WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 1

(MPCA, St. Louis River Watershed Mercury TMDL Project Charter, Fall 2022)

St. Louis River Watershed Mercury TMDL

Project charter – Fall 2022

Overview

This charter defines the goal, objectives, overall approach, and scope for the St. Louis River Watershed Mercury Total Maximum Daily Load (TMDL) study being completed by the Minnesota Pollution Control Agency (MPCA), emphasizing the overall process—including timelines—and the role of external groups.

Project goal

Minnesota's water quality standards call for lakes and streams to support healthy consumption of fish through numeric goals (water quality standards) for levels of mercury in fish tissue and in water. Wisconsin and the Fond du Lac band also have water quality standards for mercury to support these uses, and across the Great Lakes region, there is a shared goal (1.3 ng/L of mercury in the water column) to protect fish-eating wildlife. Mercury pollution prevents some water bodies in Minnesota, Wisconsin, and on the Fond du Lac reservation from meeting these goals.

The goal of the St. Louis River Watershed Mercury TMDL is to determine the mercury reductions needed to meet the water quality standards for mercury and support healthy consumption of fish by people and wildlife. Fishing is important in this watershed for economic and cultural reasons, including the exercise of tribal treaty rights; Fond du Lac's 0.77 ng/L water quality standard protects subsistence fishing. While this charter is for the development of a TMDL to be submitted by the MPCA for Minnesota's waters, a collaborative approach provides benefits for all working to drive mercury and methylmercury reductions. Working in partnership to complete technical TMDL work will support integrated and cohesive pollution reduction goals across the affected waters and ensure the protection of the water quality standards of downstream states and tribes.

Background

The MPCA monitors the state's major rivers and lakes and assesses them for meeting water quality standards. The MPCA places waters that fail to meet water quality standards on the state's impaired waters list. Impaired waters require a TMDL study, which determines how much of a specific pollutant the water body can assimilate and still achieve the water quality standard.

Many waters in Minnesota are impaired by mercury, primarily because high levels of mercury in fish tissue fail to meet the state standard for aquatic consumption. Mercury can be toxic to humans, and the Minnesota water quality standard (0.20 mg mercury/kg fish tissue) is designed to ensure that fish are safe to eat. Because the main source of mercury in fish is global air emissions that affect waters throughout the state, the MPCA developed the <u>Minnesota Statewide Mercury TMDL</u> to address impairments across Minnesota. The U.S. Environmental Protection Agency (EPA) approved this TMDL report in March 2007. The goal of the statewide TMDL is a 93% reduction in mercury air emissions from the baseline year of 1990.

https://www.pca.state.mn.us/sites/default/files/wq-iw10-16a.pdf

The statewide TMDL does not cover mercury impairments in fish where exceptionally high mercury concentrations preclude those waters from meeting the water quality standard even with the 93% reduction in mercury sources. Among the waters needing their own mercury TMDL are a subset of lakes and streams of the St. Louis River Watershed, which includes the Cloquet River Watershed. The State of Wisconsin and the Fond du Lac Band have also identified waters under their jurisdictions that are impaired for aquatic consumption due to mercury.

Mercury emissions in Minnesota, as well as in the U.S. and Canada, have dropped 87% from 1990, which is approaching the 93% reduction goal in the statewide TMDL. Several parties, including the MPCA, other state agencies, and tribal governments, have expressed strong interest in developing a St. Louis River Watershed mercury TMDL now rather than waiting until the statewide TMDL goal is fully achieved.

This TMDL project picks up from a U.S. EPA-led project that concluded in 2013 with a "Road Map for Moving Forward." The Road Map compiled a table of seven potential project paths and tasks.

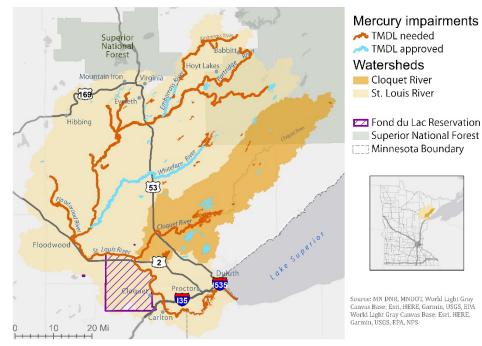


Figure 1. St. Louis River Watershed mercury TMDL project area and impairments.

Objectives

The MPCA is moving forward to develop mercury TMDLs for the remaining impairments in the St. Louis River Watershed. In order to reduce mercury beyond the state goal, Minnesota will need to address the sources of methylmercury in the watershed. There is long-standing interest in understanding and addressing the issue of methylmercury in the St. Louis River Watershed. The states of Minnesota and Wisconsin and the Fond du Lac Band all have strong interests in reducing mercury in the St. Louis River Watershed, and particularly in the St. Louis River itself, which forms the boundary between parts of Minnesota and Wisconsin and parts of Minnesota and the Fond du Lac reservation.

In addition to the project's technical objectives, the project also has objectives for communication, transparency, and partnership.

The MPCA has identified the following **technical goals for the project:**

- Identify the total mercury deposited in the watershed.
- Identify the sources of methylmercury within the watershed.
- Calculate a TMDL.
- Develop a TMDL report.

The following are the project's partnership goals:

- Fully recognize and discuss all applicable water quality standards, including those applicable to the parts of the waters in Wisconsin and within or bordering the Fond du Lac reservation.
- Work toward agreement between the three bodies that establish water quality standards (Minnesota, Wisconsin, and Fond du Lac) on the technical approach to the TMDL, to support concurrence on the approach for waters with shared jurisdiction and the creation of integrated TMDLs for all waters in the watershed.
- Communicate clearly and in a timely manner about technical concerns that may result in an inability to reach agreement on the TMDL approach, and to document the reasoning behind any decision made by MPCA to move forward on an approach for Minnesota if agreement is not reached.

The following are the project's **external engagement and communication goals**:

- Provide transparency about MPCA's approach and decisions.
- Provide a foundation of cooperative and meaningful engagement with a broad range of interested parties, including technical and scientific advisors; partners in state, federal, and tribal governments; and stakeholders including regulated parties and environmental interest groups.
 - Provide advisors, partners, and stakeholders with relevant technical information.
 - Provide advisors, partners, and stakeholders an opportunity to collaboratively discuss and contribute to the technical foundations of the TMDL.
 - Provide advisors, partners, and stakeholders an opportunity to receive information and provide input regarding topics such as available data, studies, and planned and active watershed projects related to mercury reductions.

MPCA project team

The MPCA project team consists of staff and leadership who will be the primary staff and decision makers.

Name	Division	Role
Jennifer Brentrup	Environmental Analysis and Outcomes (EAO)	Project lead
Andrea Plevan	Watershed	TMDL lead
Catherine Neuschler	EAO	Manager, Water Assessment Section
Tom Estabrooks	Watershed	WRAPS project manager
Stephen Mikkelson	Operations	Communications/Public Information
Marco Graziani	Municipal	Wastewater–TMDL liaison
Anna Bosch	Municipal	Stormwater–TMDL liaison
Erik Smith	EAO	Supervisor, Environmental Analysis & Groundwater Services
Hassan Bouchareb	EAO	Statewide Mercury TMDL implementation coordinator
Amy Adrihan	Watershed	Supervisor, NE Watershed Unit
Theresa Haugen	Watershed	Manager, North Section

Table 1. MPCA project team members

MPCA project team role

- Responsible and accountable for completion of the TMDL report and submittal to EPA for approval. Document important decisions in TMDL report and associated work products.
- Consult with Technical Advisory Team (TAT) on evaluation of technical information, proposed approaches to the TMDL, and TMDL report content.
- Inform external engagement groups of TMDL activities, decisions, and deliverables.
 - Coordinate Technical Advisory Team.
 - Connect with development of the St. Louis River Watershed Restoration and Protection Strategy (WRAPS) project and the One Watershed, One Plan (1W1P) to share important technical information that supports inclusion of strategies to reduce methylated mercury in those strategies and plans.
 - Provide updates to teams developing the St. Louis River WRAPS and the 1W1P.
 - Provide information to the public engaged in WRAPS and 1W1P.
 - Provide updates to the St. Louis River Watershed mercury Public Forum through the project website, GovDelivery,¹ and public events.

Logistics

- MPCA project team meetings: Hold meetings (approximately monthly or bimonthly) to provide project updates and to discuss technical information, challenges, and next steps.
- Decisions: The decision-making process for the MPCA project team is by group consensus for most decisions. MPCA managers from the Environmental Analysis and Outcomes (EAO) Division and the Watershed Division will make decisions if consensus cannot be reached.
- Documentation: The MPCA project team will maintain documentation of meeting agendas, minutes, work plans, and work products with coordination by Jennifer Brentrup, the project lead.

External engagement

The St. Louis River Watershed Mercury TMDL will involve two key spaces for external engagement: the Technical Advisory Team (TAT) and a St. Louis River Watershed Public Forum that is open to all who wish to participate. The MPCA will provide information to and solicit input from these two groups, as described below.

Ultimately, the MPCA has the final authority on the contents of the TMDL report for Minnesota. The final TMDL report must go through a formal public notice and comment period, which is separate from the engagement components of this charter. The MPCA submits the final TMDL, with comments and responses, to EPA for approval.

¹ Web-based email subscription system to provide news and information to subscribers

Technical Advisory Team

The Technical Advisory Team (TAT) is a group of government partners (tribal, federal, and state) and scientists (Table 2) whose primary role is to provide technical, scientific, and policy expertise to the MPCA project team.

Name	Affiliation
Donalea Dinsmore	Wisconsin Department of Natural Resources
Joel Hoffman	Great Lakes Toxicology and Ecology Division (GLTED), EPA
Nate Johnson	University of Minnesota–Duluth
Tyler Kaspar	1854 Treaty Authority
Dave Krabbenhoft	U.S. Geological Survey (USGS)
Open	Great Lakes Indian Fish & Wildlife Commission
Ken Powell	Board of Water and Soil Resources (BWSR)
Paul Proto	EPA Region 5
Nancy Schuldt	Fond du Lac Band of Lake Superior Chippewa
Christine Urban	EPA Region 5
Trent Wickman	Superior National Forest, United States Department of Agriculture
Kevin Kirsch	Wisconsin Department of Natural Resources
Xiaochun Zhang	Wisconsin Department of Natural Resources

Table 2	. Technical	Advisory	Team	members
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Technical Advisory Team role

- Provide technical expertise and input to support completion of the primary project components:
 - Science of mercury methylation and its transport and transformation throughout the St. Louis River Watershed.
 - Identification of mercury and methylmercury sources in the St. Louis River Watershed.
 - TMDL development for EPA approval.
 - Identification of implementation strategies.
- Review materials produced by the MPCA project team.
- Participate in meetings to discuss project progress and provide technical input, with a focus on the project work plan, technical approach to TMDL development, and TMDL report.

Logistics

- Meetings: Regularly, likely every six weeks, but will vary based on project activity.
- Decisions: MPCA will request technical input from this group. The decision-making process is primarily by group consensus, with MPCA having the final decision-making authority.
- Documentation: Documentation of meeting agendas, minutes, work plans, and work products is maintained by the MPCA project team. The project team will also maintain documents shared on the project's webpage.

St. Louis River Watershed mercury TMDL Public Forum

Public Forum role

The Public Forum is how the public will learn about the St. Louis River Watershed mercury TMDL and be able to ask questions of the MPCA and contribute input. All interested members of the public will have the opportunity to review project components and provide input through a variety of means.

- Who: All members of the public interested in mercury in the St. Louis River Watershed.
- Role: Review and provide feedback on materials at key milestones and discuss at scheduled forums.

Logistics

- Information from TAT meetings will be made available on the project website and communicated, approximately quarterly, through GovDelivery after the public project kick-off.
- Meetings at key milestones (e.g., mercury impacts and science; mercury sources and movement in the St. Louis River Watershed; TMDL calculations and mercury reduction options). The MPCA project team and TAT will develop agendas for each meeting with clear goals for sharing information and gathering input from this group.
- The MPCA project team will share how the input received from the Public Forum is being considered.

Deliverables

Project deliverables include technical deliverables and additional deliverables such as reports, updates, and information for the public. Deliverables will be provided by the MPCA project team through the MPCA website and GovDelivery.

- Technical deliverables:
 - Draft mercury source assessment.
 - Draft and final TMDL calculations.
 - Draft and final TMDL report (including technical support document, source assessment, TMDL calculations, reasonable assurances and a general implementation section).
- Additional deliverables:
 - Meeting agendas and minutes.
 - TAT presentation materials and other work products.
 - Presentation materials for the Public Forum.

Out of scope

TMDL Implementation—The TMDL establishes the allowable mercury loads and identifies strategies or types of actions intended to reduce mercury in fish. The MPCA, along with input from the external engagement groups described in this charter, will propose implementation strategies in the TMDL report. However, the TMDL report does not specify which implementation actions will be taken to reach the goals.

Wild Rice/Sulfate—The toxicity of high sulfate concentrations on wild rice is a concern in the St. Louis River Watershed, but the impact of sulfate on wild rice is not in scope for this effort.

Timeline

Saint Louis River Watershed Mercury TMDL project	SFY 2021			SFY 2022			SFY 2023			SFY 2024			SFY 2025				SFY 2	2026	SFY2027							
	CY 2020 CY 2		2021	.021 CY :			2022 СУ		2023 CY		2024		CY 2025				CY2026									
element	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Communications		-		-	-	-		-		=		_	_	_						-	-	-				
Prepare Communications Plan & Project Charter			х	х																						
Send MPCA Letter to Tribes				х																						1
MPCA Project Team Meetings (monthly)				x	x	x	х	x	х	x	х	х	х	x	x	x	х	x	х	х	x	x	х	х	х	х
Technical Advisory Team Meetings (6–8 weeks)				x	x	x	х	x	х	х	х	х	х	x	x	x	х	x	x	x	x	x	х	х	х	х
Public Forum (kick-off meeting, meetings at key milestones, quarterly updates)											x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Public Notice and Public Meeting																						x	х			
TMDL development				-								-									_	-				
Develop Work Plan & Modeling Approach	х	х	х	х	х	х	х	x	х																	
Modeling								х	х	х	х	х	х	х	х											1
Source Assessment—Evaluate Data and Modeling										х	х	х	х													
Develop Allocation Approach										х	х	х	х													
TMDL Calculations and Reduction Scenarios											х	х	х	х												
Prepare TMDL Report											Х	Х	Х	Х	Х	Х										
MPCA and TAT Report Review															х	x	х	х								
TMDL EPA Preliminary Review																			Х	Х						
TMDL Public Notice & Responses																					х	x	х			
TMDL EPA Approval																								х	х	

SFY: State fiscal year

CY: Calendar year

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 2

(MPCA, St. Louis River Watershed Mercury Total Maximum Daily Load Public Forum #2, June 6, 2023)



St. Louis River Watershed Mercury Total Maximum Daily Load Public Forum #2

June 6, 2023



Agenda

- Progress since Public Forum #1
- Where does mercury come from in the St. Louis River Watershed?
- Where is the total mercury likely to become methylmercury?
- How do the relative loads of total mercury and methylmercury from the different sources vary across the watershed?
- How will this information be used in the TMDL?
- Next Steps



Progress Since Public Forum #1

- Published Public Forum 1 Summary Report on MPCA website
- Published St. Louis River Watershed Mercury TMDL study <u>Frequently Asked Questions</u> on MPCA website
- Completed preliminary source assessment
- Compiled a <u>citation list</u> for the SLRW Mercury TMDL on MPCA website
- Set up online system for the public to ask questions and comment on the project
- Drafted memo describing approach to meeting Minnesota, Wisconsin, and Fond du Lac Band water quality standards in the mercury TMDLs
- Drafted mercury in stormwater literature review to explore options to address stormwater in the mercury TMDLs
- Presented the work at <u>Twin Ports Freshwater Folk</u>
- Participated in interviews with <u>Agate for their story on this project</u>

Where does mercury come from?

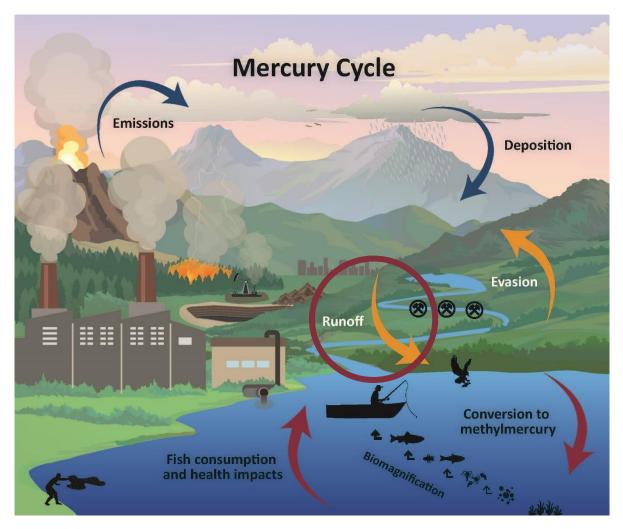


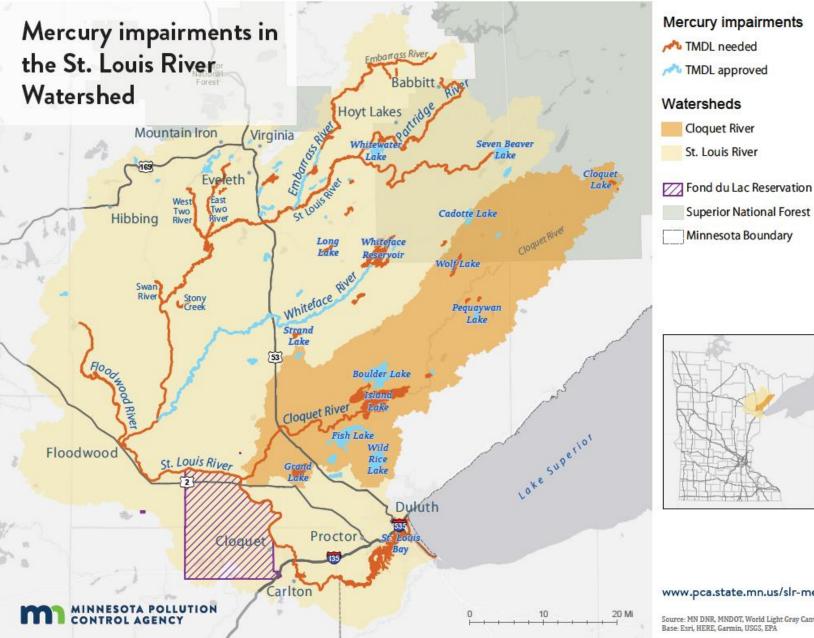
Image Credit: The Dragonfly Mercury Project (usgs.gov)

St. Louis River Watershed

- Large watershed >9000 km² and largest tributary to Lake Superior
- Land cover dominated by deciduous forest and peatlands
- Fond du Lac Tribal Nation borders St. Louis River – subsistence fishing
- Largest freshwater estuary on US side Lake Superior
- Mesabi Iron Range in northern part of the watershed



Photo Credit: Randen Pederson



i rments	Impairment Type	Streams	Lakes
ved	Water column Hg	N = 18	N = 4
r	Fish tissue Hg	N = 25	N = 28
r	Total = 75	N = 43	N = 32
	2		



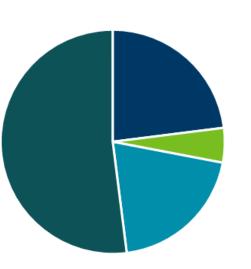
www.pca.state.mn.us/slr-mercury

Source: MN DNR, MNDOT, World Light Gray Canvas Base: Esri, HERE, Garmin, USGS, EPA



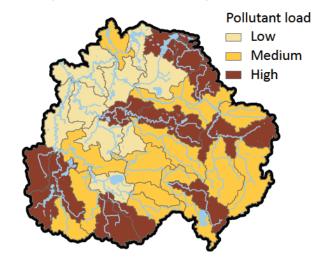
What is a Total Maximum Daily Load (TMDL)?

- Planning tools for improving water quality
- Identify sources & set limits on pollutants entering waterbodies
- Management goal: fish consumption



Example Pollutant Source Summary

Example Loading Rate Map



What is included

A TMDL report includes a description of pollutant sources, allowable amounts and reductions needed to meet standards, and recommended management practices.

What is not in a TMDL

- Precise measurements of all pollutant sources and processes.
- Detailed implementation plan that shows all the projects that are needed to restore the water body.

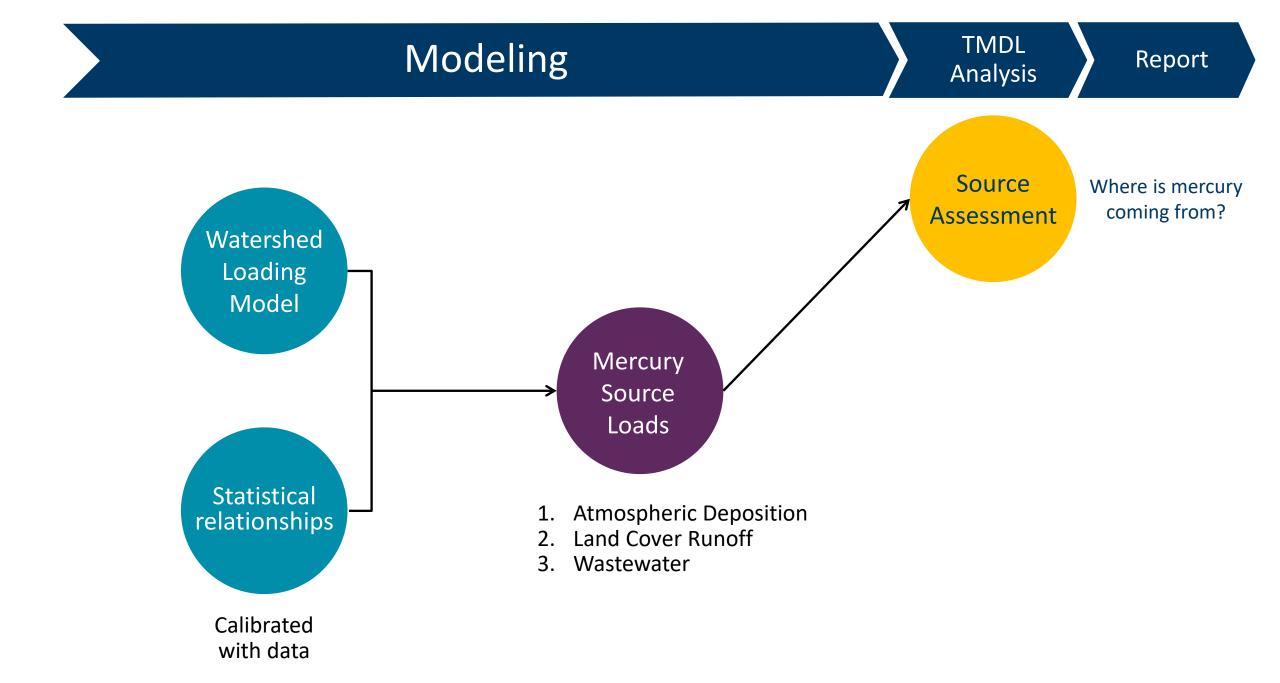
St. Louis River and Cloquet River Sub-Watersheds

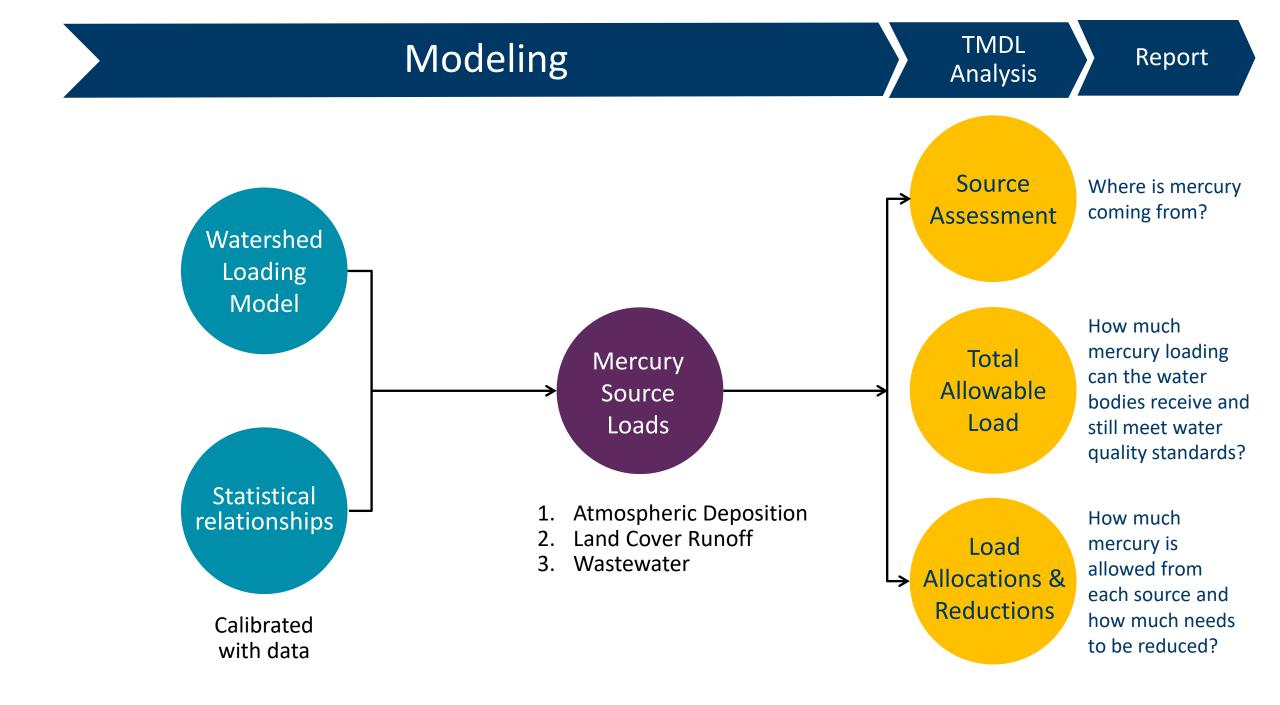
- Large watersheds divided into 15 subwatersheds based on hydrology
- Sub-watersheds vary in area, dominant land cover types, and the number of wastewater sources



Primary Mercury Sources







Data used for Watershed Model

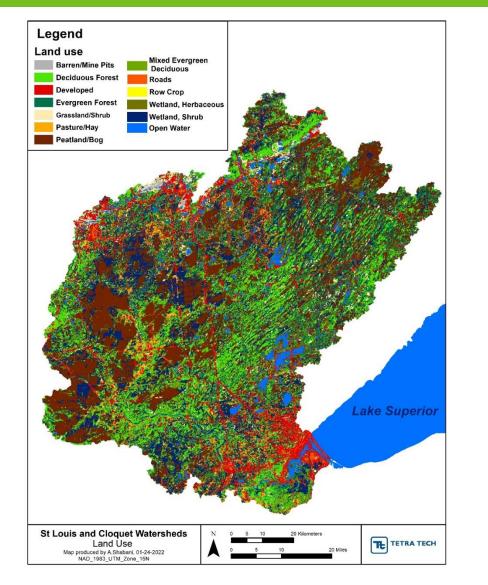
- Land cover classifications
- Atmospheric deposition data
- Water chemistry data
 - Mercury, methylmercury, dissolved organic carbon, and sulfate concentrations
- Wastewater discharge monitoring data
- Fish tissue data (used in next stage of analysis)

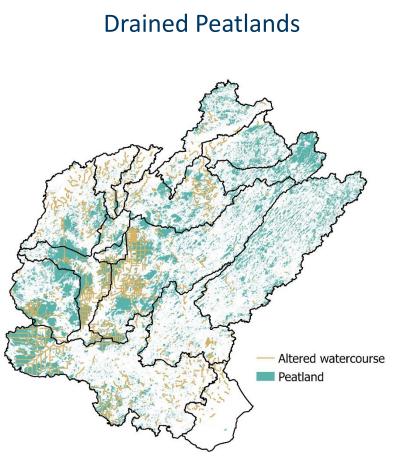


Land Cover Types

10 Land Cover Types

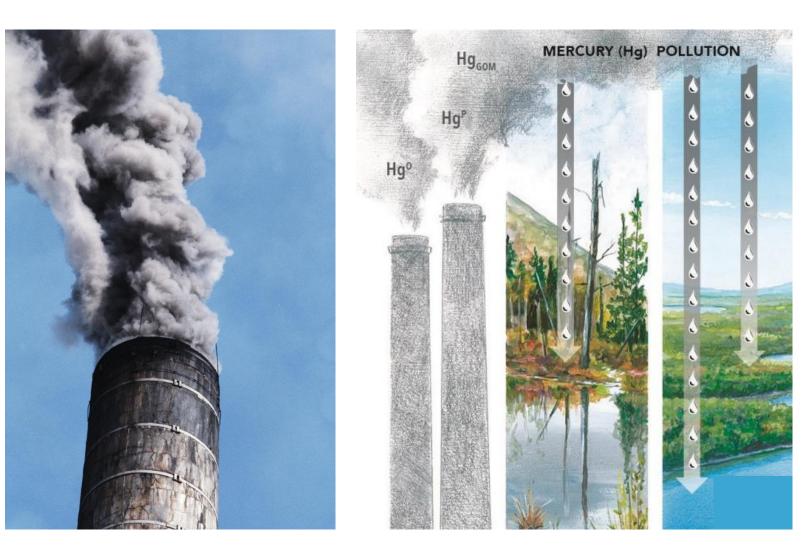
- Forest contains deciduous, evergreen, mixed
- Wetlands
- Peatlands
- Drained Peatlands
- Shrub/Grassland
- Pasture
- Agriculture
- Developed
- Open Water
- Barren/Mine Pit





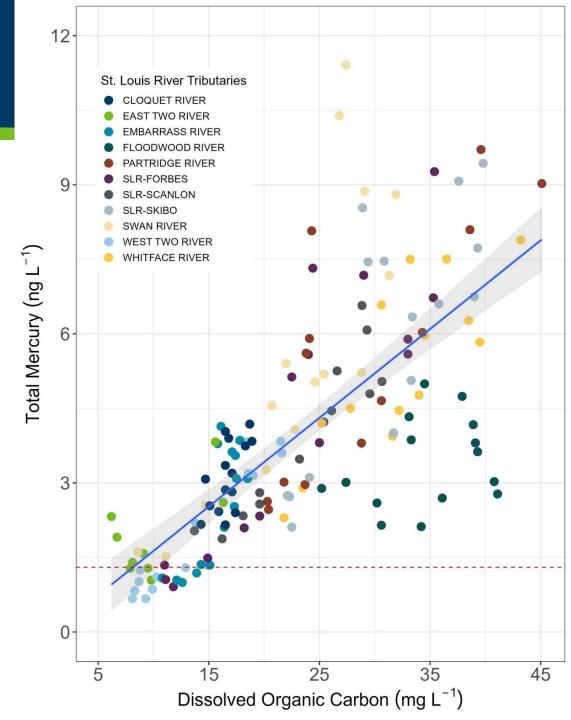
Atmospheric Deposition

- Primary source of total mercury to watershed
- Accounted for in model in 2 ways:
 - Direct deposition to surface of lakes and streams in watershed
 - Deposition to land cover types and runoff into water bodies



Modeling Mercury Transport with Dissolved Organic Carbon

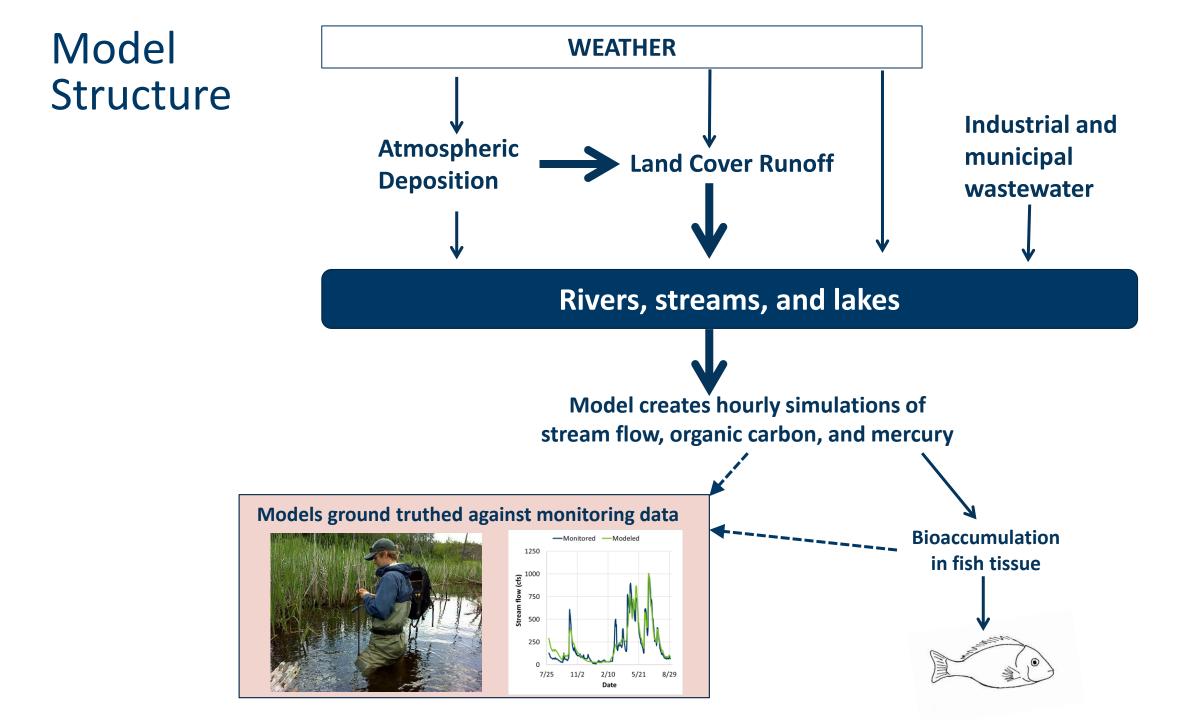




Model Questions

- Does the model account for higher sulfate concentrations in some parts of the watershed?
 - Yes studies have shown sulfate can be important for methylmercury production
 - In areas of the watershed with higher sulfate concentrations, more methylmercury per organic carbon concentration
- Does the model account for all variables that affect methylmercury production?
 - No many variables affect mercury methylation rates
 - Missing processes that may occur in riparian areas

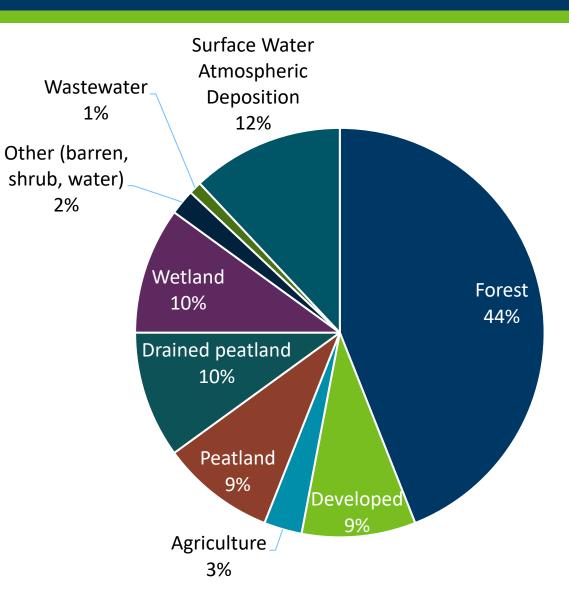




Where does the total mercury come from?

Overall Watershed Source Results

- Total mercury average annual load
- Land cover runoff originates as atmospheric deposition

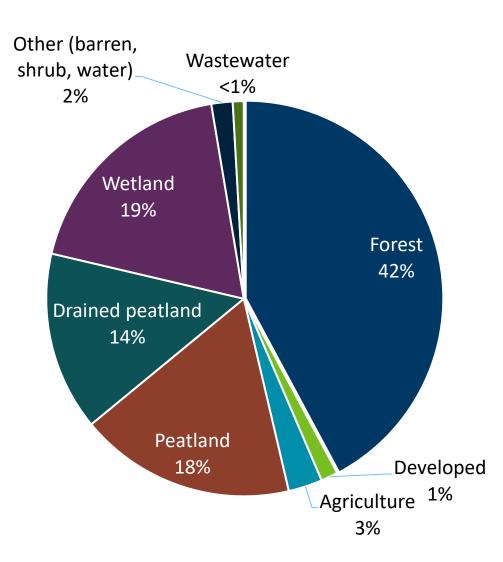


*Preliminary Load Estimates

Where is the total mercury likely to become methylmercury?

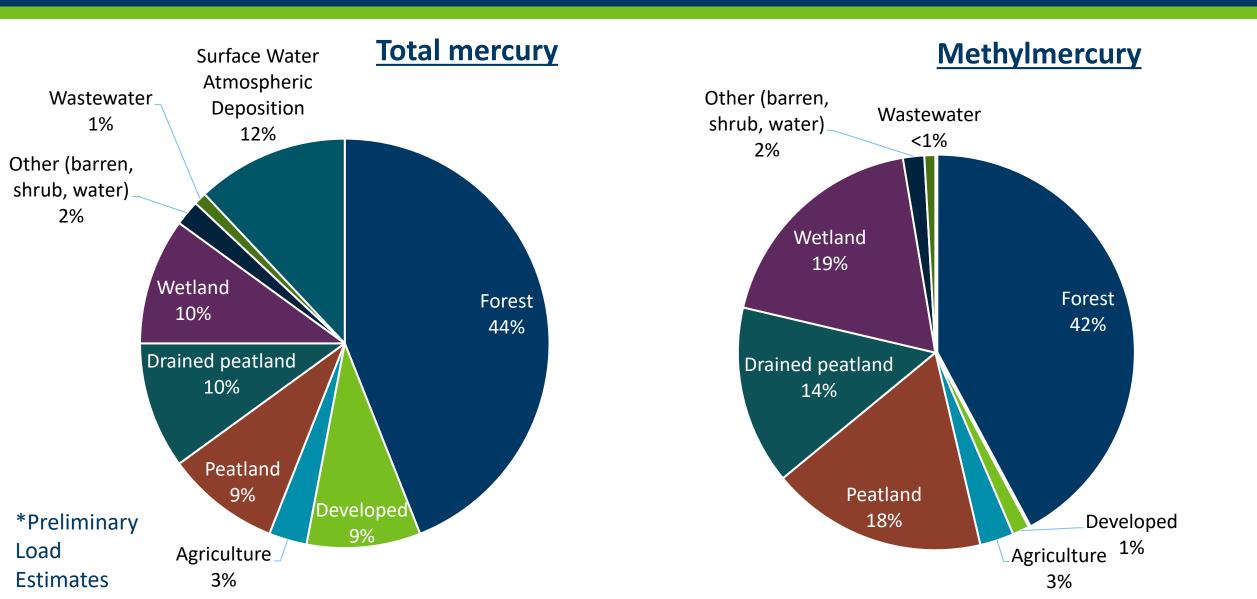
Overall Watershed Source Results

- Methylmercury average annual load



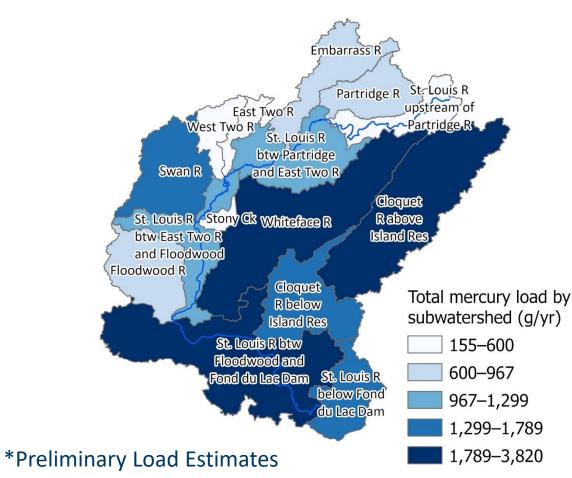
*Preliminary Load Estimates

Total mercury vs. methylmercury average annual load

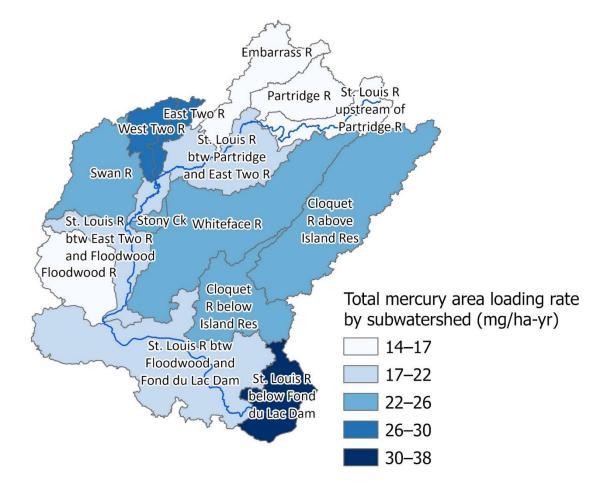


What is the geographic variation of total mercury loads?





Total Mercury Annual Area Loading Rates (mg/ha-yr)



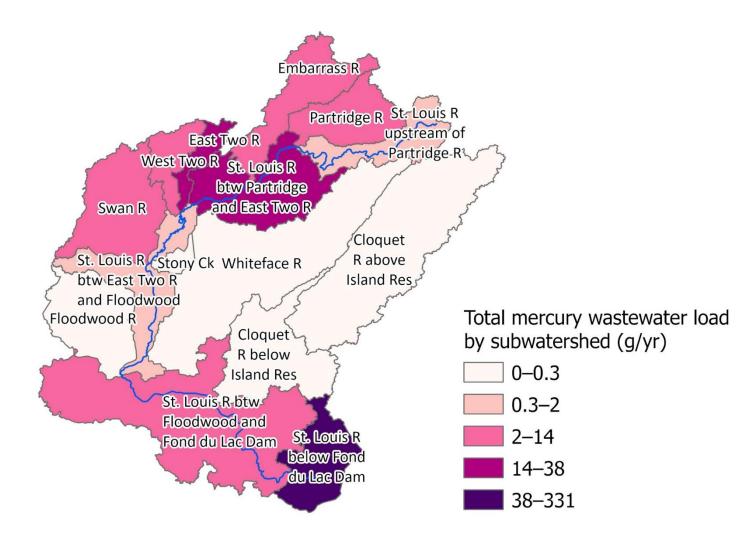
Why are those sub-watersheds high in total mercury?

• Highest loads

- Largest sub-watersheds by area
- Primary land cover is forests and wetlands/peatlands/drained peatlands; also surface water
- Highest loading rate
 - Primary land cover is developed

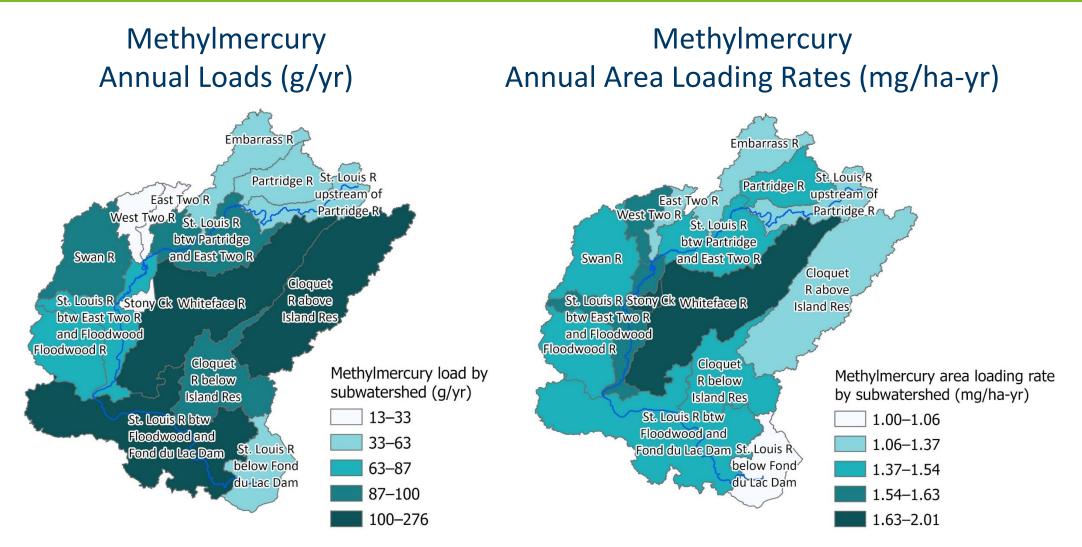
Preliminary Wastewater Total Mercury Loads

- Industrial & municipal wastewater
- St. Louis River below Fond du Lac sub-watershed
- Wastewater is a small source of mercury overall relative to land cover runoff loads



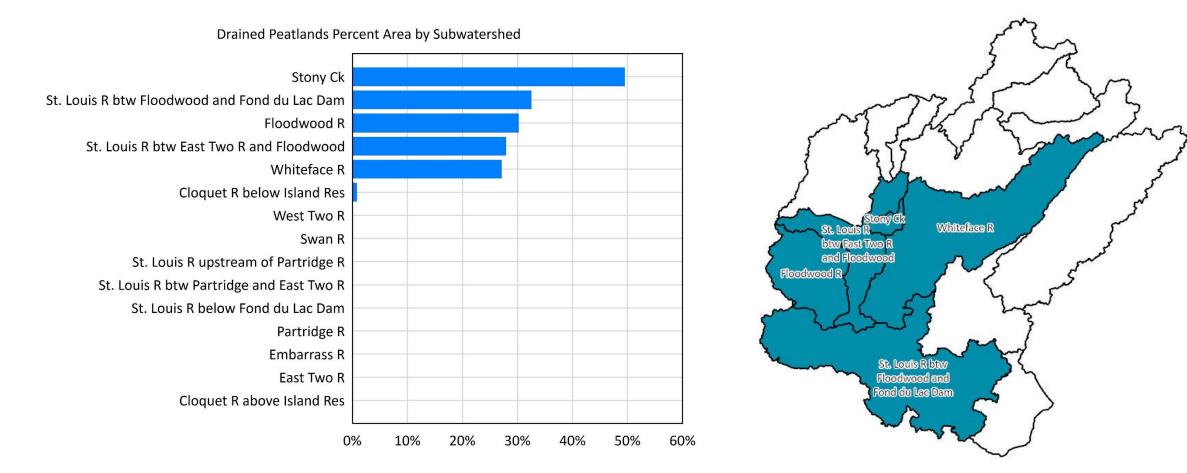
*Preliminary Load Estimates

What is the geographic variation of methylmercury loads?



*Preliminary Load Estimates

Watersheds with high percent area of drained peatlands



Draining of peatlands increases water flow and thus mercury to downstream water bodies, so areas with high percent of ditched peatlands are larger sources of methylmercury

Why are those sub-watersheds high in methylmercury?

• Highest loads

- Largest 3 sub-watersheds by area
- Primary land cover is forests and wetlands/peatlands/drained peatlands
- Highest loading rate
 - Primary land cover is drained peatlands, peatlands, wetlands

Take Home Messages

Overall

- Atmospheric mercury deposition is processed differently by land cover type
- Most of the land cover is forests and wetlands/peatlands/drained peatlands; most of the mercury comes from these areas.

