Control Agency

Manoomin

Wild rice, or manoomin, is an Anishinaabe staple described as a critical cultural and natural resource to Minnesota tribes. The grass grows in shallow streams, rivers and lakes.

It is also affected by impaired waters — though sulfates are the primary issue, not mercury. In 1973, Minnesota adopted a 10 mg/L sulfate water quality standard based upon the hypothesis that wild rice is impacted by sulfate via the conversion of sulfate to sulfide in surface waters. In 2011, the Minnesota Legislature directed MPCA to investigate this hypothesis, with a peer-reviewed summary on findings released in 2014. This report was not without conflict, as the FDL Water Resources Coordinator Schuldt said in oral comments to the MPCA Wild Rice Sulfate Standard Peer Review Panel.

"Tribes expressed serious concerns to the MPCA regarding the hydroponics testing from the very beginning because they are very short-term and limited in scope," she testified. "Even when germination occurs and seedlings begin to grow, the hydroponics studies cannot determine whether or not the seedlings will continue to grow for a full season at the exposure concentrations and produce viable seeds for the next season."

Sulfates exert their negative effects on wild rice growth because they are converted into sulfides in the sediment, and sulfides are toxic to wild rice roots. Since this conversion process is slowed or accelerated by other environmental factors, wild rice sites vary in their ability to tolerate high sulfate levels in the water column. However, as a general rule, as sulfate levels increase, so do levels of toxic sulfides, and in some areas, wild rice-inhibiting amounts of sulfide can be seen even well below the current sulfate standard of 10 mg/L.

SLRW Environmental Factors that Affect Methylmercury Production

While efforts to monitor, reduce and eventually eliminate inputs of mercury into the SLRW are important, preventing the enormous amount of inorganic mercury already in sediments there from becoming methylated and entering food chains is of greater, more immediate concern. Much of the mercury deposited in the late 20th century, when mercury pollution was at its peak, now lies in sediment with a high potential for methylation, if conditions favor it.

These conditions include sulfate availability. As noted earlier, bacteria living in oxygen-free sediments in wetlands feed on sulfate, and that process leads to the production of methylmercury. In a 2017 study of microbial sulfate reduction, it was found that providing sites with sulfate levels optimal for bacterial growth led to a nearly six-fold increase in methylmercury levels. This is of particular significance in the SLRW, because both mining and agricultural activities can introduce sulfate into the watershed.

As a result, it is the addition of sulfates, rather than mercury, that is at the core of scientist's concerns. For example, proposed mining developments, even if they emit little in the way of mercury, could lead to significant increases in levels of toxic methylmercury.

Dan Engstrom, of the St. Croix Watershed Research Station, explains that "some of the proposed mining activities would actually discharge directly into the Boundary Waters Canoe Area… and that's an especially large concern, because we're talking about ... waters that are low in sulfate, largely pristine, and adding sulfate to those waters would very likely increase in some way the production of methylmercury, and the levels of mercury we would see in the upper part of the food chain and in game fish." (Engstrom, D. Personal interview. 4 Jan. 2019).

Several researchers interviewed for this report mentioned research conducted in Voyageurs National Park by Victoria Christensen and colleagues, showing that while lakes in the park had similar levels of mercury deposition, concentrations of methylmercury in the fish were 10 times higher in some lakes than others. Sulfate availability may be responsible for the disparity.

While sulfate levels lead to increased methylation, the reduced form of sulfur — sulfide — acts as a brake on mercury methylation. That happens because sulfides bind to mercury and make it unavailable for methylation. Since methylating bacteria excrete sulfide as a waste product, sulfides build up where they are most active, and methylation slows. In addition, in areas with very high sulfate levels, other chemical processes can also convert the sulfate to sulfide. The result can be high sulfur areas where very little methylation is happening, and where reducing overall sulfur can actually lead to more methylmercury production — and greater risks to environmental and human health.

In a study in the Royal Society of Chemistry, Johnson cites this phenomenon, (Johnson, NW et al, 2016) as does Robert Mason (Mason, R. Personal interview. 31 Dec. 2018) reviewing a locale in Florida:

"[There] seems to be [a] sort of hot spot where you get very high methylation. And then deeper down when there's lots of sulfide and sulfate-reducing bacteria are some of the main mercury methylators, and they also produce the sulfide during their processing of organic matter, and so the mercury gets bound," he says. "So you have this area between the oxic and the anoxic environment [with oxygen or lacking it] which is a sort of area where the bacteria are active and the mercury is available. And some studies years ago in the Florida Everglades talked about the Goldilocks [Zone], where everything was just right for methylation."