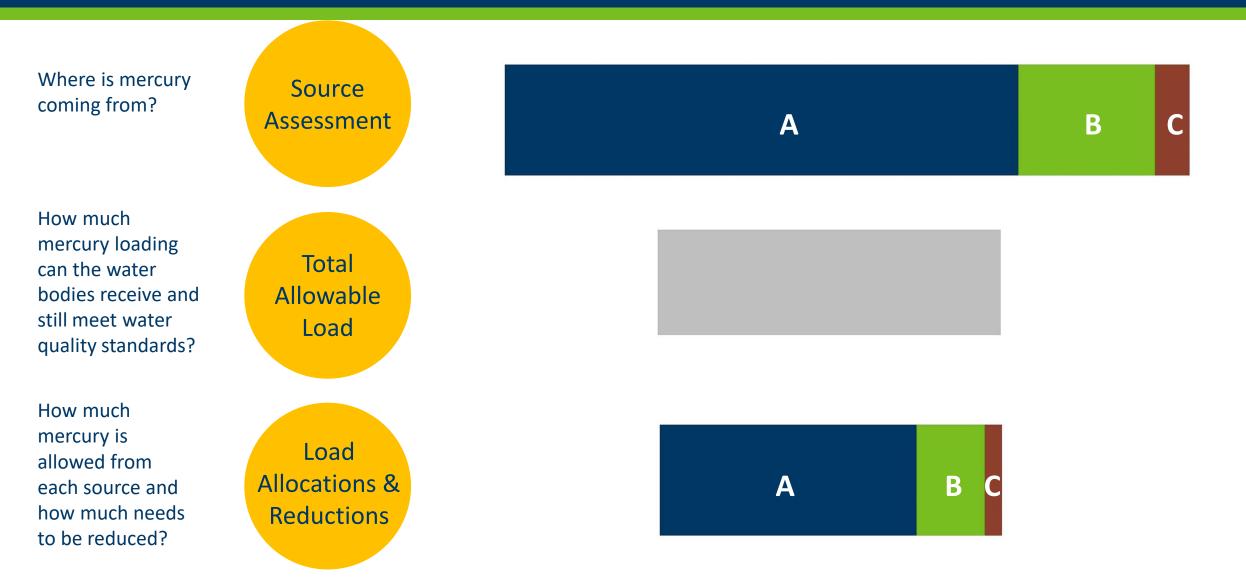
Total Mercury

- Developed land cover has a high rate of total mercury loading on an areal basis, leading to high rates of mercury runoff in and around Duluth.
- Direct atmospheric deposition to surface waters is also a substantial source
- Wastewater is a relatively small source

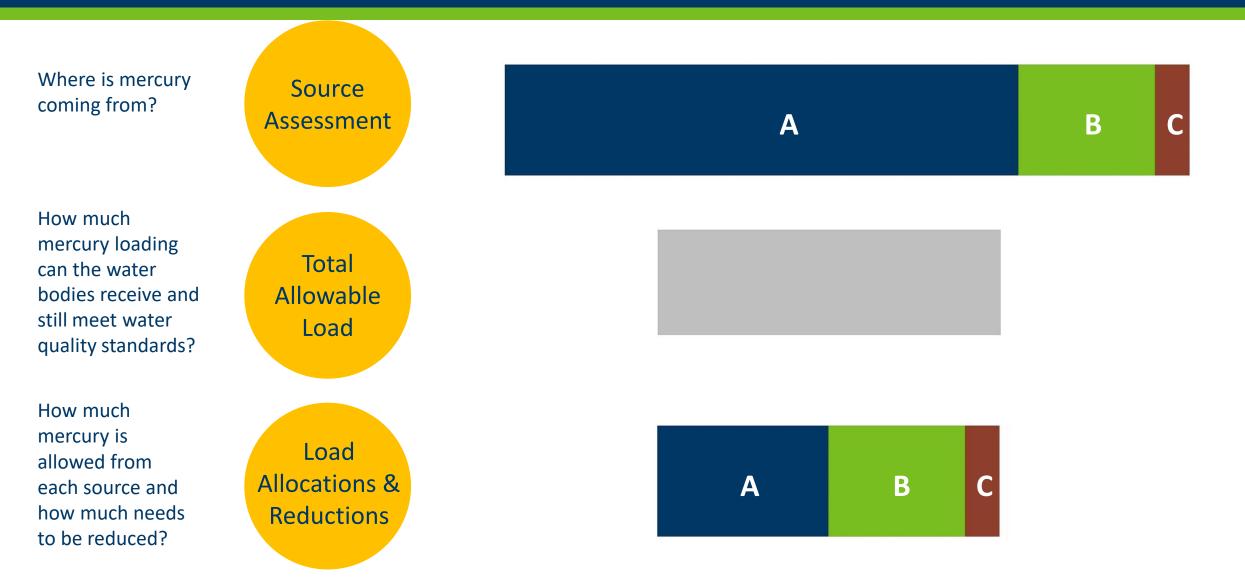
Methylmercury

- Drained peatlands have high rates of methylmercury loading on an areal basis, leading to high rates of methylmercury runoff in the Whiteface River and Stony Creek subwatersheds
- Draining of peatlands increases water flow and thus mercury to downstream water bodies

How will the mercury source information be used in the TMDL?



How will the mercury source information be used in the TMDL?



Next steps

- Mercury source load calculations for St. Louis River Estuary
- Draft TMDL calculations to meet water quality standards



Contact Information





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Thank you!

MINNESOTA POLLUTION CONTROL AGENCY

6/12/2023

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 3

(Myrbo, A, *et al*, Increase in Nutrients, Mercury, and Methylmercury as a Consequence of Elevated Sulfate Reduction to Sulfide in Experimental Wetland Mesocosms, 2017)

@AGUPUBLICATIONS

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2017JG003788

This article is a companion to Myrbo et al. (2017), https://doi.org/ 10.10022017JG003787 and Pollman et al. (2017), https://doi.org/ 10.10022017JG003785.

Key Points:

- Sulfate addition increased organic matter mineralization in wetland sediment, releasing C, N, P, and Hg to the water column
- Sulfate reduction caused not only higher methylmercury concentrations but higher total mercury concentrations in the surface water
- Increased sulfate loading to freshwaters can cause deleterious effects separate from direct sulfide toxicity to organisms

Supporting Information:

- Supporting Information S1
- Figure S1
- Data Set S1

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Citation:

Myrbo, A., Swain, E. B., Johnson, N. W., Engstrom, D. R., Pastor, J., Dewey, B., ... Peters, E. B. (2017). Increase in nutrients, mercury, and methylmercury as a consequence of elevated sulfate reduction to sulfide in experimental wetland mesocosms. *Journal of Geophysical Research: Biogeosciences*, *122*, 2769–2785. https://doi.org/10.1002/ 2017JG003788

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Increase in Nutrients, Mercury, and Methylmercury as a Consequence of Elevated Sulfate Reduction to Sulfide in Experimental Wetland Mesocosms

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Abstract Microbial sulfate reduction (MSR) in both freshwater and marine ecosystems is a pathway for the decomposition of sedimentary organic matter (OM) after oxygen has been consumed. In experimental freshwater wetland mesocosms, sulfate additions allowed MSR to mineralize OM that would not otherwise have been decomposed. The mineralization of OM by MSR increased surface water concentrations of ecologically important constituents of OM: dissolved inorganic carbon, dissolved organic carbon, phosphorus, nitrogen, total mercury, and methylmercury. Increases in surface water concentrations, except for methylmercury, were in proportion to cumulative sulfate reduction, which was estimated by sulfate loss from the surface water into the sediments. Stoichiometric analysis shows that the increases were less than would be predicted from ratios with carbon in sediment, indicating that there are processes that limit P, N, and Hg mobilization to, or retention in, surface water. The highest sulfate treatment produced high levels of sulfide that retarded the methylation of mercury but simultaneously mobilized sedimentary inorganic mercury into surface water. As a result, the proportion of mercury in the surface water as methylmercury peaked at intermediate pore water sulfide concentrations. The mesocosms have a relatively high ratio of wall and sediment surfaces to the volume of overlying water, perhaps enhancing the removal of nutrients and mercury to periphyton. The presence of wild rice decreased sediment sulfide concentrations by 30%, which was most likely a result of oxygen release from the wild rice roots. An additional consequence of the enhanced MSR was that sulfate additions produced phytotoxic levels of sulfide in sediment pore water.

Plain Language Summary In the water-saturated soils of wetlands, which are usually anoxic, decomposition of dead plants and other organic matter is greatly retarded by the absence of oxygen. However, the addition of sulfate can allow bacteria that respire sulfate, instead of oxygen, to decompose organic matter that would not otherwise decay. The accelerated decay has multiple consequences that are concerning. The bacteria that respire sulfate "breathe out" hydrogen sulfide (also called sulfide), analogous to the conversion or respiration of oxygen to CO₂. Sulfide is very reactive with metals, which makes it toxic at higher concentrations. In addition to the release of sulfide, the sulfate-accelerated decomposition of plants releases phosphorus and nitrogen, fertilizing the waterbody. Decomposition also mobilizes mercury (which is everywhere, thanks to atmospheric transport) into the surface water. The microbes that convert sulfate to sulfide also methylate mercury, producing methylmercury, the only form of mercury that contaminates fish. This study demonstrates that adding sulfate to a wetland can not only produce toxic levels of sulfide but also increase the surface water concentrations of nitrogen, phosphorus, mercury, and methylmercury.

1. Introduction

Organic matter (OM) accumulates in the sediments of aquatic systems when sediment concentrations of terminal electron acceptors (TEAs) are too low for microbes to completely decompose OM, especially when the supply of the most energy-efficient TEA, oxygen, is low. In water-saturated, organic-rich sediment, microbial sulfate reduction (MSR) can be a dominant pathway for the respiration of OM because oxygen is depleted in the uppermost sediment (Boye et al., 2017). Dissolved sulfate (SO₄) concentrations in continental surface

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waters are often low (less than 50 mgL⁻¹ or 0.5 mmol L⁻¹) (e.g., Gorham et al., 1983) compared to ocean concentrations (2,800 mg L⁻¹ or 29 mmol L⁻¹). Because of lower SO₄ concentrations, and because MSR rates can be limited by SO₄ concentrations (Holmer & Storkholm, 2001), the biogeochemical significance of MSR is often considered minimal in freshwater and low-salinity systems (e.g., Capone & Kiene, 1988; Nielsen et al., 2003; Stagg et al., 2017). However, absolute rates of MSR are not clearly lower in freshwater systems than in marine systems (Pallud & Van Cappellen, 2006), and in some cases, rapid cycling between oxidized and reduced forms of S can occur (Hansel et al., 2015).

In this study, we investigated the cascade of biogeochemical effects associated with increased MSR that result from increased surface water SO₄. We simultaneously quantified three different categories of biogeochemical responses related to MSR: (1) mineralization of organic matter and associated release of dissolved C, N, P, and Hg; (2) methylation of Hg; and (3) production of sulfide.

The stoichiometric release of the constituents of OM during MSR, notably C, N, and P, is a phenomenon long recognized by marine scientists. For instance, Boudreau and Westrich (1984) constructed a model of the MSR-mediated decomposition of marine sediment. They showed that SO_4 is reduced to sulfide (H₂S) in stoichiometric proportion to the mineralization of C, N, and P according to the reaction

$$2(CH_2O)_x(NH_3)_y(H_3PO_4)_z + xSO_4^{2-} \rightarrow 2xHCO_3^{-} + xH_2S + 2yNH_3 + 2zH_3PO_4$$
(1)

C is released as both dissolved inorganic carbon (DIC, from complete oxidation, produced as bicarbonate alkalinity in stoichiometric proportion to sulfide (reaction (1); Boudreau & Westrich, 1984)) and dissolved organic carbon (DOC, from partial oxidation). The nutrients N and P are released in forms that are readily taken up by plants; N is released as ammonia, and P as phosphate. The mineralization of sediment organic matter associated with MSR releases sulfide (S^{2-}) into sediment pore water, which speciates, depending on the pH, into hydrogen sulfide (H_2S) and bisulfide (HS^-), henceforth collectively termed sulfide. If reduced S compounds accumulate in the sediment, there may be additional consequences to an aquatic system, such as toxic concentrations of sulfide in pore water (Lamers et al., 2013; Pastor et al., 2017; Myrbo et al., 2017) or conversion of sediment Fe(III) to FeS compounds, which enhances the mobilization of P (Curtis, 1989; Maynard et al., 2011).

The multiple biogeochemical consequences of MSR in freshwater systems have been investigated and documented in more than two dozen publications (Table S1 in the supporting information), which typically address a single issue, such as the production of alkalinity that neutralizes atmospherically deposited H_2SO_4 (Baker et al., 1986; Cook et al., 1986; and others) or the methylation of Hg (Gilmour et al., 1992; Branfireun et al., 1999, 2001; and others). Experimental studies addressing SO_4 reduction, sulfide production, associated OM mineralization, and release of nutrients have been broader (Lamers et al., 2001, 2002; Weston et al., 2006, 2011; and others), but aside from the results reported in this paper, only the experiments of Gilmour, Krabbenhoft, et al. (2007) and Gilmour, Orem, et al. (2007) have investigated all three categories of biogeochemical consequences of SO_4 reduction: OM mineralization, Hg methylation, and sulfide accumulation (Table S1). We also investigated the potential for Hg to be released by mineralization, a phenomenon proposed by Regnell and Hammar (2004).

Sulfate-driven enhanced mineralization of sediment OM and release of dissolved sulfide, N, P, DOC, DIC, and associated increases in alkalinity and pH have the potential to change the nature of an aquatic ecosystem. The immediate release is to the sediment pore water, but these dissolved materials can diffuse into the surface water. Increased internal loading of N and P can drive a system toward eutrophy, which can increase carbon fixation and amplify the cascade of biogeochemical effects associated with increased MSR. Increases in DOC also have the potential to fundamentally change the nature of a waterbody. DOC influences many processes in freshwater ecosystems, including light availability for macrophyte growth, thermal stratification, and bioavailability of metals, P, and C. In addition, DOC interferes with drinking water purification (Williamson et al., 1999). Increases in DIC, alkalinity, and pH can also change the nature of a system. Aquatic macrophyte and algal species often have different optimal alkalinity concentrations (e.g., Moyle, 1945; Vestergaard & Sand-Jensen, 2000), so increases in alkalinity may change aquatic community composition. Because pH is a master variable in aquatic systems (Stumm & Morgan, 2012), increases in pH can cause changes in both aquatic chemistry and the biota that dominate a system, as best documented by changes in diatom assemblages (Patrick et al., 1968).

The release of sulfide into sediment pore water has multiple biological and geochemical consequences, several of which are related to the reactivity of sulfide with metals. If dissolved sulfide accumulates in pore water, it can negatively affect multicellular organisms inhabiting the sediment because sulfide can denature a range of metal-containing biomolecules, including cytochrome C oxidase, which is essential for respiration by both animals and plants (Bagarinao, 1992). Because aquatic sediment is a primary site of sulfide production, plants that root in sediment are vulnerable to toxic sulfide concentrations (Lamers et al., 2013; Pastor et al., 2017). However, if the watershed supplies sufficiently high loading of reactive Fe or other metals to the sediment, pore water sulfide concentrations may stay below toxic levels even while MSR proceeds as an important mineralization process (Pollman et al., 2017). The formation of FeS compounds effectively detoxifies sulfide (e.g., Marbà et al., 2007; Van der Welle et al., 2007). When Fe availability exceeds the production of sulfide, the accumulation of FeS is a measure of cumulative SO₄ reduction, which can be quantified as acid-volatile sulfide (AVS) (Heijs & van Gemerden, 2000). In addition, phosphorus is mobilized when oxidized Fe compounds with significant capacity to bind phosphate are converted to FeS compounds, which are incapable of binding phosphate (Lamers et al., 1998; Maynard et al., 2011). Thus, MSR mobilizes P both by mineralization of P-containing OM and by changing the form of Fe in sediment.

In addition to releasing C, N, and P, producing potentially toxic concentrations of sulfide, and reducing the solubility of metals, MSR is a primary process leading to the formation of MeHg, the bioaccumulative form of Hg (Gilmour et al., 1992; Hsu-Kim et al., 2013), although other microbial groups can also methylate Hg (Podar et al., 2015). In some cases, MSR can lead to toxic levels of MeHg higher in the food chain. The relationship between SO₄ concentrations and MeHg production is complex, however, and both field and laboratory studies in freshwater and saline ecosystems suggest that there is a dual effect of S on Hg methylation. At low SO₄ concentrations, the addition of SO₄ can stimulate MSR and Hg methylation (Jeremiason et al., 2006). At higher SO₄ concentrations, a greater abundance of inorganic sulfide appears to decrease the availability of inorganic Hg for Hg methylation (Hsu-Kim et al., 2013; Johnson et al., 2016). Because it has been observed that low SO₄ additions often increase Hg methylation and higher SO₄ concentrations decrease methylation, it has been proposed that there is a range of SO₄ and sulfide concentrations are optimal for Hg methylation, above which methylation is inhibited (Hsu-Kim et al., 2013). There is some debate regarding the underlying mechanism, but there is substantial evidence suggesting that dissolved inorganic sulfide above concentrations of 300–3,000 μ g L⁻¹ has an inhibitory effect on Hg methylation (Bailey et al., 2017).

This study presents results from 30 wetland mesocosms in which the surface waters were treated to maintain a wide range of SO₄ concentrations over the course of 5 years (2011–2015) to assess the impact on wild rice, *Zizania palustris* (Pastor et al., 2017). We took advantage of this experiment to analyze the geochemical conditions in surface and pore water in the mesocosms during late summer 2013, 3 years into the experiment. Pastor et al. (2017) specifically examined the effect of increased SO₄ loading on wild rice, whereas this paper examines the broader biogeochemical impact of augmenting SO₄ to a low-SO₄ system.

2. Materials and Methods

2.1. Experimental Design

The experimental setup (Figure S1 in the supporting information), described in detail by Pastor et al. (2017), consisted of thirty 375 L polyethylene stock tanks containing sediment from a wild rice lake (Rice Portage Lake; +46.6987°, -92.6886°) in which wild rice was grown in self-perpetuating populations at five SO₄ treatment levels (control, 50, 100, 150, and 300 mg L⁻¹). SO₄ concentrations in six replicate mesocosms were routinely monitored, and amendments of SO₄ were added as Na₂SO₄ during the growing season as SO₄ was removed by MSR (Figure 1). Due to MSR, the mesocosm surface waters actually had time-weighted average concentrations of 7, 27, 59, 93, and 207 mg L⁻¹, respectively. Local well water containing an average of 10.6 mg L⁻¹ SO₄ was added as needed to compensate for evapotranspiration. Precipitation in the region contains an average of 2.1 mg L⁻¹ SO₄, and Rice Portage Lake has an average SO₄ concentration of 2.2 mg L⁻¹ (Fond du Lac Band, 2016), so the control was slightly elevated above the ambient SO₄ concentration of the sediment source for the experiment. During the ice-free period (generally May through October), the surface water temperature (*T*) measured in the morning was correlated with the previous day's mean air temperature (mesocosm *T* = 0.72 air *T* + 4.4 °C; *R*² = 0.65). Peak air temperature is reached in July, when the average

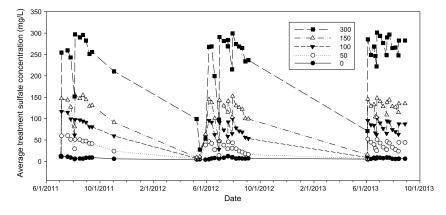


Figure 1. SO₄ concentrations in surface waters of each treatment, showing repetitive depletion and periodic amendment with Na₂SO₄ (average of six mesocosms per treatment on each sampling date).

temperature is 18.8°C (based on 1981–2010 air temperatures measured at the Duluth, Minnesota, airport, 10 km from the experimental site).

The experiments had been in progress for three growing seasons at the time of the sampling for this study, 27 and 28 August 2013, and for five growing seasons at the time of the second, less intensive, sampling (August 2015). The sediment of each mesocosm was divided into two parts for the 2013 growing season by a clear acrylic plate and all wild rice plants removed from one side in order to evaluate the effects of plant root presence on the geochemistry of the sediments. The plate was situated near one end of each mesocosm, such that about 10% of the surface area of 0.6 m² was plant-free (Figure S1). The plate was positioned to segregate the sediment without impeding the circulation of the surface water above all of the sediment. Sediment chemistry results presented here are from the side with wild rice plants present, except when analyzing the difference in AVS between the two sides.

2.2. Methods

2.2.1. Sample Collection

Rhizon^{∞} samplers with a 10 cm long, 2.5 mm diameter, cylindrical porous tip (hydrophilic membrane pore size 0.12–0.18 µm (Rhizosphere.com, Netherlands; Shotbolt, 2010)), were connected by Teflon-taped Luer-Lok connectors and silicone tubing to a syringe needle. The sampler was inserted into the sediment, and the needle was then inserted through the 20 mm thick butyl rubber septum of an evacuated serum bottle (Bellco Glass) to initiate pore water draw through the tubing and displace air. After water was observed entering the serum bottle, the needle was removed from the first sacrificial bottle and inserted through the septum of a second evacuated serum bottle to collect the sample. One Rhizon and bottle were used to collect a sample for dissolved iron, preserved with 20% nitric acid. A second Rhizon and evacuated, N₂ gas-flushed sealed bottle, preloaded with 0.2 mL 2 N zinc acetate, 0.5 mL 15 M NaOH, and a stir bar, was used to collect a sample for dissolved sulfide analysis. Each Rhizon was positioned to sample pore water from the top 10 cm of sediment and to avoid collecting water from above the sediment surface. However, it is conceivable that some surface water was able to follow the path of the Rhizon into the sediment and dilute or partially oxidize the pore water sample.

Surface water in each mesocosm was collected for analysis of nitrate + nitrite, TP, TN, DOC, pH, temperature, and alkalinity from 5 cm below the surface of the water. Surface water samples for analysis of total Hg (THg) and MeHg were collected using clean hands/dirty hands protocols in September 2013, filtered through 0.45 μ m glass fiber filters, and immediately acidified with 0.5% (by volume) trace metal hydrochloric acid. Samples were stored on ice during transport and at 4°C until analysis.

Pore water P availability was measured with three mixed bed ion exchange bags (Fisher Rexyn 300 resin) placed in the sediment of each tank in spring and harvested at the end of the growing season in 2013. A 3.8 cm diameter piston corer was used to obtain 10 cm long sediment samples for various analyses. Sediment samples for the analysis of AVS were taken monthly from June to October 2013 from replicate mesocosms of four SO₄ treatments (control, 50 150, and 300 mg L⁻¹; no mesocosm was sampled more

than once). Sediment samples were also taken on 8 October 2013 for the analysis of THg in bulk sediment and on 6 October 2015 for the analysis of total organic carbon (TOC).

2.2.2. Laboratory Analyses

Surface water and pore water analyses were conducted by the Minnesota Department of Health Environmental Laboratory (MDHEL). Total P was measured by in-line ultraviolet/persulfate digestion and flow injection (APHA, 2005, 4500 P-I), DOC by persulfate-ultraviolet oxidation and IR CO₂ detection (APHA, 2005, 5310-C), and alkalinity by automated titration (APHA, 2005, 2320-B). Pore water sulfide samples were prepared for inline distillation and flow injection colorimetric analysis using procedures that avoided exposure to oxygen. The sulfide serum bottle was weighed to determine the amount of sample collected and to adjust for the slight dilution factor of an alkaline antioxidant that was added by injection through the stoppers. The sealed samples were then placed on a stir plate for at least 1 h and subsamples withdrawn for analysis through a needle. Reanalysis of sealed, processed samples 12 months later shows no significant difference in sulfide concentrations, indicating that the sulfide samples were stable prior to analysis (data not shown). SO₄ concentration was measured using a Lachat QuikChem 8000 Autoanalyzer (Lachat Method 10-116-10-1-A). The resin was eluted using a KCl solution and analyzed for PO₄ using a Lachat Autoanalyzer, following the methods of Walker et al. (2006).

An aliquot of the nitrate + nitrite/TP/TN/DOC serum bottle was filtered in the lab within 10 days of sampling using a 0.45 μ m filter, preserved to a pH < 2 with 10% sulfuric acid, and transferred to a 250 mL polyethylene bottle for DOC analysis. The remaining sample was preserved to a pH < 2, with 10% sulfuric acid and transferred to 250 mL polyethylene bottle for nitrate + nitrite/TP/TN analysis. The contents of the metal serum bottle were transferred to a 250 mL polyethylene bottle and preserved to a pH < 2 with 10% nitric acid. Analyses were conducted within 30 days of sampling.

THg in surface water and bulk sediment were analyzed with EPA method 1631 by MDHEL, and surface water MeHg was analyzed with EPA method 1630 by Frontier Global Sciences (Bothell, Washington). Inorganic Hg (iHg) was calculated as the difference between THg and MeHg. Sediment AVS was analyzed colorimetrically, as above for pore water sulfide, following acid distillation and in-line alkaline trapping (APHA, 2005; SM 4500-S2). Sediment TOC was analyzed following SM5310C (APHA, 2005), using an OI Analytical Aurora 1030 at Pace Analytical Services, Virginia, Minnesota.

3. Data Analysis

3.1. Sulfate Depletion as the Independent Variable

Because SO_4 is relatively unreactive under oxidized conditions, its loss is attributable to diffusion or transpiration-driven advection (Bachand et al., 2014) into sediment and conversion to sulfide by bacteria. Surface water SO_4 concentrations decreased partly due to dilution by precipitation but largely from loss after movement into the sediment and reduction to sulfide. Sulfide would largely be retained in the sediment as FeS compounds, although some could be lost to the atmosphere as H₂S gas (Bagarinao, 1992) or as volatile organic sulfur compounds (Lomans et al., 2002). The cumulative SO_4 lost from surface water was calculated from a mass balance for each mesocosm from the inception of the experiment in spring 2011 through fall 2013; this quantity, termed here SO_4 depletion, $(SO_4)_{Depl}$, is used as a proxy for net MSR, following Weston et al. (2006). The surface water remained frozen from approximately 1 December to 1 April each winter, and the mesocosms were covered with plastic from November to late April each year and not amended with SO_4 . SO_4 reduction was the major biogeochemical process altered by the experimental treatments, and therefore, $(SO_4)_{Depl}$ is the independent variable used in subsequent data analyses. It was only possible to perform a complete mass balance for SO_4 , the only parameter consistently quantified in source water, precipitation, and overflow water.

3.2. Calculation of DIC From Measured Alkalinity

Dissolved inorganic carbon (DIC = $[CO_3^{2-}] + [HCO_3^{-}] + [CO_2^*]$, where $[CO_2^*] = [CO_{2(g)}] + [H_2CO_3]$) was calculated from measured alkalinity and speciated using pH, temperature, and specific conductance of the surface water. At the pH range of the mesocosms (7.60–8.84), 95–98% of DIC is in the form of HCO_3^- , so DIC concentration on a molar basis is nearly the same as alkalinity (ALK) on an equivalent basis (DIC = 0.988 ALK + 0.077, $R^2 = 0.995$). In studies of freshwater, most inorganic carbon data are presented in terms of alkalinity because

alkalinity is a familiar metric; however, in comparisons with DOC, inorganic carbon data are presented as DIC so that the units are directly comparable. PHREEQC version 3 geochemical modeling software (Parkhurst & Appelo, 2013) was used to calculate saturation indices for carbonate minerals.

3.3. Statistical Analysis

Statistical analysis was conducted with R version 3.2.3 and STATA (StataCorp, 2015). The effect of increased sulfate availability was assessed through both categorical analysis of the sulfate treatments (Kruskal-Wallis ANOVA test, followed by Dunn's test for multiple comparisons with Holm-Sidak corrections) and through linear regression and nonparametric Spearman rank correlations. We rely primarily on regressions against SO_4 depletion to detect the effects of enhanced sulfate-reduction driven mineralization, rather than categorical analysis of the sulfate treatment results, because (a) biogeochemical changes are not driven directly by SO_4 concentration, but rather by MSR, quantified as SO_4 depletion; (b) although SO_4 depletion may be highly correlated to SO_4 concentration, deviations between experimental mesocosms develop over time, so cumulative SO_4 depletion values eventually no longer align exactly with treatment categories, but rather become continuous variables; and (c) regression provides more statistical power than ANOVA and builds models that allowed us to describe the relationships between SO_4 depletion and response variables (Cottingham et al., 2005). However, when the relationship is not linear, ANOVA and comparison of treatments through Dunn's analysis can help describe the nature of a relationship.

4. Results and Discussion

4.1. The Impact of SO₄ Reduction on Mineralization of Sediment Organic Matter

Increased concentrations of surface water SO_4 resulted in increased sulfate reduction, which necessarily increased the mineralization of organic carbon, as described by reaction (1). Concentrations of surface water DOC and DIC increased in proportion to sulfate reduction, as measured by $(SO_4)_{Depl}$ (Table 1 and Figure 2). The marine literature generally assumes complete mineralization of particulate organic carbon (POC) to DIC in the water column (e.g., Boudreau & Westrich, 1984) (reaction 1), but in freshwater systems and especially wetlands, not all carbon is completely oxidized during decomposition, and a portion of POC may be mobilized as DOC (Howes et al., 1985; Selvendiran et al., 2008). In principle, the constituents of organic matter, such as the nutrients N and P, are mobilized in proportion to the mass of carbon mineralized as a result of MSR-driven decomposition. Surface water DOC and DIC, and the sum DOC + DIC, are therefore used as indicators of OM mineralization in interpreting the mobilization of N, P, and Hg to surface waters (Figure 2 and Tables 2 and 3).

In contrast to many marine systems, it is likely that SO_4 reduction in these sediments was limited more by SO_4 than by organic carbon, given that $(SO_4)_{Depl}$ was linearly proportional to the average SO_4 concentration (Figure S2a; $R^2 = 0.87$), without any obvious curvature to the relationship that would indicate saturation of MSR.

Regressions of surface water DOC and DIC against SO₄ depletion demonstrate that, on a net basis, about 60% more DIC than DOC was mobilized to the surface water as a result of MSR-driven mineralization (slope of 0.235 mM C per unit SO₄ depletion compared to 0.148; Table 2). The significantly positive slope of the DIC: DOC ratio against SO₄ depletion (Table 2) indicates that increasingly more DIC than DOC was observed in the surface water as a result of exposure to oxygen, aerobic bacteria, and sunlight, processes that could have a larger effect as DOC increases.

Not only did surface water DIC and DOC increase in concert with sulfate reduction, but parallel increases occurred in surface water concentrations of constituents of organic matter: N, P, and Hg (Table 1 and Figure 2). DIC, DOC, total P, total N, ammonia, and total Hg in surface water all had increases from the control to the highest SO₄ addition of about twofold, (2.3, 1.7, 1.9, 1.8, 1.7, and 2.6-fold, respectively, Table 1). However, available phosphate in the sediment, an estimate of P availability in pore water, had a larger increase (7.5-fold). MSR consumes acidity as the DIC-based alkalinity is produced (Baker et al., 1986), which increased the average pH from 7.57 to 7.81, a 44% decrease in hydrogen ion concentration (Table 1). If the sulfide subsequently oxidizes (which could happen in a natural system during drought (Laudon et al., 2004) or intentional dewatering), a proportional quantity of alkalinity is consumed as acid is produced

Table 1

Summary of Effects of Experimentally Increased SO₄ Concentrations on SO₄ Reduction (Quantified as SO₄ Depletion), Organic Matter Mineralization, and Mercury Methylation

		Average of each sulfate treatment ($n = 6$ for each treatmen				eatment)	Correlation with SO_4 depletion (Spearman)		
Variable	Matrix	Control	50	100	150	300	Max/Min	Rho	p value
Variables mainly associated with SO_4 reduction									
SO_4 (T-W mean mg $SO_4 L^{-1}$)	SW	6.7 ^a	26.9 ^{ab}	58.5 ^{abc}	93.2 ^{BC}	206.5 ^c	31.0	0.93	< 0.0001
SO_4 depletion (mg S cm ⁻²)	SW	0.14 ^a	2.52 ^{ab}	3.63 ^{abc}	4.28 ^{BC}	6.90 ^c	48.5	1	
Pore water sulfide (μ g S L ⁻¹)	pw	69 ^a	184 ^a	224 ^a	393 ^b	728 ^b	10.5	0.81	< 0.0001
Pore water iron ($\mu g L^{-1}$)	pw	12,883 ^a	11,122 ^{ab}	6,808 ^{abc}	4,483 ^{BC}	3,032 ^c	4.25	-0.82	< 0.0001
AVS (mg S kg $^{-1}$)	sed	102 ^a	483 ^{ab}	NA	826 ^{ab}	1,413 ^b	13.8	0.77	< 0.0001
pH	pw	7.57 ^a	7.52 ^a	7.55 ^a	7.75 ^a	7.81 ^a	1.03	0.39	=0.03
H^+ ion (µmol L ⁻¹)	pw	0.027	0.030	0.028	0.018	0.015	1.72	0.39	=0.03
		Variable	s mainly asso	ociated with	mineralizat	ion of org	anic matter		
TOC (% dry mass)	sed	9.26 ^a	7.90 ^a	8.18 ^a	7.17 ^a	8.22 ^a	1.29	-0.34	=0.065
DIC (mg CL^{-1})	SW	28.9 ^a	47.2 ^{ab}	56.3 ^{BC}	56.7 ^{BC}	66.3 ^c	2.30	0.94	< 0.0001
DOC (mg C L^{-1})	SW	16.3 ^a	21.4 ^a	26.8 ^{BC}	24.0 ^{abc}	28.3 ^{bc}	1.74	0.79	< 0.0001
Total N (mg N L^{-1})	SW	1.42 ^a	1.75 ^a	2.35 ^{BC}	2.03 ^{abc}	2.57 ^{BC}	1.81	0.77	< 0.0001
Ammonia (mg N L^{-1})	SW	0.09 ^a	0.09 ^a	0.10 ^a	0.10 ^a	0.16 ^a	1.70	0.38	=0.04
Total P (μ g P L ⁻¹)	SW	13 ^a	16 ^{ab}	22 ^{ab}	21 ^{ab}	25 ^b	1.92	0.73	< 0.0001
Available P (μ g P g ⁻¹ resin)	Resin in sed	0.34 ^a	0.40 ^a	0.59 ^{ab}	0.92 ^{ab}	2.56 ^b	7.45	0.86	< 0.0001
Total Hg (ng L^{-1})	SW	1.83 ^a	2.09 ^a	3.61 ^{ab}	3.25 ^{ab}	4.80 ^b	2.63	0.82	<0.0001
Variables mainly associated with Hg methylation									
Methylmercury (ng Hg L^{-1})	SW	0.20 ^a	0.49 ^{ab}	1.21 ^b	1.08 ^b	1.18 ^b	5.91	0.66	< 0.0001
Inorganic Hg (ng L^{-1})	SW	1.63 ^a	1.60 ^{ab}	2.40 ^{abc}	2.17 ^{BC}	3.62 ^c	2.22	0.80	< 0.0001
Percent methylmercury	SW	11% ^a	23% ^{ab}	30% ^b	32% ^b	23% ^{ab}	2.90	0.45	=0.02

Note. Matrix abbreviations: sw = surface water, pw = pore water, sed = bulk sediment. Averages with superscript letters in common are not significantly different at the 0.05 level.

(Hall et al., 2006). However, the sulfide reoxidation does not reverse the mobilization of the constituents of organic matter (C, N, P, and Hg) or the production of methylmercury (MeHg; see below). Rather, any production of SO₄ from sulfide oxidation creates the potential for additional MSR-driven OM mineralization and Hg methylation (Coleman Wasik et al., 2015; Hansel et al., 2015).

The slope of linear regressions of the C, N, and P in surface water against $(SO_4)_{Depl}$ is an estimate of the increase of that variable in mesocosm surface waters per unit SO_4 reduction (Table 2). The regression slopes provide a basis for estimates of stoichiometric ratios of the constituents mobilized from the sediment solid phase, similar to the calculation that Weston et al. (2006) performed for pore water. The calculation of stoichiometric ratios from the slopes of regressions with $(SO_4)_{Depl}$ is more accurate than calculating ratios from surface water concentrations alone, as the use of slopes accounts for the concentrations of the control (the intercept of the linear regression).

The regression slopes of surface water C versus surface water N, P, and Hg in mesocosms are estimates of the net release of each element relative to that of C (Table 3). These estimates can then be compared to the ratio of these constituents in the primary source material—the sediment—to determine the efficiency of mobilization of sediment N, P, and Hg to surface water, compared to C (Table 3). Although we present efficiency relative to only DOC and only DIC, calculating efficiency relative to the sum of mineralized OM (DOC + DIC) represents the overall net efficiency of mineralization, which ranges from 8% to 38% for the three constituents (Table 3). Although the increases in surface water N, P, and Hg are consistent with the hypothesis that those elements were released to the surface water through sulfate-enhanced mineralization of sediment OM, their lower mobilization efficiencies relative to carbon suggest that other processes were operating to either increase carbon, decrease N, P, and Hg mobilization relative to carbon, and/or increase N, P, and Hg losses. It is likely that some carbon was introduced to the surface waters from sources other than the sediment (e.g., photosynthetic fixation of atmospheric carbon) and that there were losses for N, P, and Hg from the surface water (though adsorption, settling, biological uptake, or atmospheric evasion of N and Hg).

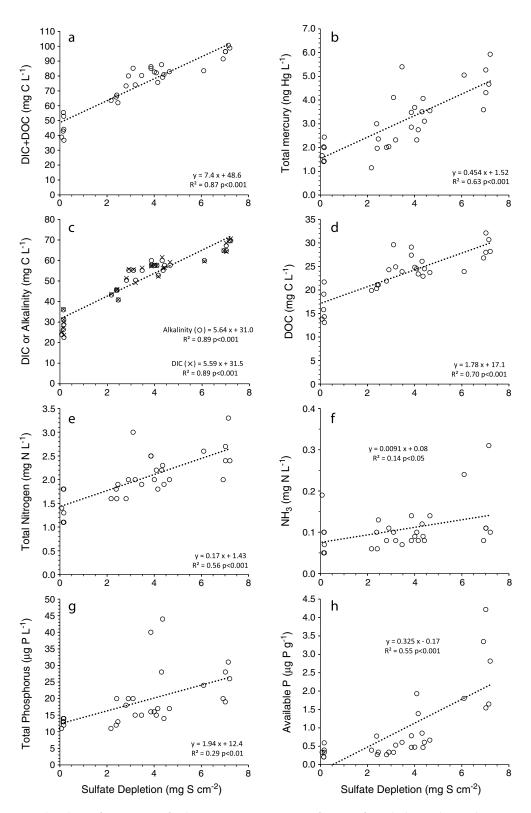


Figure 2. The release of constituents of sedimentary organic matter as a function of SO₄ depletion, showing linear regressions (dotted lines). (a) Sum of surface water DIC and DOC; (b) surface water total mercury; (c) surface water alkalinity and DIC (symbols \circ and \times , respectively; the two regressions are superimposed); (d) surface water DOC; (e) surface water total nitrogen; (f) surface water ammonia; (g) surface water total phosphorus; (h) available phosphate in the sediment, as quantified on ion-exchange resin.

Table 2

Slopes of Regressions of Surface Water Parameters (mM) Against SO₄ Depletion (mg S cm⁻²)

	Regress	ion against (SO	4) _{Depl}			
Surface water	$(mg S cm^{-2})$					
variable (molar basis)	Slope	R^2	р			
			P			
DIC	0.235	0.89	<0.0001			
DOC	0.148	0.70	<0.0001			
DIC + DOC	0.383	0.84	< 0.0001			
DIC: DOC	0.044	0.56	< 0.0001			
TN	0.0121	0.56	< 0.0001			
TN: DIC	-0.0028	0.25	<0.01			
TN: DOC	0.0004	0.01	NS			
TN: DIC + DOC	-0.0006	0.08	NS			
TP	6.26E-05	0.29	< 0.002			
TP: DIC	-7.00E-06	0.03	NS			
TP: DOC	7.00E-06	0.02	NS			
TP: DIC + DOC	-1.00E-07	0.00	NS			
THg	2.26E-09	0.63	< 0.0001			
THg: DIC	9.00E-06	0.46	< 0.0001			
THg: DOC	6.00E-06	0.23	<0.01			
THg: DIC + DOC	2.00E-05	0.42	< 0.0001			

Note. When a sediment constituent's ratio to DIC or DOC has a significant slope against sulfate depletion, it indicates that the constituent was mobilized to the surface water at a significantly different rate than the DIC or DOC.

In addition to increases of TP in the surface water, the sediment pore water in the highest SO₄ treatment contained 7.5-fold greater available phosphate than the controls, as quantified with ion-exchange resin (Table 1 and Figure 2h). In comparison, the increase in surface water TP was only 1.9fold (Table 1 and Figure 2g). The difference between phosphorus response in the resin and the surface water may be partly due to (a) loss of TP from the surface water after mobilization or (b) irreversible trapping of mobilized P on the resin. If phosphorus is released from sediment en masse in response to an S-induced shift from iron oxides to iron sulfides, the sediment pore water would experience this release first, while release to surface waters would take longer due to diffusion-limited transport and potentially an iron-oxide barrier at the sediment-water (anoxicoxic) interface.

DIC in surface water is not conservative, being subject to exchange across the air-water interface, carbonate mineral precipitation, and photosynthetic uptake. Surface water pCO₂ in all mesocosms was above saturation with respect to atmospheric equilibrium by a factor of 1.4-15.5 (based on the DIC speciation calculations discussed earlier; data not shown), so the mesocosms were losing, not gaining, C through gas exchange with the atmosphere. The pCO₂ values in the mesocosms are similar to those reported from epilimnia of small, organic-rich, temperate lakes of low to moderate salinity (Cole et al., 1994; Myrbo & Shapley, 2006). With respect to mineral precipitation, based on geochemical equilibrium calculations, surface waters were undersaturated with respect to all carbonate minerals. Thus, although DIC in surface water is subject to several transport and transformation processes, the sustained presence of CO₂ at quantities

significantly above saturation with respect to the atmosphere and the observation of increasing DIC and DOC with increasing (SO₄)_{Depl} (Table 1) provide strong evidence of sulfate-induced increases in net carbon mineralization in the mesocosms.

In addition to the carbon originally present in the sediment, organic carbon was also photosynthetically fixed by wild rice and algae in the mesocosms and subsequently subjected to respiration and some decomposition, adding to the DIC and DOC in surface waters. DOC may also have been released into sediment pore water as an exudate from the wild rice roots (Rothenberg et al., 2014; Windham-Myers et al., 2009). Exudate DOC, however, does not account for the observed increase in DOC, since a negative relationship between the number of wild rice plants and DOC was observed (Spearman's rho = -0.63, p < 0.001, Table S2).

4.2. Effects of SO₄ Reduction on Mercury and Methylmercury in Surface Water

We interpret Hg mobilization to the surface water in an analogous manner to C, N, and P, as Hg tends to associate strongly with organic matter in sediment (Feyte et al., 2010). In the mesocosm surface waters,

Elemental Ratios in Sediment and Surface Water Across the Range of SO ₄ Depletion Molar ratio in surface water ^b					Efficiency of mobilization of sediment N, P, or Hg to surface water, relative to carbon			
Molar ratio in sediment ^a		DIC	DOC	DOC + DIC	DIC	DOC	DOC + DIC	
C: N C: P C: Hg	12 ^a 463 ^a 1.90E + 07	19 3,752 1.04E + 08	12 2,366 6.5E + 07	32 6,118 1.69E + 08	63% 12% 18%	100% 20% 29%	38% 8% 11%	

Note. Together, the ratios are used to calculate the efficiency of mobilization of the constituents of particulate organic matter into the surface water. slopes of C versus N, P, and Hg in mesocosm surface waters; calculations are made based on surface water DIC alone, surface water DOC alone, and the sum of surface water DOC + DIC.

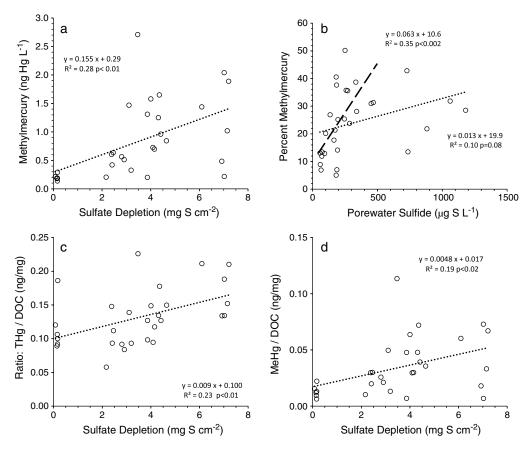


Figure 3. The response of surface water Hg variables to SO₄ depletion and the production of pore water sulfide, showing linear regressions. (a) MeHg as a function of SO₄ depletion; (b) percent MeHg as a function of pore water sulfide, showing regressions for all data (dotted line) and for the subset of data extending only to a pore water sulfide concentration of 468 μ g S L⁻¹ (dashed line); (c) ratio of THg to DOC as a function of SO₄ depletion; (d) ratio of MeHg to DOC as a function of SO₄ depletion.

THg, inorganic Hg (iHg), and MeHg all increased significantly with increased (SO₄)_{Depl} (Table 1 and Figures 2b and 3a, p < 0.0001) and were greater in the highest sulfate amendment by factors of 2.6, 2.2, and 5.9, respectively (Table 1). The relative increase in THg (2.6-fold) is greater than that for DIC, DOC, TN, and TP, which range from 1.7 to 2.3-fold (Table 1). DOC enhances the solubility of both iHg and MeHg and can facilitate the movement of Hg from sediment into surface water (Ravichandran, 2004). The 5.9-fold increase in MeHg indicates that MeHg flux to surface waters was enhanced by sulfate loading disproportionately more than sedimentary release of THg (2.6-fold) and the increase in surface water DOC (1.7-fold).

The genes required to methylate Hg have been found in a wide variety of anaerobic bacteria, including SO₄reducing bacteria, iron-reducing bacteria, and methanogens (Podar et al., 2015). Though some pure culture and experimental evidence exist for mercury methylation by other bacteria, extensive pure culture, experimental, and landscape-scale observations suggest SO₄-reducing bacteria dominate Hg methylation in many freshwater and marine environments. The relatively large increase in surface water MeHg in response to increased (SO₄)_{Depl} in this experiment supports the assumption that MSR was responsible for most of the observed production of MeHg. It is likely that increased SO₄ loading to low-SO₄ aquatic systems with organic sediment will result in increased Hg methylation even though the relative importance of Hg methylation in the environment by different groups of bacteria is still a subject of debate (Paranjape & Hall, 2017).

If movement of DOC from sediment to surface water were the sole mechanism for the Hg increase in surface water, a constant Hg:DOC ratio would be expected on the $(SO_4)_{Depl}$ gradient. However, THg:DOC, iHg:DOC, and MeHg:DOC ratios in surface water are all significantly correlated with SO₄ depletion (Table S2 and Figures 3c and 3d). Therefore, all forms of Hg (THg, iHg, and MeHg) increase in surface waters more than

does DOC, indicating that a sulfate-induced enhancement of carbon mineralization may act in combination with either enhanced methylation or an enhanced capacity of DOC to carry Hg. Changes to the binding strength of the DOC in heavily S-impacted mesocosm sediment are possible, as thiol groups on DOC are dominant binding sites for Hg (Skyllberg, 2008). The dual role of organic carbon and sulfur in driving both the production of MeHg and the transport of MeHg could be responsible for the substantially larger maximum increase in MeHg:DOC ratio relative to the increase in the THg:DOC ratio (an average 206% increase relative to a 63% increase, Figures 3c and 3d), as postulated by Bailey et al. (2017).

Regnell and Hammar (2004) identified three MSR-driven processes that might cause mobilization of Hg from sediment in a wetland, (1) mineralization of organic matter; (2) extraction of iHg by reduced S compounds, which could be associated with mobilized DOC; and (3) enhanced production of MeHg, which is more mobile than iHg. They argued that enhanced production of MeHg explained THg mobilization in the minerotrophic peat bog that they studied. However, in this study, increases in surface water MeHg concentrations (Figure 3a) are not sufficient to explain the linear increase in THg observed in this experiment (Figure 2b) because most (67%) of the increase is iHg (Table 1). Some of the increase in surface water iHg could be the result of increased production of MeHg that moved to surface water and was subsequently demethylated. Regardless of the underlying mechanism, our observations clearly show increases in surface water Hg that were greater than the increases in C, N, and P (Table 3); this corroborates other studies (Bouchet et al., 2013; Merritt & Amirbahman, 2007; Regnell & Hammar, 2004) that suggest sediment Hg may be synergistically mobilized to surface waters through mineralization, methylation, and enhanced mobility with DOC.

Recent research has shown that in many ecosystems, higher concentrations of pore water sulfide may inhibit MeHg production through either thermodynamically or kinetically controlled reactions with inorganic Hg (Benoit et al., 2003; Hsu-Kim et al., 2013). We plotted %MeHg, rather than the MeHg concentration, against pore water sulfide because we are interested in identifying the pore water sulfide zone of greatest efficiency for the methylation and mobilization of mercury. In this experiment the MSR-driven mineralization of OM released THg to surface water in addition to producing pore water sulfide. Accordingly, because THg is not constant, plotting %MeHg is the most accurate way to identify peak methylation efficiency. In principle, the restricted bioavailability of Hg to methylating bacteria results in a maximum in MeHg production at intermediate concentrations of pore water sulfide. Consistent with previous research in sulfate-impacted freshwater ecosystems (Gilmour et al., 1998; Gilmour, Krabbenhoft, et al., 2007, Gilmour, Orem, et al., 2007; Bailey et al., 2017), MeHg production was most efficient at intermediate sulfide concentrations. In the control, where average sulfide was 69 μ g S L⁻¹, MeHg averaged only 11% of THg in surface waters. In the intermediate SO₄ treatments, which had average sulfide concentrations of 224 and 393 μ g S L⁻¹, MeHg production efficiency peaked significantly higher, at averages of 30% and 32%, respectively (Table 1). %MeHg declined to an average of 23% in the highest SO4 treatment, which had an average sulfide concentration of 728 μ g S L⁻¹. Given the relatively great scatter in the relationship between %MeHg and sulfide (Figure 3b), it would be most defensible to conclude that the decrease in %MeHg began to occur somewhere between 300 and 700 μ g S L⁻¹. There is a strong positive relationship (p < 0.001) between sulfide and %MeHg if the five sulfide concentrations greater than 727 $\mu g~S~L^{-1}$ are excluded from the regression (which leaves only sulfide concentrations less than 468 μ g S L⁻¹, since there is a gap in sulfide concentrations; Figure 3b). Other studies have identified sulfide zones of peak methylation roughly comparable to that found here. In South Florida, Orem et al. (2011) found that sulfide ranging from 5 to 150 μ g S L⁻¹ did not inhibit methylation but that sulfide concentrations greater than 1,000 μ g S L⁻¹ did. In a subboreal Minnesota wetland enriched in SO₄ from mining discharge, Bailey et al. (2017) found that sulfide concentrations above ~650 μ g S L⁻¹ inhibited methylation.

The relationship between surface water SO₄ and Hg methylation can be strongly affected by site-specific conditions. Because of the variable conversion of SO₄ in surface water to sulfide in pore water—primarily due to differences in OM and Fe availability (Pollman et al., 2017)—researchers have found a broad range in the SO₄ concentration associated with maximum efficiency of Hg methylation. For example, Orem et al. (2014) observed that two different areas in the Everglades Protection Area had peak surface water MeHg concentrations at SO₄ concentrations of 2 and 10–15 mg L⁻¹. In the mesocosms presented here peak surface water %MeHg was observed in the two sulfate treatments that averaged 59 and 93 mg L⁻¹ (Table 1).

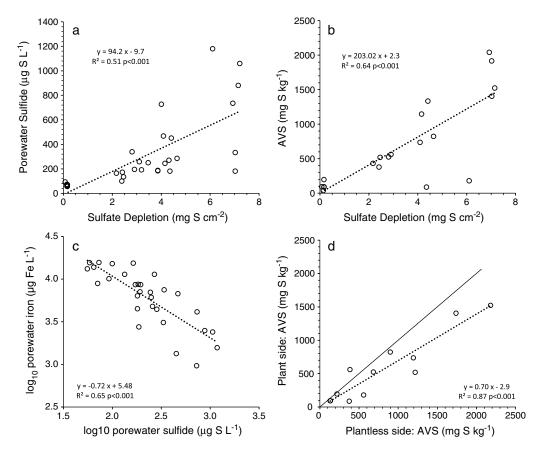


Figure 4. AVS and pore water sulfide, as related to SO_4 depletion, pore water iron, and presence of rooted plants. (a) Pore water sulfide as a function of SO_4 depletion; (b) AVS from the vegetated side of the mesocosms as a function of SO_4 depletion; (c) pore water iron as a function of pore water sulfide; (d) AVS compared between the vegetated side and nonvegetated side. The solid 1:1 line shows that in almost all mesocosms more AVS is found in the side without plants.

4.3. Effects of SO₄ Reduction on Pore Water and Sediment Sulfide

Pore water sulfide increased at higher (SO₄)_{Depl}, although with greater variance at higher (SO₄)_{Depl} (Figure 4a), possibly as a result of variable oxidation of sulfide that may depend on the proximity of the Rhizon sampler to plant roots (Schmidt et al., 2011) or of variable bioturbation by invertebrates (Lawrence et al., 1982). When SO₄ is reduced through MSR, the sulfide produced has a number of nonexclusive potential fates: the sulfide could (1) be oxidized within the sediment; (2) remain in the sediment pore water as free sulfide; (3) diffuse into oxygenated surface water, to be oxidized; (4) react with metals in the sediment, forming insoluble precipitates (dominated by iron-sulfide compounds); or (5) be lost to the atmosphere as H₂S gas or as volatile organic sulfur compounds. Because precipitation reactions are fast relative to redox reactions and diffusion, most of the sulfide probably forms metal precipitates if metals are available. When precipitation dominates the fate of sulfide produced from MSR, the continuous reduction of SO₄ and precipitation of iron sulfides form guasi-steady states between surface water SO₄ and pore water sulfide (Figure S2b) and between pore water sulfide and pore water iron (Figures 3 and 4c). The overall mass of sulfide in the mesocosm sediment, quantified through analysis of AVS (from sediment in the vegetated area), is closely correlated with SO_4 depletion (Figure 4b) even though AVS may not include all the reduced sulfide in sediments. It is likely that most of the AVS in these sediments is present as an FeS precipitate because other metals are at low concentrations in these sediments, which came from a relatively pristine (unpolluted) lake (Fond du Lac Band, 2016; Pastor et al., 2017). Note that there are two mesocosms with especially low AVS concentrations (Figure 4b). It is possible that the AVS in the specific location in these mesocosms where sediment core samples were collected was influenced by a spatially heterogeneous oxidization process (e.g., root oxygen or benthic invertebrates) that limited the accumulation of sulfide.

AVS was 30% lower in the vegetated side of the mesocosms, suggesting that wild rice released oxygen into the sediment, inhibiting the production of sulfide and/or decreasing sulfide concentrations through oxidation (Figure 4d; Wilcoxon paired test, p = 0.007). It is notable that this 30% difference developed in just one growing season, despite the previous 2 years of sulfate treatment. Pore water sulfide showed no statistically significant difference between the two sides owing to high variability within treatments. Numerous investigations have found that rooted aquatic plants release oxygen from their roots, a phenomenon that is usually interpreted as an adaptation to limit the toxicity of reduced chemical species in the pore water, especially sulfide (Lamers et al., 2013). Although oxygen release has been observed in white rice, Oryza sativa (Colmer, 2002), it has never been documented in wild rice, which is in the same tribe (Oryzeae) of grasses as white rice, and also develops aerenchyma (Jorgenson et al., 2013), plant structures that provide a lowresistance internal pathway for movement of oxygen to the roots. Since the growth and reproduction of rooted plants can be inhibited by sulfide (Pastor et al., 2017), there may be a tipping point of exposure to sulfide above which oxygen release is insufficient to mitigate phytotoxic effects, and the plant population declines over time, possibly to extirpation. In this experiment, in the third treatment year, the increase in pore water sulfide was the apparent cause of a decrease in the average number of wild rice stems from 17 in the control mesocosms to 3 in the highest-sulfate treatment mesocosms (Pastor et al., 2017).

4.4. Mesocosms as Models for Ecosystem-Scale Effects of SO₄ Reduction

Although mesocosms, as contained ecosystems, are useful because they mimic ecological and biogeochemical processes that occur in the field, extrapolating findings to nature is challenging when plastic walls have prevented exchange of water and materials (Petersen et al., 2009). These wall-based challenges are manifest in three phenomena in this experiment, (1) relatively long surface water residence times due to the lack of a constant throughflow; (2) the presence of the wall itself, which provides a surface for periphyton; and (3) lack of either overland or groundwater loading of external materials:

- Relatively long surface water residence times: the increased loading of N, P, C, Hg, and MeHg to the surface water of the mesocosms was readily detected because the lack of hydraulic loading from a watershed minimized dilution and loss through the outflow. The impact of an increase in SO₄ loading on surface water concentrations of N, P, C, Hg, DIC, and DOC would be lower in waters with shorter residence times. For instance, Baker and Brezonik (1988), in modeling increases in alkalinity from atmospheric SO₄ loading, noted that net increases in alkalinity would be most important in waters with long residence times (>5 years) and that there would be little increase in alkalinity in waters with much shorter residence times (<1 year). However, the measured concentrations may not represent the maximum impact of MSR-driven mineralization because the mesocosm wall may enhance removal from the surface water (point number 2, below).
- 2. Presence of the mesocosm wall: the mesocosms have a relatively high ratio of wall and sediment surfaces to the volume of overlying water, enhancing the removal of surface water nutrients and Hg to periphyton or inorganic sinks such as iron oxyhydroxides. Natural aquatic systems have less proportional loss to surfaces. The quantitative estimates of internal loading of N, P, and Hg in response to MSR-induced carbon mineralization may have been underestimated by the measured surface water concentrations, given that significant loss of these constituents to periphyton may have occurred. In addition, THg was filtered prior to analysis, which would have removed any Hg associated with phytoplankton or other suspended particles.
- 3. Lack of either overland or groundwater loading of particulate and dissolved material, specifically iron: the availability of iron in sediment is a primary controller of the fate of MSR-produced sulfide (Pollman et al., 2017). In natural aquatic systems, iron would be supplied at a relatively constant rate from the system's watershed over the long term, although varying in magnitude from watershed to watershed (Maranger et al., 2006; Winter, 2001). This experiment was not an accurate long-term mimic of pore water sulfide concentrations because the external supply of iron was cut off at the inception of the experiment. With no loading of iron, but continued loading of SO_4 , the continued production of sulfide would be expected to eventually consume all available Fe, allowing pore water sulfide levels to exceed those expected in a natural system at equivalent surface water SO_4 concentrations. This mesocosm experiment provides

evidence for just such a result. The experiment continued for 2 years after the 2013 sampling presented here. In the fifth year (August 2015) pore water sulfide was much greater than had been observed in 2013, and disproportionately so in the highest SO₄ treatment, which was most likely to consume available Fe. Between the 2013 and 2015, pore water sulfide increased in the control SO₄ treatment (about 7 mg SO₄ L⁻¹) from an average value of 69 µg L⁻¹ in 2013 to 116 µg L⁻¹ in 2015, a 68% increase. Pore water sulfide in the highest treatment (nominally 300 mg SO₄ L⁻¹, Table 1) increased from an average value of 728 µg L⁻¹ in 2013 to 9,350 µg L⁻¹ in 2015, a 1,184% increase (Pastor et al., 2017). In a survey of 108 Minnesota waterbodies with a wide range of surface water sulfate, only two exceeded a pore water sulfide level of 3,200 µg L⁻¹ (Myrbo et al., 2017).

5. Conclusions

This study demonstrates that increased SO₄ loading to inland waters with organic-rich sediments can significantly increase the decomposition of sedimentary organic matter, which increases internal loading to surface water of the chemical constituents of organic matter, including DIC, DOC, P, N, and Hg. Associated changes include increased production of sulfide and methylmercury and increased alkalinity and pH. Any one of these changes could alone cause significant secondary changes in the structure of an aquatic ecosystem but, taken together, could cause a cascade of primary and secondary environmental changes: increased availability of nutrients (N and P), which can alter dominant plant species, organic carbon production, oxygen consumption, and redox; increased pore water sulfide, which can be toxic to benthic animals and plants; increased MeHg production, which can affect fish and other consumers in the aquatic food web; increased DOC, which can alter light transmission, thermal stratification, and aquatic chemistry; and increased DIC production, which increases alkalinity and pH, affecting aquatic chemistry and biota. Each of these changes resulting from higher surface water SO₄ and consequent increases in MSR has been documented in the literature, but the entire suite of associated changes in aquatic chemistry has not heretofore been demonstrated in an integrated fashion. The degree to which an increase in SO₄ loading affects the ecological structure of the receiving water will depend on the relative increases in N, P, DIC, DOC, Hg, MeHg, pH, and sulfide, which will be a function of background geochemistry and hydrology of the specific system. In this experiment, the changes in these parameters were linearly proportional to SO₄ reduction, which, in turn, was linearly proportional to the time-weighted average SO_4 concentration. The linear responses of the parameters to SO_4 additions suggest that ecologically significant changes may occur even when SO₄ concentrations are elevated only modestly and that dramatic changes may occur with higher sulfate loading.

Acknowledgments

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References

- Åkerblom, S., Bishop, K., Björn, E., Lambertsson, L., Eriksson, T., & Nilsson, M. B. (2013). Significant interaction effects from sulfate deposition and climate on sulfur concentrations constitute major controls on methylmercury production in peatlands. *Geochimica et Cosmochimica Acta*, 102, 1–11.
- APHA (2005). Standard Methods for Examination of Water and Wastewater (21st ed.). Washington, DC: American Public Health Association.
- Bachand, P. A. M., Bachand, S., Fleck, J., Anderson, F., & Windham-Myers, L. (2014). Differentiating transpiration from evaporation in seasonal agricultural wetlands and the link to advective fluxes in the root zone. *Science of the Total Environment*, 484, 232–248.
- Bagarinao, T. (1992). Sulfide as an environmental factor and toxicant: Tolerance and adaptations in aquatic organisms. *Aquatic Toxicology*, 24, 21–62.
- Bailey, L. T., Mitchell, C. P. J., Engstrom, D. R., Berndt, M. E., Coleman Wasik, J. K., & Johnson, N. W. (2017). Influence of porewater sulfide on methylmercury production and partitioning in sulfate-impacted lake sediments. Science of the Total Environment, 580, 1,197–1,204.
- Baker, L. A., & Brezonik, P. L. (1988). Dynamic model of in-lake alkalinity generation. Water Resources Research, 24, 65–74. https://doi.org/ 10.1029/WR024i001p00065
- Baker, L. A., Brezonik, P. L., & Pollman, C. D. (1986). Model of internal alkalinity generation: Sulfate retention component. Water, Air, and Soil Pollution, 31, 89–94.
- Baker, L. A., Pollman, C. D., & Eilers, J. M. (1988). Alkalinity regulation in softwater Florida lakes. Water Resources Research, 24, 1069–1082. https://doi.org/10.1029/WR024i007p01069
- Baldwin, D. S., & Mitchell, A. (2012). Impact of sulfate pollution on anaerobic biogeochemical cycles in a wetland sediment. *Water Research*, 46, 965–974. https://doi.org/10.1016/j.watres.2011.11.065
- Benoit, J. M., Gilmour, C. C., Heyes, A., Mason, R. P., & Miller, C. L. (2003). Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems, Chapter 19. In *Biogeochemistry of Environmentally Important Trace Elements, ACS Symposium Series* (Vol. 835, pp. 262–297). Washington, DC: American Chemical Society.
- Bergman, I., Bishop, K., Tu, Q., Frech, W., Åkerblom, S., & Nilsson, M. (2012). The influence of sulphate deposition on the seasonal variation of peat pore water methyl Hg in a boreal mire. PLoS One, 7(9), e45547. https://doi.org/10.1371/journal.pone.0045547
- Bouchet, S., Amouroux, D., Rodriguez-Gonzalez, P., Tessier, E., Monperrus, M., Thouzeau, G., ... Anschutz, P. (2013). MMHg production and export from intertidal sediments to the water column of a tidal lagoon (Arcachon Bay, France). *Biogeochemistry*, 114, 341–358.

Boudreau, B. P., & Westrich, J. T. (1984). The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments. *Geochimica et Cosmochimica Acta*, 48, 2503–2516.

- Boye, K., Noël, V., Tfaily, M. M., Bone, S. E., Williams, K. H., Bargar, J. R., & Fendorf, S. (2017). Thermodynamically controlled preservation of organic carbon in floodplains. *Nature Geoscience*, 10, 415–419. https://doi.org/10.1038/ngeo29
- Branfireun, B. A., Bishop, K., Roulet, N. T., Granberg, G., & Nilsson, M. (2001). Mercury cycling in boreal ecosystems: The long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophysical Research Letters*, 28, 1227–1230. https://doi.org/ 10.1029/2000GL011867
- Branfireun, B. A., Roulet, N. T., Kelly, C. A., & Rudd, J. W. M. (1999). In situ sulphate stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain and methylmercury contamination in remote environments. *Global Biogeochemical Cycles*, *13*, 743–750. https://doi.org/10.1029/1999GB900033
- Capone, D. G., & Kiene, R. P. (1988). Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. *Limnology and Oceanography*, 33, 725–749.
- Caraco, N. F., Cole, J. J., & Likens, G. E. (1993). Sulfate control of phosphorus availability in lakes. Hydrobiologia, 253, 275-280.
- Cole, J. J., Caraco, N. F., Kling, G. W., & Kratz, T. K. (1994). Carbon dioxide supersaturation in the surface waters of lakes. Science, 265, 1,568–1,570.
- Coleman Wasik, J. K., Engstrom, D. R., Mitchell, C. P. J., Swain, E. B., Monson, B. A., Balogh, S. J., ... Almendinger, J. E. (2015). The effects of hydrologic fluctuation and sulfate regeneration on mercury cycling in an experimental peatland. *Journal of Geophysical Research: Biogeosciences*, 120, 1697–1715. https://doi.org/10.1002/2015JG002993

Colmer, T. D. (2002). Aerenchyma and an inducible barrier to radial oxygen loss facilitate root aeration in upland, paddy and deep-water rice (Oryza sativa L). Annals of Botany, 91, 301–309.

Cook, R. B., Kelly, C. A., Schindler, D. W., & Turner, M. A. (1986). Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. Limnology and Oceanography, 31, 134–148.

Cottingham, K. L., Lennon, J. T., & Brown, B. L. (2005). Knowing when to draw the line: Designing more informative ecological experiments. *Frontiers in Ecology and the Environment*, 3(3), 145–152.

Curtis, P. J. (1989). Effects of hydrogen ion and sulphate on the phosphorus cycle of a Precambrian Shield lake. *Nature*, 337, 156–158.

Feyte, S., Tessier, A., Gobeil, C., & Cossa, D. (2010). In situ adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments. *Applied Geochemistry*, 25, 984–995.

Fond du Lac Band (2016). Fond du Lac Lakes and Streams Data Table. Retrieved from: http://www.fdlrez.com/RM/waterquality.htm, accessed 2 Dec 2016.

Geurts, J. J. M., Sarneel, J. M., Willers, B. J. C., Roelofs, J. G. M., Verhoeven, J. T. A., & Lamers, L. P. M. (2009). Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: A mesocosm experiment. *Environmental Pollution*, *157*, 2072–2081.

Giblin, A. E., Likens, G. E., White, D., & Howarth, R. W. (1990). Sulfur storage and alkalinity generation in New England lake sediments. Limnology and Oceanography, 35, 852–869.

Gilmour, C., Krabbenhoft, D., Orem, W., Aiken, G., & Roden, E. (2007). Appendix 3B-2: Status report on ACME studies on the control of mercury methylation and bioaccumulation in the Everglades, 2007 South Florida Environmental Report. South Florida Water Management District, West Palm Beach, FL.

- Gilmour, C., Orem, W., Krabbenhoft, D., & Mendelssohn, I. (2007). Appendix 3B-3: Preliminary assessment of sulfur sources, trends and effects in the Everglades. 2007 South Florida Environmental Report. South Florida Water Management District, West Palm Beach, FL.
- Gilmour, C. C., Henry, E. A., & Mitchell, R. (1992). Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science & Technology*, 26, 2,281–2,287.
- Gilmour, C. C., Riedel, G. S., Ederington, M. C., Bell, J. T., Benoit, J. M., Gill, G. A., & Stordal, M. C. (1998). Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40(2–3), 327–345.
- Gorham, E., Dean, W. E., & Sanger, J. E. (1983). The chemical composition of lakes in the north-central United States. *Limnology and Oceanography*, 28, 287–301.

Hall, K. C., Baldwin, D. S., Rees, G. N., & Richardson, A. J. (2006). Distribution of inland wetlands with sulfidic sediments in the Murray-Darling Basin, Australia. Science of the Total Environment, 370, 235–244.

Hansel, C. M., Lentini, C. J., Tang, Y., Johnson, D. T., Wankel, S. D., & Jardine, P. M. (2015). Dominance of sulfur-fueled iron oxide reduction in low-sulfate freshwater sediments. *The ISME Journal*, 9, 2400–2412. https://doi.org/10.1038/ismej.2015.50

Harmon, S. M., King, J. K., Gladden, J. B., Chandler, G. T., & Newman, L. A. (2004). Methylmercury formation in a wetland mesocosm amended with sulfate. *Environmental Science & Technology*, 38, 650–656.

Heijs, S. K., & van Gemerden, H. (2000). Microbiological and environmental variables involved in the sulfide buffering capacity along a eutrophication gradient in a coastal lagoon (Bassin d'Arcachon, France). *Hydrobiologia*, 437(1–3), 121–131.

Hildebrandt, L., Pastor, J., & Dewey, B. (2012). Effects of external and internal nutrient supplies on decomposition of wild rice, Zizania palustris. Aquatic Botany, 97, 35–43.

Holmer, M., & Storkholm, P. (2001). Sulphate reduction and sulphur cycling in lake sediments: A review. *Freshwater Biology*, 46, 431–451.
Howes, B. L., Dacey, J. W. H., & Teal, J. M. (1985). Annual carbon mineralization and belowground production of Spartina alterniflora in a New England salt marsh. *Ecology*, 66(2), 595–605.

Hsu-Kim, H., Kucharzyk, K. H., Zhang, T., & Deshusses, M. A. (2013). Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: A critical review. *Environmental Science & Technology*, 47(6), 2,441–2,456.

Jeremiason, J. D., Engstrom, D. R., Swain, E. B., Nater, E. A., Johnson, B. M., Almendinger, J. E., ... Kolka, R. K. (2006). Sulfate addition increases methylmercury production in an experimental wetland. *Environmental Science & Technology*, 40, 3,800–3,806.

Johnson, N. W., Mitchell, C. P., Engstrom, D. R., Bailey, L. T., Coleman Wasik, J. K., & Berndt, M. E. (2016). Methylmercury production in a chronically sulfate-impacted sub-boreal wetland. *Environmental Science: Processes & Impacts*, 18(6), 725–734.

Jorgenson, K. D., Lee, P. F., & Kanavillil, N. (2013). Ecological relationships of wild rice, *Zizania* spp. 11. Electron microscopy study of iron plaques on the roots of northern wild rice (*Zizania palustris*). Botany, 91, 189–201.

Lamers, L. P. M., Falla, S.-J., Samborska, E. M., Van Dulken, I. A. R., Van Hengstum, G., & Roelofs, J. G. M. (2002). Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. *Limnology and Oceanography*, 47, 585–593.

Lamers, L. P. M., Govers, L. L., Janssen, I. C. J. M., Geurts, J. J. M., Van Der Welle, M. E. W., Van Katwijk, M. M., ... Smolders, A. J. P. (2013). Sulfide as a soil phytotoxin. Frontiers in Plant Science, 4, 1–14.

Lamers, L. P. M., Ten Dolle, G. E., Van Den Berg, S. T. G., Van Delft, S. P. J., & Roelofs, J. G. M. (2001). Differential responses of freshwater wetland soils to sulphate pollution. *Biogeochemistry*, 55, 87–102.

Lamers, L. P. M., Tomassen, H. B. M., & Roelofs, J. G. M. (1998). Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. Environmental Science & Technology, 32, 199–205.

Laudon, H., Dillon, P. J., Eimers, M. C., Semkin, R. G., & Jeffries, D. S. (2004). Climate-induced episodic acidification of streams in central Ontario. Environmental Science & Technology, 38, 6009–6015.

Lawrence, G. B., Mitchell, M. J., & Landers, D. H. (1982). Effects of the burrowing mayfly, Hexagenia, on nitrogen and sulfur fractions in lake sediment microcosms. *Hydrobiologia*, 87, 273–283.

Lomans, B. P., van der Drift, C., Pol, A., & Op den Camp, H. J. M. (2002). Microbial cycling of volatile organic sulfur compounds. Cellular and Molecular Life Sciences, 59, 575–588.

Maranger, R., Canham, C. D., Pace, M. L., & Papaik, M. J. (2006). A spatially explicit model of iron loading to lakes. *Limnology and Oceanography*, 51, 247–256.

Marbà, N., Calleja, M. L., Duarte, C. M., Álvarez, E., Díaz-Almela, E., & Holmer, M. (2007). Iron additions reduce sulfide intrusion and reverse seagrass (Posidonia oceanica) decline in carbonate sediments. *Ecosystems*, 10, 745–756.

Maynard, J. J., O'Geen, A. T., & Dahlgren, R. A. (2011). Sulfide induced mobilization of wetland phosphorus depends strongly on redox and iron geochemistry. *Soil Science Society of America Journal*, *75*, 1986–1999.

Merritt, K. A., & Amirbahman, A. (2007). Mercury dynamics in sulfide-rich sediments: Geochemical influence on contaminant mobilization with the Penobscot River estuary, Maine, USA. *Geochimica et Cosmochimica Acta*, 71, 929–941.

Mitchell, C. P. J., Branfireun, B. A., & Kolka, R. K. (2008). Assessing sulfate and carbon controls on net methylmercury production in peatlands: An in situ mesocosm approach. *Applied Geochemistry*, 23, 503–518.

Moyle, J. B. (1945). Some chemical factors influencing the distribution of aquatic plants in Minnesota. *The American Midland Naturalist*, 34, 402–420.

Myrbo, A., & Shapley, M. D. (2006). Seasonal water-column dynamics of dissolved inorganic carbon stable isotopic compositions ($\delta^{13}C_{DIC}$) in small hardwater lakes in Minnesota and Montana. *Geochimica et Cosmochimica Acta*, 70, 2699–2714.

Myrbo, A., Swain, E. B., Engstrom, D. R., Coleman Wasik, J., Brenner, J., Dykhuizen Shore, M., ... Blaha, G. (2017). Sulfide generated by sulfate reduction is a primary controller of the occurrence of wild rice (Zizania palustris) in shallow aquatic ecosystems. *Journal of Geophysical Research: Biogeosciences*, 122. https://doi.org/10.1002/2017JG003787

Nielsen, D. L., Brock, M. A., Rees, G. N., & Baldwin, D. S. (2003). Effects of increasing salinity on freshwater ecosystems in Australia. Australian Journal of Botany, 51, 655–665.

Orem, W., Fitz, H. C., Krabbenhoft, D., Tate, M., Gilmour, C., & Shafer, M. (2014). Modeling sulfate transport and distribution and methylmercury production associated with Aquifer Storage and Recovery implementation in the Everglades Protection Area. *Sustainability Water Quality and Ecology*, 3-4, 33–46.

Orem, W., Gilmour, C., Axelrad, D., Krabbenhoft, D., Scheidt, D., Kalla, P., ... Aiken, G. (2011). Sulfur in the South Florida ecosystem: Distribution, sources, biogeochemistry, impacts, and management for restoration. *Critical Reviews in Environmental Science and Technology*, *41*(S1), 249–288. https://doi.org/10.1080/10643389.2010.531201

Pallud, C., & Van Cappellen, P. (2006). Kinetics of microbial sulfate reduction in estuarine sediments. *Geochimica et Cosmochimica Acta*, 70, 1,148–1,162.

Paranjape, A. R., & Hall, B. D. (2017). Recent advances in the study of mercury methylation in aquatic systems. FACETS, 2, 85–119. https://doi. org/10.1139/facets-2016-0027

Parkhurst, D. L., & Appelo, C. A. J.(2013). Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p. Retrieved from: http://pubs.usgs.gov/tm/06/a43/, Accessed 20 Nov 2016.

Pastor, J., Dewey, B., Johnson, N. W., Swain, E. B., Monson, P., Peters, E. B., & Myrbo, A. (2017). Effects of sulfate and sulfide on the life cycle of Zizania palustris in hydroponic and mesocosm experiments. *Ecological Applications*, 27, 321–336.

Patrick, R., Roberts, N. A., & Davis, B. (1968). The effect of changes in pH on the structure of diatom communities. *Notulae Naturae* (*Philadelphia*), 416, 1–16.

Petersen, J. E., Kennedy, V. S., Dennison, W. C., & Kemp, W. M. (Eds.) (2009). Enclosed Experimental Ecosystems and Scale: Tools for Understanding and Managing Coastal Ecosystems (pp. 221). New York: Springer.

Podar, M., Gilmour, C. C., Brandt, C. C., Soren, A., Brown, S. D., Crable, B. R., ... Elias, D. A. (2015). Global prevalence and distribution of genes and microorganisms involved in mercury methylation. *Science Advances*, 1, e1500675.

Pollman, C. D., Swain, E. B., Bael, D., Myrbo, A., Monson, P., & Dykhuizen Shore, M. (2017). The evolution of sulfide in shallow aquatic ecosystem sediments—An analysis of the roles of sulfate, organic carbon, iron and feedback constraints using structural equation modeling. *Journal of Geophysical Research: Biogeosciences*, 122, https://doi.org/10.1002/2017JG003785

Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter—A review. Chemosphere, 55, 319–331.

Regnell, O., & Hammar, T. (2004). Coupling of methyl and total mercury in a minerotrophic peat bog in southeastern Sweden. Canadian Journal of Fisheries and Aquatic Sciences, 61, 2014–2023.

Rothenberg, S. E., Windham-Myers, L., & Creswell, J. E. (2014). Rice methylmercury exposure and mitigation: A comprehensive review. *Environmental Research*, 133, 407–423.

Schindler, D. W. (1986). The significance of in-lake production of alkalinity. Water, Air, and Soil Pollution, 30, 931–944.

Schindler, D. W., Turner, M. A., Stainton, M. P., & Linsey, G. A. (1986). Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian Shield. Science, 232, 844–847.

Schmidt, H., Eickhorst, T., & Tippkötter, R. (2011). Monitoring of root growth and redox conditions in paddy soil rhizotrons by redox electrodes and image analysis. *Plant and Soil*, 341, 221–232.

Selvendiran, P., Driscoll, C. T., Bushey, J. T., & Montesdeoca, M. R. (2008). Wetland influence on mercury fate and transport in a temperate forested watershed. *Environmental Pollution*, 154, 46–55.

Shotbolt, L. (2010). Pore water sampling from lake and estuary sediments using Rhizon samplers. Journal of Paleolimnology, 44(2), 695–700. https://doi.org/10.1007/s10933-008-9301-8

Skyllberg, U. (2008). Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. *Journal of Geophysical Research: Biogeosciences, 113,* 2005–2012. https://doi.org/10.1029/2008JG000745

Stagg, C. L., Schoolmaster, D. R., Krauss, K. W., Cormier, N., & Conner, W. H. (2017). Causal mechanisms of soil organic matter decomposition: Deconstructing salinity and flooding impacts in coastal wetlands. *Ecology*, *98*, 2003–2018. https://doi.org/10.1002/ecy.1890 StataCorp (2015). Stata Statistical Software: Release 14. College Station, TX: StataCorp LP.

Stumm, W., & Morgan, J. J. (2012). Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. New York: John Wiley.

Van der Welle, M. E. W., Smolders, A. J. P., Op den Camp, H. J. M., Roelofs, J. G. M., & Lamers, L. P. M. (2007). Biogeochemical interactions between iron and sulphate in freshwater wetlands and their implications for interspecific competition between aquatic macrophytes. *Freshwater Biology*, 52, 434–447.

Vestergaard, O., & Sand-Jensen, K. (2000). Alkalinity and trophic state regulate aquatic plant distribution in Danish lakes. Aquatic Botany, 67, 85–107.

Walker, R. D., Pastor, J., & Dewey, B. W. (2006). Effects of wild rice (Zizania palustris) straw on biomass and seed production in northern Minnesota. Canadian Journal of Botany, 84, 1019–1024.

Weston, N. B., Porubsky, W. P., Samarkin, V. A., Erickson, M., Macavoy, S. E., & Joye, S. B. (2006). Porewater stoichiometry of terminal metabolic products, sulfate, and dissolved organic carbon and nitrogen in estuarine intertidal creek-bank sediments. *Biogeochemistry*, *77*, 375–408.
 Weston, N. B., Vile, M. A., Neubauer, S. C., & Velinsky, D. J. (2011). Accelerated microbial organic matter mineralization following salt-water intrusion into tidal freshwater marsh soils. *Biogeochemistry*, *102*, 135–151.

Williamson, C. E., Morris, D. P., Pace, M. L., & Olson, O. G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: Resurrection of a more integrated paradigm. *Limnology and Oceanography*, 44, 795–803.

Windham-Myers, L., Marvin-Dipasquale, M., Krabbenhoft, D. P., Agee, J. L., Cox, M. H., Heredia-Middleton, P., ... Kakouros, E. (2009). Experimental removal of wetland emergent vegetation leads to decreased methylmercury production in surface sediment. *Journal of Geophysical Research*, 114, G00C05. https://doi.org/10.1029/2008JG000815

Winter, T. C. (2001). The concept of hydrologic landscapes. Journal of the American Water Resources Association, 37, 335–349.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 4

(MPCA, Minnesota's Statewide Mercury TMDL, Public Forum #1 handout, Feb. 7, 2023)

Minnesota's Statewide Mercury TMDL

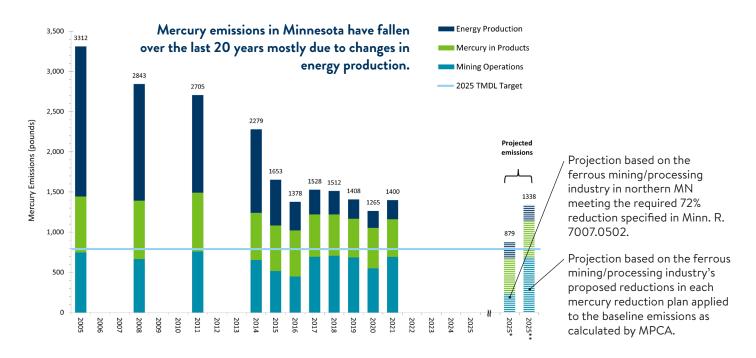
Reducing mercury in our air and water

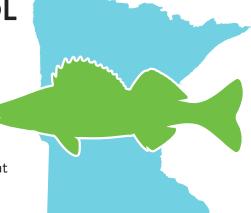
Mercury released into the air settles into water and accumulates in fish, making them unsafe for people to eat and damaging the ecosystem. Mercury exposure can harm the organs and nervous systems of people, especially children, and wildlife. In 2007, MPCA finalized a statewide mercury **total maximum daily load** (TMDL) study that determined the emissions reductions necessary to meet water quality standards and protect people from consuming mercury-contaminated fish. The MPCA also conducts fish tissue analysis to understand how mercury levels in fish are changing over time. All the waters in the state will benefit from the statewide mercury reduction plan, but not all waters respond the same to reduced emissions. The primary goal is to substantially lower mercury in fish and make them safer to eat. About 73% of our waters impaired for mercury will reach the goal if the plan is fully implemented. For the remaining 27%, more work is needed to understand why these waters

remain high in mercury despite lower emissions.

Progress in reducing mercury emissions

To accomplish the reductions specified in the TMDL and implementation plan, MPCA proposed and later adopted rules regarding mercury reduction plans in Minn. R. 7007.0502. These rules established mercury emissions reductions for certain sources of mercury air emissions in order to ensure we meet the goals of the 2007 TMDL. In order to evaluate the progress of reducing mercury in our waters, mercury emissions inventories are developed and tracked. Despite significant reductions from some sectors, the MPCA projects that the state will not meet the 2025 statewide reduction goal. Meeting that goal will require significant reduction of mercury emissions from the ferrous mining/processing sector and further reductions from mercury use in products.







Mercury emissions from energy production

State statutes and rules, along with national standards for mercury and air toxics emissions from coal-fired utility boilers, have resulted in significant reductions in emissions of mercury in Minnesota. In 2006, Minnesota passed the Mercury Emissions Reduction Act (MERA), which set a schedule for the largest coal-fired utility boilers in the state to reduce mercury emissions by 90% from 2005 levels. To achieve these reductions, they retrofitted some coal plants with improved pollution controls, switched some to natural gas, and shut down others. Utilities continue to shut down coal plants in Minnesota as they rely more on renewable energy and natural gas.

Mercury emissions from mercury use in products

The MPCA keeps track of information, such as the amount of household waste generated in the state, alongside information tracked by other local, state, and federal partners to estimate the amount of mercury emissions from smaller, widespread sources in Minnesota. Within this category, the two largest contributors are mercury in solid waste and dental mercury (via dental preparations and cremation). While the amount of solid waste produced and collected in Minnesota went up from 2017 to 2021, there has been a general downward trend in the mercury content of solid waste. Conversely, emissions from cremation have continued to increase as the practice becomes more popular in Minnesota.

Mercury emissions from mining operations

The emissions reduction goal that MPCA established in 2007 also included milestones for industrial facilities. Ferrous mining or processing facilities were required to submit a mercury emissions reduction plan by December 30, 2018, for approval and inclusion in a permit or other enforceable document. Under Minn. R. 7007.0502, these facilities had to prepare reduction plans that reduce mercury emissions by 72% from 2008/2010 emission levels by January 1, 2025. The rule also provides the option to submit an alternative plan to reduce mercury emissions if the facility demonstrated that the required 72% mercury reduction was not technically achievable.

Ferrous mining/processing facilities-mercury reduction plans

The ferrous mining/processing sector submitted mercury reduction plans to MPCA in December 2018. The MPCA received eight plans, each varying in the amount of mercury reductions proposed. Two facilities submitted plans with proposed reductions meeting the required 72% reduction specified in Minn. R. 7007.0502, two facilities submitted alternative plans with proposed reductions less than the 72%, and four facilities submitted alternative plans with no proposed reductions.

In January 2023, MPCA determined that the conclusion identified in five plans (i.e., that mercury emissions reductions of 72% are not technically achievable) had not been adequately demonstrated and determined that those plans were deficient. Across these plans, MPCA found that the facilities identified three strategies that represent technically achievable methods to achieve a 72% reduction from historical mercury emission levels. These three identified technologies are commercially available, don't impair pellet quality or production, don't cause corrosion in equipment, and achieve at least a 72% reduction in mercury emissions.

Without reductions in the ferrous mining/processing sector, the statewide mercury TMDL goals are likely unachievable. The MPCA requested that these facilities submit revised mercury reduction plans based on one of the three technically achievable options by roughly mid-2024.



Mercury emissions from energy production has generally decreased.



Emissions from mercury use in various products have generally decreased.



Mercury emissions from ferrous mining/processing have remained flat.



WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 5

(MPCA, Frequently Asked Questions, St. Louis River Watershed Mercury TMDL June 2023)

MINNESOTA POLLUTION CONTROL AGENCY

St. Louis River Watershed Mercury Total Maximum Daily Load (TMDL) Study Frequently Asked Questions

The Minnesota Pollution Control Agency (MPCA) compiled this list of frequently asked questions (FAQ) from initial interviews conducted with partners and stakeholders by DeYoung Consulting Services, the first public forum in February 2023, and discussions with the technical advisory team. The document will continue to be updated throughout the project, and new questions that arise will be added. Answers to some of the questions will also continue to be updated as the project progresses.

Information sharing

Why has it taken MPCA so long to start the St. Louis River Watershed Mercury TMDL project?

Work started on a St. Louis River Watershed mercury TMDL project in the early 2010s, with technical work led by US EPA Region 5 in collaboration with MPCA, Wisconsin Department of Natural Resources (WDNR), and the Fond du Lac Band of Lake Superior Chippewa (FDL). Preliminary analysis on mercury impairments was completed in 2013, but that initial work did not continue due to technical disagreements among these parties about how to best model how mercury works in this environment.

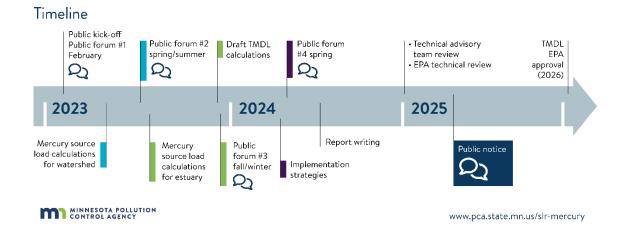
Further data collection and analysis continued in the years after completion of the project in 2013. In 2020, MPCA restarted planning for the St. Louis River Watershed Mercury TMDL project. In 2021 MPCA secured funding from the legislature for water quality modeling to support mercury TMDL development in this watershed. Also in 2021, MPCA convened a Technical Advisory Team (TAT), made up of government partners (tribal, federal, and state) and scientists whose primary role is to provide technical, scientific, and policy expertise to the MPCA project team. In 2022, MPCA hired a consultant for the mercury water quality modeling and worked with the consultant and the TAT to develop a technical approach. MPCA also hired a consultant to support public engagement. The MPCA is continuing to work with the consultants and TAT on the technical work and presenting the information to the public.

How is MPCA sharing information on this project with the public? What is the project timeline?

MPCA is sharing information on this project through our <u>website</u>, public forum events, and GovDelivery emails, and is looking for additional opportunities to engage with the public.

The public forums provide opportunities for the public to hear directly from the MPCA and to ask questions of and provide input to the MPCA project team. MPCA hosted the first St. Louis River Watershed Mercury TMDL Public Forum at Fond du Lac Tribal and Community College in February 2023 (see <u>agenda</u> and <u>summary report</u>). Additional public forums will occur in 2023 and 2024:

https://app.sharebase.com/#/document/899539/share/185--uenTdmttkGkGK3R5wTekbbZz1U



Sign up for updates on our project website, under "Stay connected."

MPCA is looking for opportunities to share our work and hear from the public in between these public forum events, so please let us know if you have an event or a group that would like to hear about it.

How can the public comment on the project and submit questions?

In addition to opportunities at the public forums to ask questions and comment on the project, the MPCA is setting up an online system for this purpose. MPCA anticipates soliciting input through the MPCA's website from the public at specific times throughout the course of the project.

MPCA is looking for opportunities to share our work and hear from the public in between the public forum events, so please let us know if you have an event or a group that would like to hear about it.

Why is the compilation of literature on the <u>document sharing site</u> (linked to from the <u>project website</u>) not complete?

MPCA originally compiled this information to share reference lists and unpublished information with the Technical Advisory Team. That compilation was not meant to cover all of the literature that will be cited in the TMDL report. To respond to requests from the public for a more complete reference list, the MPCA compiled a list of relevant published studies that may be cited in the TMDL report; this list is available on the document sharing site: <u>Citation List for the St. Louis River Watershed Mercury TMDL</u>. To access the links in the Citation List, please download it first from the document sharing site.

Where can I find information about this project online?

MPCA is sharing information on this project through a project website: St. Louis River Watershed Mercury TMDL (<u>https://www.pca.state.mn.us/business-with-us/st-louis-river-watershed-mercury-tmdl</u>). At the bottom of this page are three important links:

- Under "Stay connected," you can sign up for project updates through GovDelivery.
- Under "For more information," you can view the project charter.
- Under "For more information," you can access the project's <u>document sharing site</u>.

What progress has been made on this project since the first public forum in February 2023?

- Published Public Forum 1 Summary Report on MPCA website
- Published St. Louis River Watershed Mercury TMDL study Frequently Asked Questions (this document) on MPCA website
- Completed draft source assessment, which includes preliminary estimates of mercury loads from the different source types, and by subwatershed
- Compiled citation list for the St. Louis River Watershed Mercury TMDL on MPCA website
- Set up online system for the public to ask questions and comment on the project
- Drafted memo describing approach to meeting Minnesota and Fond du Lac Band water quality standards in the mercury TMDLs
- Drafted mercury in stormwater literature review to explore options to address stormwater in the mercury TMDLs
- Presented the work at <u>Twin Ports Freshwater Folk</u>
- Participated in interviews with <u>Agate for their story on this project</u>

Why aren't representatives from regulated wastewater dischargers and environmental organizations on the Technical Advisory Team?

The Technical Advisory Team (TAT) is a group of government partners (tribal, federal, and state) and academic scientists whose primary role is to provide technical, scientific, and policy expertise to the MPCA project team. Conversations with regulated entities and environmental organizations are occurring through the public forum events and targeted outreach.

Process

Is the St. Louis River Watershed Mercury TMDL project being coordinated with implementation of the statewide Minnesota mercury TMDL and the St. Louis River Area of Concern (AOC) program? What is the difference between these programs?

Yes, MPCA scientists from these three efforts are collaborating on the St. Louis River Watershed Mercury TMDL project. As illustrated in <u>Addressing mercury</u>—how <u>multiple programs work together</u>, the <u>St. Louis River Area of Concern</u> (AOC) addresses legacy aquatic sediment contamination, the <u>statewide mercury TMDL</u> focuses on reducing mercury that enters surface waters directly from the atmosphere, and the St. Louis River Watershed Mercury TMDL focuses on the specific watershed impacts of mercury from the atmosphere that is deposited on the land surface and then travels across the land and eventually reaches surface waters.

The AOC program and the TMDL program stem from different environmental initiatives. The St. Louis River Area of Concern (AOC) was designated under the United States and Canada Great Lakes Water Quality Agreement in 1987. Participation in the AOC program is voluntary, and the program's goal is to address "legacy impacts"—historic contamination and habitat loss that occurred before environmental regulations existed. Actions address "beneficial use impairments" that apply to an AOC, and the program ends with removals of beneficial use impairments and delisting. The TMDL program is based in Section 303(d) of the Clean Water Act (1972), which requires TMDLs to be developed for surface waters that do not meet applicable water quality standards necessary to support their designated uses. Surface waters that do not meet water quality standards are referred to as "impaired." Both the AOC and the TMDL program use the word "impairment," but the impairments are under different program authorities and have different meanings:

- AOC beneficial use impairment (BUI): a change in the chemical, physical or biological integrity of the Great Lakes system which caused significant environmental degradation; the "Restrictions on Dredging" BUI focuses on implementing remedies that reduce exposure to contaminated aquatic sediments, and the "Restrictions on Fish and Wildlife Consumption" BUI assesses the impact of remediation on fish consumption advisories
- 303(d) impaired water: lakes, streams, and rivers that do not meet water quality standards for designated uses; the mercury impairments in this project affect the aquatic consumption designated use

At this time, removal of the Restrictions on Dredging BUI is anticipated in 2027, and removal of the Restrictions on Fish and Wildlife Consumption BUI is anticipated in 2029, with delisting the AOC to follow. Even after the AOC has addressed legacy mercury contamination, the 303(d) aquatic consumption impairments will likely persist until the mercury concentrations in water and fish are reduced enough for the fish and water to meet water quality standards. Although the AOC and TMDL work is important to reducing fish consumption advisories, the state follows independent processes to determine whether a fish consumption advisory exists (see <u>MN Department of Health's fish</u> <u>consumption guidance</u>).

The new St. Louis River Watershed mercury TMDLs will not revise the mercury reduction goals that already exist in the statewide mercury TMDL and the AOC program. Rather, they will call for additional reductions from watershed mercury that originates as atmospheric deposition and is transported across the land to surface waters.

Is MPCA collaborating with the Fond du Lac Band and incorporating indigenous knowledge?

Nancy Schuldt, Water Projects Coordinator with the Fond du Lac Band of Lake Superior Chippewa, is a member of the Technical Advisory Team. In addition to the input that Fond du Lac provides through the Technical Advisory Team, MPCA and Fond du Lac staff will be meeting to discuss ways that Fond du Lac can share their knowledge about the watershed and mercury impairments. Other Technical Advisory Team members include representatives from the 1854 Treaty Authority and the Great Lakes Indian Fish & Wildlife Commission (GLIFWC).

Why is MPCA developing mercury TMDLs in the St. Louis River Watershed when we already have the statewide mercury TMDL?

The Minnesota Statewide Mercury TMDL (2007) set a mercury emissions reduction goal of 93% (from 1990) to meet the mercury water quality standard in fish tissue. Across the state, 378 impairments for mercury in fish are not included in the statewide TMDL because of their exceptionally high mercury concentrations. For these waters, a 93% reduction in human-caused mercury emissions is predicted to help reduce mercury concentrations but would be insufficient to meet the standard for mercury in fish tissue. The intention for those waters not included in the statewide TMDL was to consider individual mercury TMDLs after the goals of the statewide TMDL had been achieved. Mercury emissions in Minnesota, as well as in the U.S. and Canada, have dropped 87% from 1990, which is approaching the 93% reduction goal in the statewide TMDL. Several parties, including the MPCA, other state agencies,

and tribal governments, have expressed strong interest in developing the St. Louis River Watershed mercury TMDLs now rather than waiting until the statewide TMDL goal is fully achieved.

After the TMDLs are approved, what will happen if there are new sources of mercury in the watershed?

If new sources of mercury are added to the watershed after the TMDLs are approved by EPA, additional mercury load reductions would be needed to meet the mercury loading goals. The mercury loading goals would stay the same; that is, the total allowable load (or "TMDL") does not change.