Other current research into mercury methylation shows that wetland sediments that are glutted with methylation-stifling sulfides can become "re-animated" if they dry out as a result of drought or human activities that lower water levels. Later, when water returns, mercury methylation ramps up vigorously.

Researchers point out that climate change is expected to boost the occurrence of these drought and flooding episodes, leading to increases in methylmercury production, and accompanying rising levels in fish — all without any additional mercury being added to the system.

Perhaps the most contentious proposed change to the SLRW is the PolyMet mine project, to be located in a former steel facility near Hoyt Lakes. Proponents of the project claim the mining operations, thanks to strict containment of both solid and liquid waste and implementation of new wastewater treatment technologies, will have no effect on surrounding wetlands and downstream waters — and will, in fact, reduce both mercury and sulfate levels in the environment. To support these claims, they refer to the findings contained within the 2015 Final Environmental Impact Statement (FEIS) conducted for the project.

PolyMet spokesman Bruce Richardson says the company stands by the FEIS, which states: "sulfate and mercury loadings, two key constituents of concern, are predicted to decrease overall as a result of the NorthMet Project Proposed Action," adding, in a company statement, "it will lead to a net reduction in overall mercury levels to the downstream St. Louis River. This is because we will discharge treated water with a mercury concentration at or below water quality standards for mercury while also cutting off mercury load that is currently contributing from the former iron ore mining operations."

To that, Richardson adds: "There will be a net decrease in mercury. That's something that's never reported." (Richardson, B. Personal interview. 23 Jan. 2019).

Western University of Ontario researcher Brian Branfireun is among those who counter that such certainty is not supported by the FEIS and questions the report's rigor and conclusions. In a 29-page expert opinion provided to the environmental advocacy group WaterLegacy, Branfireun claims that the FEIS relies on extremely optimistic projections regarding discharge from the project's unlined containment areas and for the efficiency of new technology designed to treat the project's wastewater.

In addition, Branfireun claims that the FEIS ignores or minimizes a number of potential environmental threats, including changes in the hydrology of the surrounding wetlands — as a result of water seepage into the mine pit — that could boost production of methylmercury in those surrounding wetlands; creation of a large pit that, once flooded, could become an anoxic environment conducive to mercury methylation (despite claims that the waters are expected to remain oxygenated indefinitely); and a critical lack of uncertainty estimates in the construction of models — an omission that renders the conclusions of those models, in his estimation, of little value.

Current Research Pertaining to SLRW Mercury Concerns

Human activities that are known to boost methylmercury production and are relevant to the St. Louis River watershed include:

- Direct addition of mercury into the environment through extraction of ores;
- Addition of mercury via deposition from mercury-bearing aerosols produced largely from coal-burning power plants;
- Introduction of sulfates resulting from ore extraction into rivers and wetlands;
- Introduction of sulfates from agricultural activities;
- Changes to wetland hydrology that cause chemical changes in sensitive areas and boost methylation;
- Lowering of pH as a result of acid rain and the release of greenhouse gases;
- Changes in lake dynamics resulting from warming temperatures;
- Increased precipitation instability resulting from climate change.

New research and findings are being released at a breakneck pace that will help scientists and policy-makers get a better handle on current and future trends. This research has come about partly as a result of the Minamata Convention, and partly due to new methods and technologies to measure minute levels of compounds, track trace mercury isotopes, conduct rapid genetic analyses, and produce highly sensitive biosensors. While some of this work has served to complicate the methylmercury picture, some is allowing researchers to home in on some of the field's most slippery problems.

For example, in December 2018 researchers published a protocol for creating a fluorescent biosensor to track production of methylmercury in anaerobic conditions, paving the way for studies into how various environmental conditions boost or reduce methylmercury production (Stenzler, BR et al, 2018). This could lead to significant improvements in the predictive power of environmental models.

Other researchers, taking advantage of new, high-speed genetic analysis techniques, are studying the organisms involved in mercury methylation and, specifically, the genes involved in the process (Grégoire, D. 2018). The work could help understand and predict methylation activity.

Still other research teams are teasing out the toxicological effects of mercury at the cellular level, in both humans and wildlife, to understand the full spectrum of the toxin's health effects, and illuminate new paths toward treating them (Unoki, T et al, 2018).