If a new or expanded mercury source requires an NPDES permit, and if the new or expanded discharge causes or has reasonable potential to cause or contribute to excursions above water quality standards, the new mercury load may be eligible for an offset through water quality trading. Water quality trading reduces pollutants in rivers and lakes by allowing a point source discharger to enter into agreements under which the point source "offsets" its pollutant load by obtaining reductions in a pollutant load discharged by another point source operation or a nonpoint source or sources in the same watershed. While the US EPA and the MPCA do not currently support water quality trading for persistent bioaccumulative toxins such as mercury, limited pilot projects designed to ensure substantial reductions may be considered. Any approved offsets would be limited in scope and would have to provide assurances that aquatic life and human health criteria will not be exceeded as a result of the discharge or the trades. The MPCA must establish specific conditions governing trading in the point source discharger's NPDES permit or in a general permit that covers the point source discharger. The MPCA implements water quality trading through permits. See the USEPA's 2003 <u>Water Quality Trading Policy</u> and MPCA's <u>Water Quality Trading Guidance</u> for more information.

If a new or expanded mercury source requires an NPDES permit, and if the new or expanded discharge <u>does not</u> cause or have reasonable potential to cause or contribute to excursions above water quality standards, the increased load would be permissible. This scenario could occur if the discharge concentrations were below the applicable mercury target (1.3 or 0.77 ng/L total mercury).

If a new mercury source does not require an NPDES permit, adaptive management will be used to change or refine management activities to meet the TMDLs. If the mercury sources can be mitigated through watershed practices, adaptive management can be considered as part of the Watershed Restoration and Protection Strategies (WRAPS) report and/or the watershed's comprehensive watershed management plan, or "One Watershed, One Plan."

Technical approach

What data is the MPCA using for the TMDL?

We are using data from the following sources:

- Water chemistry data
 - Parameters: mercury (Hg), methylmercury (MeHg) [total and filtered fractions], total and dissolved organic carbon (TOC, DOC), sulfate (SO₄)
 - \circ Time period: 2005–2021
 - Source: MPCA, DNR, Fond du Lac, RTI (EPA contract)
- Fish tissue data

- Parameters: Fish tissue mercury concentrations (assumed to be MeHg), fish length, fish species (channel catfish, northern pike, walleye, other)
- Time period: 1991–2019
- Source: EPA GLTED (Great Lakes Toxicology and Ecology Division Laboratory), MDNR, MPCA, WDNR, Fond du Lac
- Atmospheric deposition data
 - Parameters: wet (NADP and FDL) and dry (FDL) mercury deposition
 - Time period: 1998–2021 (FDL wet), 1996–2021 (NADP)
 - Source: Fond du Lac (FDL) Air Program, National Atmospheric Deposition Program (NADP)
- Wastewater discharge monitoring data
 - Parameters: flow and mercury in permitted wastewater discharges
 - Time period: 2010–2021
 - Source: DMRs (discharge monitoring records)
- Land cover
 - Parameters: 12 land cover types
 - Source: LANDFIRE 2016, National Wetland Inventory, Gridded Soil Survey Geographic (gSSURGO) database
- Estuary & harbor
 - Parameter: sediment mercury data
 - Time period: 1989–2018
 - Source: NOAA GLI DIVER database
- Peatlands Load Monitoring Study
 - \circ Parameters: THg, MeHg, DOC, total suspended solids, iron, nutrients, SO₄
 - Time period: 2019–2021
 - Source: USGS, MPCA

What have we learned from comparative work with the Bad River Slough?

The Bad River Slough in northeastern Wisconsin was chosen for comparison to the St. Louis River Estuary. It has similar wetland and hydrodynamic features as the SLR Estuary, but with no historical or current industrial activity. The USEPA, USGS, and University of Minnesota–Duluth conducted a joint study of the two estuaries in 2017, using the state-of-the-science mercury stable isotope analysis, as well and carbon and nitrogen stable isotope analysis.

The first published study using mercury isotopes in the St. Louis River Estuary to identify mercury sources showed prey fish (shiners and yellow perch) in the estuary had a strong industrial source signal, indicating the mercury in the contaminated sediments remained a significant source of mercury to the food web (Janssen et al. 2021). The SLR AOC project is leading ongoing remediation work to remove legacy mercury contaminated sediments from the SLR Estuary. In contrast, the primary source of mercury in the Bad River fish was from atmospheric deposition to the watershed. Mercury levels in the St. Louis River Estuary were higher than the Bad River; walleye from the estuary had approximately double the mercury concentrations of walleye in the Bad River.

How will the MPCA account for the more stringent Fond du Lac mercury water quality standard?

Because TMDLs must take into account water quality standards of downstream waters, the mercury targets in Minnesota's St. Louis River Watershed mercury TMDLs will be the most restrictive of the criteria that apply to each water. Of the mercury criteria that apply in MN, FDL, and WI, the most

restrictive criteria are FDL's human health-based chronic criterion (0.77 ng/L) for water impairments and MN's fish tissue criterion (0.2 mg/kg) for fish impairments. Because MN's mercury criteria in the Lake Superior Basin are as strict as or stricter than WI's, there are no adjustments to TMDL targets to account for downstream water quality standards in WI. The TMDL target for the St. Louis River reaches with water impairments that border FDL will be 0.77 ng/L, and the TMDL target for the remaining water impairments will be 1.3 ng/L. The TMDL target for all fish tissue impairments will be 0.2 mg/kg.

Although the TMDL target for the water impairments upstream of the St. Louis River FDL border impairments will be 1.3 ng/L, some of the allocations (i.e., loading goals) upstream of the FDL waters will need to be more stringent to accommodate the load reductions needed to meet the downstream FDL border impairments with the lower 0.77 ng/L TMDL target. Although the MPCA has not yet decided how to distribute the load reductions needed to meet the FDL border reaches' target, MPCA will use the model under development for this TMDL project to show that the collective TMDL allocations will lead to all impaired water bodies meeting their respective water quality standards.

Will the St. Louis River Watershed Mercury TMDL report evaluate sulfate? Will sulfate loading limits be set?

The TMDL report will include a sulfate evaluation, but sulfate loading limits will not be set as part of the St. Louis River Watershed Mercury TMDL project.

MPCA is analyzing surface water concentrations of sulfate in the watershed and will be incorporating the analysis into the TMDL study. One of the ways that sulfate is being considered is in the watershed modeling. Dissolved organic carbon (DOC) is being used as a proxy for mercury transport in watershed runoff, and the ratio of methylmercury to DOC is higher in parts of the watershed with higher sulfate concentrations. That is, where there is higher sulfate, we expect more methylmercury per unit DOC.

The MPCA's models do not directly simulate mercury methylation, which depends on many variables including redox conditions, microbial populations, temperature, availability of inorganic mercury, and the carbon and sulfur cycles. In other states, attempts to simulate mercury methylation at the watershed scale with process-based models have generally been unsuccessful as predictors of methylmercury concentrations. MPCA's models instead use relationships of dissolved organic carbon, total mercury, and methylmercury based on monitoring data from water bodies in the St. Louis River Watershed.

The mercury TMDLs will quantify the reductions in mercury and methylmercury needed to meet water quality standards. Because the models do not quantitatively predict the impact that reductions in sulfate will have on methylation rates and mercury concentrations in fish throughout the watershed, the St. Louis River Watershed mercury TMDLs will not quantify the effect of sulfate load reductions on mercury impairments. The TMDL report will identify the areas of high sulfate and will present these results to inform TMDL implementation and how it should consider sulfate. The adaptive management approach typically used in TMDL implementation calls for continued monitoring and "course corrections" responding to monitoring results. Management activities can be changed or refined as appropriate over time to efficiently meet the TMDL and lay the groundwork for de-listing the impaired water bodies.

MPCA is committed to implementing the 10 mg/L sulfate standard, which applies to <u>waters used for</u> <u>production of wild rice</u>. Sulfate impairments are primarily point source driven, and the MPCA is primarily addressing these impairments through discharge permits. MPCA is not developing sulfate TMDLs at this time.

Is the influence of mining on the St. Louis River Watershed mercury impairments being addressed?

Yes, the influence of sulfate discharges from mining is being addressed through point source discharge permits. Wastewater effluent from the mining industry can be high in sulfate, and sulfate is one of the many variables that is involved in mercury methylation. Reductions in sulfate may lower the potential for mercury methylation, which could lead to lower mercury concentrations in fish.

Please see the answer to the previous question for information about the MPCA's considerations of sulfate in the St. Louis River Watershed Mercury TMDL project.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 6

(Tetra Tech, Technical Approach for the St. Louis River Watershed Mercury Total Maximum Daily Loads, June 7, 2022)

Technical Approach for the St. Louis River Watershed Mercury Total Maximum Daily Loads

June 7, 2022 (Revised)

PREPARED FOR

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ACRONYMS/ABBREVIATIONS

Acronyms/Abbreviations	Definition
µg/L	Micrograms per liter
AUID	Assessment unit ID
BAFs	Bioaccumulation factors
CBOD	Carbonaceous biochemical oxygen demand
DMR	Discharge monitoring report
DOC	Dissolved organic carbon
FILET	Fillet without skin
FILSK	Fillet with skin
Hg	Mercury
Hg(0)	Elemental mercury
Hg(II)	Divalent mercury
HgS	Cinnabar
HSPF	Hydrologic Simulation Program - FORTRAN
IMPLND	Impervious land segment in HSPF
kg	Kilogram
m	Meter
m³/s (cms)	Cubic meters per second
MDN	Mercury deposition network
MeHg	Methylmercury
mg/L	Milligram per liter
mg	Milligram
MGD	Million gallons per day
MOS	Margin of safety
MPCA	Minnesota Pollution Control Agency
MS4	Municipal separate storm sewer system
NADP	National Atmospheric Deposition Program
ng/L	Nanogram per liter
NOHV	Organism without head or viscera
NPDES	National Pollutant Discharge Elimination System
OC	Organic carbon
PERLND	Pervious land segment in HSPF
PLUG	Dorsal muscle plug without skin
ppm	Parts per million
RCHRES	Reach segments in HSPF
SO4 ²⁻	Sulfate

Acronyms/Abbreviations	Definition
THg	Total mercury
TMDL	Total maximum daily load
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WHORG	Whole organism
WLA	Wasteload allocation
WRAPS	Watershed restoration and protection strategy
WWTP	Wastewater treatment plant
WY	Water year

1.0 MERCURY

Minnesota issued statewide mercury Total Maximum Daily Loads (TMDLs) for the northeast and southwest regions in 2007 to address over 75 percent of the state's waterbodies listed as impaired on Minnesota's 2004 303(d) list for elevated mercury (Hg). The TMDLs applied a fish tissue target of 0.2 mg-THg/kg to be achieved in top predator fish. The primary nonpoint source of mercury identified was atmospheric deposition and the TMDLs specified reductions of 51 percent for the southwest region and 65 percent for the northeast region. The technical analysis found that waters with fish tissue levels exceeding 0.572 mg-THg/kg would require greater reductions than necessitated by the northeast and southwest regional TMDLs. Minnesota is now seeking to develop TMDLs for waterbody segments that were not included in the original TMDL and listed for exceedances of fish tissue (53) and water column (22) mercury criteria in the St. Louis River and Cloquet River watersheds. This report describes the technical approach for establishing mercury loading capacities and quantifying mercury loads from point and nonpoint sources to support MPCA in the development of the mercury TMDLs.

1.1 WATER QUALITY STANDARDS

Surface water quality is protected and regulated for fresh waters under standards approved by the United States Environmental Protection Agency (USEPA) and adopted by the state of Minnesota. Waters of the state are assigned designated use classifications, also called beneficial uses, that include aquatic life, wildlife, recreational, and drinking water uses as well as other uses. Definitions of the designated uses for fresh waters are found in the Minnesota Administrative Rules (7050.0140).

The designated uses of a water body or water segment determine the applicable surface water quality standards; these standards can include both numeric and narrative criteria that are used to identify impaired water segments. Moreover, water quality standards inform the development of loading capacity for a TMDL. Minnesota's water quality standards are described in Minnesota Rules chapters 7050 (Waters of the State) and 7052 (Lake Superior Basin Water Standards). Mercury standards applicable to the St. Louis River watershed are listed in Table 1; the most stringent chronic water column standard defined by the state is 0.0013 µg/L (1.3 ng/L). As discussed in Minnesota Rule 7052 (Lake Superior Basin water standards), water column metals standards are expressed in the total metal form but are implemented as the dissolved form. Pre-established, constituent specific factors are applied to convert from the total metal standard to the dissolved metal standard that is used for evaluation purposes. The acute and chronic conversion factors for mercury are 0.85 and 1.0, respectively. In addition, the edible fish tissue standard is 0.2 mg/kg. The fish tissue standard is expressed as total mercury; however, the vast majority of mercury in edible fish tissue is in the form of methylmercury, so this is essentially a methylmercury standard. Because Minnesota has adopted water quality standards for both total mercury in the water column and mercury in fish tissue, the most stringent of these requirements applies. In addition to the state's water quality standards, there are five segments (AUID -503, -504, -505, -506, and -517) of the St. Louis River that are along the border of the Fond du Lac Reservation and these are also subject to the Band's chronic total mercury standard of 0.00077 µg/L in the water column (0.77 ng/L). The Band also utilizes the U.S. EPA's health criterion for fish tissue in their assessments (0.3 mg/kg methylmercury in fish tissue).

Media Form and U		Beneficial Use/Type	Numeric Standard	Averaging Period for Chronic Standards	
		Minnesota			
		Aquatic life chronic standard	0.91	Four-day average	
	Total mercury, μg/L	Aquatic life maximum standard	1.7	One-day average	
Water column		Aquatic life final acute value	3.4		
		Human health chronic standard	0.00153	30-day average	
		Wildlife chronic standard	0.0013	30-day average	
		Applicable chronic standard	0.0013	30-day average	
Fish tissue	Total mercury, mg/kg	Human health edible fish tissue standard	0.2		
	Fon	d du Lac Band of Lake Superior Chippew	а		
Water column	Total mercury, μg/L	Aquatic Life: Subsistence Fishing/Netting designated use	0.00077		

Table 1. Applicable mercury w	vater quality standards
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U.S. EPA (applicable to the Fond du Lac Reservation)

Fish tissue	Methylmercury, mg/kg	Human health (used for the Fond du Lac's Aquatic Life: Subsistence Fishing/Netting designated use)	0.3	
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1.2 MERCURY IMPAIRED WATERBODIES

Mercury TMDLs are to be developed for 33 stream segments and 28 lakes in the St. Louis River watershed (Table 2,

Figure 1). Of the streams, 18 are listed for exceedances of the water column mercury standard and 25 are listed for exceedances of the fish tissue mercury standard. Four lakes are listed for elevated water column levels and 28 are listed for fish tissue levels in excess of the standard.

Waterbody	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID	Туре
Waterbouy			Fish Tissue	Water Column	(AUID)	Type
St Louis River	Cloquet R to Pine R	2Bg	х	х	04010201-503	Stream
St Louis River	Stoney Bk to Cloquet R	2Bg	Х		04010201-504	Stream
St Louis River	Artichoke R to Stoney Bk	2Bg	Х		04010201-505	Stream
St Louis River	East Savanna R to Artichoke R	2Bg	Х		04010201-506	Stream
St Louis River	Floodwood R to East Savanna R	2Bg	х		04010201-507	Stream
St Louis River	Whiteface R to Floodwood R	2Bg	Х		04010201-508	Stream
St Louis River	West Two R to Swan R	2Bg	Х		04010201-510	Stream
St Louis River	Embarrass R to East Two R	2Bg	Х	Х	04010201-511	Stream
St Louis River	Scanlon Dam to Thomson Reservoir	2Bg	Х	х	04010201-515	Stream
St Louis River	Potlatch Dam to Scanlon Dam	2Bg	Х		04010201-516	Stream
St Louis River	Pine R to Knife Dam	2Bg	Х	х	04010201-517	Stream
St Louis River	Thomson Reservoir to Fond du Lac Dam	2Bg	Х		04010201-523	Stream
St Louis River	Knife Dam to Potlatch Dam	2Bg	Х		04010201-524	Stream
St Louis River	Swan R to Whiteface R	2Bg	Х		04010201-525	Stream
St Louis River	Partridge R to Embarrass R	2Bg	х		04010201-526	Stream
Superior Bay	Mouth of St Louis Bay at Blatnik bridge to Duluth Ship Channel	2Bg	Х	Х	04010201-530	Stream
Superior Bay	Mouth of St Louis Bay at Blatnik bridge to Superior Entry	2Bg	Х	Х	04010201-531	Stream
West Two River	McQuade Lk outlet to St Louis R	2Bg		Х	04010201-534	Stream
Partridge River	Headwaters to St Louis R	2Bg	Х	Х	04010201-552	Stream

Technical Approach (Revised)

Weterbedy	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID	Turne
Waterbody			Fish Tissue	Water Column	(AUID)	Туре
St Louis River	East Two R to West Two R	2Bg	Х		04010201-554	Stream
East Two River	Unnamed branch to St Louis R	2Bg		Х	04010201-555	Stream
Swan River	Confluence of East and West Swan R to St Louis R	1B, 2Bdg		Х	04010201-557	Stream
Floodwood River	Headwaters (Floodwood Lk 69-0884- 00) to St Louis R	2Bg		Х	04010201-560	Stream
Embarrass River	Headwaters to Embarrass Lk	2Bg		Х	04010201-579	Stream
St Louis River	Headwaters (Seven Beaver Lk 69- 0002-00) to T58 R13W S36, west line	2Bg	Х		04010201-631	Stream
St Louis River	T58 R13W S35, east line to Partridge R	2Bg	Х	Х	04010201-644	Stream
Stony Creek	Unnamed cr to Unnamed cr	2Bg		Х	04010201-963	Stream
Trimble Creek	-92.13 47.647 to Embarrass R	2Bg		Х	04010201-A41	Stream
Unnamed creek (Mud Lake Creek)	Wetland to Unnamed cr	2Bg		X	04010201-B50	Stream
Cloquet River	Us-kab-wan-ka R to St Louis R	2Bg	Х	Х	04010202-501	Stream
Cloquet River	Beaver R to Us-kab-wan-ka R	2Bg	Х		04010202-502	Stream
Cloquet River	Island Lake Reservoir to Beaver R	2Bg	Х		04010202-504	Stream
St Louis River	Fond du Lac dam to beginning of estuary	2Bg	Х	Х	04010201-B66	Stream
Thomson Reservoir	At Thompson	2B	Х		09-0001-00	Lake
Cloquet	Finland	2B	Х		38-0539-00	Lake
Sink	Two Harbors	2B	Х		38-0540-00	Lake
White	4 miles SW of Rollins	2B	Х		69-0030-00	Lake
Big Bear	Two Harbors	2B	Х		69-0113-00	Lake

Waterbody	Segment Description	Use	Mercury Impairment		Assessment Unit ID	Turne
Waterbody		Class	Fish Tissue	Water Column	(AUID)	Туре
Alden	Duluth	2B	х		69-0131-00	Lake
Wolf	5.5 miles SW of Rollins	2B	Х		69-0143-00	Lake
Otto	Brimson	2B	Х		69-0144-00	Lake
Colby	At town of Hoyt Lakes	1B, 2Bd	Х		69-0249-00	Lake
Island Lake Rsvr(W.Basin)	17 miles N of Duluth	2B	Х		69-0372-01	Lake
Island Lake Rsvr(E.Basin)	16 miles N of Duluth	2B	Х		69-0372-02	Lake
Whiteface Reservoir	9 MI miles N of Duluth	2B	х		69-0375-00	Lake
Upper Comstock	Whiteface	2B	Х		69-0412-01	Lake
Lower Comstock	Markham	2B	Х		69-0412-02	Lake
South Twin	Aurora	2B	Х		69-0420-00	Lake
Loon	Auora	2B	Х		69-0426-00	Lake
Sabin	Biwabik	2B	Х	Х	69-0434-01	Lake
Wynne	Biwabik	2B	Х	Х	69-0434-02	Lake
Long	Evelth	2B	Х		69-0495-00	Lake
Embarrass	At Biwabik	2B	Х		69-0496-00	Lake
Grand	16 miles N of Duluth	2B	Х		69-0511-00	Lake
Strand	3.5 miles SE of Cotton	2B	х		69-0529-00	Lake
Esquagama	4 miles S of Biwabik	2B	х		69-0565-00	Lake
Ely	At Gilbert	2B	х		69-0660-00	Lake
Elbow	1 mile NW of Iron Junction	2B	Х		69-0717-00	Lake
St. Louis Bay	None	2B	х	Х	69-1291-02	Lake

Waterbody	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID	Туре
			Fish Tissue	Water Column	(AUID)	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Spirit Lake	At Duluth	2B	Х		69-1291-03	Lake
Upper Estuary	None	2B	Х	Х	69-1291-04	Lake

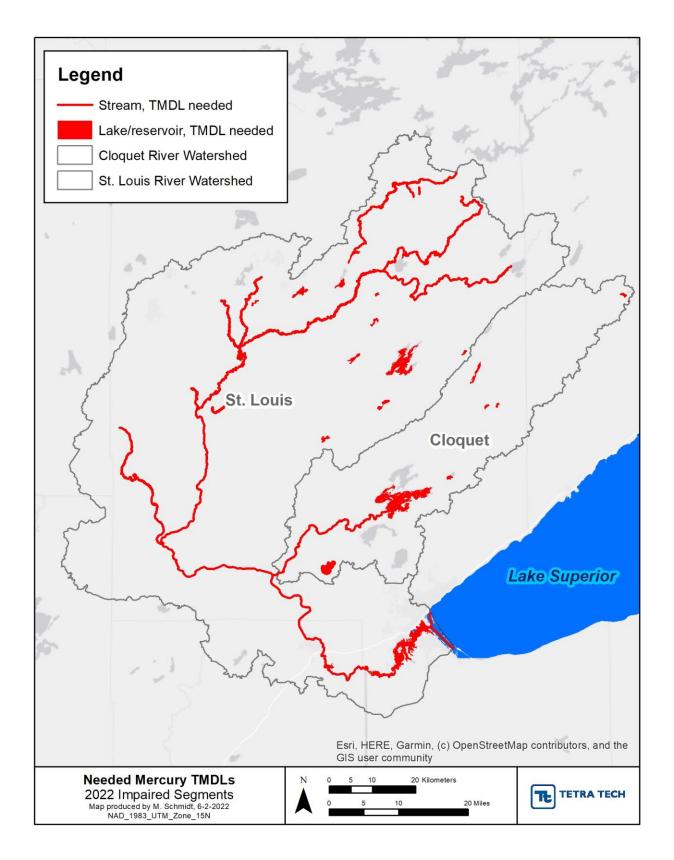


Figure 1. Stream and lake segments that need mercury TMDLs

1.3 MERCURY CYCLING

Mercury is a naturally occurring element that cycles through the atmosphere, hydrosphere, and geosphere, existing in three major forms: elemental mercury, inorganic (ionic) mercury, and organic mercury (primarily methylmercury, or MeHg). Elemental mercury is a potent neurotoxin in humans that can cause significant health effects. Elemental mercury forms compounds and salts with other elements such as sulfur, generating inorganic mercury. Inorganic mercury in waterbodies is not a direct threat to aquatic life, wildlife, and human health. However, environmental processes, such as sulfate and iron reduction by bacteria in hypoxic sediments, create MeHg as a byproduct of organic carbon digestion. Low oxygen environment like peatlands in the watershed are hot spots for methylation. Chronic exposure to elevated MeHg levels leads to ingestion by filter-feeding organisms, bioaccumulation in the food web, and ultimately to biomagnification of mercury in higher tropic level fish such as walleye, pike, and smallmouth bass. Worrisome human and wildlife exposure to mercury occurs primarily though repetitive consumption of contaminated fish and shellfish.

1.4 SUMMARY OF MERCURY IN THE ST. LOUIS RIVER WATERSHED

The Minnesota statewide mercury TMDL found that the primary source of mercury to waterbodies of the state is atmospheric deposition, much of which now originates from global activities outside of the state's boundaries that are not subject to local control. MPCA has been tracking in-state mercury emissions. Between 2005 and 2014 the state reduced mercury emissions by about 33 percent from mercury in products, mining, and energy production (<u>https://www.pca.state.mn.us/air/emissions-data</u>). While this is a significant achievement, the state is not on track to meet the 76 percent reduction goal to be achieved by 2025. Furthermore, legacy sources of mercury are pooled in soils and sediments and continue to contribute mercury to waterbodies. While the rates of mercury loading from these sources will gradually decline as atmospheric deposition declines, it may require many decades to reach a new equilibrium. Controlling mercury exposure to mitigate bioaccumulation in the food web needs to consider reductions in sources but also controlling transport and transformation processes.

The Mesabi Iron Range is a mining district of the Biwabik Iron Formation that crosses the northern St. Louis River watershed. Both underground mines and open-pit mines have been operated in this area. While these ore deposits do not have high levels of mercury, taconite processing in this area may contribute some mercury through discharging spent water, tailings, and stack emissions (Berndt, 2003). Mining discharges are regulated and monitored through the National Pollutant Discharge Elimination System (NPDES). Mercury concentrations in tailings basins have been lower or similar to concentrations in other surface waters (Berndt, 2003). Thus, atmospheric emission is the dominant pathway of mercury loading from mining activities according to Berndt. Berndt elaborates on this stating "Hg(II) in ore concentrate is converted to Hg(0) during the firing of pellets and released to the atmosphere in stack emissions. Emission factors reflect primary distribution of mercury in the ore body, and generally increase in a westward direction across the district from 1 to 17 kg Hg per million long tons of pellets. Atmospheric Hg emissions from taconite processing exceeded 100 kg/yr in the late 1960's, and have ranged from between approximately 200 and 400 kg/yr ever since. The great majority of this mercury is transported out of the state..."

Sulfate (SO₄²⁻), an oxidized form of sulfur, is a waste product associated with iron mining that has led to elevated sulfate levels in this region (Myrbo et al., 2017). Hirshon et al. (2020) discuss that waters in the watershed impacted by mining activities exhibit sulfate concentrations that are 5 to 80 times higher than waters not impacted by mining. Sulfate-reducing microbes in low oxygen, organic matter rich sediment environments like wetlands, lake bottoms, and slow moving streams facilitate MeHg production. Sulfate is also contributed to the landscape and waterbodies by way of atmospheric deposition and agricultural activities, though most of the watershed is forest and wetland. According to the National Atmospheric Deposition Program, the concentration of sulfate in precipitation in this region was about 0.3 mg/L in 2020 (NADP, 2022).

While limiting production of MeHg is critical, so too is limiting transport of bioavailable mercury to waterbodies where aquatic organisms are exposed. According to Berndt and Bavin (2009), "for a low-sediment river such as the St. Louis River, Hg is almost certainly bound primarily to organic carbon and, thus, an important starting point for evaluation of Hg transport involved understanding DOC [dissolved organic carbon] transport". Berndt and Bavin conducted monitoring and an empirical analysis that revealed while sulfate was mainly originating from the mining region, mercury was tending to originate from non-mining areas (Figure 2). Furthermore, both THg and MeHg were found to have strong relationships with DOC in the St. Louis River and its tributaries (Figure 3), however, there was a poor correlation between SO₄²⁻ and MeHg concentrations in the water column (Figure 4). Moreover, the timing of peak SO₄²⁻ and MeHg concentrations at sites along the St. Louis River do not correspond (Figure 5; personal communication, B. Monson, Minnesota Pollution Control Agency); MeHg tends to peak in the late spring to early summer while SO₄²⁻ tends to peak in the late summer to fall. This may indicate that the MeHg was produced elsewhere (e.g., in wetlands) and transported to the monitoring sites where SO₄²⁻ loads are present from other sources. Higher wetland density related to higher DOC levels (Figure 6). Further efforts reiterated the finding that MeHg readily binds to and is transported with DOC in the St. Louis River watershed (Berndt and Bavin, 2012). This is consistent with a global meta-analysis of the relationship between mercury and DOC that found that an additional milligram (mg) of DOC in freshwater bodies increases Hg and MeHg by 0.25 nanogram (ng) and 0.029 ng, respectively (Lavoie et al., 2019).

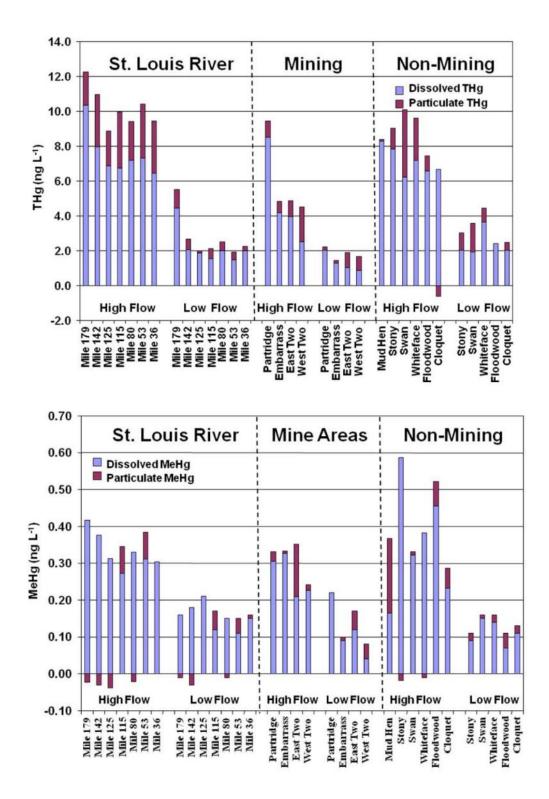


Figure 2. Dissolved and particulate THg (top) and MeHg (bottom) concentrations in the St. Louis River and its tributaries (Berndt and Bavin, 2009; Figure 8 and Figure 11)

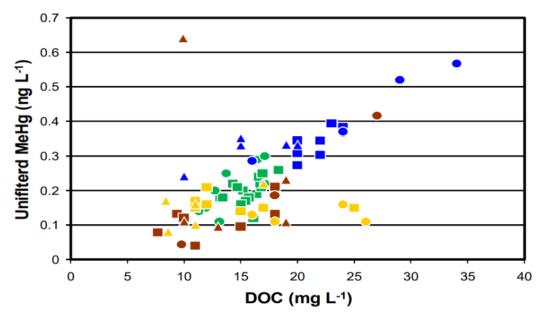


Figure 3. DOC and unfiltered MeHg concentration in the St. Louis River watershed (Berndt and Bavin, 2009; Figure 21)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries, circles are for non-mine impacted tributaries, and squares are for the St. Louis River.

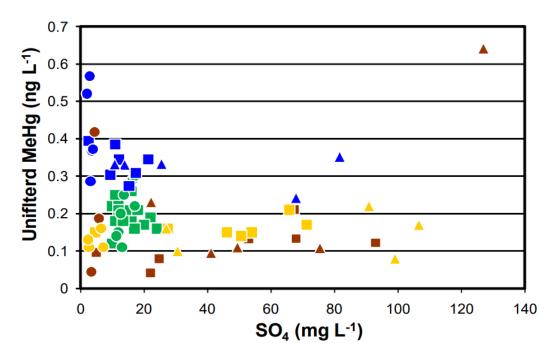


Figure 4. SO₄²⁻ and unfiltered MeHg concentration in the St. Louis River watershed (Berndt and Bavin, 2009; Figure 22)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries, circles are for non-mine impacted tributaries, and squares are for the St. Louis River.



Figure 5. Time series of SO₄²⁻ and MeHg at St. Louis River near Skibo, Forbes, and Scanlon (source: personal communication, B. Monson, Minnesota Pollution Control Agency)

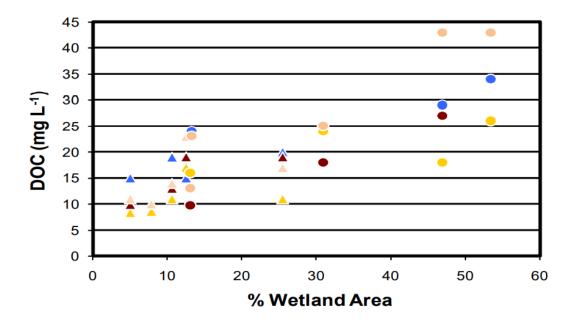


Figure 6. Wetland area and DOC concentration in the St. Louis River watershed (Berndt and Bavin, 2009; Figure 18)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries and circles are for non-mine impacted tributaries.

1.5 DATA SUMMARY

1.5.1 Water Column Data

Water quality data that have been collected in the study area were provided by MPCA for the technical assessment. Samples have been collected for various purposes including for total metals monitoring, stressor identification, lake monitoring, the mercury in rivers project, fish kill investigations, ambient trace metals monitoring and through other efforts and studies. The majority of the mercury and organic carbon water column data were collected in 2013 as part of the load monitoring study (Figure 7).

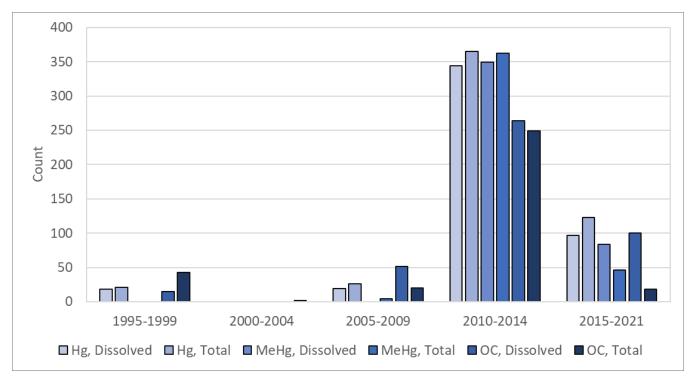


Figure 7. Sample counts of water column mercury and organic carbon by collection year range

1.5.2 Fish Tissue Data

Fish tissue mercury samples collected from the St. Louis River and Estuary date back to 1970. Over 1,400 individual specimen or composite samples were collected between 1970 and 2020 by MPCA, Minnesota Department of Natural Resources, Wisconsin, USEPA, the Department of Fisheries Oceans Canada, Fond du Lac Band, and through other agencies and research efforts (Figure 8). The species with the most records include walleye, northern pike, white sucker, smallmouth bass, and channel catfish. Sample anatomies included dorsal muscle plug without skin (PLUG), whole organism (WHORG), fillet with skin (FILSK), fillet without skin (FILET), organism without head or viscera (NOHV), and dorsal muscle plug using biopsy sampler or scalpel without skin (BIOPSY). The median recorded fish tissue Hg level is 0.29 mg/kg (Table 3). The 26th percentile corresponds with the fish tissue standard of 0.2 mg/kg, meaning that about 74 percent of fish tissue samples collected from the St. Louis River and Estuary exceed the water quality standard.

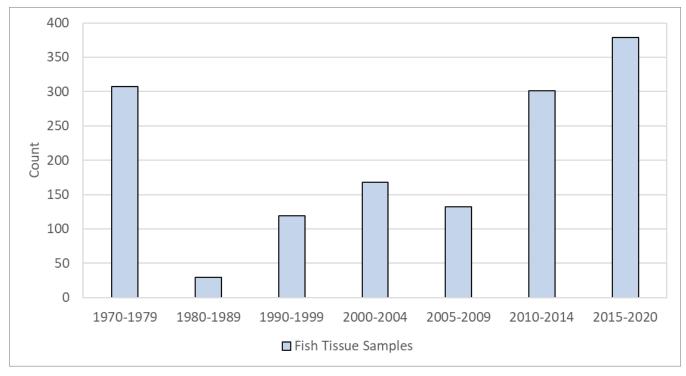


Figure 8. Sample counts of fish tissue mercury samples by collection year range

Includes individual specimen samples and composite samples.

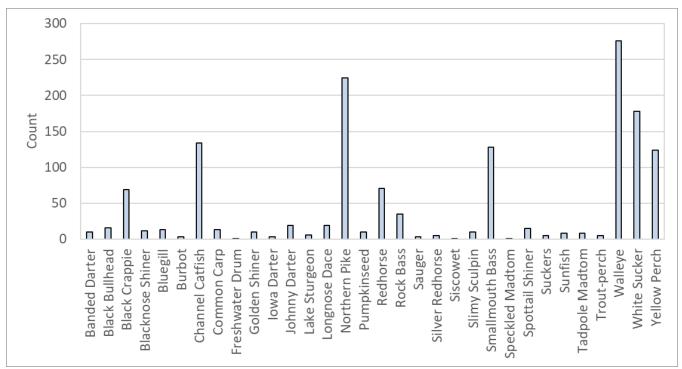


Figure 9. Sample counts of fish tissue mercury samples by fish species Includes individual specimen samples and composite samples.

Percentile	Fish Tissue Mercury Level (ppm or mg/kg)
5 th	0.10
10 th	0.13
25 th	0.19
50 th	0.29
75 th	0.43
90 th	0.63
95 th	0.75

Table 3. Distribution of fish tissue mercury levels (PPM) in the St. Louis River and Estuary

2.0 TECHNICAL APPROACH

2.1 OVERVIEW

The statewide TMDLs identify atmospheric deposition as the primary source of mercury in the state and call for reductions in local mercury emissions to the atmosphere. Peatlands and other wetlands in the St. Louis River watershed are hot spots for methylation due to the low oxygen conditions and presence of sulfate and iron reducing bacteria. However, the main exposure pathway for fish and other aquatic species is within streams and lakes. The proposed technical approach will evaluate mercury sources in further detail, examine Hg/MeHg

transport and delivery to waterbodies, and determine loading capacities and required load reductions for waters impaired for mercury in the St. Louis River watershed.

There are two potential strategies for addressing mercury bioaccumulation in fish tissue in the St. Louis watershed. The first is to address sources that enhance methylation potential (such as sulfate loads from mining operations and atmospheric deposition). There are challenges associated with this strategy as a 2011 study in the St. Louis River watershed found a poor relationship between sulfate and dissolved MeHg in streams (Berndt and Bavin, 2012; note Fig. 4 in the paper) so watershed-scale reductions in sulfate may not correlate well with actual reductions in methylation. Furthermore, a recent report commissioned by the Minnesota Environmental Partnership states "Many environmental groups question whether even the most effective operations can assure sequestration [of sulfate] for decades or centuries, when the companies themselves may no longer exist" (Hirshon et al., 2020), which poses barriers for implementation. The second strategy is to address the transport and delivery of bioaccumulatable MeHg from source areas to waterbodies to control exposure levels. The approach proposed herein focuses on transport and delivery of MeHg and THg, with considerations for MeHg production, and exposure and bioaccumulation in fish tissue.

The relationship between MeHg and THg concentrations is a key issue in mercury TMDLs based on fish tissue criteria. It has frequently been observed that fish THg concentrations are not strongly correlated with sediment or water column THg, but instead depend on the processes that control the creation and destruction of MeHg, resulting in a stronger correlation between fish tissue concentrations and ambient MeHg concentrations in sediment than to THg concentrations in the water column (Eagles-Smith et al., 2016; Alpers et al., 2016). Unfortunately, it has proven difficult to use process-based models to predict mercury methylation and demethylation rates in the environment. Methylation is a bacteria-mediated process that occurs under low oxygen conditions as a byproduct of the reduction of sulfate (SO4²⁻) as an oxygen source for the consumption of organic carbon compounds. Rates of methylation depend on several variables including: redox conditions, microbial populations, temperature, availability of inorganic Hg, and the C and S cycles. Attempts to simulate mercury methylation at the watershed scale with process-based models have generally been unsatisfactory as predictors of MeHg concentrations (e.g., Knightes et al., 2014, Knightes et al., 2016). It appears that empirical relationships of MeHg to THg based on monitoring from specific waterbodies is generally a more useful approach than process-based simulation. For example, USGS developed an empirical-statistical approach to predict MeHg concentrations as a function of water temperature, antecedent flow, and the prior history of water table elevation (all of which influence the rates of methylation in riparian groundwater) in an Adirondack stream (Burns et al., 2014).

A recent review of the state of process-based mercury modeling (Zhu et al., 2019) laments "the insufficient quantity of adequate measurements and the unsatisfactory accuracy of mercury models". In particular, current models do not accurately capture the complex relationships between mercury methylation and the sulfur cycle: where sulfate is in short supply increasing the supply tends to increase methylation, but only up to a point. As sulfate concentrations increase, bacterial sulfate reduction activity begins to produce excess reduced sulfide, which depresses methylation rates because high concentration of sulfide will convert a large portion of Hg into insoluble HgS and reduce the amount of reactive Hg available for methylation.

Past research in the St. Louis River watershed has found strong relationships between DOC and Hg and MeHg concentrations (Berndt and Bavin, 2009; Berndt and Bavin, 2012). Wetland and peat bog areas provide high loads of DOC and are also areas where MeHg production is likely. Thus, DOC can serve as a surrogate for modeling landscape transport and delivery mechanisms of Hg from nonpoint sources in the rural, wetland-dominated portions of the watershed (Figure 10).

Hydrologic Simulation Program – FORTRAN (HSPF) models of the St. Louis, Cloquet, and Duluth Urban Area watersheds, currently being updated by Tetra Tech under a separate contract with MPCA, will be used to simulate

landscape processes with DOC as a surrogate for mercury transport, and will be further expanded to include THg and MeHg as instream water quality parameters. DOC from the upland and wetland areas will be translated to

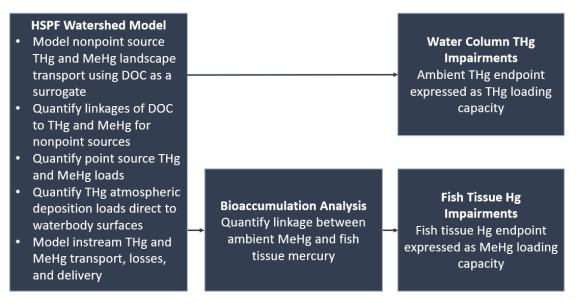


Figure 10. Conceptual schematic of the technical approach

THg and MeHg within the HSPF model and THg and MeHg will be calibrated using available monitoring data collected throughout the study area. Spatial or source-specific linkages will be explored, such as to account for differences in sulfate availability given its influence on methylation.

For the waterbody segments listed for exceedances of ambient THg, the calibrated HSPF modeling results can be directly applied to determine TMDL loading capacities expressed as THg loads. For waterbody segments listed for elevated fish tissue mercury, the HSPF MeHg results will be paired with a statistical analysis that links MeHg exposure concentrations to bioaccumulation in fish tissue. This linkage will be used to establish target MeHg concentrations and loading capacities.

In the proposed approach, HSPF will not fully replicate the complex kinetics and transformations of mercury in water. Rather, it will be used for mass balance purposes to approximate instream THg and MeHg advective transport, losses, and delivery to waterbodies listed as impaired using the observed relationship to DOC as a surrogate. The approach does not directly represent specific reactions such as methylation in riverine and lake environments and activities that influence these reactions (e.g., fluctuating reservoir levels). However, the proposed approach is useful and efficient because it 1) comprehensively accounts for instream dynamics that impact chronic water column mercury levels and bioaccumulation in the food web, 2) is a defensible and feasible option for developing TMDLs for 50+ mercury impaired segments within the relatively short time frame of the project, 3) leverages the recently updated watershed-scale HSPF models, 4) uses available data as evidence for attributing mercury loading to point and nonpoint sources in the watershed to support allocations and implementation planning efforts, and 5) provides the opportunity to define loading capacities for two end-points of interest – THg (water column impairments) and MeHg (fish tissue impairments) - to support TMDL development.

The current version of this approach focuses on providing a robust technical analyses for TMDL development upstream of the estuary and harbor. Additional funding and an extension is planned to conduct WASP modeling for the lower St. Louis River, Estuary and Harbor. Past modeling efforts found that about 70 percent of Hg in the harbor/estuary originates from the St. Louis River watershed. Remediation and restoration activities are ongoing and are working to address legacy contaminated sediments in the estuary. The updated approach for the estuary

and harbor is to be determined in the coming weeks, however in the absence of schedule and budget extensions, the approach will provide information to support TMDL development in the estuary and harbor including mercury and methylmercury loading to the estuary from the St. Louis and Cloquet watersheds and Duluth urban area. The estuary will be evaluated at a coarser level. Information available from past studies will be compiled regarding legacy sediment issues and internal loading, contributions from Wisconsin, and hydrodynamics and hydraulics, including use of the existing WASP model. Information from past studies plus ongoing research in the harbor is expected to result in mercury loading targets for the estuary and harbor. The technical approach will then help support the translation of the harbor and estuary target(s) into corresponding allocations for sources in the watershed. Follow on work (still to be determined) is planned to update the WASP model for the TMDL evaluation.

2.2 HSPF

HSPF is a watershed scale, process-based model for simulating hydrology and water quality. HSPF is capable of producing accurate daily streamflow and pollutant concentration predictions, allowing detailed calibration to instream observations. HSPF provides dynamic simulation of upland and instream processes at a level of detail and complexity suitable for addressing the project objectives. HSPF can be used to address water quality impairments associated with combined point and nonpoint sources and has historically been used for TMDL development. For example, HSPF served as the foundation of the mercury mass balance model developed for the recent Willamette River Basin mercury TMDL, and was used to model THg transport for TMDLs in the Shenandoah Valley, Virginia (Eggleston, 2009), and has been applied in the development of TMDLs for other water quality impairments (e.g., elevated nutrients and low dissolved oxygen) in Minnesota and across the country. HSPF is supported by USEPA with open-source code. MPCA has long allocated funds towards the development of HSPF models for the purposes of supporting TMDLs, watershed restoration and protection strategies (WRAPS), and other initiatives across the state that can be leveraged to support the St. Louis watershed mercury TMDLs.

HSPF models of the St. Louis River watershed, Cloquet River watershed, and Duluth Urban Area were developed by Tetra Tech over the last decade and are currently being updated by Tetra Tech to cover the more recent time period (Figure 11). The update is being completed in anticipation of the upcoming mercury TMDLs. Recent data related to land use/cover, hydraulics, permitted point source discharges, atmospheric deposition of nutrients, reservoir dam releases, and weather have been incorporated to update the models and extend the simulation periods through Water Year 2021 (WY 2021). To support the mercury TMDLs, the National Wetland Inventory was used to differentiate peatlands from herbaceous and shrub wetlands. Model land use/cover categories are shown in Figure 12 and Figure 13. The watershed models are currently being re-calibrated for hydrology (i.e., streamflow, snow, evapotranspiration), sediment, nutrients, dissolved oxygen, algae, and organic carbon. The HSPF models will be further updated to include instream simulation of mercury for the TMDL project.

According to MPCA, there are about 144,000 acres of peatlands in the St. Louis River watershed that are ditched (about 25 percent of peatlands in the study area). A comparison of the Minnesota Altered Watercourses coverage with peatlands in the watershed, indicates that ditched peatlands are predominately concentrated in the central and southwestern portions of the St. Louis River watershed, corresponding with HSPF model weather zones 8, 11, and 12. Research has found that undrained peatlands tend to be carbon sinks and ditching of peatlands makes them carbon sources (Planas-Clarke et al., 2020; Krause et al., 2021). This information may be used to calibrate alterative DOC parameters for peatlands, and potentially hydrologic parameters and the Hg translators, within weather zones that have dense ditching based on evidence provided by available instream DOC/Hg/MeHg records. Should the allocations selected by MPCA seek to reduce Hg loading from ditched peatlands to meet the TMDLs, those reductions can be concentrated in the subbasins/weather zones with dense ditched peatlands.

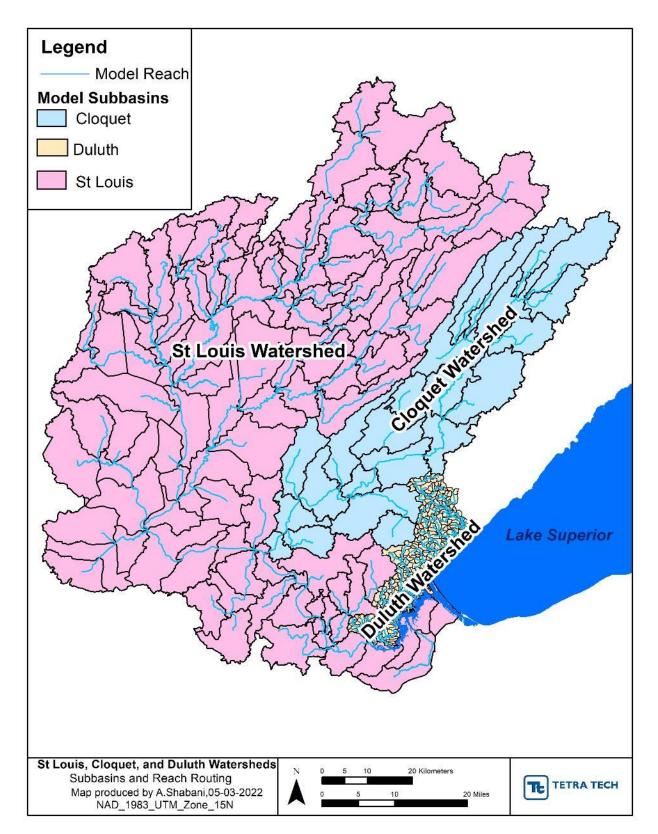


Figure 11. Subbasins and reaches for the St. Louis and Cloquet HSPF model and Duluth urban area HSPF model

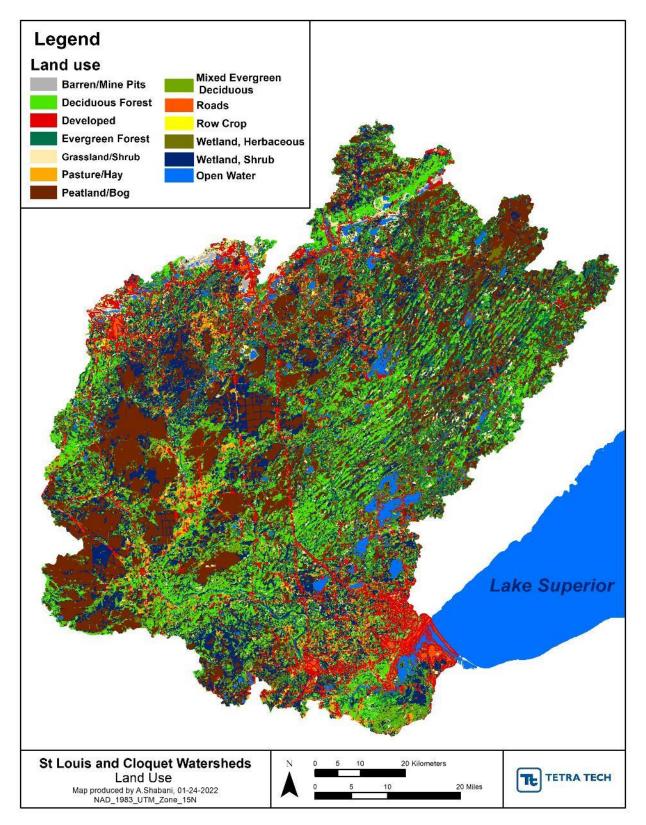


Figure 12. Model land use/cover in the St. Louis and Cloquet HSPF model

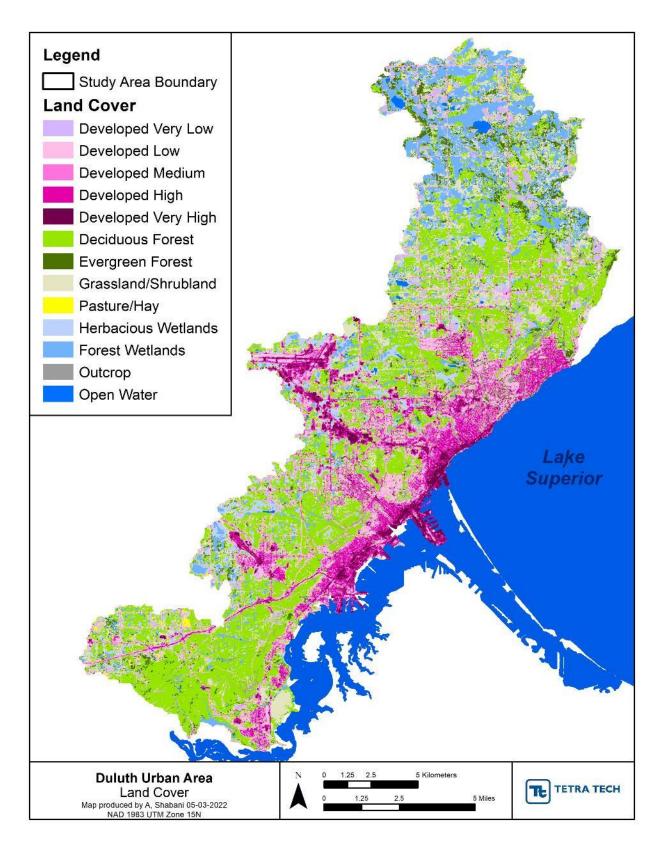


Figure 13. Model land use/cover in the Duluth urban area HSPF model

2.2.1 Landscape Mercury Transport Modeling

Global, regional, and natural emissions of mercury to the atmosphere are deposited to the landscape and direct to waterbody surfaces. Atmospheric deposition is the predominant source of Hg to Minnesota waterbodies, although mercury currently stored in soils and sediments reflects the net effects of long periods of deposition. The existing statewide mercury TMDLs attribute 10 percent of U.S. emissions to Minnesota based on estimates completed in the early 2000s. Humans have emitted Hg to atmosphere since ancient times as a result of mining, smelting, and fossil fuel burning, resulting in elevated Hg in soils and sediment. The statewide TMDLs call for reductions in atmospheric emissions of mercury. The objective here is to build on those required reductions while focusing on the mechanisms that transport MeHg and THg to streams, lakes, and reservoirs from nonpoint sources in the watershed though application of DOC as a transport surrogate.

DOC is a useful surrogate because there is a strong relationship between DOC and MeHg/THg concentrations in the watershed (Berndt and Bavin, 2009; Berndt and Bavin, 2012). Using DOC as a surrogate for Hg transport assumes that in general THg concentrations in soils are similar across the watershed because the primary originating source is the same – atmospheric deposition. This is consistent with the distribution of mercury in surface soils (depth 0 to 5 cm) in this vicinity that have concentrations within a narrow range from 0.03 to 0.07 mg/kg (dry weight) compared to the conterminous United States range of <0.01 to 3.55 mg-Hg/kg (Smith et al., 2014).

Mercury readily binds to DOC, leading to similar transport mechanisms for the two constituents. Thus, DOC serves as a relative indicator of Hg delivery from pervious nonpoint sources. The HSPF model is valuable because it 1) can be directly used to quantify sources of DOC in the watershed and 2) it eliminates the need for empirical upland delivery ratios for Hg and instead provides relevant process-based and calibrated outputs. It provides multi-decadal, hourly surface and subsurface flows and loads for point and nonpoint sources for modeled constituents.

HSPF can simulate total organic carbon, dead refractory organic carbon, and total inorganic carbon. (Total organic carbon includes the carbon within phytoplankton and labile carbon that is represented as a stoichiometric fraction of carbonaceous biochemical oxygen demand [CBOD]). HSPF does not split organic carbon into truly dissolved, colloidal, and particulate portions. Therefore, under an existing scope of work Tetra Tech is calibrating the HSPF model such that dead refractory organic carbon and phytoplankton associated organic carbon are considered particulate organic carbon whereas the organic carbon simulated as a fraction of CBOD will be used to represent the apparent dissolved (truly dissolved and colloidal) organic carbon fraction. DOC is computed based on simulated CBOD and a stoichiometric ratio conversion factor.

CBOD dynamics are simulated on pervious lands (PERLNDs) and impervious surfaces (IMPLNDs) in HSPF. This includes transport of CBOD by overland flow, the buildup/washoff of particulate CBOD, and CBOD in shallow lateral interflow and resurfacing groundwater. Instream organic carbon monitoring records collected in the watershed are being used for model calibration.

For directly connected impervious surfaces, delivery of mercury to streams is largely due to direct runoff of mercury in wet atmospheric deposition coupled with washoff of mercury derived from dry atmospheric deposition or anthropogenic sources such as spills, mercury switches, or fluorescent light bulbs. These sources and their transport to streams are not associated with DOC, so DOC cannot be used as a surrogate. Minimal MeHg loading is expected in impervious surface runoff. Therefore, loading in runoff from impervious surfaces will be simulated directly as THg based on wet deposition concentrations in precipitation coupled with buildup of THg that occurs during dry weather conditions as the net balance of dry deposition rates, re-emission to the atmosphere, and anthropogenic sources (see Eckley and Branfireun, 2008; Eckley et al., 2016).

The Fond du Lac Band has collected wet and dry mercury deposition data, as well as methylmercury deposition, as described by Hedin (2021):

"The Fond du Lac Air Program has been collecting wet mercury deposition data on Fond du Lac since 1998, and they collected methylmercury deposition in 2003. The cumulative deposition rate at FDL's air monitoring site for total mercury was 36 ug/m² for six years, and 190 ng/m² of methylmercury (MeHg) over three years. They then calculated a mean annual deposition rate for total mercury (6 ug/m²) and methylmercury (63.3 ng/m²), and determined the mass of mercury and methylmercury deposited in each watershed annually. In addition to the wet deposition site, in 2012 the FDL Air Program began collecting dry deposition mercury data on three sites on the Reservation where they placed six to seven bins that caught leaf litter from deciduous and coniferous trees. The leaves were ground and processed for mercury for Fond du Lac and there was an assumption it was bound up in leaf litter."

These data will be further investigated and utilized if deemed appropriate by MPCA. In the absence of these data, the following approach will be used.

Data from the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) sites closest to the study area are Marcell Experimental Forest (MN16) west of Hibbing, Minnesota that has been in operation since February 1996 and Brule River (WI08) east of Superior, Wisconsin that has been in operation since March 1996. Deposition of mercury to the pervious portions of the landscape and associated loading to the stream network, will be implicitly represented within the surrogate transport approach and translator to Hg and MeHg. Dry deposition of Hg is not often directly measured in Minnesota and indeed is very difficult to measure due to complex patterns of deposition and re-emission. Therefore, dry deposition to impervious surfaces will not be explicitly simulated but will instead be included within overall accumulation rates and accumulation limits for Hg on impervious surfaces that will be checked for consistency with literature estimates of total and wet Hg deposition and reported THg loading rates in urban runoff.

Few measurements are available for wet deposition of MeHg in precipitation. Such deposition does occur and is well documented in the vicinity of a bitumen processing plant in the Athabasca Oil Sands region of Canada (Kirk et al., 2014). Available monitoring studies show that in most cases MeHg concentrations in wet deposition are a small fraction of THg deposition (e.g., Conaway et al., 2010; Gerson et al., 2016). Gerson et al. in a detailed study of atmospheric mercury fluxes in New York's Adirondack mountains found that MeHg concentrations in precipitation were consistently less than 1% of THg concentrations and were not correlated with soil MeHg, from which they concluded that in situ methylation of ionic Hg in soils is a more important source than direct deposition of MeHg. Similarly, RTI (2013) concluded that the atmospheric deposition of MeHg in the watershed was "near zero." Furthermore, MPCA has evaluated MeHg data in precipitation for the period of 1996-2015; a majority of the samples were less than the method detection limit and those detected were less than 2 percent of total mercury in precipitation. Accordingly, only THg will be explicitly simulated in wet deposition.

2.2.2 Instream Mercury Modeling

TMDLs will be developed for segments listed as impaired for elevated ambient THg and/or elevated fish tissue mercury concentrations, which are primarily due to MeHg. Fish tissue concentrations reflect bioaccumulation from lower trophic levels and are often poorly correlated with water column THg due to complexities that drive mercury methylation by bacteria such as temperature and oxygen, sulfate, and iron availability. Therefore, new instream state variables will be added to the HSPF models for both THg and MeHg. The models will then be calibrated for THg and MeHg using instream monitoring records.

At the edge of the stream, linkage relationships will be applied to translate from DOC (simulated on the upland pervious land covers as a surrogate for mercury transport) to mercury (Figure 14); this will be done through the HSPF Mass Link block that is used to connect PERLNDs and IMPLNDs to model reaches (RCHRES). Separate DOC translators will be established for THg and MeHg. To account for environmental differences that effect the DOC/MeHg relationship such as the presence of mines that contribute sulfate and peatlands that exhibit low oxygen levels, spatial or source specific linkages will be explored for the HSPF modeling. For example, different

DOC/MeHg linkages may be developed for peatlands that are hotspots for methylation (Mitchell et al. 2008). Information from past studies, such as the 2013 load monitoring study, can inform where it might be valuable to differentiate the translators. Where there are locations or land covers, such as urban impervious surfaces, that deliver Hg to streams independent of DOC these can be represented directly as Hg. Instream records will be used to guide differentiated translators in the model. DOC loads and the mercury translators will be combined to tabulate and attribute nonpoint source and Municipal Separate Storm Sewer System (MS4) mercury loads to land use/cover categories to support allocations and implementation planning.

Mercury loads from permitted wastewater dischargers will be simulated. Wastewater discharge flow records are being processed into input time series for the HSPF model. These will be leveraged with mercury effluent data to develop input loading time series. Atmospheric deposition of mercury direct to the surface of waterbodies represented as part of the model reach network (i.e., stream and lake segments explicit in the model but not including waterbodies such as peat bogs) will also be simulated using the data sources described above for impervious surfaces.

Transport of THg and MeHg through the reach network, including in lakes, reservoirs, and streams, will be simulated on a mass-balance basis subject to transit losses described by a first-order decay function that accounts for a variety of loss mechanisms including re-emission of gaseous mercury and net settling loss of insoluble precipitates such as cinnabar (HgS). Available instream THg and MeHg records collected across the study area described in Section 1.5 will be used to calibrate the decay rates and temperature correction factors. It is anticipated different rates will be applicable to different waterbody types (e.g., natural lakes, reservoirs, free-flowing higher order streams).

Hg and MeHg Sources	Hg and MeHg Loads	Transport and Losses
 Nonpoint Sources Pervious surfaces: runoff, interflow, and groundwater DOC loading to edge of stream by land use/cover Impervious surfaces: Hg build-up/wash-off 	→ DOC to Hg/MeHg translators	
 Permitted Stormwater (MS4s) Pervious surfaces: runoff associated DOC loading to edge of stream by land use/cover Impervious surfaces: Hg build-up/wash-off 	→ DOC to Hg/MeHg translators	Transport and losses of Hg an MeHg through the stream
 Wet Atmospheric Deposition Waterbody surfaces: wet deposition Hg loading] ,	network and in-line lakes
 Permitted Wastewater Discharges Discharges: Hg and MeHg loads in effluent 	,	
Reservoirs* • Sediment releases: Hg and MeHg loads released from reservoir sediment * Pending data availability		

Figure 14. Conceptual schematic of mercury sources and modeling

Duda et al. (2012) provides general performance targets for water quality constituents in HSPF simulations that will be used to provide a qualitative evaluation of the performance of the model to predict THg and MeHg concentrations (Table 4). Annual relative errors are to be calculated from observed and simulated daily concentrations at a monitoring location. Evaluation of water quality simulations presents a challenge because water quality is not monitored continuously. Rather, grab samples represent conditions at a specific location at a point in time and may not be representative of average conditions across a broader waterbody and timeframe. Therefore, the metric ratings are applicable to sites with a minimum of 20 observations to reduce the impact of anomalous outliers.

Table 4. Performance targets for HSPF water quality simulation, relative error on daily values

Variable	Very Good	Good	Fair	Poor
THg or MeHg	≤ 15%	15 – 25%	25 – 35%	> 35%

2.3 **BIOACCUMULATION**

The bioaccumulation component of the technical assessment seeks to link ambient MeHg exposure concentrations with fish tissue mercury levels. As with methylation, process-based models of bioaccumulation of MeHg are available but are complex and have high data requirements. Fish targeted for human consumption are primarily larger fish at higher trophic levels that accumulate most of their body burden through consumption of smaller fish. As such, there tends to be a progressive accumulation of MeHg tissue concentrations at each step of the food chain. Direct uptake of MeHg from the water column occurs primarily in plankton and algae. A process-based simulation of MeHg bioaccumulation requires understanding the population structure and bioenergetics of all trophic levels, the rates at which different species are able to clear mercury from their systems, and, most importantly, a description of the dietary composition of each species, which often varies with age, size, and physical location. Such data are not available in detail for the majority of the St. Louis watershed. Without such data simpler empirical approaches, which implicitly incorporate the food web complexities through the specification of bioaccumulation factors (BAFs), have proved more robust.

As part of the development of the MeHg criterion, USEPA (2001, Appendix A) undertook a thorough evaluation of data on MeHg BAFs. Table A-9 in USEPA (2001) gives the final recommendations for national BAFs, summarized as the median of the distribution but also providing the 95th percentile value. However, USEPA's discussion of uncertainty in the BAF calculation notes that the lotic BAFs are primarily based on data from canals in the Everglades and a point-source-contaminated stream in Tennessee, while the lentic BAF data are biased toward northern oligotrophic lakes, primarily in the Great Lakes region. In addition, the range of species used was relatively small: much of the available TL 4 data was limited to walleye, pike, or bass, while much of the TL 3 data were for bluegill and perch. USEPA (2010) revisited the issue of MeHg BAFs and "cautions water quality managers that methylmercury bioaccumulation is generally viewed as a site-specific process and that BAFs can vary greatly across ecosystems, leading to significant risk of being either under-protective or over-protective when the national BAF numbers are used." For this reason, USEPA (2010) instead indicated a preference for site-specific BAFs.

For the statewide Hg TMDL, MPCA (2007) used a "generalized" BAF approach based on the geometric mean of a set of BAFs for fish mercury concentrations and total ambient mercury concentrations from 14 lakes representing three geographic areas of Minnesota (Table 6 in MPCA, 2007) to translate the fish tissue target to a corresponding water column THg concentration. This approach has considerable uncertainty because the tissue concentration depends more on MeHg exposure than THg; however, accurate estimates of MeHg BAFs were not widely available statewide.

For the St. Louis TMDL, addressing fish tissue concentrations with a BAF approach is also proposed; however, this will use a BAF based on MeHg not THg. This involves using fish tissue data collected in the project area to determine a regression relationship between ambient MeHg, fish length (i.e., a surrogate for age and accumulation timespan), and tissue Hg concentrations (which are predominantly MeHg) for the target endpoint species.

In the statewide TMDL, the standard size applied in mercury studies for adult northern pike and walleye were 55 centimeters (cm) and 40 cm, respectively. A distribution of observed tissue concentrations in adult endpoint fish in the watershed will be established. Local BAFs can then be derived to translate from the existing water column MeHg concentrations to the observed adult fish tissue concentrations. The focus is expected to be on the 90th percentile adult fish tissue concentration in the endpoint which is consistent with the statewide TMDL. The local BAFs can then be used to estimate the MeHg target concentration to attain the 0.2 mg/kg fish tissue water quality standard. Food webs across the watershed may differ. Therefore, different environment-specific (e.g., reservoir) relationships and BAFs may be derived to account for these differences.

2.4 LOADING CAPACITIES AND REDUCTIONS

Modeling results will be used to establish THg loading capacities for waterbodies impaired for ambient THg. HSPF MeHg results will be paired with results from the bioaccumulation assessment (Section 2.3) to determine the MeHg concentration needed to ensure the fish tissue target of 0.2 mg/kg is achieved in higher tropic level fish. The MeHg concentration required to meet the chronic water column standard of 1.3 ng-THg/L (or 0.77 ng-THg/L for segments along the Fond du Lac Reservation) will also be evaluated for waterbody segments impaired for fish tissue mercury to ensure both are achieved. HSPF simulated flows will be combined with the applicable Hg/MeHg water column target to compute a loading capacity for each impaired segment. A loading capacity will be computed as follows:

$$LC_w = Q_w tc$$

where LC_w is the loading capacity for segment w in lb/yr, Q_w is the flow for segment w in acft/yr, t is the target Hg or MeHg concentration in ng/L, and c is a unit conversion factor, 2.72(10⁻⁶) [1,233,481.85 L/acft x 2.05(10⁻¹²) lb/ng].

Many of the impaired segments align with a HSPF model reach. Therefore, calibrated streamflows for model reaches will be used. For waterbodies that do not align with a HSPF model reach (e.g., Big Bear Lake), runoff, interflow, and groundwater contributions simulated on a unit-area basis by the HSPF model will be applied to the land use distribution of the drainage area will be tabulated for loading capacity establishment.

Existing mercury loads predicted by the HSPF model and calibrated to instream monitoring records will be tabulated for each impairment as well. The percent reduction needed to meet the load capacity will be computed as follows:

$$R_w = \frac{(LC_w - M_w)}{LC_w} \times 100$$

where R_w is the percent load reduction needed for segment w and M_w is the existing mercury load for segment w in lb/yr.

2.5 SOURCE ASSESSMENT

Following the HSPF model calibration, existing at-source Hg and MeHg loads will be tabulated for nonpoint and point sources. The modeling will evaluate loads for nonpoint sources by land use/cover, permitted stormwater entities (MS4s), wet atmospheric deposition, permitted wastewater dischargers, and reservoirs (tentatively). To better understand Hg/MeHg sources and to support the assignment of load allocations and wasteload allocations, Hg and MeHg loads will be tabulated for subset drainage areas within the broader watershed. A benefit of this approach is that it will provide finer scale loading information compared to evaluating source contributions only at

the watershed-scale. The loading capacity and percent reductions needed to meet mercury water quality standards will computed as described in Section 2.4 for each impairment. Then loading capacities will need to be collectively met for every impairment within the zone. Given that some impairments may require lower reductions than specified for the zone, this serves as a conservative component in the TMDL margin of safety (MOS). The source assessment zones will include (Figure 15):

- Cloquet River above Island Reservoir
- Cloquet River below Island Reservoir
- East Two River
- Embarrass River
- Floodwood River
- Partridge
- Stony Creek
- Swan River
- West Two River
- Whiteface River
- St. Louis River upstream of confluence with Partridge River
- St. Louis River between confluences with Partridge River and East Two River
- St. Louis River between confluences with East Two River and Floodwood
- St. Louis River between confluence with Floodwood to Fond du Lac dam
- St. Louis River below Fond du Lac Dam

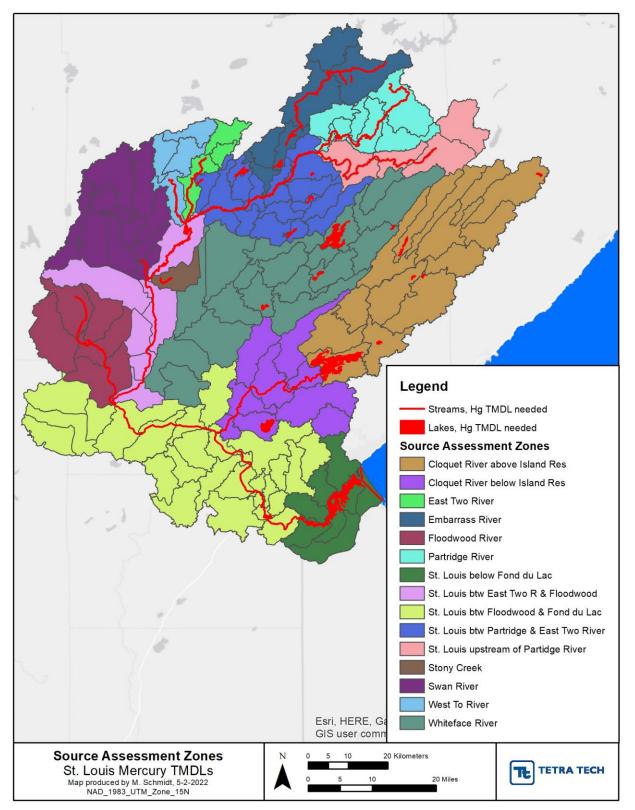


Figure 15. Source assessment zones for the Hg TMDLs

2.6 ALLOCATION SCENARIOS

Modeling results will be applied to develop an interactive spreadsheet (i.e., allocation tool) that can be used to establish allocations strategies to meet the TMDL loading capacities expressed as Hg (water column listings) and MeHg (fish tissue listings). The allocation tool will include existing Hg and MeHg loads by source category for each of the source assessment zones listed in Section 2.5. For nonpoint sources, Hg/MeHg loads will be tabulated by land use/cover. The allocation tool will be designed so that reductions can be entered by source category and zone to evaluate alternative scenarios. Resulting loads and load reductions will be automatically computed by the tool and checks generated to evaluate if a given scenario satisfies the reductions required for impaired segments as described in Section 2.4. Resulting loads for point and nonpoint sources can be directly used, or aggregated, for wasteload allocations and load allocations in the TMDL. Three example allocation options will be prepared in coordination with MPCA that achieve the Hg/MeHg targets.

3.0 BIBLIOGRAPHY

- Alpers, C.N., J.L. Yee, J.T. Ackerman, J.L. Orlando, D.G. Slotton, and M.C. Marvin-DiPasquale. 2016. Prediction of fish and sediment mercury in streams using landscape variables and historical mining. *Science of the Total Environment* 571:364-379.
- Berndt, M. and T. K. Bavin. 2012. Methylmercury and dissolved organic carbon relationships in a wetland-rich watershed impacted by elevated sulfate from mining. Environmental Pollution, 161, pp. 321-327.
- Berndt, M. and T. Bavin. 2009. Sulfate and Mercury Chemistry of the St. Louis River in Northeastern Minnesota. A Report to the Minerals Coordinating Committee prepared by Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, Minnesota.
- Berndt, M. 2003. Mercury and Mining in Minnesota. Prepared for the Minerals Coordinating Committee by the Minnesota Department of Natural Resources, St. Paul, Minnesota.
- Burns, D.A., E.A. Nystrom, D.M. Wolock, P.M. Bradley, and K. Riva-Murray. 2014. An empirical approach to modeling methylmercury concentrations in an Adirondack stream watershed. *Journal of Geophysical Research: Biogeosciences* 119:1970-1984. doi:10.1002/2013JG002481.
- Conaway, C. H., F. J. Black, P. Weiss-Penzias, M. Gault-Ringold, and A. R. Flegal (2010), Mercury speciation in Pacific coastal rainwater, Monterey Bay, California, *Atmos. Environ.*, 44(14):1788–1797, doi:10.1016/j.atmosenv.2010.01.021.
- Duda, P.B., P.R. Hummel, A.S. Donigian, Jr., and J.C. Imhoff. 2012. BASINS/HSPF: Model use, calibration, and validation. *Transactions of the ASABE*, 55(4): 1523-1547.
- Eagles-Smith, C.A., J.T. Ackerman, J.J. Willacker, M.T. Tate, M.A. Lutz, J.A.Fleck, et al. 2016. Spatial and temporal patterns of mercury concentrations in freshwater fish across the Western United States and Canada. *Science of the Total Environment* 568:1171-1184.
- Eckley, C.S. and B. Branfireun. 2008. Gaseous mercury emissions from urban surfaces: controls. *Applied Geochemistry*, 23: 369-383.
- Eckley, C.S., M.T. Tate, C.-J. Lin, M. Gustin, S. Dent, C. Eagles-Smith, et al. 2016. Surface-air mercury fluxes across Western North America: A synthesis of spatial trends and controlling variables. *Science of the Total Environment*, 568: 651-665.
- Eggleston, Jack. 2009. Mercury loads in the South River and simulation of mercury total maximum daily loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River—Shenandoah Valley, Virginia: U.S. Geological Survey Scientific Investigations Report 2009–5076, 80 p., available online at http://pubs.usgs.gov/sir/2009/5076/
- Gerson, J. R., C. T. Driscoll, J. D. Demers, A. K. Sauer, B. D. Blackwell, M. R. Montesdeoca, J. B. Shanley, and D. S. Ross. 2017. Deposition of mercury in forests across a montane elevation gradient: Elevational and seasonal patterns in methylmercury inputs and production. J. Geophys. Res. Biogeosci., 122: 1922–1939, doi:10.1002/2016JG003721.
- Hedin, K. 2021. Fond du Lac Reservation Nonpoint Source Assessment Report. Prepared for the Fond du Lac Office of Water Protection, Environmental Program, Resource Management Division, February 2021.
- Hirshon, B., Schafroth, D., and R. Washington. 2019-2020. Mercury in the St. Louis River Watershed. Prepared for the Minnesota Environmental Partnership by Trains, Planes, & Automobiles LLC.

- Kirk, J.L., D.C.G. Muir, A.Gleason, X. Wang, G. Lawson, R.A.. Frank, I. Lehnherr, and F. Wrona. 2014. Amospheric deposition of mercury and methylmercury to landscapes and waterbodies of the Athabasca oil sands region. *Environmental Science and Technology*, 48, 7374–7383.
- Knightes, C., H.E. Golden, C.A. Journey, G.M. Davis, P.A. Conrads, M. Marvin-DiPasquale, et al. 2014. Mercury and methylmercury stream concentrations in a Coastal Plain watershed: A multi-scale simulation analysis. *Environmental Pollution* 187: 182-192.
- Knightes, C.A., G.M. Davis, H.E. Golden, P.A. Conrads, P.M. Bradley, and C.A. Journey. 2016. Simulating mercury and methyl mercury stream concentrations at multiple scale in a wetland influenced coastal plain watershed (McTier Creek, SC, USA). Edited by K.W. Krauss, and J.S. Latimer C.E. Stringer. *Headwaters to Estuaries: Advances in Watershed Science and Management - Proceedings of the Fifth Interagency Conference on Research in Watershed Models. North Charleston, SC*: USDA Forest Service, Southern Research Station. 74.
- Krause, L., McCullough, K.J., Kane, E.S., Kolka, R.K., Chimner, R.A., Lilleskov, E.A. 2021. Impacts of historical ditching on peat volume and carbon in northern Minnesota USA peatlands. *Journal of Environmental Management.* 296. https://doi.org/10.1016/j.jenvman.2021.113090.
- Lavoie, R.A., Amyot, M., and J.F. Lapierre. 2019. Global Meta-Analysis on the Relationship Between Mercury and Dissolved Organic Carbon in Freshwater Environments. JGR Biogeosciences, 124(6), pp. 1508-1523. https://doi.org/10.1029/2018JG004896
- Mitchell, C. P. J.; Branfireun, B. A.; Kolka, R. K. 2008. Assessing sulfate and carbon controls on net methylmercury production in peatlands: An in situ mesocosm approach. Appl. Geochem. 2008, 23 (3), 503–518.
- MPCA. 2007. Minnesota Statewide Mercury TMDL. wq-iw4-01b. Minnesota Pollution Control Agency, St. Paul, MN.
- Myrbo, A., Swain, E. B., Engstrom, D. R., Wasik, J. C., Brenner, J., Shore, M. D., Peters, 50 E. B., and Blaha, G., 2017, Sulfide Generated by Sulfate Reduction is a Primary Controller of the Occurrence of Wild Rice (Zizania palustris) in Shallow Aquatic Ecosystems: Journal of Geophysical Research-Biogeosciences, v. 122, p. 2736-2753.
- National Atmospheric Deposition Program (NRSP-3). 2022. NADP Program Office, Wisconsin State Laboratory of Hygiene, 465 Henry Mall, Madison, WI 53706.
- Planas-Clarke, A.M., Chimner, R.A., Hribljan, J.A. et al. 2020. The effect of water table levels and short-term ditch restoration on mountain peatland carbon cycling in Cordillera Blanca, Peru. *Wetlands Ecol Manage* 28, 51-69. https://doi.org/10.1007/s11273-019-09694-z
- RTI. 2013. St. Louis River Estuary TMDL Project, Preliminary WARMF Modeling Report. Prepared for U.S. Environmental Protection Agency, Region 5 by RTI International, Research Triangle Park, NC and URS Corporation, Southfield, MI.
- Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, Federico, and Ellefsen, K.J., 2014, Geochemical and mineralogical maps for soils of the conterminous United States: U.S. Geological Survey Open-File Report 2014–1082, 386 p., <u>http://dx.doi.org/10.3133/ofr20141082</u>.
- USEPA (United States Environmental Protection Agency). 2001. Water Quality Criterion for the Protection of Human Health: Methyl mercury. EPA-823-R-01-001.
- USEPA (United States Environmental Protection Agency). 2010. Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion. Office of Science and Technology, U.S. Environmental Protection Agency, Washington, DC.

Zhu, S., Z. Zhang, and D. Žagar. 2019. Mercury transport and fate models in aquatic systems: A review and synthesis. *Science of the Total Environment*, 639:538-549. <u>https://doi.org/10.1016/j.scitotenv.2018.04.397</u>.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 7

(Berndt, Mike, email to Patrick Carey and Ed Swain, MPCA re Coordinated TMDL effort, Oct. 7, 2011)

Subject: Coordinated TMDL effort

Date: Friday, October 7, 2011 1:16:38 PM CT
From: Berndt, Mike (DNR)
To: Carey, Patrick (MPCA), Swain, Ed (MPCA)

Pat and Ed,

Here is a first cut at drafting something to arrange a coordinated MPCA/DNR effort. I had only a few hours to write it, but wanted to make sure to give something to you before I left (I am at GSA Sunday through Wednesday next week). I attached the proposed arrangement that was accepted by the mining industry to give you a flavor of that connection (where our money for the study comes from). Once the money arrives, there are no strings attached, but the panel needs to be informed and allowed to have input on the studies to be conducted. I have already broached the subject of applying some or all of the funds to each individually and they sounded like they would support it.

Now I would like to receive comments from you two (if/how to proceed) by Thursday (Oct. 13). If you want to discuss something sooner than that, you can get me by cell phone next week. I probably won 't be checking email or phone messages.

Mike Berndt Research Scientist III Minnesota Department of Natural Resources Division of Lands and Minerals 500 Lafayette Rd. St. Paul, MN 55155-4045 651-259-5378 cell- 952-288-3640

<u>Draft</u> plan for combining DNR and MPCA resources for development of a Mercury TMDL for the St. Louis River and its estuary

Michael E. Berndt, Minnesota Department of Minnesota Resources, Division of Lands and Minerals, St. Paul, MN 55155

The Minnesota Department of Natural Resources in Minnesota has been conducting and sponsoring research on mercury and sulfate in the St. Louis River watershed for approximately ten years. These studies have (1) evaluated methods to reduce mercury in taconite stack emissions (Berndt, 2011), (2) provided better resolution on sources and fate of sulfate in the St. Louis River watershed and estuary (Berndt and Bavin, 2009, 2011a, Johnson and Beck, 2011), and (3) shed considerable light on mechanisms of MeHg production and transport in watersheds containing mining features (Berndt and Bavin, 2011c).

These advances have been made with considerable guidance and assistance from the Minnesota Pollution control agency who have been tasked with developing a statewide Hg TMDL for Minnesota as well as a watershed specific TMDL for the St. Louis River and its estuary. The former Hg TMDL has been previously developed and approved by EPA, but the St. Louis River TMDL is still in the early stages of development. On Sept. 29, 2011, DNR and MPCA scientists met to discuss the state of research on this watershed to determine if and where data gaps exist. A list of gaps was generated and circulated and discussions were held relating to development of potential paths forward. This document is a direct outcome from that meeting. Here we propose a mechanism to fund and coordinate DNR and MPCA efforts in a manner that will effectively fill as many of those data gaps as possible.

Funding:

The Minnesota Department of Natural Resources has approximately \$900,000.00 of cash and in-kind support that is being dedicated towards research on release and environmental effects on Minnesota's Iron Range. This Iron Range outlines the northern fringe of the St. Louis River watershed and so depending on interest, some or all of these funds could be devoted towards this effort. These funds were obtained from Environmental and Iron Ore Cooperative Research programs (\$400,000) that were matched with additional funding (\$500,000) from a consortium of iron mining companies. The group directing the research that will be conducted using these funds will involve a panel consisting of DNR, MPCA, and industry experts (see attached document). In addition, the DNR is expecting to using the competitive RFP process to name researchers to this panel. Once projects are chosen, the research will be conducted by DNR and the outside experts. This funding is available immediately and must be spent by June 30, 2013.

It is proposed that the MPCA obtain and use funds from EPA to conduct research that is coordinated with the DNR effort. Ideally, these EPA funds would be obtained in time to begin work in the summer (2012) so that the programs could be coordinated both in space and time.

Research Coordination:

Specific DNR and MPCA activities would be selected and guided by their respective managers with technical assistance and input from research scientists at both agencies (Michael Berndt and Travis Bavin at the DNR, Bruce Monson and Edward Swain at the MPCA).

We propose a three pronged approach, directed towards (1) evaluating specifically how and where MeHg is loaded into streams in the St. Louis River watershed, (2) collecting species-specific data on MeHg bioaccumulation, (3) providing full current stream inventories of key components that will be needed in a TMDL evaluation. The TMDL would then be developed on a species specific basis.

It is noteworthy that three out of six projects that will be considered by the DNR's sulfate studies can be used to frame a TMDL study:

- (1) MeHg Transport and Degradation Processes in Iron Range Streams
- (2) A Sediment and Water Column Geochemical study of Lake Manganika: A Highly Productive Lake that Generates MeHg on Minnesota's Iron Range.
- (3) Real Time Monitoring of Chemistry and Flow Volumes in Mineland Streams.

Although the "Sulfate Panel" has not met to discuss which projects to spend its resources on at this point, these three studies are all directly relevant to a mercury TMDL approach.

Project (1), above, would involve the full evaluation of MeHg Transport at one or more sites on the Iron Range. Although not designed as part of a Hg TMDL study, it could be designed to fill an important gap in our understanding of MeHg transport and bioaccumulation processes on the Iron Range (and perhaps elsewhere). Berndt and Bavin (2011a) presented evidence that MeHg transport is very likely to be speciation dependent. While MeHg is bound to organic carbon in most streams, there is mounting evidence that MeHgHS contributes to stream inventories in areas where H₂S is being produced. MeHgHS is volatile and relatively unstable so an important question relates to the speed at which it degases or oxidizes compared to the rate at which it is taken up by biota.

Project (2), above, would involve conducting a combined field and laboratory study to evaluate MeHg release processes from Lake Manganika. This lake was recently found to be the dominant loading source for MeHg to the East Two River during the summer months. This river feeds directly into the St. Louis River. Berndt and Bavin (2011b) have hypothesized that a primary factor involving MeHg loading (of MeHgHS) involves SO4 reduction in Fe-limited settings. Streams feeding this lake contain elevated SO₄ and nutrient levels, conducive for SO₄ reduction in bottom sediments. The sediments also lack Fe and so all of the SO₄ reduced to sulfide in sediments is released as H₂S. Geochemical calculations for this and other sites have predicted that MeHg releases in this and other sites are linked to formation of H₂S at circum-neutral (non-basic) pH. Thus, evaluating the factors associated with MeHg generation at this and other sites will improve our understanding of MeHg loading in this watershed.

Project (3), above, involved coupling flow monitoring and sulfate measurements to provide better information on SO₄ inventories in the mining region. DNR funding is probably insufficient for collecting the data of this type that would be needed for a mercury TMDL study. Improving on this portion of the study is where the MPCA may want to focus its resources. The idea would be to select and install

stream gages at selected sites and to sample periodically for a list of parameters chosen jointly by MPCA and DNR staff.

Together, these three studies provide a beginning framework for a TMDL study, because they couple regionally specific mechanics of MeHg production, transport, and bioaccumulation, with a detailed watershed-wide loading estimates for those species thought to be most important in development of a TMDL (Species Specific Data on MeHg, Hg, DOC, SO4, pH, Other cations and anions).

Timeline:

October/November 2011: MPCA and DNR Staff Coordinate Activities. MPCA and DNR work with their constituent and management teams to identify and assign specific projects that are needed for the TMDL. MPCA works to obtain EPA funding for their portion of the effort.

November 2011 to December 2012: Identify scientists and consultants to conduct the studies. This will involve using the state's RFP process to fill the needs not met by staff scientists.

January to April 2012: Work together to better design the studies and write all contracts needed for work to begin in May 2012.

May to November 2012: Conduct field studies.

Project Title: A Coordinated Sulfate Research Effort for the Mining Regions of Northeastern Minnesota

Total Funds: \$900,000.00 Two Years.

Date: 3/27/2011

Michael E. Berndt, Minnesota Department of Natural Resources

Exposure of metal sulfides to air and water in tailings basins, stockpiles, and pit walls produced during mining results in the release of sulfate $(SO_4^{=})$ to nearby surface and ground waters. While it has long been known that $SO_4^{=}$ is released by iron mining in Northeastern Minnesota, proposed mining of the metal sulfides in the Duluth complex could contribute additional $SO_4^{=}$. These $SO_4^{=}$ releases have recently factored heavily in regulatory discussions owing to their potential to drive chemical reactions that could increase the concentration of Hg in fish or negatively impact wild rice populations.

Extensive sampling and reporting of stream chemistry in the area surrounding the mining region in NE Minnesota has illustrated a relatively systematic behavior of sulfate, methyl mercury (MeHg), and other elements in the St. Louis River basin, but it has become apparent that additional studies are needed to better define the detailed chemical mechanisms underlying the largely empirical results. Further studies are needed to evaluate mechanisms of MeHg release in wetlands receiving SO₄ from mining and to determine the relative rates of transport, degradation, and biologic uptake of MeHg in mine land streams and flooded wetlands. Additionally, Minnesota companies are currently being required to meet the 10 mg/L wild rice standard when wild rice is found downstream from their operations. This standard is currently being reviewed by the MPCA while the DNR is examining the sources and distribution of SO₄ released from the mining regions and evaluating several means to reduce future SO₄ releases.

Here, the DNR proposes to develop a coordinated research effort focused on obtaining a full understanding of sulfate releases from mining and their effect on the environment. This effort will be similar to that used previously when the DNR developed a coordinated mercury research effort to address mercury in taconite stack emissions beginning in 2003. This effort pooled funding from multiple sources, met periodically with industry, state, and other organizations to discuss the research studies conducted to date, and then used the funds to coordinate studies on Hg control at taconite processing plants. This research effort led to development of an understanding of how mercury cycles in taconite processing plants and to the performance of many bench and plant-scale tests that developed into several promising technologies for mercury control.

The new effort will focus on evaluating $SO_4^{=}$ in mine land discharges. Research funded under this project will build on reconnaissance work that has been completed by the DNR from 2007-2011 and is currently being conducted through an ENTRF (Environment and Natural Resources Trust Fund) which

will be completed in June 2012. The objective will be to acquire a more detailed understanding of the sulfate release mechanisms in the mining regions, obtain a fundamental understanding of how these releases affect MeHg generation, transport, and bioaccumulation in surface waters near mining districts, and to provide a more comprehensive understanding of potential means to either decrease sulfate discharges into surface and/or ground water or to minimize their potential impacts through careful timing. This group will interface with, but not duplicate, the efforts currently being made by the Minnesota Pollution Control Agency as they evaluate Minnesota's wild rice sulfate standard.

A technical steering committee will be assembled to guide this effort immediately upon learning that this effort is funded. Members will initially include staff from the state agencies (DNR, MPCA), the University of Minnesota, and industry participants, but may be expanded to include other members if/when it is believed their expertise is necessary. This group will continue to meet periodically throughout the two-year period to help assess the results of past and on-going studies related to sulfate releases on the Iron Range and to design and conduct additional studies. Funds are requested to manage, conduct, and fund the research activities selected by the steering committee.

DNR Committee Members:

Michael E Berndt, PhD: Minnesota DNR Geochemist, University of Minnesota Adjunct Professor in Geology. 32 years of research experience in geochemistry, 15 years of direct experience working on environmental geochemistry relating to taconite processing plants and tailings basins, pits, wetlands, and streams on the Mesabi Iron Range. Dr. Michael Berndt will manage and coordinate the research efforts and also provide scientific input on studies conducted in connection with the proposed studies.

Kim Lapakko: Civil and mineral engineer with 35 years of experience detailing SO₄ release mechanisms associated with on-land and in-pit disposal of tailings and waste rock. Kim Lapakko will provide scientific input on sulfate release mechanisms associated with Iron Formation and Gabbroic Rocks.

Preliminary List of Coordinated Research Studies:

A preliminary topic list includes the following. This list will likely be modified upon consultation with the members of the steering committee for the coordinated research effort:

- (4) Sulfate Release Rates from Iron Range Stockpiles, Tailings, and Overburden.
- (5) Promoting Biologic Sulfate Reduction in Wetlands, Pits, and Lakes: a Long-Term Approach for Managing SO₄ Discharges in Mining Watersheds?
- (6) Calibrating Sulfur and Oxygen Isotopic Methods to Quantify Sulfate Reduction Rates in Groundwater, Lakes, and Wetlands on Minnesota's Iron Range.
- (7) MeHg Transport and Degradation Processes in Iron Range Streams
- (8) A Sediment and Water Column Geochemical study of Lake Manganika: A Highly Productive Lake that Generates MeHg on Minnesota's Iron Range.
- (9) Real Time Monitoring of Chemistry and Flow Volumes in Mineland Streams.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 8

(J.K. Coleman Wasik *et al.*, Methylmercury Declines in a Boreal Peatland When Experimental Sulfate Deposition Decreases, 2012)

Methylmercury Declines in a Boreal Peatland When Experimental Sulfate Deposition Decreases

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Supporting Information

ABSTRACT: Between 2001 and 2008 we experimentally manipulated atmospheric sulfate-loading to a small boreal peatland and monitored the resulting short and long-term changes in methylmercury (MeHg) production. MeHg concentrations and %MeHg (fraction of total-Hg (Hg_T) present as MeHg) in the porewaters of the experimental treatment reached peak values within a week of sulfate addition and then declined as the added sulfate disappeared. MeHg increased cumulatively over time in the solid-phase peat, which acted as a sink for newly produced MeHg. In 2006 a "recovery" treatment was created by discontinuing sulfate addition to a portion of the experimentally treated section to assess how MeHg production might respond to decreased sulfate loads. Four years after sulfate additions ceased, MeHg concentrations and %MeHg had declined significantly from 2006 values in porewaters and peat, but remained elevated relative to control levels. Mosquito larvae collected from each treatment at the end of the experiment exhibited Hg_T concentrations reflective of MeHg levels in the peat and porewaters where they were collected. The proportional responses of invertebrate Hg_T to sulfate deposition rates demonstrate that further controls on sulfur emissions may represent an additional means of mitigating Hg contamination in fish and wildlife across low-sulfur landscapes.



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INTRODUCTION

Atmospheric sulfate deposition increased dramatically with the advent of the industrial period, ultimately causing widespread ecosystem acidification, especially downwind of large population centers in North America and Europe.^{1,2} Regulatory efforts aimed at controlling sulfur dioxide emissions were very successful at reducing sulfate deposition,^{3–5} but ecosystems have responded variably depending on landscape and climatic factors.⁶ Whereas most research in sulfate-impacted systems has focused on recovery from environmental acidification,^{7,8} sulfate deposition is also of considerable consequence to the production of methylmercury (MeHg),⁹ the predominant form of mercury that bioaccumulates in food webs.

Wetlands are a major linchpin in the coupled biogeochemical cycles of sulfur and mercury and serve two potential countervailing roles in ecosystem recovery from sulfate deposition. They are sites of active sulfate reduction and so provide an important sink for legacy sulfate leaching from upland soils toward downstream aquatic systems.10 Wetlands are also important sites of mercury methylation in the landscape.¹¹ Augmented sulfate inputs can stimulate MeHg production in sulfurlimited systems due to the increased activity of sulfate-reducing bacteria (SRB), which are known mediators of the methylation process.^{9,12-16} Therefore continued inputs of sulfate from uplands may prolong elevated MeHg production in, and export from, wetland systems.¹⁷ Our understanding of how MeHg production in ecosystems responds to declining sulfate deposition, and the subsequent effects on mercury concentrations in biota, is limited to a handful of largely correlative studies in lakes.^{18,19} We therefore lack an experimental basis for predicting the rate of ecosystem recovery, the factors that enhance or inhibit it, or the biogeochemical mechanisms involved.

To investigate the in situ response of net MeHg production as an ecosystem recovers from elevated sulfate deposition, we experimentally amended a peatland in northern Minnesota with sulfate for four years and then monitored the system over an equivalent period after sulfate additions ceased. Changes in porewater, peat, and biotic MeHg levels across treatments with differing sulfate depositional histories were used to (1) understand the impacts of increasing and decreasing sulfate deposition on net MeHg production within the peatland, (2) identify mechanisms that promote and inhibit recovery of systems previously impacted by elevated levels of sulfate deposition, and (3) connect changes in sulfate deposition to mercury levels in biota. The extended nature of this project provided an opportunity to study wetland recovery processes against a backdrop of variable climate and hydrology.

MATERIALS AND METHODS

Study Site. This study was performed in the S6 watershed of the Marcell Experimental Forest (MEF), a field-research facility of the Northern Research Station of the USDA Forest Service (Figure 1). The 2.0-ha S6 peatland has an overstory of mature black spruce (*Picea mariana*) and tamarack (*Larex laricina*) within a central bog area and is dominated by alder (*Alnus rugosa*) within its lagg margin.²⁰ The perched water table in the central bog is hydrologically isolated from the uplands and the lagg, creating a mineral-poor, ombrotrophic system ideal for experimental manipulation of atmospheric deposition.