Overall, this mysterious, fussy but incredibly important process may soon be elucidated. That will allow the creation of much stronger models of mercury methylation under different conditions, leading to better predictions and, ultimately, better decisions regarding environmental policies.

Recommendations

Scientists interviewed in this report offered recommendations for steps that can be taken immediately to address methylmercury remediation in the St. Louis River watershed.

Charles Kerfoot, Michigan Technological University:

“The first thing would be [to identify] sources. With the stable isotopes [of mercury now available], you could determine which plant is discharging the most.

“Especially with the St. Louis River, I have not seen a good downwind study of where that mercury is being discharged. … All you have to do is put a series of deposition meters there. We have a whole series [of meters] in Wisconsin and Michigan that have regularly been determining the amount of mercury deposition… The tribes have approached me on this, [asking] can we shift one from Michigan to Minnesota? … I don’t think there’s one downwind from where the taconite plants are.”

Nancy Schuldt, water resources coordinator for the Fond du lac Band of Lake Superior Chippewa:

“The most important thing we can do is restart the St. Louis River TMDL study and recognize that we will need to do all sorts of regulatory and nonregulatory actions to reduce mercury bioaccumulation in the St. Louis River watershed. But we need the framework of an honest and public TMDL study.”

“The second thing [is] the statewide mercury TMDL study. … Each sector had reduction goals and timelines that would get them for 2010 to 2025,” she says, noting that the taconite sector’s report for the TMDL has not yet been made public.

“Enforcement of the existing standards would go a long way.”

One solution to health risks that she unequivocally dismisses is for people to stop eating fish.

“It is entirely unacceptable to tell band members not to eat fish,” citing its nutritional and cultural values.

Nate Johnson, University of Minnesota Duluth:

Johnson says more research is needed. “This might sound self serving, because I work on the research. … A risk is that a management decision will be made one way or the other without a solid understanding of what the basis is for that decision. If a significant regional source is the mines but we keep ignoring the mines, then that would be a bad management decision.”

“We don't know, from a TMDL standpoint, how much the regional inputs influence compared to global sources. There is the question of sulfur in the system and whether the new mines that are proposed now will contribute a drip in the bucket compared to existing and legacy mines.”

Brian Branfireun, Western University, London, Ont.

Branfireun says research should be focused on the many unanswered questions surrounding mercury methylation.

“Our biggest challenge is understanding the controls in the landscape that regulate the formation of methylmercury and then the delivery of that methylmercury to living things,” Branfireun explains. “And that is a particularly challenging problem in a very heterogeneous landscape, and it’s further complicated by the fact that we’re now into a time of changing climate that is affecting hydrology and other ecological processes.”

Regarding the Polymet project, he suggests the implementation of greater rigor in models and predictions of the project’s environmental impacts.

Niladri Basu, McGill University:

“I think it’s important to continue to promote the monitoring activities that occur in both human populations but also environmental settings to have a relatively good strong sense of what the current state is, because with regulatory changes in the U.S., and internationally now, we want to be able to document that these are proper, that they’re doing their job, and if they’re not, are there lessons learned that we can then use to update or modify or tweak or something to improve the situation?”

Conclusion

For all practical purposes, there is universal agreement among scientists and stakeholders that methylmercury levels in fish in the St. Louis River Watershed (SLRW) are too high. If not, there would be no need for advisories by governmental agencies to those who potentially consume the fish.

There are similar concerns about sulfates in the SLRW, and their potential to boost methylmercury production, leading to higher mercury levels in fish, wildlife and ultimately humans. Sulfates also increase levels of sulfide in the environment, which is toxic to wild rice.

If human contributions of mercury and sulfates to the SLRW ended, these problems would be mitigated. However, knowing precisely what changes would occur in which environments under what conditions will require many years of additional research.

Making specific policy decisions about how much methylmercury and sulfate is too much, and who is responsible for taking action, relies on science that, by its very nature, can never be exact. There are too many variables to say the exact result of a single change in water chemistry, and it's not possible to say precisely what percentage of sulfate came from a particular point source. Policymakers therefore may be forced to rely on their judgment regarding when to say "we know enough."

Although this is a report on the state of the science, and much new work has been documented, none of the overarching facts are unknown to interested parties. The issue of mercury in the St. Louis River watershed is not about mercury emissions; Minnesota has done an impressive job reducing them. Rather, it's about methylmercury and mercury in fish. Many studies have been published and many others — some abandoned — are still necessary. The greater hurdle is the will to act on them.

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