Sulfate Additions. Long-term atmospheric deposition records from the National Atmospheric Deposition Program (NADP) site (MN-16) at MEF show that sulfate deposition

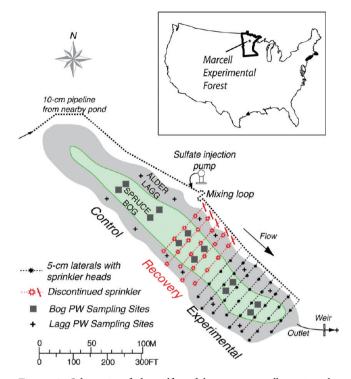


Figure 1. Schematic of the sulfate delivery system illustrating the experimental design within the S6 peatland. Porewater (PW) sampling sites in the bog (■) and lagg (+) were located along transects within each treatment. The first 5 lateral pipelines encompass the recovery treatment. See text for further details. The inset map shows the location of the Marcell Experimental Forest.

decreased by roughly 50%, from 11 kg ha⁻¹ yr ⁻¹ in the early 1980s to approximately 5.5 kg ha⁻¹ yr ⁻¹ in the mid-2000s (Supporting Information Figure S1).²¹ Our experimental additions increased sulfate loading to 32 kg ha⁻¹ yr ⁻¹, or approximately 4× the average ambient 1990s deposition rate at MEF. This rate is representative of late 20th-century sulfate deposition across large areas of eastern North America, and thus provides an appropriate model for the effects of increasing sulfate deposition on MeHg production as well as the recovery processes that a sulfate-impacted peatland would experience as sulfate deposition declined.

The specific details of the initial experimental design and sulfate delivery system for this study were described previously by Jeremiason et al.⁹ Briefly, in the summer of 2001 the peatland was divided into control and experimental sections, and a sulfate delivery system was constructed of PVC pipe across the downgradient experimental half (Figure 1). Source water was pumped from a nearby, dilute pond (specific conductivity = $20 \ \mu \text{S cm}^{-1}$), a concentrated sodium sulfate solution was injected into the 10-cm main pipeline just above the experimental treatment, and the sulfate-enriched solution was sprayed onto the peatland surface via sprinkler heads atop 1-m risers. Sulfate amendments began in the fall of 2001 and continued three times each year (spring, summer, and fall) through 2008. Each sulfate addition simulated approximately 6-8 mm of rainfall, which did not significantly alter the peatland water table. In the early spring of 2006 a recovery treatment was created by discontinuing sulfate addition to the upgradient, one-third of the original experimental treatment (Figure 1).

Field Sampling. *Porewaters.* Two porewater sampling transects were established in the control and experimental treatments, with four 1-m² sample plots distributed evenly across the

central bog area and lagg margins along each transect (Figure 1). To isolate the effect of atmospheric sulfate deposition on MeHg production from effects caused by upland inputs, only data from the central bog sites were considered for this paper. In 2006 two additional transects were established in the newly created recovery treatment, and transects located in the experimental treatment were repositioned down-gradient to ensure sampling occurred well within the treated area. Peat porewater samples were collected from each plot on day -1, +1, +3, and +7 relative to each sulfate addition. Extra sampling days were added to spring and fall samplings on days -7and +14.

Porewater samples were collected by portable peristaltic pump through a 1.9-cm ID, Teflon probe with a custommachined tip perforated with 5-mm holes. The probe was inserted into the peat to a depth approximately 5 cm below the water table and porewater was pumped via Teflon tubing through acid-washed, 47-mm Teflon filter-holders (Savillex Co.) pre-loaded with ashed, 0.7- μ m, glass-fiber filters directly into new, 125-mL PETG bottles. Bottles were rinsed in triplicate with porewater prior to filling, and samples were preserved with high-purity HCl to 0.5% (v/v). Samples were collected for dissolved Hg_T, MeHg, and major anions on each sampling day throughout the course of the project. Hg_T and MeHg samples were collected using accepted clean sampling techniques.²² Field duplicates and equipment blanks accounted for 10% of samples.

Peat Samples. Surficial peat cores were collected annually from each treatment in 2003, 2005–2007, and 2009 by coring or cutting and hand-collection (SI Table S2). All peat samples were kept in frozen storage and freeze-dried prior to analysis of Hg_T and MeHg.

Invertebrate Samples. In late spring 2009, near the end of the study, mosquito (*Culex* spp.) larvae were collected in triplicate batches from each treatment by netting with vinyl-coated aquarium nets. Mosquito larvae were hand-picked at the MEF laboratory, placed in vials of deionized water overnight to purge gut contents, and then frozen. Samples were freeze-dried prior to analysis of Hg_T content. Where enough mass remained, samples were also analyzed for MeHg content.

Laboratory Analyses. Porewaters. Aqueous Hg_T was analyzed according to EPA method 1631 Revision E.²³ Samples were oxidized overnight with BrCl and then neutralized with NH₂OH. Stannous chloride reduced the oxidized mercury species to Hg^0 , which was purged and trapped on gold traps. Mercury was thermally desorbed from the traps in a stream of Ar and analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) on a Tekran 2600 Automated Total Mercury Analyzer. Daily calibrations were checked with lab-made standards. Each run included 20% deionized-water blanks, 10% sample duplicates, and 5% sample matrix spikes.

Aqueous MeHg was analyzed according to methods described in Bloom²⁴ and Liang et al.²⁵ at the Branfireun laboratory (2005 samples), the Jeremiason laboratory (2006 samples), or the Balogh laboratory (2007 and 2008 samples). Samples were distilled with 8 M H_2SO_4 and 20% KCl in an acid-cleaned, Teflon, extraction manifold and distillates were analyzed within 48 h. Mercury species were ethylated with sodium tetraethylborate and then purged from solution and trapped on Tenax traps. Mercury species were thermally desorbed from the traps and carried in a stream of Ar or He through a short chromatographic column. The separated mercury species passed through a pyrolytic trap where they were thermally transformed into Hg^{0} , and analyzed by CVAFS on a Tekran 2500 spectrometer (Branfireun and Jeremiason laboratories) or a Brooks Rand Model III (Balogh laboratory). Each run included 5% deionized-water blanks, 10% sample duplicates, and 5% sample matrix spikes.

Water samples for major anions (SO₄^{2–}, Cl[–], Br[–]) were analyzed on a Dionex DX-500 ion chromatograph according to standard methods by the USFS Northern Research Station laboratory in Grand Rapids, Minnesota. Each run included 10% deionized-water blanks, 10% sample duplicates, and check standards. Replicate standard measures and lab duplicates were within 10% and method detection limits were 0.1 mg L⁻¹ each year

Peat Samples. For Hg_T analysis, peat samples were microwave digested in concentrated HNO_3 and diluted prior to analysis by dual gold-trap amalgamation CVAFS, as described above for porewaters. For MeHg analysis, peat samples were distilled as outlined for porewaters, but with the inclusion of a known mass spike of enriched Me^{199} Hg in each vessel. Samples were analyzed by isotope dilution—gas chromatography—inductively coupled plasma mass spectrometry (ID-GC-ICPMS) with mercury detection on an Agilent 7700 ICPMS according to the methods of Hintelmann et al.²⁶ In addition to blanks and duplicates, certified reference materials (MESS-3 for Hg_T ; ERM-CC580 for MeHg) were analyzed in 10% of samples.

Quality assurance and control results for aqueous and solid phase Hg_T and MeHg for each year can be found in Tables S2–S4 of the Supporting Information.

Mosquito Larvae Samples. For Hg_T analysis, mosquito larvae samples were microwave digested in concentrated HNO_3 and diluted prior to analysis by dual gold-trap amalgamation CVAFS, as described for porewaters. MeHg in mosquito larvae samples was heat extracted in a solution of 25% KOH in methanol, with a known mass spike of enriched Me¹⁹⁹Hg in each vessel. Samples were analyzed by ID-GC-ICPMS. In addition to blanks and duplicates, the certified reference material DORM-3 was analyzed in 10% of samples.

Numerical Analysis. Weighted means were calculated for annual porewater results because sampling dates were not evenly distributed throughout the season. Annual porewater values from each treatment were calculated by multiplying the mean result on each sampling day within a treatment by a weighting factor and then summing. The weighting factor was equal to the fraction of the season represented by a sample since the previous sampling date (e.g., the day -1 sample collected for a summer addition had a much larger weighting factor than a sample collected 2 days later on day +1). The season began on the first date on which peat soil temperatures at 10-cm depth were greater than 1 °C, and ended with the last sampling date each year. Bulk density of the peat did not change appreciably within the top 8 cm (one-way Anova, p =0.18), and so mean results for each peat core were calculated by multiplying concentrations for each interval by a weighting factor related to interval thickness (2 or 4 cm) and summing. Treatment means were then calculated from the weighted averages. Mosquito larvae results from each sample batch were averaged for each treatment.

The program R was used for all statistical analyses.²⁷ The distributions for both porewater and solid data were right-skewed, so each data set was natural-log-transformed prior to statistical analyses to obtain a normal distribution. A linear-least-squares model of the transformed data was fit on treatment and year factors. Residual plots of the transformed data

did not show any systematic bias. General linearized hypothesis tests were used to compare the estimated slopes for each treatment in each year and generate p-values. A p-value <0.05 was considered significant.

RESULTS AND DISCUSSION

MeHg Response to Sulfate Applications. The short and long-term processes whereby elevated sulfate deposition affected MeHg production within the S6 peatland were explored through intensive sampling of porewaters and periodic collections of peat cores, respectively (Figure 1). Although the MeHg pool in porewaters can be affected by factors other than methylation, such as changes in water chemistry, partitioning between the aqueous and solid phases, and the character and abundance of organic ligands,^{13,28,29} MeHg in porewater nevertheless represents the most dynamic and mobile MeHg pool and is thus important for considering downstream effects. The solid peat represented the major sink for MeHg and Hg_T—of the total mercury mass in the upper 8 cm of peat matrix, >99.7% of MeHg and >99.8% of Hg_T was bound to the peat.

Porewaters. An increase in porewater MeHg concentration in response to sulfate addition was clearly evident following spring sulfate application to the central-bog as illustrated here for the spring of 2006 and 2008 (Figure 2), the first and last year of

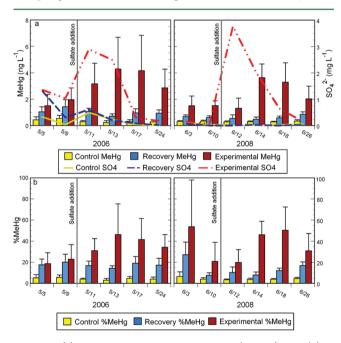


Figure 2. (a) Sulfate and MeHg concentrations (± 1 s.d.), and (b) % MeHg (the ratio of MeHg to Hg_T; ± 1 s.d.) in control, recovery, and experimental treatment porewaters of the S6 peatland over the period of spring sulfate addition in 2006 and 2008. The spring 2006 and 2008 addition periods were chosen because they illustrate patterns in the first and last year of recovery, respectively.

recovery, respectively. In each year porewater sulfate concentrations in the experimental treatment peaked one day following the additions ($2.9 \pm 2.1 \text{ mg L}^{-1}$ in 2006 and $3.8 \pm 2.2 \text{ mg L}^{-1}$ in 2008). As sulfate concentrations declined, the porewater MeHg pool increased dramatically (Figure 2a). MeHg concentrations peaked by the third day post-addition in each year ($4.3 \pm 2.1 \text{ ng L}^{-1}$ in 2006 and $3.6 \pm 1.0 \text{ ng L}^{-1}$ in 2008). MeHg as percentage of Hg_T (%MeHg) followed a very similar pattern, peaking at $46 \pm 29\%$ three days after the addition in 2006 and at $50 \pm 22\%$

seven days after the addition in 2008 (Figure 2b). In contrast, mean sulfate and MeHg concentrations and %MeHg in the control area were consistently low each spring (<0.5 mg L⁻¹, < 0.6 ng L⁻¹, and <7%, respectively). MeHg concentrations and %MeHg were significantly higher in the experimental treatment than in the control on each day shown in Figure 2 (p < 0.05). Peak MeHg concentrations and %MeHg in the experimental treatment, postaddition, were significantly higher than preaddition levels (p < 0.05). Annual, seasonally weighted, average porewater MeHg concentrations and %MeHg in the experimental treatment were 4–9× higher than corresponding levels in the control section (Figure 3).

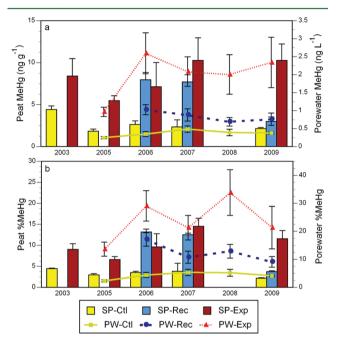


Figure 3. (a) MeHg concentrations and (b) %MeHg levels in the solid peat (SP; interval-weighted average values) and porewaters (PW; annual, seasonally weighted average values) in the control, recovery, and experimental sections of the S6 peatland 2003–2009. Error bars for peat are standard errors of weighted treatment means. Error bars on porewaters are standard deviations calculated from weighted annual means.

The order-of-magnitude increases in MeHg concentrations and %MeHg in porewaters of the experimental treatment following sulfate application are of similar magnitude and timing to the responses reported by Jeremiason et al.⁹ for the first year of this study and other mesocosm-scale studies in nutrientpoor, boreal peatlands.^{14,30} Our interpretation of these results is that the added sulfate stimulated SRB activity resulting in a net increase in Hg methylation. The steady buildup of a large pool of solid-phase MeHg in the peat matrix (see below) provides strong evidence for this de novo production of MeHg.

An alternative explanation for the observed increase in porewater MeHg is a change in partitioning of MeHg and Hg_T between the aqueous and solid phase resulting from an increase in the dissolved sulfide pool.²⁸ We modeled mercury speciation in response to increasing dissolved sulfide concentrations and found that the molar ratio of MeHg to Hg peaked at 0.3 μ M sulfide and subsequently decreased, which is similar to previously reported findings (model parameters shown in SI Table S6).²⁸ However, at low sulfide concentrations the model did not accurately predict MeHg and Hg concentrations in the dissolved phase possibly because of uncertainty in the log K value for the reaction between MeHg and thiol groups or because of kinetic limitations controlling adsorption/desorption of MeHg. Many studies have demonstrated the difficulty of accurately representing mercury speciation in the presence of high DOC.^{29,31–33} Although we can not rule out the possibility that sulfide-driven changes in solid-phase partitioning caused porewater MeHg to increase, the weakness of the simple equilibrium model and the fact that the total pool of MeHg in the experimental section increased progressively over time argues strongly that increased MeHg production, rather than sorption/desorption reactions, is responsible for the MeHg patterns seen following sulfate addition.

Peat. The solid-phase data integrate the responses to sulfate additions that were noted above for porewater MeHg concentrations and %MeHg in the experimental treatment (Figure 2). In the control section, MeHg concentrations and %MeHg remained consistently low in both peat and porewaters (Figure 3). Average MeHg concentrations and %MeHg in the peat of the experimental treatment were 4–9× greater than the corresponding values in the control section. There was no significant effect of treatment on Hg_T concentrations in peat, which ranged between 63 and 110 ng g⁻¹ across the peatland over the 5-year period.

The MeHg pool within a peatland represents a dynamic equilibrium between MeHg production, predominantly through biotic methylation, and removal processes, including biotic and abiotic demethylation, bioaccumulation, and advective transport.^{13,14,34} In sulfur-limited systems, such as the experimental peatland in this study, sulfate addition represents an important factor influencing MeHg production and contributes to higher MeHg concentrations in wetland porewaters and soils than would be expected based on atmospheric Hg inputs alone.^{12–14,35} The increases in %MeHg in peat and porewaters of the experimental treatment relative to those in the control indicate that experimentally increasing sulfate loads shifts that equilibrium toward greater MeHg production.

Recovery from Elevated Sulfate Deposition. Porewaters. The recovery treatment-a subsection of the experimental treatment to which sulfate application was halted-was created in the spring of 2006. Sulfate concentrations in recovery porewaters declined almost immediately thereafter, generally remaining low and following a temporal pattern similar to that of the control in each year (Figure 2a). In contrast to sulfate, MeHg concentrations and %MeHg in recovery treatment porewaters remained elevated well above control levels during the first year of recovery (p < 0.001). In 2007 annual, seasonally weighted %MeHg declined 37% from 2006 levels (p < 0.001), but then held steady between 2007 and 2009. MeHg concentrations fell more gradually over the recovery period, declining 32% between 2006 and 2008 (*p* < 0.001). Both MeHg concentrations and %MeHg in the recovery section remained elevated relative to control values through the end of the study (Figure 3). The continued difference in porewater MeHg between the control and recovery treatments likely reflects equilibrium with the peat rather than continued elevation of MeHg production.

Peat. MeHg concentrations and %MeHg in recovery treatment peat declined by 62% and 76%, respectively, between 2006 and 2009 (p < 0.005 and p < 0.02). Demethylation was a more important MeHg loss process than desorption coupled with advective transport out of the system. This conclusion follows from the observation that concentrations of MeHg in porewaters were too low to account for the mass of MeHg lost from the recovery-section peat. Jeremiason et al.⁹ found that

nearly 1800 μ g MeHg was exported from the S6 peatland in 2002. The mass of MeHg lost in the top 8 cm of the recovery treatment alone between 2006 and 2009 was approximately 120 mg, or more than 65× the amount exported in outflow in 2002 from the entire peatland.

Methylmercury concentrations in the peat of the recovery treatment did not show significant declines within the first two years after sulfate additions were halted. This could either imply that the kinetics of desorption of the newly accumulated MeHg from the peat was much slower than the decreases in methylation rates in porewaters, or that elevated MeHg production was sustained for a period of time by internal recycling of the previously added sulfate. Such recycling has been proposed by others^{13,14} and would also explain our observed short-term response to sulfate addition in which sulfate disappeared from experimental porewaters within three days of application, while porewater MeHg levels remained elevated two weeks later (Figure 2). Urban et al.¹⁰ investigated sulfur biogeochemistry in a small peatland 1 km from the S6 site and determined that annual recycling of sulfur was equivalent to annual external sulfur inputs. Blodau et al.³⁶ found evidence that an anaerobic sulfur cycle sustained SRB activity under reducing conditions in an ombrotrophic peatland, providing an explanation for the high sulfur recycling rates observed by Urban et al.¹⁰ Thus one possible mechanism for recovery following the cessation of sulfate addition to the S6 peatland is that sulfur compounds within the peat become more recalcitrant over time. That is, as the pool of added sulfur is repeatedly turned over, labile sulfur compounds are preferentially consumed and progressively converted into refractory organic forms, which are much more slowly cycled by anaerobic and aerobic processes. In line with this hypothesis, differential sulfate release was observed among treatments in the S6 peatland following drying events, which can expose reduced sulfur moieties to oxygen (SI Table S5). The highest sulfate release into porewaters occurred in the experimental treatment, and the lowest release was observed in the control section. Because there was no significant difference among treatments in size of the total sulfur pool in the peat, these results suggest that the newly added sulfate was more susceptible to release/recycling than the pre-existing pool of ambient sulfur.

Interannual Variability. Despite the significant trends in peat MeHg concentrations and %MeHg (increases in the experimental treatment and decreases in the recovery treatment), there is some unexplained variability in the data-for example, the decrease in peat %MeHg between 2003 and 2005 and the fluctuating porewater values in the experimental treatment (Figure 3). These variations are likely the result of year-to-year differences in precipitation and hydrology, such as the series of summer droughts that persisted at the MEF from 2005 to 2007. Hydrologic variability can affect mercury cycling in peatlands by altering peat accumulation and decomposition, redox con-ditions, and methylation potentials.³⁷⁻⁴⁰ Such effects are most clearly evident in the S6 control treatment where interannual fluctuations in both porewater and peat MeHg cannot be the result of sulfate manipulation. In the experimental and recovery treatments the effects of these large-scale physical processes are superimposed on trends due to sulfate addition alone. For example, the 2007-2009 decline of MeHg in the recovery section can be explained, at least in part, by the cessation of sulfate amendments, but this should not be the case for the experimental treatment where sulfate additions continued. Thus it appears that some of the interannual variability in MeHg

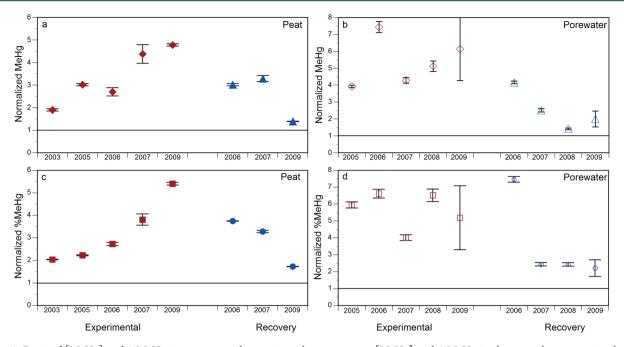


Figure 4. Ratio of [MeHg] and %MeHg in recovery and experimental treatments to [MeHg] and %MeHg in the control treatment in the peat (a and c) 2003–2009 and porewaters (b and d) 2005–2009 ([MeHg] experimental peat (\blacklozenge), [MeHg] experimental porewater (\diamondsuit), %MeHg experimental porewater (\square), %MeHg is recovery peat (\blacklozenge), %MeHg recovery peat (\blacklozenge), %MeHg recovery peat (\circlearrowright), %MeHg recovery peat (\bigcirc), %MeHg recovery peat (\bigcirc). Peat error propagated from standard errors of mean [MeHg] and %MeHg in control and respective treatment (experimental or recovery). Porewater error propagated from standard deviations for control and respective treatment. The horizontal line at *y* = 1 in each figure represents a ratio of 1:1 or a return to control levels in the treatments.

concentrations and %MeHg in each treatment (Figure 3) was the result of overriding climatic and/or hydrologic effects.

To remove the influence of natural hydrologic variability from the longer-term effects of experimental sulfate addition, we normalized MeHg concentrations and %MeHg in the experimental and recovery treatments to corresponding values in the control treatment for porewaters and peat in each year (Figure 4). Normalized MeHg concentrations and %MeHg in the experimental peat increased cumulatively with time such that by 2009 these values in the experimental treatment were 5-6× higher than those of the control (p < 0.005). In the recovery treatment the opposite trend occurred, and by 2009 normalized MeHg concentrations and %MeHg approached a value of 1, indicating a near-return to control levels. However, the trend was not significant (p = 0.28) owing to small sample sizes (n = 4) from each treatment. Normalized MeHg concentrations in the porewaters of the experimental treatment did not show any discernible trend with time, presumably because most newly produced MeHg accumulated in the peat. The large loss of MeHg from the recovery-section following the discontinuation of sulfate addition indicates that reductions in sulfate deposition could produce a relatively rapid decline in MeHg export to connected lakes and streams.

Biotic Response. In the spring of 2009 mosquito larvae (*Culex* spp.) were collected in the S6 peatland to compare mercury concentrations in biota among treatments, as mosquitoes are sensitive indicators of mercury loading to, and MeHg production within, aquatic systems.⁴¹ Dry-weight, Hg_T concentrations in *Culex* spp. larvae mimicked %MeHg trends in peat samples, with experimental-treatment larvae having significantly elevated mercury concentrations relative to those found in the control and recovery sections (p < 0.05; Figure 5). Significant differences in mosquito-larvae Hg_T also persisted between the control and recovery sections (p < 0.05). Although sample masses were

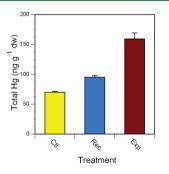


Figure 5. Dry-weight, Hg_T concentrations (±1 s.d.) in mosquito larvae (*Culex* spp.) in control (Ctl), recovery (Rec), and experimental (Exp) treatments in spring 2009.

insufficient to allow MeHg analysis of all mosquito larvae samples, for the six samples measured for both Hg_T and MeHg in this study, MeHg comprised $62 \pm 19\%$ of Hg_T in mosquito larvae, and Hg_T explained 75% of the variability in MeHg concentrations (SI Figure S2).

These biotic results provide direct evidence that increasing/ decreasing sulfate loading to peatlands translates into significant increases/declines in biotic mercury concentrations. Whereas MeHg in experimental-treatment peat was >4.5× that in the control by 2009, Hg_T in mosquito larvae from the experimental treatment in the same year was just over 2× the levels found in the control. Apparently some of the MeHg produced as a result of sulfate-stimulation became less bioavailable with time. This finding agrees with other studies which have found that recently produced MeHg is more available to biota than older MeHg.^{42,43}

Because detritivorous mosquito larvae spend a short time in their aquatic habitat, they present a snapshot of mercury bioaccumulation in the season during which they hatch. Mercury bioaccumulation within sulfate-impacted peatlands may be even

greater for invertebrates with long aquatic larval stages and those higher in the food chain, such that recovery from sulfate deposition may take longer than for mosquito larvae. Although the S6 wetland does not itself support fish, its outflow contributes to the MeHg load of downstream lakes that have susceptible fish populations. Moreover, direct transfer of MeHg to terrestrial foodwebs through the emergence and predation of aquatic insects has been identified as an important trophic pathway that may contribute to lowered reproductive success for insectivorous birds that exploit riparian and wetland habitats.^{44,45}

Broader Impacts. Our long-term sulfate-loading experiment created an opportunity to observe the in situ processes whereby sulfate deposition enhanced MeHg production within a peatland, MeHg declined once sulfate additions were discontinued, and mercury levels in biota mirrored changes in sulfate inputs. Increasing sulfate deposition by $4 \times$ led to a MeHg increase of similar magnitude in both porewaters and peat. These changes in MeHg production occurred despite flat trends in Hg deposition over the study period.⁴⁶ The steady accumulation of MeHg in the peat over time, relative to the control, suggests sustained disequilibrium between methylation and demethylation over the course of the experiment. At what point equilibrium between MeHg production and removal processes would be achieved at these elevated levels of sulfate deposition is an open question. The finding that most of the MeHg lost from the recovery treatment was likely due to in situ demethylation rather than export from the system implies that the majority of the MeHg produced in response to elevated sulfate deposition may not be transported to downstream aquatic systems. This is supported by the finding that peat and porewater MeHg increased by $\sim 4\times$ in response to a $4\times$ increase in sulfate deposition but MeHg flux from the wetland in the first year of this study only increased by 2×.9

The proportional, synchronous decreases in mosquito-larvae mercury with cessation of sulfate addition indicate that declines in sulfate deposition can directly reduce MeHg in biota. Wetland recovery from elevated, anthropogenic sulfate deposition may explain some of the downward trends seen in fish and wildlife mercury across North America and Europe in the late 20th century as regulations on sulfur emissions took effect.^{19,47–49} It is important to note that atmospheric mercury deposition declined concurrently with the reductions in sulfate deposition in many areas⁵⁰ and may also be responsible for declining mercury concentrations in biota.

In this study MeHg responses to climatic variability were superimposed on the trends caused by sulfate addition alone. The fluctuations in peat MeHg seen in the control section, and the declines in MeHg concentrations in the experimental treatment over the periods 2003–2005 and 2007–2009, demonstrate that physical processes can also alter the balance between methylation and demethylation from year to year. Climatic events such as severe droughts, which lead to oxidation of reduced sulfur species and sulfate formation, may slow or reverse declining MeHg levels in wetlands. The influence of drought on sulfate release from wetlands and sulfate export from watersheds are well documented.^{5,51–54} Altered sulfur cycling consequent to climatic shifts may thus explain some of the recently reported reversals in downward fish mercury trends noted above.^{49,55}

Sulfate deposition to ecosystems downwind of industrial centers increased by more than an order of magnitude over natural background rates by the mid-20th century.²¹ It is reasonable to infer that such large increases in sulfate loading

caused comparably large increases in MeHg production in sulfur-limited peatlands—increases above and beyond those arising from the $3-4\times$ rise in mercury deposition during that same time period.^{56,57} Subsequent regulations of sulfur emissions, such as the 1970 Clean Air Act and its 1990 amendments in the United States, led to substantial reductions in sulfate deposition across regions once affected by very high levels of atmospheric loading.⁵ As of 2009 sulfate deposition across eastern North America remained well above background levels²¹ highlighting the potential benefits to additional reductions. Our finding that peatland MeHg responds rapidly to reductions in sulfate inputs implies an opportunity to mitigate mercury contamination through policies aimed at further reducing sulfur emissions and deposition.

ASSOCIATED CONTENT

Supporting Information

Information regarding peat sample collection, quality control data for aqueous and solid total- and methyl-mercury analyses, average sulfate concentrations in porewaters during a water table rise in 2007, annual sulfate deposition rates at the Marcell Experimental Forest, the correlation between Hg_T and MeHg concentrations in invertebrates samples, and equilibrium model parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Likens, G. E.; Bormann, F. H. Acid rain: A serious regional environmental problem. *Science* **1974**, *184* (4142), 1176–1179.

⁽²⁾ Rodhe, H. Acidification in a global perspective. Ambio 1989, 18 (3), 155-160.

⁽³⁾ Driscoll, C. T.; Lawrence, G. B.; Bulger, A. J.; Butler, T. J.; Cronan, C. S.; Egar, C.; Lambert, K. F.; Likens, G. E.; Stoddard, J. L.; Weathers, K. C. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. *Bioscience* **2001**, *51* (3), 180–198.

(4) Schopp, W.; Posch, M.; Mylona, S.; Johansson, M. Long-term development of acid deposition (1880–2030) in sensitive freshwater regions in Europe. *Hydrol. Earth Syst. Sci.* **2003**, 7 (4), 436–446.

(5) Mitchell, M. J.; Likens, G. E. Watershed sulfur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. *Environ. Sci. Technol.* **2011**, *45*, 5267–5271.

(6) Stoddard, J. L.; Jeffries, D. S.; Lukewille, A.; Clair, T. A.; Dillon, P. J.; Driscoll, C. T.; Forsius, M.; Johannessen, M.; Kahl, J. S.; Kellogg, J. H.; Kemp, A.; Mannio, J.; Montieth, D. T.; Murdoch, P. S.; Patrick, S.; Rebsdorf, A.; Skjelkvale, B. L.; Stainton, M. P.; Traaen, T.; van Dam, H. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* **1999**, *401* (6753), 575–578.

(7) Dillon, P. J.; Somers, K. M.; Findeis, J.; Eimers, M. C. Coherent response of lakes in Ontario, Canada to reductions in sulphur deposition: The effects of climate on sulphate concentration. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 583–595.

(8) Keller, W.; Heneberry, J. H.; Dixit, S. S. Decreased acid deposition and the chemical recovery of Killarney, Ontario, Lakes. *Ambio* **2003**, *32* (3), 183–189.

(9) Jeremiason, J. D.; Engstrom, D. R.; Swain, E. B.; Nater, E. A.; Johnson, B. M.; Almendinger, J. E.; Monson, B. A.; Kolka, R. K. Sulfate addition increases methylmercury production in an experimental wetland. *Environ. Sci. Technol.* **2006**, *40*, 3800–3806.

(10) Urban, N. R.; Eisenreich, S. J.; Grigal, D. F. Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota. *Biogeochemistry* **1989**, 7, 81–109.

(11) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Bloom, N. S.; Flett, R. J. Importance of Wetlands as Sources of Methyl Mercury to Boreal Forest Ecosystems. *Can. J. Fish. Aquat. Sci.* **1994**, *51* (5), 1065–1076.

(12) Gilmour, C. C.; Henry, E. A.; Mitchell, R. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* **1992**, *26*, 2281–2287.

(13) Gilmour, C. C.; Riedel, G. S.; Ederington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. A.; Stordal, M. C. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* **1998**, *40*, 327–345.

(14) Branfireun, B. A.; Roulet, N. T.; Kelly, C. A.; Rudd, J. W. M. In situ sulphate stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain and methylmercury contamination in remote environments. *Global Biogeochem. Cycles* **1999**, *13* (3), 743–750.

(15) Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **1999**, 33, 951–957.

(16) Branfireun, B. A.; Bishop, K.; Roulet, N. T.; Granberg, G.; Nilsson, M. Mercury cycling in boreal ecosystems: The long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophys. Res. Lett.* **2001**, *28* (7), 1227–1230.

(17) Mitchell, C. P. J.; Branfireun, B. A.; Kolka, R. K. Spatial characteristics of net methylmercury production hot spots in peatlands. *Environ. Sci. Technol.* **2008**, *42*, 1010–1016.

(18) Hrabik, T. R.; Watras, C. J. Recent declines in mercury concentration in a freshwater fishery: Isolating the effects of deacidification and decreased atmospheric mercury deposition in Little Rock Lake. *Sci. Total Environ.* **2002**, *297*, 229–237.

(19) Drevnick, P. E.; Canfield, D. E.; Gorski, P. R.; Shinneman, A. L. C.; Engstrom, D. R.; Muir, D. C. G.; Smith, G. R.; Garrison, P. J.; Cleckner, L. B.; Hurely, J. P.; Noble, R. B.; Otter, R. R.; Oris, J. T. Deposition and cycling of sulfur controls mercury accumulation in Isle Royale fish. *Environ. Sci. Technol.* **2007**, *41* (21), 7266–7272.

(20) Kolka, R. K.; Mitchell, C. P. J.; Jeremiason, J. D.; Hines, N. A.; Grigal, D. F.; Engstrom, D. R.; Coleman-Wasik, J. K.; Nater, E. A.; Swain, E. B.; Monson, B. A.; Fleck, J. A.; Johnson, B.; Almendinger, J. E.; Branfireun, B. A.; Brezonik, P. L.; Cotner, J. B. Mercury cycling in peatland watersheds. In *Peatland Biogeochemistry and Watershed Hydrology at the Marcell Experimental Forest*; Kolka, R. K., Sebestyen, S. D., Verry, E. S., Brooks, K. N., Eds.; CRC Press: Boca Raton, FL, 2011; pp 349-370.

(21) National Atmospheric Deposition Program (NRSP-3). NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820; 2011; http://nadp.sws.uiuc.edu/.

(22) Bloom, N. S.; Fitzgerald, W. F. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapour atomic fluorescence detection. *Anal. Chim. Acta* **1988**, *208*, 151–161.

(23) U.S.EPA. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry; Office of Water: Washington, DC, 2002.

(24) Bloom, N. S. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* **1989**, *46* (7), 1131–1140.

(25) Liang, L.; Horvat, M.; Bloom, N. S. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. *Talanta* **1994**, *41* (3), 371–379.

(26) Hintelmann, H.; Evans, R. D.; Villeneuve, J. Y. Measurement of mercury methylation in sediments by using enriched stable mercury isotopes combined with methylmercury determination by gas chromatography-inductively coupled plasma mass spectrometry. *J. Anal. Atom. Spectrom.* **1995**, *10* (9), 619–624.

(27) R-Development-Core-Team R: A Language and Environment for Statistical Computing. http://www.R-project.org.

(28) Skyllberg, U. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. J. Geophys. Res. 2008, 113, G00C03.

(29) Miller, C. L.; Mason, R. P.; Gilmour, C. C.; Heyes, A. Influence of dissolved organic matter on the complexation of mercury under sulfidic conditions. *Environ. Toxicol. Chem.* **2007**, *26* (4), 624–633.

(30) Mitchell, C. P. J.; Branfireun, B. A.; Kolka, R. K. Assessing sulfate and carbon controls on net methylmercury production in peatlands: An in situ mesocosm approach. *Appl. Geochem.* **2008**, 23 (3), 503–518.

(31) Drexel, R. T.; Haitzer, M.; Ryan, J. N.; Aiken, G. R.; Nagy, K. L. Mercury (II) sorption to two Florida Everglades peats: Evidence for strong and weak binding and competition by dissolved organic matter released from the peat. *Environ. Sci. Technol.* **2002**, *36* (19), 4058–4064.

(32) Hsu, H.; Sedlak, D. L. Strong Hg(II) Complexation in Municipal Wastewater Effluent and Surface Waters. *Environ. Sci. Technol.* **2003**, 37 (12), 2743–2749.

(33) Ravichandran, M. Interactions between mercury and dissolved organic matter--a review. *Chemosphere* **2004**, *55*, 319–331.

(34) Gilmour, C. C.; Henry, E. A. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* **1991**, *71*, 131–169.

(35) Benoit, J. M.; Gilmour, C. C.; Heyes, A.; Mason, R. P.; Miller, C. L. Geochemical and Biological Controls over Methylmercury Production and Degradation in Aquatic Ecosystems. In *Biogeochemistry* of Environmentally Important Trace Elements; American Chemical Society: Washington, DC, 2002; Vol. 835, pp 262–297.

(36) Blodau, C.; Mayer, B.; Peiffer, S.; Moore, T. R., Support for an anaerobic sulfur cycle in two Canadian peatland soils. *J. Geophys. Res.* **2007**, *112*, G02004, doi:10.1029/2006JG000364.

(37) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Bodaly, R. A.; Paterson, M. J.; Beaty, K. G.; Hesslein, R. H.; Heyes, A.; Majewski, A. R. The rise and fall of mercury methylation in an experimental reservoir. *Environ. Sci. Technol.* **2004**, *38* (5), 1348–1358.

(38) Brigham, M. E.; Krabbenhoft, D. P.; Olson, M. L.; DeWild, J. F. Methylmercury in flood-control impoundments and natural waters of northwestern minnesota, 1997–99. *Water, Air, Soil Pollut.* **2002**, 138 (1), 61–78.

(39) Hall, B. D.; St. Louis, V. L.; Rolfhus, K. R.; Bodaly, R. A.; Beaty, K. G.; Paterson, M. J.; Cherewyk, K. A. P. Impacts of reservoir creation

on the biogeochemical cycling of methyl and total mercury in boreal upland forests. *Ecosystems* **2005**, *8* (3), 248–266.

(40) Balogh, S. J.; Swain, E. B.; Nollet, Y. H. Elevated methylmercury concentrations and loadings during flooding in Minnesota rivers. *Sci. Total Environ.* **2006**, *368*, 138–148.

(41) Hammerschmidt, C. R.; Fitzgerald, W. F. Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. *Environ. Sci. Technol.* **2005**, *39*, 3034–3039.

(42) Orihel, D. M.; Paterson, M. J.; Blanchfield, P. J.; Bodaly, R. A.; Gilmour, C. C.; Hintelmann, H. Temporal changes in the distribution, methylation, and bioaccumulation of newly deposited mercury in an aquatic ecosystem. *Environ. Pollut.* **2008**, *154* (1), 77–88.

(43) Harris, R. C.; Rudd, J. W. M.; Amyot, M.; Babiarz, C. L.; Beaty, K. G.; Blanchfield, P. J.; Bodaly, R. A.; Branfireun, B. A.; Gilmour, C. C.; Graydon, J. A. Whole-ecosystem study shows rapid fish-mercury reponse to changes in deposition. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 16586–16591.

(44) Custer, C.; Custer, T.; Hill, E. Mercury exposure and effects on cavity-nesting birds from the carson river, nevada. *Arch. Environ. Contam. Toxicol.* **2007**, *52* (1), 129–136.

(45) Cristol, D. A.; Brasso, R. L.; Condon, A. M.; Fovargue, R. E.; Friedman, S. L.; Hallinger, K. K.; Monroe, A. P.; White, A. E. The movement of aquatic mercury through terrestrial food webs. *Science* **2008**, *320* (5874), 335.

(46) Risch, M. R.; Gay, D. A.; Fowler, K. K.; Keeler, G. J.; Backus, S. M.; Blanchard, P.; Barres, J. A.; Dvonch, J. T. Spatial patterns and temporal trends in mercury concentrations, precipitation depths, and wet deposition in the North American Great Lakes region, 2002–2008. *Environ. Pollut.* **2012**, *161* (0), 261–271.

(47) Monson, B. A.; Staples, D.; Bhavsar, S.; Holsen, T.; Schrank, C.; Moses, S.; McGoldrick, D.; Backus, S.; Williams, K. Spatiotemporal trends of mercury in walleye and largemouth bass from the Laurentian Great Lakes Region. *Ecotoxicology* **2011**, *20* (7), 1555–1567.

(48) Chalmers, A. T.; Argue, D. M.; Gay, D. A.; Brigham, M. E.; Schmitt, C. J.; Lorenz, D. L. Mercury trends in fish from rivers and lakes in the United States, 1969–2005. *Environ. Monit. Assess.* **2011**, *175*, 175–191.

(49) Evers, D.; Wiener, J.; Basu, N.; Bodaly, R.; Morrison, H.; Williams, K. Mercury in the Great Lakes region: bioaccumulation, spatiotemporal patterns, ecological risks, and policy. *Ecotoxicology* **2011**, *20* (7), 1487–1499.

(50) Driscoll, C. T.; Han, Y. J.; Chen, C. Y.; Evers, D. C.; Lambert, K. F.; Holsen, T. M.; Kamman, N. C.; Munson, R. K. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *Bioscience* **2007**, *57* (1), 17–28.

(51) Bayley, S. E.; Behr, R. S.; Kelly, C. A. Retention and release of S from a freshwater wetland. *Water, Air, Soil Pollut.* **1986**, 31, 101–114.

(52) Devito, K. J.; Hill, A. R. Sulphate mobilization and pore water chemistry in relation to groundwater hydrology and summer drought in two conifer swamps on the Canadian Shield. *Water, Air, Soil Pollut.* **1999**, *113*, 97–114.

(53) Warren, F. J.; Waddington, J. M.; Bourbonniere, R. A.; Day, S. M. Effect of drought on hydrology and sulphate dynamics in a temperate swamp. *Hydrol. Process.* **2001**, *15*, 3133–3150.

(54) Eimers, M. C.; Watmough, S. A.; Buttle, J. M.; Dillon, P. J. Drought-induced sulphate release from a wetland in south-central Ontario. *Environ. Monit. Assess.* **2007**, *127*, 399–407.

(55) Monson, B. A. Trend reversal of mercury concentrations in piscivorous fish from minnesota lakes: 1982–2006. *Environ. Sci. Technol.* 2009, 43 (6), 1750–1755.

(56) Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36* (1), 19–32.

(57) Munthe, J.; Bodaly, R. A.; Branfireun, B. A.; Driscoll, C. T.; Gilmour, C. C.; Harris, R.; Horvat, M.; Lucotte, M.; Malm, O. Recovery of mercury-contaminated fisheries. *Ambio* 2007, 36 (1), 33–44.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 9

(Fond du Lac Band, Notification of Objection to the NorthMet Mine Project Section 404 permit and Clean Water Act Section 401(a)(2) "Will Affect" Analysis for PolyMet Mining, Inc.'s NorthMet Mine Project, August 3, 2021)

Fond du Lac Band of Lake Superior Chippewa **Reservation Business Committee** 1720 Big Lake Rd.

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Chairman Kevin R. Dupuis, Sr.

Secretary/Treasurer Ferdinand Martineau, Jr.

Dist. I Representative Wally J. Dupuis

Dist. II Representative **Bruce M. Savage**

Dist. III Representative Roger M. Smith, Sr.

Executive Director, **Tribal Programs** Miyah M. Danielson

Executive Director, **Tribal Enterprises Terry Savage**

August 3, 2021

Michael S. Regan Administrator U.S. Environmental Protection Agency 1200 Pennsylvania Ave., N.W. Washington, D.C. 20460 Regan.Michael@epa.gov

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Chad Konickson **Regulatory Branch Chief** St. Paul District U.S. Army Corps of Engineers 180 5th St. E., Suite 700 St. Paul, MN 55101 chad.konickson@usace.army.mil

Re: Notification of Objection to NorthMet Mine Project, U.S. Army Corps Proposed Permit MVP-1999-05528-TJH

Dear Administrator Regan, Acting Regional Administrator Newton, District Engineer Col. Jansen, and Mr. Konickson:

The Fond du Lac Band of Lake Superior Chippewa ("Band") received notice from the U.S. Environmental Protection Agency ("EPA") on June 4, 2021 that discharges associated with a proposed U.S. Army Corps of Engineers' Clean Water Act ("CWA") Section 404 permit No. MVP-1999-05528-TJH ("404 Permit") for PolyMet Mining, Inc.'s NorthMet Mine Project may affect the quality of the Band's Letter and Analysis from Fond du Lac Band of Lake Superior Chippewa Re: Will Affect Notification and Objection to Section 404 Permit August 3, 2021 Page 2

waters. Pursuant to CWA Section 401(a)(2), 33 U.S.C. § 1341(a)(2), the Band has determined the discharges related to the proposed NorthMet Mine Project ("Project") will affect the quality of the Band's waters so as to violate the Band's water quality requirements.

This matter is on remand from the U.S. District Court for the District of Minnesota in *Fond du Lac Band of Lake Superior Chippewa v. Kurt Thiede, et al.*, Case No. 0:19-cv-02489-PJS-LIB (D. Minn.). The remand concerns the Band's claims that EPA and the Corps failed to comply with CWA Section 401(a)(2) regarding the Project.

In accordance with CWA Section 401(a)(2), the Band has reviewed water quality effects related to discharges from the Project. I am enclosing the Band's analysis, which sets forth the Band's determination that the Project will affect the quality of the Band's waters. The Band's analysis identifies the specific receiving waters and water quality requirements that will be affected. In addition, the Project will impact the Band's treaty resources and create environmental justice issues that your agencies must give appropriate consideration. Accordingly, the Band hereby notifies you of its objection to the proposed 404 Permit and requests a public hearing on the objection pursuant to CWA Section 401(a)(2).

The Corps' regulations require the public hearing be held within the Fond du Lac Reservation, 33 C.F.R. § 325.2(b)(1)(i). The Black Bear Casino in Carlton, MN would be a suitable location for the public hearing. We look forward to coordinating with you to finalize the necessary details for the hearing.

Miigwech.

Sincerely,

Kevin R. Dupuis, Sr. Chairman

cc: Jaime A. Pinkham: Jaime.a.pinkham.civ@mail.mil Tera Fong: Fong.Tera@epa.gov Melanie Burdick: Burdick.Melanie@epa.gov

Enclosures

August 3, 2021

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS FOR POLYMET MINING, INC.'S NORTHMET MINE PROJECT

Developed by:

Fond du Lac Environmental Program

Dr. Brian Branfireun

Matthew Schweisberg, SPWS

Dr. Elsie Sunderland

Great Lakes Indian Fish and Wildlife Commission

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **2** OF **39**

I. INTRODUCTION

On June 4, 2021, the U.S. Environmental Protection Agency ("EPA") notified the Fond du Lac Band of Lake Superior Chippewa ("Band") pursuant to Clean Water Act ("CWA") Section 401(a)(2), 33 U.S.C. § 1341(a)(2), that discharges associated with PolyMet Mining, Inc.'s NorthMet Mine Project ("Project") may affect the Band's water quality.¹ Accordingly, the Band reviewed water quality effects related to discharges that may result from the Project in order to evaluate whether the discharges "will affect the quality of [the Band's] waters so as to violate any water quality requirements" in the Fond du Lac Reservation.² This review included reviewing information related to the Project, including but not limited to, the Final Environmental Impact Statement ("FEIS"), related PolyMet Permits and 401 Certification, and several maps and images of the watersheds for the Embarrass, Partridge, and St. Louis Rivers that show the numerous small streams and creeks that provide surface hydrologic connections from the Mine site, the Plant site, and Hydrometallurgical Tailings Facility to the aforementioned Rivers.

The Band was assisted in its review by subject matter experts Dr. Brian Branfireun, Senior Professional Wetland Scientist ("SPWS") Matthew Schweisberg, Dr. Elsie Sunderland, and the Great Lakes Indian Fish and Wildlife Commission ("GLIFWC") through John Coleman and Esteban Chiriboga. The credentials for these experts are located in Attachment 2, Exs. 30 at 7-21; Attachment 2, Ex. 31 at 7-12; and Attachment 3. Together, the Band and the subject matter experts developed this analysis.

This analysis incorporates by reference in its entirety the Band's April 30, 2021 submission, including expert work from Dr. Brian Branfireun and SPWS Matthew Schweisberg, to the U.S. EPA regarding the Band's determination that the Project may affect the Fond du Lac Reservation's wetland and other water resources due to non-compliance with the Band's water quality standards.³ This analysis also relies on substantive content from prior expert opinions that Dr. Branfireun provided on the Project⁴ in addition to other scientific literature that relates to:

- fate and transport of mercury and sulfate, and generation of mercury, methylmercury and sulfide in peat wetlands and associated streams and rivers;
- the fish and wildlife resources of the St. Louis River and the Fond du Lac Reservation; and

¹ Attachment 1 (EPA "May Affect" Notification and Analysis).

² 33 U.S.C. § 1341(a)(2).

³ A full copy of the Band's April 30, 2021 Submission to the U.S. EPA ("April 30 Submission") is also being provided to the U.S. Army Corps of Engineers as part of this analysis. *See* Attachment 2. Attachment 2 has thirty-two separate exhibits. Dr. Branfireun's expert memorandum developed for the Band is Ex. 30 and Mr. Schweisberg's expert memorandum is Ex. 31.

⁴ Those prior expert memoranda can be found in Attachment 2, at Exs. 24, 25 and 27.

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **3** OF **39**

• the fate and transport of (methyl)mercury, sulfate and dissolved organic matter.

As part of this analysis, GLIFWC provided maps to the Band showing four zones of estimated drawdown of groundwater around the Mine site resulting from dewatering activities during construction and operation. Those maps are discussed and included below. GLIFWC also provided maps showing the areas of extend and wetland types adjacent to the Mine tailings pond, in the riparian zones, and in the 100-year floodplain of the Embarrass, Partridge and St. Louis Rivers. Those maps were reviewed as part of this analysis.

Based on this analysis, the Band has determined the Project's discharges will affect the Band's water quality so as to violate water quality requirements within the Fond du Lac Reservation. The Section 404 Permit issued by the U.S. Corps of Engineers should be revoked and not be issued because those violations of the Band's water quality requirements violate Section 401(a)(2) of the CWA and Section 230.10(b) of the CWA regulations (aka the "404(b)(1) Guidelines") governing issuance of Section 404 permits (40 C.F.R. Part 230).⁵ Moreover, there are not adequate protective permit conditions nor corrective actions that can be imposed based on the Project as designed to prevent these violations. A summary of the main conclusions reached as part of this determination is set forth in the next section.

II. SUMMARY CONCLUSIONS

- Based on a conservative estimate the Project will fill and alter nearly 7,000 acres of diverse wetlands. This acreage figure does not include indirect impacts downstream of the Mine, e.g., riparian wetlands along the St. Louis River, especially along the Fond du Lac Reservation.
- The Project will result in the discharge of millions of gallons of water containing inorganic mercury, sulfate, and dissolved organic matter to tributaries of the Embarrass and Partridge Rivers that already contain elevated levels of methylmercury and will lead to additional formation and accumulation of this potent neurotoxicant in the ecosystem. The Embarrass and Partridge Rivers are direct tributaries of the St. Louis River, which forms the northern and eastern boundaries of the Fond du Lac Reservation.
- The discharges from the Project will result in:
 - direct and seepage discharges of sulfate and inorganic mercury to extensive headwater wetlands of the Embarrass River Watershed; and,
 - seven direct wastewater outfalls to the headwater wetlands of Trimble Creek, increasing water loading by several million gallons per day that will supply hundreds of pounds of sulfate per year (based on PolyMet's own data).

⁵ Moreover, the adverse impacts to aquatic resources described herein will cause or contribute to significant degradation of Waters of the U.S., a violation of Section 230.10(c) of the 404(b)(1) Guidelines that underscores why the Section 404 Permit should be revoked and not issued.

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **4** OF **39**

- There are extensive riparian (floodplain) wetlands along the Embarrass, Partridge and St. Louis River that contain organic-rich soils, i.e., mucks and peats. Fluctuating water levels in these riparian muck and peat wetlands will create ideal conditions (i.e., oxidation and reduction) for enhancing the methylation of mercury, thereby facilitating the accumulation of this bioavailable species of mercury in the food-web.
- As there is a direct surface water connection between the Project and the riparian wetlands along and within the Fond du Lac Reservation, it is expected that the contaminated discharges from the Project will be transported to these riparian wetlands.
- In addition, it is expected that late fall, winter, and spring flooding on the St. Louis River will back up waters into at least the three major streams on the Fond du Lac Reservation—Fond du Lac Creek, Stoney Brook, and Simian Creek—and the wetlands adjacent to those streams. As such, the contaminated discharges from the Project will reach and contaminate at least these three streams and their adjacent wetlands within the Fond du Lac Reservation.
- Fish and wildlife resources that use the St. Louis River, its riparian wetlands, the three streams, and their adjacent wetlands will be exposed to elevated levels of methylmercury, the mercury form that biomagnifies by a million-fold or more in predatory species. Biomagnification occurs when plant and animal foods containing methylmercury are consumed by higher trophic level species, resulting in the highest levels of exposure in predatory organisms including wildlife such as piscivorous birds and humans that catch and consume fish. Thus, methylmercury exposure is a concern for wetland dependent wildlife from the St. Louis River, the three principal streams, and their adjacent wetlands. Among other species, the Band's restoration efforts for lake sturgeon will likely be compromised.
- Project discharges will affect biogeochemical functions of these wetlands, which in turn will substantially affect their ecological functions. The discharges (in addition to any seepage that is not contained by the proposed and wholly unproven seepage capture system) will result in an increase in methylmercury production at a location in the watershed that will result in significant environmental harm—headwater wetlands that provide water and solutes to downstream reaches, especially the St. Louis River and its riparian wetlands.
- The weight of the scientific evidence indicates that the Project will affect water column and fish methylmercury concentrations in surface waters downstream of the Project, including the St. Louis River.
- The Project will affect methylmercury concentrations in downstream waters in two ways that are directly linked to Mine operations:
 - The direct effect of loading water, sulfate and (inorganic) mercury to headwater wetlands and surface waters will increase net methylmercury production resulting in a measurable contribution to the cumulative loading of methylmercury to the St. Louis

River. Increasing methylmercury concentrations are expected to result in increases in exposure of fish and wildlife, as well as Band member consumers, and is neither accounted for in existing mass balances, nor is there an adequate monitoring plans to detect harm.

- Changes in regional wetland hydrology in the area of groundwater impact in the vicinity of the Project will have indirect effects that will enhance mercury, sulfate and methylmercury release in an area that data clearly indicate is already naturally susceptible to enhanced methylmercury production.
- Project-related changes in hydrology and the release of excess sulfate which stimulates the process of mercury methylation will enhance production of methylmercury both adjacent to the Project as well as more distal locations in the St. Louis River watershed and contribute to the load of methylmercury in surface waters. This methylmercury will bioaccumulate in biota, increasing exposures of fish-consuming wildlife and humans.
- The consumption of methylmercury contaminated foods by fish and wildlife and by Band members will impair the Band's Designated Uses for the St. Louis River and the three principal streams on the Fond du Lac Reservation as well as wetlands adjacent to those areas.
- The degradation of Fond du Lac Reservation waters and wetlands will result in non-compliance with the Band's Designated Uses and Antidegradation Water Quality Standards.
- Though somewhat speculative at this time, based on the economics of the Project,⁶ there is a clear potential for PolyMet to have a need to expand the Project to recover a greater proportion of ore to ensure that the Project is economically feasible. If an expansion occurs, the adverse impacts described herein will increase substantially.

III. ANALYSIS

A. Background.

<u>1.</u> <u>The Band's Water Quality Program.</u>

Since May 1996, the Band has had treatment as State ("TAS") authority pursuant to the CWA.⁷ EPA has approved the Band's water quality standards ("WQS"), which apply to all waters of the Fond du Lac Reservation.⁸ The Band's WQS consist of designated uses, narrative and numeric criteria to protect those uses, and anti-degradation provisions. Among other things, the

⁶ See Jim Kuipers P.E., Kuipers & Associates. PolyMet NorthMet Mine Economic Analysis, Form NI 43-101F1 Technical Report. Performed by M3, March 26, 2018.

⁷ See 33 U.S.C. § 1377.

⁸See Attachment 2, Ex. 28 (Water Quality Standards of the Fond du Lac Reservation), <u>https://www.epa.gov/sites/default/files/2014-12/documents/chippewa-tribe.pdf</u>.

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Band's WQS protect Band members in the exercise of their Treaty rights and the uses of water for subsistence purposes and to maintain their cultural and religious traditions.

The Band administers its water quality program and enforces its water quality requirements in order to protect, restore, and maintain the Reservation's water quality now and for future generations. For over 20 years, the Band has conducted a comprehensive monitoring program to evaluate the water quality of the Reservation's waters. The Band has also participated in various studies and collected data to analyze the effects of water quality on the condition and integrity of the Reservation's waters. The Band also issues certifications pursuant to CWA Section 401(a)(1)for discharges originating within the Reservation.

The Band has determined that mercury, (specifically the organic form, methylmercury), is a pollutant of particular concern because it contaminates aquatic life and bioaccumulates up the food chain. Exposure to methylmercury during pregnancy or in childhood has been associated with neurodevelopmental delays that persist over a lifetime (Debes et al., 2016). Other health effects include endocrine disruption and adverse impacts on cardiovascular health in adults and a broad suite of effects on behavior, fecundity, and reproduction in wildlife (Depew et al., 2012). Thus, increases in methylmercury in the aquatic systems surrounding the Project are expected to produce toxic effects on Band members and wildlife that consume the fish. The Band presently has fish consumption guidelines in place to protect public health, including a recommendation to limit consumption for women who are or may become pregnant and for all children under 15 years old. *See* Attachment 4 (Geyaabi Go Onishi Brochure). This recommendation advises that those tribal members consume significantly less traditional fish species on a week-to-week basis than the amount necessary for their subsistence, cultural, and religious practices.

2. Environmental Setting Summary.

a. The Project Area.

The Mine site is located on the eastern flank of the Mesabi Iron Range near the town of Hoyt Lakes in St. Louis County, Minnesota. The Mesabi Iron Range region has been mined for iron ore and lower-grade iron ore (called taconite) for over a century. Mining and ore processing for the Project will go on for at least 20 years and post-closure maintenance will continue for 200 or more years—essentially indefinitely. And processes included in the Project require large quantities of water that can divert and disrupt surface water and groundwater flows.

The Project includes several major components: a Mine site, a Plant site, a Hydrometallurgical facility, and a Transportation and Utility Corridor. According to the FEIS, the former LTV Steel Mining Company ("LTVSMC") processing plant and existing tailings basin (collectively "the Plant site") are located about 8 miles from the Mine site. The Plant site is approximately 4,500 acres, consisting mostly of the existing facilities and infrastructure. The existing tailings basin, which is unlined and was constructed beginning in the 1950s, has been inactive since 2001 and currently releases seepage with elevated concentrations of sulfate and total dissolved solids, among other constituents. The tailings basin consists of three cells totaling over

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3,000 acres. The transportation and utility corridor connects the Mine site and Plant site and contains about 120 acres of land. The Project also includes plans for a seepage capture system as part of the tailing basin for the purpose of capturing and treating polluted wastewater.

The Project's Mine site will be located in the upper portion of the St. Louis River watershed. Two major rivers bracket the Mine site—the Partridge River to the south, and the Embarrass River to the north. In between the Mine site and the two major rivers are several named creeks (e.g., Spring Mine, Ridge, Yelp, Trimble, Rice Farm, Wetlegs, Longnose, Wyman) as well as numerous smaller unnamed creeks. These headwater creeks are fed by flows from wetlands and provide direct surface connections to the Embarrass and Partridge Rivers, and in turn to the St. Louis River.

The more than 3,000-acre Mine Site contains at least 1,100 acres of wetlands that mostly have been characterized as high quality. Vegetation communities present in the Project area include forests composed of aspen, paper birch, jack pine, balsam fir, white spruce, red pine, and white pine in the uplands. Wetland communities include conifer bogs, shrub swamps, cedar swamps, shallow marsh, sedge wet meadow, open bog, and hardwood swamp. Most of the wetlands are underlain by extensive peat soils.

The Partridge and Embarrass Rivers and many of the creeks contain valuable habitat for a diversity of fish and wildlife species. Among others, fish include northern pike, bluegill, northern rock bass, yellow perch, walleye, largemouth bass, black crappie, and channel catfish. According to the FEIS, fish surveys of the rivers and creeks that will be affected are limited.

Wildlife habitat in these watersheds supports species such as the monarch butterfly, northern leopard frog, common loon, hooded merganser, osprey, red-tailed hawk, ruffed grouse, spruce grouse, American woodcock, killdeer, common tern, belted kingfisher, pileated woodpecker, black-backed woodpecker, brown creeper, golden-crowned kinglet, Swainson's thrush, magnolia warbler, pine warbler, savannah sparrow, beaver, porcupine, black bear, and white-tailed deer. Federally- and state-listed species and species of special concern include Canada lynx, northern long-eared bat, gray wolf, moose, little brown bat, Eastern pipistrelle, northern goshawk, boreal owl, wood turtle, yellow rail, and the Quebec emerald dragonfly.

b. The Fond du Lac Reservation

Drainage from the Mine site via the Embarrass and Partridge Rivers enters the St. Louis River approximately at river mile 160, and drains downstream to the Fond du Lac Reservation, which begins approximately at river mile 65. The St. Louis River flows for approximately 30 miles along the northern and eastern boundary of the Fond du Lac Reservation. There are three major streams on the Fond du Lac Reservation that drain to the St. Louis River and provide direct surface water connections between the River and the Reservation—Stoney Brook (and Martin Branch, which drains to Stoney Brook), Simian Creek, and Fond du Lac Creek. In addition, there are numerous smaller unnamed creeks that drain to the three major streams as well as directly to the

St. Louis River. The Fond du Lac Reservation is approximately 43% wetlands.⁹ Principal wetland types are forested, scrub shrub, emergent (i.e., shallow marsh), and aquatic bed (e.g., lilies).

At least four game fish species can be found in appreciable numbers: northern pike, walleye, smallmouth bass, and channel catfish. The channel catfish fishery remains the highest priority of Band members who regularly use the St. Louis River's fishery resources.¹⁰

Many, if not most, of the bird species listed above for the entire St. Louis River watershed are found on the Fond du Lac Reservation. In particular, several waterfowl and wading bird species use Reservation waters and wetlands, e.g., mallard, teal, wood duck, ringneck, coot, Canada geese, heron, sandhill cranes and egret. Trumpeter swan populations have been increasing on the lakes and ponds as well. Several birds of prey use Reservation lands, especially bald eagle and osprey.

Terrestrial and aquatic wildlife on the Reservation include moose, black bear, coyote, white-tailed deer, ruffed and sharp-tailed grouse, beaver, muskrat, mink, river otter, marten, fisher, snowshoe hare, and bobcat. Occasionally gray wolf and Canada lynx are observed on the Reservation.

c. Existing Conditions

As the Band indicated in its March 6, 2012, letter to the St. Paul District of the Army Corps of Engineers, Attachment 2, Ex. 3, mercury and specifically methylmercury in Reservation waters and wetlands are the principal health concerns of the Band. Mercury concentrations in the St. Louis River have exceeded the Band's chronic human health standard (0.77 ng/L) for more than a decade. Consumption of fish contaminated by methylmercury is the primary exposure pathway for Band members and wildlife, and existing monitoring data indicate levels are already elevated in many species that are consumed as food.¹¹ The Band continues to be especially concerned about any new or expanded discharges to the St. Louis River system upstream of the Reservation that will contribute to cumulative increases in mercury and sulfate loadings, enhance mercury methylation, and increase methylmercury bioaccumulation in fish and wetland dependent wildlife.

⁹ Fond du Lac Resource Management, 2018 Integrated Resource Management Plan, <u>http://www.fdlrez.com/rm/downloads/FDL_IRMP-101817.pdf</u>.

 $^{^{10}}$ *Id*.

¹¹ The Fond du Lac Environmental Program has collected and analyzed preferred game fish species from Reservation waters, including the St. Louis River, and worked closely with the Minnesota Department of Health to develop and communicate reservation-specific fish consumption guidance based upon the high mercury concentrations found. This data collection, funded through EPA tribal water quality monitoring grants, was in direct response to Band members' expressed concerns for health risks (to themselves and family members) associated with practicing traditional subsistence lifeways, specifically consuming locally harvested fish. Final reports for each of these sampling efforts were provided to EPA Region 5 in accordance with grant reporting requirements, and sampling was conducted under an EPA-approved Quality Assurance Project Plan.

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The discharges from the Project will increase the loading of mercury, manganese,¹² and sulfate in the St. Louis River.¹³ Both the Embarrass and Partridge Rivers are listed by the Minnesota Department of Natural Resources as impaired waters, from their headwaters to their confluence with the St. Louis River. The St. Louis River is listed as impaired for methylmercury in fish tissue where it forms the northern and eastern boundaries of the Reservation. There have been and continue to be fish consumption advisories for the St. Louis River that greatly affect the Band's members by inhibiting the traditional and safe consumption of fish.

d. Background on the Mercury Cycle

In the northern hemisphere, anthropogenic activities have resulted in large quantities of inorganic mercury being released to the atmosphere and a resulting 200% to 500% increase in deposition to ecosystems since ca. 1850. In terrestrial and freshwater environments, such as that found in Minnesota, inorganic mercury is converted to methylmercury (typically only a few percent of all mercury forms in the environment) in low-oxygen environments such as the sediments of lakes and slow-moving waters, and in wetlands (in particular peatlands) that support the activity of sulfate-reducing bacteria, principle methylators of mercury in freshwater environments. The methylation process is an enzymatic by-product of the sulfate-reduction reaction. Thus, nutrient-limited anaerobic environments that have a supply of inorganic mercury, sulfate, and organic matter (required for microbial metabolism) are likely net sources of methylmercury, with sulfate and organic matter being limiting (in that order). A primary mechanism of methylmercury loss in aquatic systems is through photodegradation by UV light. Methylmercury is the only form of mercury that bioaccumulates in aquatic systems and presents serious risks to consumers of higher trophic level fish because it can cross the blood-brain and placental barriers, unlike inorganic mercury (Debes et al., 2016).

B. Discharges from the Project.

The U.S. Army Corps of Engineers ("Corps") is required to ensure the Project's compliance with the Band's water quality requirements.¹⁴ Several CWA permits have been issued to PolyMet for the Project, including: a CWA Section 404 permit from the Corps to discharge dredge and fill material;¹⁵ a CWA Section 402 individual permit from the Minnesota Pollution Control Agency ("MPCA") to discharge pollutants; and multiple CWA Section 402 general

¹² Principal effects of manganese exposure in children include deficits in bone growth and immune function and somatic cell mutation. *See* <u>Ykateryna D. Duka</u>, <u>Svetlana I. Ilchenko</u>, <u>Mykola M. Kharytonov</u>, and <u>Tetyana L. Vasylyeva</u>. Impact of Open Manganese Mines on the Health of Children Dwelling in the Surrounding Area. Emerg. Health Threats J. 2011; 4: 10.3402.

¹³ See prior Branfireun memoranda, supra n.4.

¹⁴ 33 U.S.C. § 1341(a)(2).

¹⁵ Of note, the Corps suspended PolyMet's CWA Section 404 Permit on March 17, 2021, and EPA's June 4 notification to the Band refers to that permit as a "proposed" permit. As explained above, that permit should be revoked, not just suspended.

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construction stormwater permits from MPCA to discharge pollutants. The State of Minnesota has also issued a certification for the Project pursuant to CWA Section 401(a)(1). Significantly, neither the FEIS or any of these permits either addresses or ensures compliance with the Band's WQS. Similarly, the Project's FEIS fails to evaluate the Project's effects on the Band's waters.¹⁶

For example, the Section 404 permit would authorize PolyMet to dredge and fill wetlands. PolyMet's dredge and fill activities would result in the largest permitted destruction of wetlands in Minnesota's history. PolyMet will discharge dredged or fill material into wetlands, which would then either be removed and replaced by mine pits or excavated and replaced with fill material discharged to construct overburden and waste rock storage facilities, roads, storm and mine water management systems, tailings basin buttresses, the tailings basin seepage capture system, and utility corridors. PolyMet's discharges into wetlands will generate turbidity and suspended particulates that will then be conveyed via overland flow to downstream waters. PolyMet's dredge and fill activities will remove and dewater wetlands that are dominated by peat bogs, which will release and discharge significant amounts of dissolved organic matter as well as mercury into waters of the United States (some of which are already listed on the MPCA Section 303(d) list for mercury impairments), affecting the Band's downstream waters. The Section 404 permit does not discuss the Band's downstream water quality standards.

The Project's individual NPDES permit does not include water quality-based effluent limits for mercury sulfate, or specific conductance. The individual NDPES permit contains statelaw based "operating limits" on an internal waste stream (not discharges to the environment) which are only arguably enforceable under the CWA. These "operating limits" are set to Minnesota's WQS, which are not nearly as stringent as the Band's WQS in certain respects. Both EPA and the Band recommended to MPCA that the individual NPDES permit contain water quality-based effluent limits for several pollutants, including mercury and sulfate. However, the NPDES permit does not contain any water quality-based effluent limits, nor does it consider risks posed by methylmercury exposures at all, despite mercury ultimately being the contaminant of concern with respect to human health.

The Project has four general construction stormwater NPDES permits from MPCA. PolyMet's general NPDES permit coverage would authorize PolyMet's discharges from the draining of over 900 acres of wetlands dominated by peat bogs. As EPA acknowledged, this activity is expected to release significant amounts of mercury into downstream navigable waters, including the Band's. A general NPDES construction stormwater permit, however, assumes compliance with WQS and does not include conditions to address specific issues regarding WQS.

¹⁶ See, e.g., FEIS 4-1 (FEIS's "discussion of the affected environment is limited to those resources that may be subject to potential environmental effects from . . . the NorthMet Project Proposed Action"), 4-19 (characterizing the hydrology and water quality "within the Partridge River and Embarrass River watersheds because these watersheds are expected to be affected by the NorthMet Project Proposed Action").

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The Project also may result in other discharges that are not controlled at all under the CWA. PolyMet assumes at least 10% of untreated polluted water will seep through its proposed seepage capture system. As described below, this assumption is overly optimistic and entirely unproven. As such, it is expected that significantly more untreated polluted water will seep from the Project and discharge to jurisdictional waters with a direct hydrologic connection to the Band's waters.

Further, as described above the proposed tailings basin, which will be built on an existing tailings basin, currently discharges and seeps polluted water into jurisdictional waters with a direct hydrologic connection to the Band's waters. PolyMet's proposed tailings basin will be constructed using the upstream construction method and material for the dam would come from tailings and material borrowed from the LTVSMC dam and basins, as well as other waste rock. PolyMet's proposed tailings basin has a significant probability of failure, which would result in heavily polluted wastewater flowing or issuing out of the tailings basin.¹⁷ These discharges would then flow into other jurisdictional waters with a direct hydrologic connection to the Band's waters.

Similarly, the drawdown effects from the Project discussed below will create significant ecological impacts and cause water containing mercury, including methylmercury, to flow or issue out of wetlands outside PolyMet's seepage capture system and into the small creeks that flow to the Embarrass and Partridge Rivers, all waters with a direct hydrologic connection to Fond du Lac Reservation waters.

C. Project De-Watering Operations Will Cause Changes in Regional Hydrology and the Release of Sulfate, Inorganic Mercury and Methylmercury from Impacted Wetlands.

In addition to the over 900 acres (according to the FEIS) of diverse and ecologically valuable wetlands that would be directly destroyed and altered by construction of Project, including the Mine site and operation of the Mine, the development and de-watering of the open pit will lower groundwater and surface water levels around the mine directly affecting an area that contains over 6000 acres of wetlands.¹⁸ PolyMet has previously argued that site conditions preclude the application of the numerical model used to determine pit dewatering requirements to explicitly identify the extent of wetland impact, and as such only apply knowledge from analog sites. This argument has been dismissed in another expert Opinion (J.S. Price, 2017). Despite the

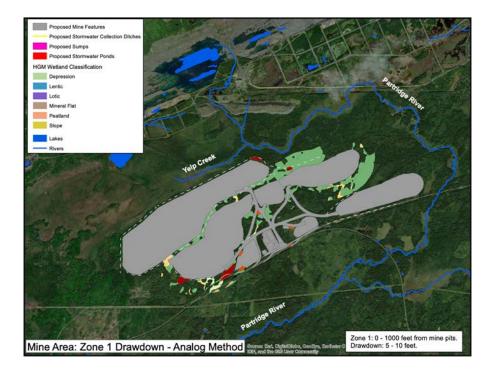
¹⁷ S.D. Warren Co. v. Maine Bd. of Envtl. Protection, 547 U.S. 370, 376 (2006) (discharge under CWA Section 401 means water "flowing or issuing out"). Recent catastrophic upstream dam failures at Mount Polley in British Columbia and at Córrego do Feijão in Brumadinho, Brazil, show the costs and risk of upstream dam construction in this industry context. *See* Cherise Seucharan, *Mount Polley Mine Disaster: 3 Years Later Concerns Still Remain, CBC News*, Aug. 4, 2017 (https://www.cbc.ca/news/canada/british-columbia/mount-polley-mining-fears-1.4235913); Shasta Darlington, et al., *Brumadino Dam Collapse: A Tidal Wave of Mud*, N.Y. Times Feb. 9, 2019 (https://www.nytimes.com/interactive/2019/02/09/world/americas/brazil-dam-collapse.html).

¹⁸ See Attachment 5 (PolyMet Wetlands Area Map by GLIFWC).

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clear potential for impacts on surface water and wetland function, in the absence of a model, PolyMet asks that it be taken on faith that wetlands in the zones of impact would be largely unaffected by aquifer depressurization because they are hydrologically 'disconnected' from underlying groundwater systems. This unsubstantiated contention was consistently challenged in prior opinions (Branfireun, 2014; 2019), as it is neither supported by best available science, nor PolyMet's own data (or lack thereof) and expert opinions.

Maps developed by GLIFWC (included below)¹⁹ show the approximate area of groundwater drawdown in four zones, which have ranges of potential surface dewatering effects ranging from severe (Zone 1 – closest to the mine pit) to modest-minimal (Zone 4, farthest)—

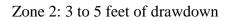


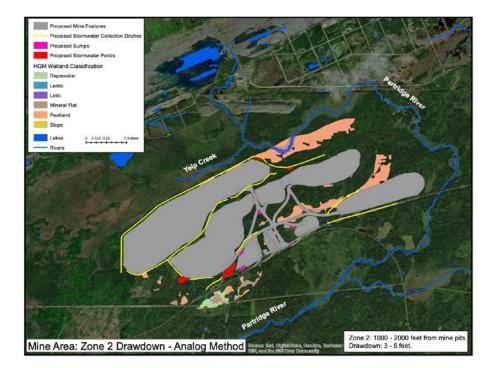
Zone 1: 5 to 10 feet of drawdown

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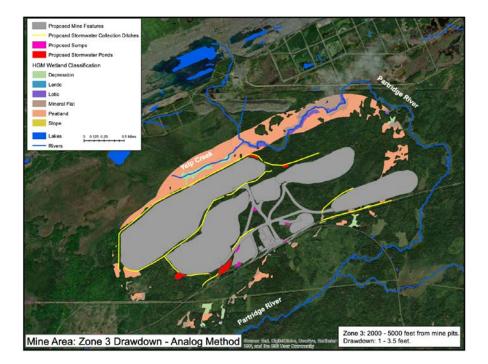
¹⁹ As part of its review of the Project, GLIWFC developed an analysis of indirect impacts to wetlands due to drawdown at the Project's Mine site. *See* Attachment 6 (Letter from GLIWFC to Tony Hingsberger, Project Manager U.S. Army Corps (Apr. 30, 2013)).

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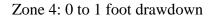


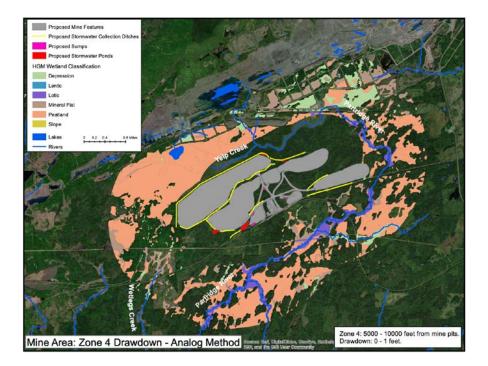


Zone 3: 1 to 3.5 feet of drawdown



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The wetlands in the analog drawdown zones contain extensive areas of saturated organic soils (i.e., peat). The affected peat soils lack free oxygen (i.e., are anaerobic) and already contain inorganic mercury and methylmercury. From a survey of wetland mercury concentrations undertaken in the St. Louis River watershed (Branfireun et al., 2009) upper soil concentrations of Total mercury and methylmercury for peatlands with 100% organic soils (peat) average 5.2 and 72 ng g^{-1} (7.1% methylmercury), respectively, and for other wetland types average 4.8 and 127 ng g^{-1} ¹ (3.7% methylmercury), respectively. From this, the masses of inorganic mercury and methylmercury in the top 30 cm of wetland soils for the entire area of water table drawdown are 131.2 and 7.2 kg, respectively with the distribution of this mass being a function of wetland type and area. Given that the solid phase is >99% of the mass of mercury and methylmercury in the terrestrial environment (Coleman-Wasik et al., 2012), this is a substantial pool in wetlands in the analog drawdown zone that is available for exchange and transport. Using partition coefficients (LogKd) for wetland soils typical of northern Minnesota (4.1 L kg⁻¹ for inorganic mercury; see Branfireun et al., (2005) and 3.5 L kg⁻¹ for methylmercury; see Skyllberg et al., (2008), then the pore water concentrations will be 5.33 ng L⁻¹ Inorganic mercury, and 1.64 ng L⁻¹ methylmercury, for peatlands, and 9.72 ng L⁻¹ inorganic mercury, and 1.50 ng L⁻¹ methylmercury, for other wetland classes. These estimates are consistent with reported concentrations in the literature (Table 1). Importantly, they also are in line with those reported by Coleman-Wasik et al. (2015) in an experimental peatland in north-central Minnesota where the impacts of lower water tables on sulfate, mercury and methylmercury was studied. There, typical total mercury concentrations were up to 12 ng L^{-1} and methylmercury up to 4 ng L^{-1} .

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Prolonged (i.e., greater than approximately 30 to 45 consecutive days) drawdown of greater than approximately 10-12 inches, especially in organic soils, will cause organic matter to begin oxidizing. It is well documented that increased loading of sulfate both increases net methylmercury formation and redistributes methylmercury from the peat soil to its porewater through oxidative release. Coleman-Wasik et al. (2015) found that prolonged deep drought resulted in substantial increases in pore water sulfate, total mercury and methylmercury concentrations upon re-wetting during wet periods in the fall and/or spring snow melt. The occurrence of the spring "acid pulse" of sulfate during snowmelt post-drought is a welldocumented phenomenon, and the observations of increases in mercury and methylmercury are striking. Increases in total mercury concentrations of 166-400% were observed upon rewetting after drought, attributed to oxidative release from the large pool of mercury associated with the solid phase. Methylmercury concentrations also rose significantly (129%) post drought, attributed to both oxidative release through decomposition, along with new methylmercury production caused by the drought-induced sulfate pulses (Coleman-Wasik et al., 2015). Lower and more variable water table regimes²⁰ and the loss of Ericaceae (i.e., bog) shrubs (from land clearing) act significantly and independently to increase both total mercury and methylmercury concentrations in peat pore water and subsequent export during times of high flows such as in spring snowmelt runoff.²¹ It is reasonable to conclude that the oxidation of 25% more wetland soil volume due to persistent under-drainage would result in the oxidative release of sulfate, inorganic mercury and methylmercury in similar proportions.

Wetlands that are in the analog zone of surface water table impacts will be influenced by the open pit dewatering to varying degrees resulting in a *compounding* impact of both climatedriven drought and aquifer depressurization. In wetlands with groundwater influence, under-drainage will increase the amplitude of water table fluctuation, and enhance the magnitude and duration of drought-induced peat drying/oxidation, sulfate regeneration, and mercury methylation to varying degrees. In Analog Zones 1 and 2 in particular, a persistent lowering of the water table will increase the thickness of the aerated zone in peatlands which indeed may have a connection (albeit constrained by peat accumulation) to regional groundwater (see Siegel and Glaser, 1985), where the typical average annual water table is 5-20 inches below the peat surface. In other dominant wetland types found in these zones such as marshes which are more likely to have direct groundwater connections, the annual average water table is typically at or above the soil surface. Enhanced drying in wetlands such as these would have substantial hydrological and biogeochemical implications. Despite having smaller total areas as compared to peatlands in each of the analog zones, the higher bulk densities of these wetland soils and different mercury concentrations means that they may have total masses of mercury that are the similar to or even greater than the more extensive peatlands. This is particularly relevant for Analog Zone 3 and 4 where less pronounced

²⁰ Åkerblom, S., Nilsson, M B., Skyllberg, U., Bjorn, E., Jonsson, S. et al. 2020. Formation and mobilization of methylmercury across natural and experimental sulfur deposition gradients. Environmental Pollution, 263: 114398.

²¹ Haynes, K. M., E. S. Kane, L. Potvin, E. A. Lilleskov, R. K. Kolka, and C. P. J. Mitchell (2017). Mobility and transport of mercury and methylmercury in peat as a function of changes in water table regime and plant functional groups, Global Biogeochem. Cycles, 31, 233–244.

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potential drawdown levels would proportionally impact wetland classes more freely connected to groundwater more significantly. Analog Zone 4 presents the greatest uncertainty given the lack of empirical data, distance from the open pit, and total wetland area. Although a range of potential water table drawdown of 0-1 ft are assigned to this zone, the large area of peatlands and other wetland classes relative to other zones in the analog drawdown zone suggests that even subtle impacts on this zone could have greater impacts on exports of sulfate, inorganic mercury and methylmercury than the zones with more significant de-watering. Of the total amount of inorganic mercury and 78% of the methylmercury in the entire analog drawdown zone. Non-peatland wetlands make up only 30% of the wetland area but contribute 61 and 45% of the total mass of inorganic mercury and methylmercury, respectively. Uncertainty concerning potential hydrological impacts in this zone combined with the substantial wetland area and pool of mercury presents substantial risk of downstream impacts. A lack of monitoring of wetland chemistry under baseline conditions, and no requirement for monitoring during operations means that none of these impacts would be captured.

Wetlands are generally not closed systems, and in this context are the sources of runoff that supply the headwaters of the Partridge and Embarrass Rivers. Research shows that the upper several inches of peat soils contain larger pores that more easily transmit solutes and affect water flow,²² and it is through these pores that water and solutes such as methylmercury are exported to receiving creeks and streams under normal hydrological conditions. The inorganic mercury and methylmercury produced in and liberated from wetland soils is transported into the numerous small streams and creeks that drain to the Embarrass and Partridge Rivers, then to the St. Louis River. This mercury in the St. Louis River is conveyed downstream to the Fond du Lac Reservation. High concentrations of high molecular weight natural dissolved organic matter ("DOM") in surface waters is associated with runoff from wetlands and peatlands, and is responsible for the tea color that is characteristic of streams and rivers in north central Minnesota. Inorganic mercury and methylmercury form very strong chemical bonds with DOM (Ravichandran, 2004), to such a degree that inorganic mercury is preserved in the dissolved form protected from particle binding and precipitation with sulfides enhancing transport, and is protected from photodegradation by UV light which is the main mechanism of methylmercury loss in freshwaters (Klapstein et al., 2018). The naturally high DOM environment in the headwaters creates the ideal conditions for the excess inorganic mercury released by the Project to be transported downstream where it may be methylated in riparian wetlands of the St. Louis River, contributing to resource impairment far from the point of release. Methylmercury formed by sulfate release by the project may be transported in the dissolved form long distances associated with, and protected by DOM, with the potential for bioaccumulation far from where it was formed, including in the St. Louis River. During spring snowmelt and/or heavy rains that cause water levels to rise in the St. Louis River, those waters flood the riparian wetlands along the St. Louis and can back up into the principal

²² Fereidoun Rezanezhad, Jonathan S. Price, William L. Quinton, Bernd Lennartz, Tatjana Milojevic, Philippe Van Cappellen. Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists, in *Chemical Geology*. 429 (2016) 75–84.

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streams on the Fond du Lac Reservation—Fond du Lac Creek, Stoney Brook, and Simian Creek the wetlands adjacent to those streams, and numerous adjacent smaller creeks and wetlands, contaminating Fond du Lac Reservation lands.

PolyMet suggested that "the potential export of SO₄ [sulfate] and MeHg [methylmercury] is expected to be the same as background wetlands and *likely* no different with the Project in operations as occurs now in existing conditions" (Cross-Media Analysis Appx. F, p. 12; emphasis added). Given the substantial changes in surface water hydrology that will be the direct result of pit dewatering and wetland under-drainage, it is inconceivable how such a conclusion could be arrived at, when the opposite conclusion is the most parsimonious and precautionary. The lack of consideration of these potential impacts in loading estimates of sulfate, mercury and methylmercury and complete absence of any monitoring of wetland water quality over the operation of the Mine means that not only are these loads unaccounted for in the mass balances used to justify meeting permitting thresholds, but also that cumulative contributions to downstream loads cannot be detected nor mitigated under the current proposal, resulting in irreparable harm to downstream resources.

As described in Mr. Schweisberg's April 29, 2021 Memorandum for the Band ("Schweisberg 2021"),²³ in turn, benthic macro-invertebrates, fish, amphibians (e.g., frogs, salamanders), reptiles (e.g., turtles, snakes), wetland dependent mammals (e.g., river otter, mink, beaver), and wading and other water birds (e.g., herons, egrets, ducks and geese) that feed in these systems become contaminated with mercury, which biomagnifies from prey to higher trophic level predators (including piscivorous birds, e.g., bald eagles and ospreys).

As also described in Schweisberg 2021, over 2,400 acres of the floodplain wetlands along the St. Louis River contain organic soils and are seasonally flooded. Fluctuating water levels in these riparian muck and peat wetlands will create ideal conditions (i.e., oxidation and reduction) for enhancing the methylation of mercury. As these seasonally flooded floodplain and riparian wetlands dry out periodically in summer, the oxidizing and re-wetting action makes the wetlands efficient sources of methylmercury that is transported along the stream corridors and spread throughout much of hydrologic system in the Fond du Lac Reservation.²⁴

The wildlife resources and diverse fish assemblages that use the Partridge, Embarrass, and St. Louis Rivers, their riparian wetlands, and the smaller streams and creeks and their adjacent wetlands are already contaminated with sulfides and sulfate, and methylmercury. The Project's discharges will add to the existing loads of those contaminants and be available to fish and wildlife that consume the plant and animal food sources containing elevated levels of methylmercury. In turn, those contaminated food sources—fish (e.g., northern pike, largemouth bass, walleye),²⁵

²³ See Attachment 2, Ex. 31.

²⁴ The last catastrophic flood in the St. Louis River watershed occurred in the summer of 2012.

²⁵ The Band's restoration efforts for lake sturgeon will likely be compromised by the contamination. With respect to those efforts, the Band also has significant concerns regarding

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waterfowl (e.g., ducks), and wetland dependent mammals (e.g., river otter, mink, moose)—will be available to Band members that catch or trap and consume them from the St. Louis River and the three principal streams and adjacent wetlands. Accumulation of high levels of methylmercury in the food chain is a continuing and major concern.

D. Discharges of Mercury and Sulfate are Not Adequately Regulated by the General Construction Stormwater Permit.

As noted above PolyMet was issued general permit coverages for construction stormwater discharges for the Project. The stormwater general permit authorizes discharges from the draining of over 900 acres of wetlands, which are dominated by peat bogs. This activity will release significant amounts of mercury and sulfates into downstream waters that will reach the St. Louis River and its riparian wetlands along the Reservation, as well as affect several of the streams and creeks that flow into the St. Louis River when flood waters back up into the Reservation. Storage of oxidized peat overburden in the unlined laydown area for 11 years would result in repeated flushes of methylmercury as well as inorganic mercury. Although the PolyMet FEIS suggests (FEIS 5-227) that the impact of stored mercury on loading of inorganic mercury has been considered as part of its mercury mass balance, there are assumptions about the flushing effect diminishing over time. Given the mass of mercury and methylmercury in the peat materials, the pool is effectively limitless over the time span of operations. Nothing in the permitting record demonstrates that this issue has been addressed or even considered. There is no provision in the construction stormwater general permit for addressing specific water quality issues. The general permit leaves mercury completely unaccounted for and unregulated, and that is an unacceptable result. For a project of this extent, scope, and duration, and considering the contaminants (e.g., mercury, methylmercury) that stormwater will carry, construction stormwater discharges should be regulated under an individual NPDES permit.

E. Direct Discharges of Water, Sulfate and Mercury to Surface Waters and Wetlands Will Increase Methylmercury Production During Project Operations.

Prior Branfireun expert memoranda provide a detailed conceptual overview of the mechanisms by which Project discharges of sulfate and mercury will enhance methylmercury production in the Partridge and Embarrass watersheds (tributaries of the St. Louis River) and that this methylmercury production presents an environmental risk that is completely unaccounted for in permitting associated with the Project.²⁶ Headwater tributaries that will receive discharges from the Project are low in sulfate, and are already elevated in the percentage of total mercury that is present as methylmercury (up to nearly 10%) indicating a high methylmercury production potential in their watersheds.²⁷

elevated specific conductance, which may inhibit survival of fry and fingerlings (for which there is evidence of sensitivity to high salinity).

²⁶ See supra n.4.

²⁷ Branfireun, 2015 at Section 2.1.1 (Attachment 2, Ex. 24).

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Seven direct wastewater outfalls (SD004-SD010) associated with the mine processing facility will discharge to the headwater wetlands of a single tributary north of the tailings basins (Trimble Creek) increasing water loading by several million gallons per day, and supplying hundreds of pounds of sulfate per year (based on PolyMet's own data), affecting ecological and biogeochemical function of these wetlands. These loads (in addition to any seepage that is not contained by the proposed capture system) would result in an increase in methylmercury production precisely at a location in the watershed that would result in the greatest environmental harm—a headwater wetland that then supplies water and solutes to downstream.²⁸

The specifics of these discharges merit deeper consideration beyond the analyses in prior Branfireun Opinions in order to quantify potential increases in loading. The NPDES/SDS documents for the Project stated that rainwater coming in contact with tailings and plant site materials, Colby Lake water used for processing, and water from the pit dewatering process and Mine site construction activities will be captured in a seepage capture system. Some of that seepage will be returned to the tailings basin and some will be treated in a Wastewater Treatment System ("WWTS") and subsequently discharged from the site.

Although there are no effluent limits in the NPDES/SDS permit for any surface discharge outfalls, internal waste stream operating limits (WS074) propose that mercury concentrations will be set at 1.3 ng/L for total mercury, and 10 mg/L for sulfate. The internal treated waste stream from WS074 will be sent to SD001 and then divided into multiple discharge outfalls (SD002 to SD011), each of which will discharge into the headwaters of the Embarrass River. The MPCA NPDES/SDS permit (Table 2.1, p. 10) identifies estimated average discharges of 0.24 million gallons per day (MGD) in mine year 1, increasing to 0.39 MGD in mine year 10 and maximum discharges of 0.29 MGD in mine year 1, increasing to 0.57 MGD in mine year 10 from *each* of the 10 outfalls northwest and north of the tailings basin in the Embarrass River watershed.

Even if PolyMet is able to reduce effluent concentrations of mercury and sulfate to the stated levels using its proposed waste-water treatment plant, this additional water input will deliver over 100 kg of sulfate, and nearly 5 g of mercury per year from the seven outfalls discharging to the headwater wetlands of Trimble Creek. These wetlands alone cover an area of 1198 acres (485 ha). Prorating these discharges and conservatively estimating that additional discharges may only interact with 50% of the total wetland area, the loading of sulfate and mercury from the mine are equal to \sim 11% and \sim 16% respectively of that annually deposited from the atmosphere in rain based on regional historical data for Minnesota.

Brigham et al. (2021) considered long-term data from four lakes in Voyageurs National Park in northern Minnesota and demonstrated that lake methylmercury concentrations are declining as a result of the "decline in atmospheric Hg [mercury] deposition as well as a decline in *sulfate deposition, which is an important driver of mercury methylation in the environment.* (emphasis added). Results from this case study suggest that regional- to continental-scale

²⁸ Branfireun 2019 at Section 2.1.2 (Attachment 2, Ex. 25).

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decreases in both mercury and sulfate emissions have benefitted aquatic resources." These substantial increases in loadings of both sulfate and mercury in wetlands proximal to the Project effectively undo progress toward reductions in these deleterious compounds. Brigham et al. (2021) found that overall, a 22% decrease in total mercury deposition over a 20-year period in Minnesota was associated with a nearly proportional 27% decrease in lake water total mercury concentrations. However, methylmercury concentrations declined by 44%, linked to an also nearly proportional mean decrease in water sulfate concentrations of 45% due to the fundamental biogeochemical role of sulfate in the mercury methylation process. Moreover, Brigham et al. conclude that "For the three lakes with long-term biomonitoring, temporal patterns in biotic THg concentrations were similar to patterns in MeHg_{aq} concentrations". If the same relative changes observed for Minnesota surface waters measured by Brigham et al. (2021) are applied to the increases stated here, a >10% increase in methylmercury concentrations in surface waters and concomitant increases in biota would be anticipated as a result of already approved discharges of sulfate and mercury from Mine operations in these headwater streams of the Embarrass River, a tributary of the St. Louis River.

PolyMet contends that sulfate loadings only lead to increases in methylmercury production in "certain limited circumstances" (Barr, 2018). However, sulfate stimulation of methylmercury production is well-established scientifically as the rule, not the exception, with numerous consistent examples. The most pertinent examples are from the Marcell Experimental Forest in Minnesota, where an experimental increase in sulfate loading of ~4x historical levels resulted in an average increase in peat methylmercury concentrations of 35% (an increase from 5.59 to 8.61 ng/g d.w.) which was reflected in pore water concentrations (Coleman-Wasik et al., 2012; 2015). These changes translated into increases in methylmercury concentrations in waters flowing from the experimental wetland (Jeremiason et al., 2006), supporting the findings of Brigham et al. (2021). Further, Berndt et al. (2016) make it clear that methylmercury in the St. Louis River watershed is dominantly derived from wetlands, net methylmercury production is most pronounced at relatively lower sulfate concentrations, and that concentrations are highest in shallow groundwater seeping from wetlands under rewetting conditions and that most of this methylmercury is associated with wetland-derived dissolved organic matter ("DOM") (Berndt and Bavin, 2009). Indeed, from the perspective of methylmercury production and downstream impacts on aquatic life, the proposed water discharges create a worst-case scenario in this location.

For the Trimble Creek headwater wetlands, the additional water loading from the Mine processing operation alone will further contribute to the export of inorganic mercury and methylmercury through the exchange of mercury and methylmercury from the solid peat material. The concentrations of a chemical will always move towards an equilibrium between that in the solid (soil) and dissolved (porewater) forms. The loading of more dilute water will result in the release of mercury and methylmercury from the solid peat. Using average concentrations of total mercury (92.05 ng g⁻¹) and methylmercury (5.05 ng g⁻¹) in wetland soils from a range of wetland types across the St. Louis River Watershed, (Branfireun et al. 2009), wetland area data indicated above, and data on Minnesota wetland soil physical properties (bulk density of 0.15 g cm⁻³; Boelter, 1968), the total mass of mercury and methylmercury in only the top 30 cm of moderately decomposed peat soils is *20.1 and 1.1 kg respectively* in these 1198 acres of impacted headwater

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wetlands without consideration of any additional methylation due to excess sulfate supply. Given that the solid phase is >99% of the mass of mercury and methylmercury in the terrestrial environment (Coleman-Wasik et al., 2012), this is a substantial pool in proximal wetlands that is available for exchange and transport.

If partition coefficients (LogKd) values for wetland soils typical of northern Minnesota are applied as described in prior sections then the effective concentration of the discharged process waters after interacting with wetland soils will be 6.91 ng L⁻¹ inorganic mercury, and 1.59 ng L⁻¹ methylmercury, for a sum *Total mercury concentration of 8.50 ng L⁻¹*. These concentrations exceed the proposed 1.3 ng L⁻¹ concentration to meet State water quality guidelines by over 650%, and the Band's water quality standard by 1300%.

Even if mixing is with a more limited area of the wetlands, and/or soil contact time is too short for equilibrium to be reached, it is certain that the total mercury concentration of discharged water will be elevated above 1.3 ng L^{-1} before reaching headwater tributaries. Although the porewater concentrations that are calculated above are in the range of those observed in many wetlands, this is a calculation that is highly sensitive to the value of LogKd and is not predictive; empirical values for peat and porewater mercury concentrations are not known for the wetlands in question (but could be easily measured). The intent of the calculation is to illustrate that there are a wide range of mechanisms that can only result in an *increase* in mercury concentrations. The degree to which concentrations increase may be over or underestimated, however given that these changes are exclusively the result of the Project's operations, they are a direct effect that will add to the cumulative load of inorganic mercury and methylmercury of the St. Louis River and its tributaries.

F. Increase in Methylmercury Production From Sulfate and Inorganic Mercury Loading Poses Risks for Human and Ecological Health.

Many peer-reviewed scientific studies have shown that any increases in water column methylmercury concentrations will increase methylmercury concentrations in food webs (Harris et al., 2007; Knightes et al., 2009, Schartup et al., 2019). For example, the EPA assumed a linear relationship between inorganic mercury inputs and fish methylmercury concentrations for regulatory determinations when assessing the potential impacts of increased air deposition of mercury across the United States on fish mercury concentrations in lakes and rivers (https://cfpub.epa.gov/si/si public record report.cfm?Lab=OST&dirEntryId=74661). The slope of the relationship between increasing methylmercury concentrations in water and biological concentrations at the base of the food web is affected by water quality parameters such as dissolved organic carbon (Schartup et al., 2018) but a linear increase in food web concentrations is expected to result from increasing aqueous methylmercury concentrations. This is particularly problematic for the Project's operations that are expected to substantially increase methylmercury inputs to the Saint Louis River, which is already impaired, and several tributaries upstream of the Fond du Lac

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Reservation. Piscivorous fish already have high body burdens of methylmercury,²⁹ thus additional increases pose elevated exposure risks for both Band members and wildlife.

Band members rely on aquatic resources harvested from these freshwater ecosystems for subsistence foods and as part of their traditional fishing activities that are essential for maintaining and protecting culture. In addition to the deleterious impacts of methylmercury on human health (summarized below), studies for other indigenous groups have shown substantial social costs associated with restricted traditional hunting and fishing due to environmental contaminants including increases in depression, suicide, and addiction (Van Oostdam et al., 2005). As noted herein, hunting and fishing activities have already been limited due to environmental pollution within the Band's Reservation (and its Ceded Territory). Any further increase in pollution poses unacceptable risks to the Band's traditional lifestyle, culture, and health and violates environmental justice considerations. Methylmercury is the only form of mercury that bioaccumulates in food webs. It undergoes facilitated transport in the human body because it resembles an essential amino acid and is able to cross the protective blood-brain and placental barriers in the human body (Clarkson et al., 2007). The predominant pathways for human exposure to methylmercury is from consuming contaminated fish (Mahaffey et al., 2009). The developing brain is the most sensitive endpoint for methylmercury toxicity and methylmercury exposure for children and pregnant women has been linked to neurodevelopmental delays that persist over a lifetime (Debes et al., 2016). Methylmercury exposure is also associated with a variety of other adverse health effects; for example, high concentrations of methylmercury in blood and tissue samples from adults have been strongly associated with adverse cardiovascular impacts (Virtanen et al, 2005). Cardiovascular abnormalities are also associated with prenatal exposures to methylmercury (Stern et al. 2005). Biologically, there does not appear to be a safe level of methylmercury exposure for humans. Studies have shown adverse effects on brain development in children with prenatal methylmercury exposures similar to or below the RfD (Karagas et al. 2012).

G. Downstream Impacts on Water Quality and Designated Uses of Natural Resources in the St. Louis River.

Changes in the concentrations of sulfate, inorganic mercury and methylmercury in wetlands have been directly linked to surface water quality in Minnesota. For example, Jeremiason et al. (2006) clearly demonstrate that increases in methylmercury production resulting from an experimental addition of sulfate resulted in a 3-fold increase in methylmercury concentrations in wetland pore waters, and these increases translated into a 2.4-fold increase in methylmercury export to surface waters. Wiener et al. (2006) identify "pH, dissolved sulfate, and total organic carbon (an indicator of wetland influence) as factors influencing methylmercury concentrations in lake water and fish" indicating not only a connection with sulfate and methylmercury in fish, but also the degree of wetland influence at the catchment scale.

²⁹ See supra n.11.

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PolyMet has based its contention that the Project will not cumulatively impact downstream water quality exclusively on a mass-balance model to predict the potential impacts of project development and operations on sulfate, mercury, and other solutes. This approach is fatally-flawed. The mass-balance model is inappropriate to apply to reactive solutes and does not account for mercury release from any of the effects identified above, nor does the model consider methylmercury at all. Technical documents submitted to dispel concerns about both the potential for exceedances in the release of mercury and sulfate (see Barr, 2018) lay bare the complete reliance on unconstrained mass balance estimates, unproven storm and wastewater capture techniques, and the avoidance of the quantification of releases of mercury, methylmercury and sulfate outlined above in order to draw the conclusion of *de minimus* impacts. This conclusion is unsupported by data, scientific consensus in the literature, or even a sound conceptual model.

The combination of both direct and indirect effects on mercury release and methylmercury production will have impacts that will reach far downstream. All of the potential impacts and subsequent discharges identified above (which are beyond those currently considered in the PolyMet application) will have a cumulative effect on downstream waters, including the St. Louis River. Headwater streams such as the upstream tributaries of the Partridge and Embarrass Rivers will be directly impacted by the Project, and these streams strongly regulate the downstream water quality of the larger rivers that they supply (Bishop et al., 2008; Klaminder et al., 2006). Headwater stream chemistries can be predicted from the mixed chemistry of the downstream river (see Temnerud et al., 2010), revealing the important control of source waters on downstream resources. Thus, there can be no scientific disconnection made between the mercury, methylmercury and sulfate loading to the source waters impacted by the Project and the larger rivers that they supply. Sulfate is often treated as a quasi-conservative solute (i.e. it moves with surface waters in a relatively unreactive way) in the context of hydrological studies (e.g. Christopherson and Hooper, 1992), and as such additional loading to the headwaters of the St. Louis River will contribute to the cumulative sulfate load. Under higher flow conditions, this additional sulfate will be delivered to extensive riparian wetlands associated with the lower reaches of the St Louis River, contributing to enhanced sulfate reduction and methylmercury production far from the Project. The total area of hydrologically connected riparian wetlands in the Embarrass, Partridge Rivers and the receiving St. Louis River above the Fond du Lac Reservation is approximately 9,183 acres, with an additional approximately 41,782 acres within the 100-year floodplain. Berndt et al. (2016) determined that a substantial amount of the methylmercury in the St. Louis River is derived from wetlands such as these during high flow periods, making any cumulative increase in sulfate loading critical to fully quantify.

The potential for transport of either methylmercury or inorganic mercury considerable distances from the Project to downstream locations where they contribute to ecosystem impairments is not speculation. A very recent published paper used natural abundance stable isotopes of mercury to trace the origins of mercury in biota in the St. Louis River Estuary (Janssen et al., 2021), and shows unequivocally that SLRE sediment mercury showed significant proportions attributed to industrial sources likely associated with in the estuary. Importantly, some locations well upstream of the estuary also had significant proportions of industrial mercury, indicating the long-distance river transport of industrially-derived mercury from unidentified

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upstream sources. The mercury in biota and fish was a more complex pattern but also reflected these differences, clearly demonstrating that the locations of mercury release, methylation, and bioaccumulation need not be spatially contiguous.

The releases of mercury, methylmercury and sulfate from the headwater region of the St. Louis River will be cumulatively impacted by the Project, and the releases of total mercury and sulfate will far exceed estimates provided by PolyMet in support of the Project's 401 Certification. Further, methylmercury loading to surface water will be increased due to direct and indirect effects of the Project. This aspect of the Project has never been considered in any environmental assessment or permit application associated with the Project, despite it being the only variable that directly links to mercury bioaccumulation and biomagnification in biota. These releases will cumulatively affect water quality standards, downstream ecosystem function, and designated uses of aquatic resources by the Band and other downstream aquatic resource stakeholders.

H. Expected Downstream Exceedances of Fond du Lac's Approved Specific Conductance Standard.

The Band's concerns for protecting aquatic resources from Project pollutants discharged upstream of the Fond du Lac Reservation is not limited to mercury bioaccumulation and human health impacts. The Band also clearly communicated its concerns about elevated specific conductance from existing upstream mining sources, and the additional loading that would likely occur from the proposed PolyMet project, early and consistently throughout the environmental review process to the federal and state co-lead agencies. Specific conductance is the ability of a material to conduct an electric current measured in microSiemens per centimeter (μ S/cm) standardized to 25°C. Specific conductance reflects concentrations of dissolved ions, including metal and other contaminants from mining, other industrial activities, and agriculture. Sulfate is a major constituent of the measured specific conductance in the St. Louis River.

The Band adopted a numeric aquatic life use criterion for specific conductance of 300 μ S/cm to protect sensitive macroinvertebrate species and the relatively high biodiversity in the Band's waters. These macroinvertebrates are an integral part of the aquatic food web, processing nutrients and detritus and providing food for fish, birds, and other animal species. The Band considers its water quality standards the foundation for protecting its high-quality waters without degradation, through both narrative and numeric criteria and a robust antidegradation policy.

Through the Band's long-term water quality monitoring program, the Band has collected thousands of data points on all Reservation waterbodies for more than 20 years, and that data confirms that natural or ambient conductivity is very low—below the Band's new criterion everywhere with the exception of the St. Louis River, where it is routinely exceeded, depending upon discharge rates. Historic data from the St. Louis River clearly shows that, prior to iron mining evolving to include taconite processing in the 1950's and 60's, natural background conductivity levels were also low (generally below 200 μ S/cm). The Band has long recognized, through years of extensive review of mining permits and environmental assessments, that elevated specific conductance is a water chemistry "signature" for mining discharges. The Band's concerns

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regarding specific conductance also relate to the Band's long-term efforts to reestablish native lake sturgeon (*Acipenser fulvescens*), a culturally important species, in the St. Louis River.

The Band notes:

Lake sturgeon have been successfully reproducing in the estuary for several years, and Fond du Lac Resource Management Division's successful reintroduction and tracking efforts in the upper river have been documented.³⁰ After the construction of hydroelectric facilities on the St. Louis River in the early 1900's, the lake sturgeon population in the upper St. Louis River was isolated from the lower estuary and Lake Superior.³¹ The remaining sturgeon population was likely extirpated due to exploitation and pollution from the wood products industry and municipal waste. In addition, many of the upper tributaries were dammed during the extensive white pine logging era (1800's) in order to float logs down during the high water spring runoff. Pollution and degraded water quality has been identified as a factor limiting sturgeon abundance in many locations.³²

The conclusion at FEIS 4-275 that "There are no known occurrences of lake sturgeon and not likely habitat for lake sturgeon within the NorthMet Project area" neglects to consider that downstream water quality effects may result from the Proposed Project. This will result in another degradation of the Band's downstream water quality that is explicitly relevant to our stated resource management goals for lake sturgeon.

A dramatic recovery in lake sturgeon abundance in Rainy River and Lake of the Woods followed improvements in water quality in the Rainy River, which resulted from substantial reductions in the amount of wood fiber and untreated chemical wastes discharged by upstream pulp and paper mills.³³ Evidence from hatchery rearing studies show that juvenile sturgeon can only tolerate salinity < 23 ppt.³⁴ The Band is concerned about protecting the both the habitat and water quality necessary to support its reintroduction efforts. Uncontrolled contaminant loading

³⁰ *Lake Sturgeon Restoration in the Upper St. Louis River, Minnesota*, FDL poster presented at the Great Lakes Lake Sturgeon Coordination Meeting, 3 – 4 December 2012, Sault Ste Marie, MI

 $^{^{31}}$ *Id*.

³² Dick, T. A., et al 2006. COSEWIC assessment and update status report on the lake sturgeon (*Acipenser fulvescens*) in Canada. Ottawa, Ontario. 107 p.

³³ Mosindy, T. E. and J. Rusak. 1991. An assessment of the lake sturgeon population in Lake of the Woods and Rainy River. Lake of the Woods Fisheries Assessment Unit Report 1991- 01. Ontario Ministry of Natural Resources. Kenora, Ontario. 66 p.

³⁴ A Review of Lake Sturgeon Habitat Requirements and Strategies to Protect and Enhance Sturgeon Habitat March 2011. Steven J. Kerr, Michael J. Davison and Emily Funnell, Fisheries Policy Section, Biodiversity Branch Ontario Ministry of Natural Resources.

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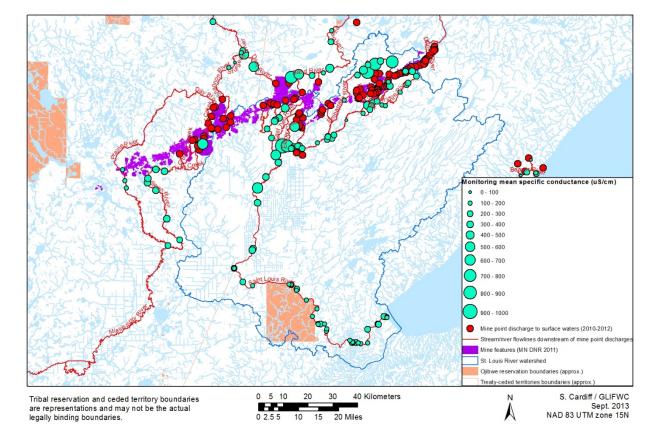
from existing mine facilities, along with elevated constituents from the Project, will affect the successful establishment of a sustainable lake sturgeon fishery throughout the St. Louis River.

Scientific literature suggests that early life stages are particularly sensitive to high salinity (another common term referencing high dissolved salts or high ionic strength). The Band's ongoing radiotelemetry surveys of slowly maturing lake sturgeon that it stocked as eggs, fry and fingerlings over more than 20 years shows that these fish are using the entire reach of the St. Louis River from the Reservation, all the way upstream to the low-head dam at Forbes (near the United Taconite Fairlane facility). These fish are approaching reproductive age, and the Band's goal of reestablishing a self-sustaining lake sturgeon fishery in the St. Louis River depends upon high water quality, not only for the fish themselves but also to support their food base, which includes benthic macroinvertebrates.

During the SDEIS process for the NorthMet project, tribal staff conducted analysis of specific conductance downstream of mine discharges using agency monitoring data (1990-2013) as part of a tribal cumulative effects analysis. See Attachment 2, Ex. 7 at 16-18. Analysis of specific conductance downstream of Mine discharge sites indicated that specific conductance was highest nearest to Mine discharge sites, and tended to only gradually decrease downstream of mine discharge sites. Linear regressions demonstrated that specific conductance was significantly negatively related to distance across all sample sites (P < 0.01, $R^2 = 0.15$; n = 123 sites; Fig. 4) and within the St. Louis River and Swan River systems (P < 0.05, $R^2 = 0.18$ and 0.52, respectively; Fig. 5). This analysis included stream and river monitoring only (not lakes). The regression suggests that specific conductance could drop to 150 µS/cm only 203 km (126 mi) downstream of the nearest upstream mine discharge site.

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Specific conductance downstream of mine point discharges (1990-2013)

Methods as follows (in appendix to Tribal Cumulative Effects Analysis):

We associated downstream water quality monitoring points with upstream discharge points based on the listed receiving waters in discharge data, the position of the discharge sites and water features in satellite imagery, and flow direction in the National Hydrography Dataset. We traced upstream and downstream of discharge and monitoring points using the Utility Network Analyst in Arc GIS. We joined a table of related discharge points and monitoring points with tables of summary measurements (maximum, minimum, and mean) of discharge measurements and monitoring measurements restricted to individual characteristics (e.g. specific conductance) and the time period of DMR data availability (2001-2012). We selected the downstream monitoring point with the desired measurement (e.g. specific conductance) that was nearest to a group of discharge points related to a particular facility. We excluded further monitoring points if downstream of a selected monitoring point to avoid using the same discharge data twice in the analysis. We also excluded non-surface water discharge sites and NPDES discharge sites were listed as surface water monitoring rather than discharge measurements. We analyzed the mean discharges at the selected downstream monitoring points and the mean discharges of the related upstream discharge points. Since each discharge point was already a mean of multiple measurements, we multiplied that mean by the number of measurements at that site, summed that

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across the multiple sites related to the monitoring point, and divided by the total number of measurements for those sites. This yielded a discharge mean that was not biased by more measurements at one discharge site than at others. We conducted a linear regression of the discharge and monitoring data. Sample size varied by site because of differences in number of measurements between sites.

IV. NONCOMPLIANCE WITH BAND WATER AND WETLANDS QUALITY STANDARDS³⁵

A. The Band's Water Quality Standards.

The principal contaminants of concern from the Project are mercury, methylmercury due to their impacts on wildlife and fish consumers, and sulfides/sulfates due to the direct effect on wild rice as well as the role in the mercury cycle affecting fish and fish consumers. In addition, elevated specific conductance is a water chemistry "signature" for mining discharges with adverse impacts to sensitive aquatic life, particularly many benthic aquatic insects.

Considering the direct and indirect discharges from the Project, it is expected that there will be non-compliance with the following Fond du Lac Water Quality Standards:

Antidegradation

<u>Section 105(a).3.</u> Degradation of water quality shall not be permitted where it will be injurious to existing or designated uses. The Reservation Business Committee or appropriate permitting authority shall impose the most stringent regulatory controls for all new and existing point sources, and shall impose cost effective and reasonable best management practices for non-point sources and wetland alterations.

As described above, Project discharges will increase the loading of sulfates, mercury, methylmercury and specific conductance to the Embarrass and Partridge Rivers. Those rivers drain to the St. Louis River and its riparian wetland systems, then flow downstream to the Fond du Lac Reservation. Consequently, increased loading of those contaminants will occur to the streams and adjacent wetlands of the Fond du Lac Reservation that have surface connections to the St. Louis River. In particular, the water quality classification for Stoney Brook is Aquatic Life, Cold Water Fisheries, which likely is for brown and brook trout.

<u>Section 105(b).1.</u> Lowering of Water Quality. A significant Lowering of Water Quality is de-fined as: . . . 2) a new or increased loading of a pollutant from any regulated existing or new facility, either point source or non-point source, for which

³⁵ The Band's water and wetlands quality standards cited and discussed in this Section are included in Attachment 2, Exhibit 28.

there is a control document or re-viewable action, as a result of any activity including, but not limited to . . .

A. Construction of a new regulated facility modification of an existing regulated facility such that a new or modified control document is required; . . .

E. Other deliberate activities that, based on the information available, could be reasonably expected to result in an increased loading of any pollutant to any waters of the Fond du Lac Reservation.

There will be a lowering of water quality as defined under either Section 105(b)(1)(A) or (E). Regarding Section 105(b)(1)(A), PolyMet proposes a "new . . . loading of a pollutant from . . . [a] new facility . . . as a result of . . . [c]onstruction of a new regulated facility." The Project permits are "control documents" and reviewable actions. Section 105(b)(1)(E) also applies. As described above, the increased loading of sulfates, mercury, and methylmercury to the streams and wetlands of the Fond du Lac Reservation described above will significantly lower the water quality of affected Reservation waters and wetlands.

Those conditions will cause non-compliance with the Band's Anti-degradation standards.

<u>Section 105(c).</u> "[A]ny entity seeking to lower water quality in an Exceptional Resource Water or create a new or increased discharge of bioaccumulative substances of immediate concern or other pollutants must first submit an antidegradation demonstration for consideration and approval or disapproval by the Reservation Business Committee."

As described above, the Project's discharges will result in both (1) lower water quality in Fond du Lac Creek, Stoney Brook, and Simian Creek, and their adjacent wetlands, which are all Exceptional Resource Waters for relevant pollutants and (2) a new or increased discharge of bioaccumultative substances (e.g., mercury) of immediate concern or other pollutants. PolyMet has not submitted an antidegradation demonstration to the Band for its consideration and approval with respect to all pollutants in PolyMet's discharges. Accordingly, PolyMet has not complied with Section 105(c) and the Band's antidegradation policy and implementing procedures. Until PoyMet complies with Section 105(c), the Band's antidegradation policy and implementing procedures for all pollutants in its proposed new discharges.

Narrative Standards

<u>Section 301.a.</u> Waters of the Fond du Lac Reservation shall be free from suspended and submerged solids or other substances that enter the waters as a result of human activity and that will settle in the bed of a body of water or be deposited upon the shore of that body of water to form putrescent or otherwise objectionable deposits, or that will adversely affect aquatic life. THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **30** OF **39**

The discharges from the Project will carry sulfates, mercury, and methylmercury down-stream to Reservation streams and wetlands connected to the St. Louis River. As water flow velocities decrease in the streams and wetlands, some of those contaminants will settle on the stream bottoms and in the sediment of the wetlands. Methylmercury in the sediments especially will be ingested by benthic aquatic invertebrates, then by other aquatic life that feeds on those invertebrates, then by higher trophic level aquatic life. Those contaminants will substantially harm benthic invertebrates, the higher trophic level aquatic life that feed on those invertebrates, and also be assimilated by some wetland vegetation. In turn, Band members will be prevented or con-strained from the traditional use of those contaminated fish and wildlife and plants.

<u>Section 301.n.</u> Water quantity and quality and habitat alterations that may limit the growth and propagation of, or otherwise cause or contribute to an adverse effect to wild rice and other flora and fauna of cultural importance to the Band shall be prohibited.

The discharges from the Project described above will undeniably contribute to an adverse effect on flora and fauna of cultural importance to the Band. The adverse effects upon aquatic invertebrates, fish, wetland dependent mammals, waterfowl and waterbirds and other piscivorous birds will harm those species, as explained above. Of particular cultural importance is the use of flora and fauna in ceremonies; continuing subsistence fishing in the St. Louis River and being able to consume the catch; hunting and harvesting; and the preservation of wetlands for the maintenance of traditional medicinal plants. The discharges from the Project may not necessarily outright prevent Band members from maintaining these cultural traditions, but it will inhibit them through subsistence-level consumption restrictions of aquatic species due to cumulative increases in mercury bioaccumulation.

Designated Uses

<u>Section 302.B. Wildlife.</u> All surface waters capable of providing a water supply, vegetative habitat and food, including but not limited to wild rice, and prey for the support and propagation of wildlife located within the Fond du Lac Reservation.

As described above, discharges from the Project will increase loading of sulfates, mercury and methylmercury in the St. Louis River and its riparian wetlands, as well as the streams and wetlands with direct surface water connections to the St. Louis River. Those contaminants will harm plant, fish and wildlife species that Band members use and depend upon.

<u>Section 302.C.2.</u> Warm Water Fisheries. A stream, reach, lake or impoundment where water temperature, habitat and other characteristics are suitable for support and propagation of warm water fish and other aquatic life, or serving as a spawning or nursery area for warm water fish species. Examples of warm water fish species include large mouth bass and bluegills.

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Most of the streams and creeks on the Reservation support warm water fish. The diversity of aquatic life residing in those streams and creeks, and their adjacent wetlands will be degraded by the Mine facilities discharges causing increased loadings of sulfates, mercury, and methylmercury.

<u>Section 302.C.3.</u> Subsistence Fishing (netting). That portion of the Fond du Lac Reservation necessary to provide a sufficient diet of fish in order to sustain a healthy, current, on-Reservation population, including any stream, reach, lake or impoundment where spearing, netting or bow fishing is allowed as provided under applicable Band conservation laws.

The loading of contaminants listed above in Fond du Lac Reservation streams and wetlands in turn will impair resident and transient fish species. The existing fish consumption advisories already constrain the ability of Band members to safely consume a full diet of fish. The discharges from the Project will further constrain that ability.

Numeric Standards

Appendix 1. Human Health Chronic Standard, Mercury.

As described above, there is a direct surface water connection between the Project's Mine facilities and the Fond du Lac Reservation, principally via the Embarrass and Partridge Rivers which drain to the St. Louis River. The FEIS states that the WWTF and the WWTP (which were later combined into a single facility at the Plant site) would be designed to meet Minnesota water quality-based effluent limits that are protective of the GLI 1.3 ng/L mercury standard.³⁶ In contrast, the standard as approved by the EPA for Fond du Lac Reservation waters and wetlands is half that at 0.77 ng/L. It is inconceivable that the discharged water from the Project's Mine facilities could meet that lower standard when those waters reach Reservation waters and wetlands. Regardless, there is no data or other relevant information in the FEIS or record to support that the lower standard would be met in the St. Louis River at the Reservation, and no consideration is given to methylmercury in water or other media. As such, the Project's discharges will contribute to an exceedance of the Band's numeric mercury water quality standard.

<u>Section 301(k)</u>. Existing mineral quality shall not be altered by municipal, industrial and in stream activities or other waste discharges so as to interfere with the designated uses for a water body. Since Aquatic biota in this ecoregion are known to be sensitive to the effects of elevated ionized substances (cations and anions) in the water, the specific conductance in all waters of the Reservation shall not exceed an annual average continuous exposure of 300 μ S/cm. Exceedances of this numeric condition are indicative of polluted conditions.

Based on the land and environmental impacts, discharges, and releases of pollutants, such as sulfate (an acid anion), from the Project, there will be additional increases, and variability in,

³⁶ There is *no* documentation contained in the FEIS or record to support this contention.

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conductance in the St. Louis River that will reach the Band's downstream waters. In fact, PolyMet estimates specific conductance in its discharges to range from 753-960 μ S/cm, which is more than double the Band's numeric standard of 300 μ S/cm. Levels of specific conductance persist for at least 126 miles downstream of the nearest upstream discharge site.³⁷ Accordingly, PolyMet will violate the Band's numeric standard for specific conductance.

B. The Band Wetlands Water Quality Standards.

Considering the discharges from the Project, it is expected that there will be non-compliance with the following:

Wetlands Water Quality Standards

Section 701. Designated Uses. For all wetlands, as defined by the Cowardin classification scheme, the uses to be protected include, but are not limited to—baseflow discharge, cultural opportunities, flood flow attenuation, groundwater recharge, *indigenous floral and faunal diversity and abundance*, nutrient cycling, organic carbon export/cycling, protection of down-stream water quality, recreation, resilience against climatic effects, sediment/shoreline stabili-zation, surface water storage, *wild rice*, and *water dependent wildlife* to the extent that such uses, functions, and values occur as represented by reference wetlands. (emphasis added).

As described above, it is expected that discharged waters from the Project containing elevated levels of sulfates and mercury will interact with dissolved organic matter to generate additional methylmercury that will be transported downriver to the Band's Reservation waters and wetlands, especially in the event of high flows. Methylmercury will bioaccumulate and biomagnify in fish and other aquatic life in or dependent upon the St. Louis River, streams and wetlands and impair designated uses such as subsistence fishing, warm water fish, wildlife, especially piscivorous birds and mammals such as herons, ducks, mink, river otter, bald eagle. The consumption of methylmercury contaminated foods by humans has resulted in fish consumption advisories and impairs Designated Uses for the St. Louis River and the three major streams on the Reservation as well as wetlands adjacent to those areas.

3. Section 703 Antidegredation

Tier I: For all wetlands, using the Cowardin classification scheme, there shall be no degradation of existing uses.

Tier II: Using the Cowardin classification scheme: there shall be no net loss to the water quality, functions, area, or ecological integrity of high quality lacustrine, lacustrine fringe, palustrine, riverine, and slope wetlands, unless, after satisfying applicable antidegradation provisions including avoidance, minimization, and

³⁷ Attachment 2, Ex. 7 at 13 (Tribal Cumulative Effects Analysis).

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mitigation/replacement requirements, the authorized tribe determines that allowing degradation is necessary to accommodate important social or economic development in the area in which the wetlands are located.

As described in the FEIS, the Band's April 30, 2021 Submission and above, the Project's unavoidable leakages and releases of process water, leachate, and stormwater containing inorganic mercury and methylmercury, and sulfides/sulfates will almost certainly result in degrading the ecological functions and services of the affected Fond du Lac Reservation wetlands, including existing uses, as well as the loss of their ecological integrity.

V. TREATY RIGHTS AND ENVIRONMENTAL JUSTICE IMPACTS

Under the Treaty of LaPointe of September 30, 1854 ("1854 Treaty"), 10 Stat. 1109, in exchange for ceding large portions of land in northeastern and east-central Minnesota, several member Bands of the Minnesota Chippewa Tribe, including the Fond du Lac Band, retained the right to hunt, fish, and gather in their Ceded Territory in northeastern Minnesota. *Id.* art.1. Those Band members, including members of the Fond du Lac Band, rely to this day on their Treaty rights to hunt, fish and gather within the Ceded Territory for subsistence and as an integral part of their culture. The 1854 Treaty also established a Reservation along the St. Louis River for the Fond du Lac Band as the Band's permanent homeland where Band members all have the right to hunt, fish and gather. *Id.* art. 2.

The St. Louis River watershed (called *Chi-gamii-ziibi* by the Ojibwe) is encompassed within the Ceded Territory and has been home to the Band for centuries.³⁸

Ancestors of present day Band members resided in th[e Project] area for centuries and many Band members followed traditional practices extensively until about a generation ago when the effects of mining devastated the rice beds in the Embarrass and St. Louis River watersheds and closed access to large tracts of public (USFS) land where traditional harvest and collection areas occur. Th[e] proposed Tribal Historic district encompasses complex trail system, Indian villages, trading posts, encampments for fishing, hunting, wild rice harvest and processing, sugar bush, and other traditional subsistence practices. It includes what was essentially a 'water highway' used by the Ojibwe at the time of European contact, and subsequently by Voyagers during the era of heavy fur trading. In addition, numerous medicinal plant gathering sites, Midewewin lodges, vison quest locales and other sacred places occur.³⁹

³⁸ Attachment 2, Ex. 9, Earth Economics – The Value of Nature's Benefits in the St. Louis River Watershed Report (Jun. 2015) (discussing the socio-economic value of the St. Louis Rivers and watershed to the Band).

³⁹ Attachment 2, Ex. 7, Tribal Cumulative Effects Analysis, at 8-9 (Sep. 2013).

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As discussed in the Band's April 30 Submission, the area in and around the Project is located in the Band's Ceded Territory and includes the St. Louis Watershed, which has suffered from historical negative mining impacts. Over time, the Band has seen its wild rice waters (called *manoomin* in Ojibwe) degraded and its lake sturgeon wiped out by water quality degradation and pollution. The remaining fish are now so high in mercury that the Band members cannot safely feed the fish to their children. Many of these impacts are attributable to mines upstream of the Reservation and failed enforcement of Minnesota's water quality standards on the mining industry.

Construction and operation of the Project will have a combined impact on the natural and physical environment that will significantly and adversely affect the Band. The adverse cultural, social, economic, and ecological impacts to the Band are interrelated to the adverse impacts to the natural and physical environment that will result from the Project. The additional environmental effects of the Project will be significant and will have an adverse impact on the Band that appreciably exceed or will likely appreciably exceed the effects on the general population. These impacts raise significant concerns with respect to the Band's Treaty rights and environmental justice. For example, the Project will result in a loss of Band members' ability to exercise their Treaty rights within the Project area, will result in the destruction of diverse wetlands in the Ceded Territory and have adverse impacts to the Band's Reservation, including violations of the Band's federally approved water quality standards. Both the EPA and Army Corps have a trust responsibility to protect the Band's Treaty rights and must comply with environmental justice principles.

VI. RECOMMENDATIONS

The Corps should revoke the 404 Permit because there are not adequate protective permit conditions nor corrective actions that can be imposed based on the Project, as designed and permitted, to prevent the violations of the Band's water quality requirements discussed throughout this analysis. Those violations also result in infringements on the Band's Treaty rights and violate environmental justice principles. Put simply, the Project has not been evaluated, designed, or permitted to comply with the Band's water quality requirements.

In addition, the monitoring provisions described in the FEIS and other Project permits are entirely inadequate. Monitoring of *post-development* wetland water quality is explicitly *excluded* from the 401 Certification, preventing discovery of any impacts on wetland biogeochemistry— particularly methylmercury production—during the Project's mine and processing operations. In the final 401 Certification, the MPCA ultimately requires only two monitoring locations upstream of the Project, and only three downstream (potentially impacted) sites where change might be detected. Downstream monitoring sites are only on larger channels and considerable distance from potential locations of direct operational impact such as the Embarrass River wetlands discussed previously. The specification for sampling the streams only four times annually is indefensible— detection and confirmation of systematic change above natural variability will be impossible over any reasonable time period, particularly in the absence of reference monitoring of comparable systems (Branfireun 2019; Section 2.2).

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A comprehensive monitoring program is essential, for example, to ensure that methylmercury in the environment is not increased as a result of the Project. In order for monitoring to be meaningful and used for, among other aspects, assessing performance of control measures (e.g., the capture and treatment of seepage), WWTF performance, and long-term ecological conditions, there should be robust baseline data, in this case for at least two to three years. In addition, and because the key adverse impacts will likely be to flora and fauna in the St. Louis River, its adjacent wetlands, and streams and wetlands within the Fond du Lac Reservation with surface water connections to the St. Louis River, biological monitoring of, among other things, benthic and macro-invertebrates, water birds and waterfowl, fish, and wetland dependent mammals should have been conducted to obtain a robust baseline profile. A vigorous long term monitoring plan should be an integral part of the approach to evaluating performance of controls, impacts to stream and wetland conditions, and to flora and fauna. Moreover, a comprehensive monitoring plan also should address the potential range of responses to problems that could arise during construction and operation of the Project's mine and its facilities, i.e., an adaptive management plan.

A template for monitoring is the DeBeer's Victor Mine which is located in a wetland-rich region of northern Ontario. DeBeer's implemented an extensive groundwater and surface water network of monitoring stations at nested spatial scales where dozens of surface water and shallow groundwater locations were sampled on a monthly basis for a minimum of 36 months predevelopment to establish baseline conditions, and then throughout the entire life of mine into closure. In addition to other routine water chemistry, every water sample is analyzed for filtered and unfiltered total mercury and methylmercury using ultra-trace techniques. 500-700 smallbodied fish (young of year) are collected each year late in the open water season and analyzed for methylmercury content as biosentinels under provincial regulation; the mercury in these biota reflect mercury exposure conditions in that year only, permitting annual assessments of change both prior to, and during Mine operations. This is in addition to a large food fish monitoring program. Reference locations are also sampled for all parameters indicated above in order to deconvolve mine-related impacts from natural year to year variability. These data are reported to the provincial regulator annually and are in the public record. An excellent illustration of a biosentinel program in Minnesota was undertaken by Jeremiason et al. (2016) where concentrations of methylmercury in dragonfly larvae reflected surface water methylmercury in a high flow year. A failure to require biological monitoring of methylmercury is a regulatory omission that prevents detection of, or protection from, methylmercury impacts of the project on the environment and on human health.

In the absence of robust baseline data, operational upsets at the Project (such upsets are unavoidable) cannot be anticipated, evaluated correctly, and addressed and resolved efficiently. Due to the lack of robust baseline data, a comprehensive monitoring program, and a well-designed adaptive management plan, operational upsets will result in periodic discharges from the Project that reach Reservation water and wetlands and do not comply with the Band's Water and Wetland Quality Standards. That circumstance will result in long-term harm to Fond du Lac Reservation

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waters and wetlands, the flora and fauna that depend upon those resources, and the Band's members.

ADDITIONAL REFERENCES REVIEWED

Alan H. Stern, A Review of the Studies of the Cardiovascular Health Effects of Methylmercury with Consideration of their Suitability for Risk Assessment, 98 Envtl. Res. 133 (2005).

BARR Engineering (2018) Technical Memorandum: Potential for Mercury Loading to the St. Louis River Associated with the Construction Stormwater General Permit. November 9, 2018.

Berndt, M, Bavin T (2009) Sulfate and Mercury Chemistry of the St. Louis River in Northeastern Minnesota A Report to the Minerals Coordinating Committee. Minnesota Dept. of Natural Resources. 81 pp.

Berndt ME, Rutelonis W, Regan CP (2016) A comparison of results from a hydrologic transport model (HSPF) with distributions of sulfate and mercury in a mine-impacted watershed in north-eastern Minnesota, Journal of Environmental Management 181 (2016) 74-79.

Bishop, K, I Buffam, M. Erlandsson, J. Folster, H. Laudon, J. Seibert, Temnerud, J (2008). Aqua Incognita: the unknown headwaters, Hydrological Processes, 22, 1239-1242.

Branfireun BA, Fowle DA, Krabbenhoft DP (2009) Reservoir Water Level Fluctuation and Methylmercury Cycling - Final Project Report. Minnesota Power St. Louis River Hydroelectric Sediment Mercury Research Project. 78 pp.

Branfireun, B.A. Final Expert Review of the NorthMet Mining Project and Land Exchange Supplemental Draft Environmental Impact Statement, March 10, 2014 and Referenced Materials.

Branfireun, B.A. Final Expert Review of the NorthMet Mining Project and Land Exchange Final Environmental Impact Statement, Dec. 12, 2015 and Referenced Materials.

Branfireun, B.A. Final Expert Review of the Minnesota Pollution Control Agency Clean Water Act Section 401 Certification for the NorthMet Project, January 20, 2019 and Referenced Materials.

Brigham, ME, VanderMeulen, DD, Eagles-Smith CA, Krabbenhoft DP, Maki RP, DeWild JF (2021) Long-Term Trends in Regional Wet Mercury Deposition and Lacustrine Mercury Concentrations in Four Lakes in Voyageurs National Park, Applied Sciences, 11(4), 1879; https://doi.org/10.3390/app11041879.

Christopherson, N, RP Hooper (1992) Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. Water Resources Research, 28(1), 99-107.

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **37** OF **39**

CD Knightes, EM Sunderland, MC Barber, JM Johnston, RB Ambrose Jr, Environmental Toxicology and Chemistry: An International Journal 28 (4), 881-893.

Coleman Wasik, J.K., C.P.J. Mitchell, D.R. Engstrom, E.B. Swain, B. A. Monson, S.J. Balogh, J.D. Jeremiason, B. A. Branfireun, SL Eggert, R.K. Kolka, J.E. Almendinger (2012) Methylmercury Declines in a Boreal Peatland When Experimental Sulfate Deposition Decreases, Environ. Sci. Technol. 46, 6663–6671.

Coleman Wasik, J.K., D.R. Engstrom, C.P.J. Mitchell, E.B. Swain, B. A. Monson, S.J. Balogh, J.D. Jeremiason, B. A. Branfireun, R.K. Kolka, J.E. Almendinger (2015) Hydrologic fluctuations and sulfate regeneration increase methylmercury in an experimental peatland, Journal of Geophysical Research – Biogeosciences, 120: 10.1002/2015JG00299

Debes, F., Weihe, P., Grandjean, P., 2016. Cognitive deficits at age 22 years associated with prenatal exposure to methylmercury. Cortex 74, 358–369. https://doi.org/10.1016/j.cortex.2015.05.017.

Depew, D. C.; Basu, N.; Burgess, N. M.; Campbell, L. M.; Devlin, E. W.; Drevnick, P. E.; Hamerschmidt, C. R.; Murphy, C. A.; Sandheinrich, M. B.; Wiener, J. G. Toxicity of dietary methylmercury to fish: derivation of ecologically meaningful threshold concentrations. Environ. Toxicol. Chem. 2012, 31 (7), 1536–1547.

Graham, A.M., Cameron-Burr, K.T., Hajic, H.A., Lee, C., Msekela, D., Gilmour, C.C., 2017. Sulfurization of Dissolved Organic Matter Increases Hg-Sulfide-Dissolved Organic Matter Bioavailability to a Hg-Methylating Bacterium. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.7b02781.

Fletcher, A., Christin, Z. 2015. The Value of Nature's Benefits in the St. Louis River Watershed. Earth Economics, Tacoma, WA.

Janssen SE, JC Hoffman, RF Lepak, DP. Krabbenhoft, D Walters, CA. Eagles-Smith, G Peterson, JM. Ogorek, JF. DeWild, A Cotter, M Pearson, MT. Tate, RB. Yeardley, MA. Mills (2021) Examining historical mercury sources in the Saint Louis River estuary: How legacy contamination influences biological mercury levels in Great Lakes coastal regions. Science of the Total Environment. doi.org/10.1016/j.scitotenv.2021.146284.

Jeremiason, JD, Engstrom, DR, Swain, EB, et al. (2006) Sulfate addition increases methylmercury production in an experimental wetland ENVIRONMENTAL SCIENCE & TECHNOLOGY 40(12) 3800-3806, 2006.

Jyrki K. Virtanen et al., Mercury, Fish Oils, and Risk of Acute Coronary Events and Cardiovascular Disease, Coronary Heart Disease, and All-Cause Mortality in Men in Eastern Finland, 25 Arteriosclerosis, Thrombosis, & Vascular Biology 228, 232 (2005). THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **38** OF **39**

Karagas et al., Evidence on the Human Health Effects of Low-level Methylmercury Exposure, 120 Envtl. Health Persp. 799, 806 (2012).

Kathryn R. Mahaffey, Robert P. Clickner, Rebecca A. Jeffries Environ Health Perspect. 2009 Jan; 117(1): 47–53. Published online 2008 Aug 25. doi: 10.1289/ehp.11674. Adult Women's Blood Mercury Concentrations Vary Regionally in the United States: Association with Patterns of Fish Consumption (NHANES 1999–2004). https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2627864/.

Klaminder J, Bindler R, Laudon H, Bishop K, Emteryd O, Renberg I. 2006. Flux rates of atmospheric lead pollution within soils from a small catchment in northern Sweden and their implication for future stream water quality. Environmental Science and Technology 40(15): 4639–4645. DOI: 10.1021/es0520666.

Klapstein, SJ, SE Ziegler, NJ O'Driscoll (2018). Methylmercury photodemethylation is inhibited in lakes with high dissolved organic matter. Environmental Pollution, 232, 392-401.

Osterwalder, S., Bishop K., Alewell, C., et al. Mercury evasion from a boreal peatland shortens the timeline for recovery from legacy solution. Sci Rep. 2017:7(1). Published 11/22/2017.

Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter—a review. Chemosphere, 55(3), 319-331.

Reed C. Harris, John W. M. Rudd, Marc Amyot, Christopher L. Babiarz, Ken G. Beaty, Paul J. Blanchfield, R.A. Bodaly, Brian A. Branfireun, Cynthia C. Gilmour, Jennifer A. Graydon, Andrew Heyes, Holger Hintelmann, James P. Hurley, Carol A. Kelly, David P. Krabbenhoft, Steve E. Lindberg, Robert P. Mason, Michael J. Paterson, Cheryl L. Podemski, Art Robinson, Ken A. Sandilands, George R. Southworth, Vincent L. St. Louis, Michael T. Tate, Proceedings of the National Academy of Sciences Oct 2007, 104 (42) 16586-16591; DOI: 10.1073/pnas.0704186104

Price, J.S. Evaluation of the Impact of the Proposed NorthMet Mine on Local Wetlands, July 2017, with attached articles.

Schartup, A.T., Thackray, C.P., Qureshi, A. *et al.* Climate change and overfishing increase neurotoxicant in marine predators. *Nature* 572, 648–650 (2019). <u>https://doi.org/10.1038/s41586-019-1468-9</u>.

Schartup, A. T. et al. A model for methylmercury uptake and trophic transfer by marine plankton. Environ. Sci. Technol. 52, 654–662 (2018).

Skyllberg, U. (2008) Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and

THE FOND DU LAC BAND OF LAKE SUPERIOR CHIPPEWA'S CLEAN WATER ACT SECTION 401(A)(2) "WILL AFFECT" ANALYSIS AUGUST 3, 2021 PAGE **39** OF **39**

implications for MeHg net production. JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, G00C03, doi:10.1029/2008JG000745.

Temnerud, J, J. Folster, I Buffam, H. Laudon, M. Erlandsson, K. Bishop (2010). Can the distribution of headwater stream chemistry be predicted from downstream observatsions? Hydrological Processes, 24, 2269-2276.

T.W. Clarkson, J.B. Vyas, N. Ballatori, 2007. Mechanisms of mercury disposition in the body. 50(10): 757-764.

Van Oostdam, J., Donaldson, S.G., Feeley, M., Arnold, D., Ayotte, P., Bondy, G., Kalhok, S., 2005. Human health implications of environmental contaminants in Arctic Canada: a review. Sci. Total Environ. 351–352, 165–246. https://doi.org/10.1016/j. scitotenv.2005.03.034.

Vincent L. St. Louis, John W. M. Rudd, Carol A. Kelly, Ken G. Beaty, Nicholas S. Bloom, and Robert J. Flett. May, 1994. Importance of Wetlands as Sources of Methyl Mercury to Boreal Forest Ecosystems. Canadian Journal of Fisheries and Aquatic Sciences.

Wiener, JG, Knights, BC, Sandheinrich, MB, et al. (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors, ENVIRONMENTAL SCIENCE & TECHNOLOGY 40(20) 6261-6268.

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 10

(EPA, Clean Water Act Section 401(a)(2) Evaluation and Recommendations with respect to the Fond du Lac Band's Objection to the Proposed Clean Water Act Section 404 Permit for the NorthMet Mine Project, April 29, 2022)



Clean Water Act Section 401(a)(2) Evaluation and Recommendations with respect to the Fond du Lac Band's Objection to the Proposed Clean Water Act Section 404 Permit for the NorthMet Mine Project

PREPARED BY U.S. ENVIRONMENTAL PROTECTION AGENCY REGION 5

APRIL 29, 2022

Abstract

Pursuant to Clean Water Act (CWA) Section 401(a)(2), 33 U.S.C. § 1341(a)(2), EPA Region 5 prepared this evaluation and recommendations with respect to the objection raised by the Fond du Lac Band of Lake Superior Chippewa to the U.S. Army Corps of Engineers' (Corps') issuance of a CWA Section 404 permit for the proposed PolyMet NorthMet project. The Band submitted its "will affect" determination, objection letter, and hearing request to EPA and the Corps on August 3, 2021 (Band's Objection). The Corps scheduled a public hearing on the Band's Objection for May 3-5, 2022, at which EPA's evaluation and recommendations will be submitted. In developing EPA's evaluation and recommendations with respect to the Band's Objection and pursuant to CWA Section 401(a)(2), EPA reviewed the Band's Objection and other supporting and relevant information available to EPA. To further inform EPA's evaluation and recommendations, EPA requested and obtained two scientific reviews from EPA's Office of Research and Development.

In EPA's evaluation of the Band's Objection to the CWA Section 404 permit based on projected exceedances of its water quality requirements for mercury, EPA considered projected discharges of mercury resulting from the NorthMet project's CWA Section 404 permitted activities, the potential for mercury discharges associated with Minnesota Pollution Control Agency's (MPCA's) CWA Section 402 discharge permits for construction stormwater and process wastewater, and the extent to which the MPCA's CWA Section 401 water quality certification for the CWA Section 404 permit would prohibit or limit mercury discharges. The available data and analyses supporting the CWA Section 404 permit and CWA Section 401 certification are insufficient to fully evaluate the mercury impacts in terms of area of wetlands affected and effects on the Band's water quality. Based on EPA's review of the information, EPA's evaluation is that the CWA Section 404 permit and MPCA's CWA Section 401 certification lack conditions sufficient to protect from mercury mobilization, methylation, and export at levels that would exceed the Band's water quality requirements. In EPA's evaluation of the Band's Objection to the CWA Section 404 permit based on projected exceedances of its water quality requirements for specific conductance, EPA considered that the CWA Section 404 application and Corps' suspended CWA Section 404 permit, as proposed, would result in activities that contribute additional mineral loadings to the St. Louis River and decrease the specific conductance dilution capacity currently provided by the existing, undisturbed forested wetland mine site. The available data and analyses supporting the CWA Section 404 permit and CWA Section 401 certification do not provide sufficient information on the extent to which the cumulative mineral loadings will contribute to specific conductance downstream of the NorthMet project. Further, there are no corrective actions specified in the permits that would reverse trends showing that specific conductance is increasing. Even relatively small increases in specific conductance loading-and/or decreases in dilution capacity-would likely result in violations of the Band's water quality requirements pertaining to specific conductance and antidegradation.

Accordingly, EPA recommends that the Corps not reinstate the suspended CWA Section 404 permit for the NorthMet project, as currently proposed. Given uncertainties regarding pollutant discharges from permitted activities, in addition to the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are

unaccounted for in the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities. EPA's recommendations do not foreclose any future modifications to the permit application or the NorthMet project design. Any future modifications should include meaningful involvement of the Band and Minnesota to ensure compliance with both tribal and state water quality requirements.

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I. Executive Summary

Pursuant to Clean Water Act (CWA) Section 401(a)(2), 33 U.S.C. § 1341(a)(2), EPA Region 5 prepared this evaluation and recommendations with respect to the objection raised by the Fond du Lac Band of Lake Superior Chippewa (Fond du Lac Band or Band) to the U.S. Army Corps of Engineers' (Corps) issuance of a CWA Section 404 permit for the proposed PolyMet Mining, Inc. (PolyMet) NorthMet mine, a mine and processing plant to extract copper, nickel, and precious metals, including platinum, palladium, gold, and silver from the NorthMet Deposit in northeastern Minnesota. The Band submitted its "will affect" determination, objection letter, and hearing request to EPA and the Corps on August 3, 2021 (Fond du Lac Objection or Band's Objection). The Corps scheduled a public hearing on the Band's Objection for May 3-5, 2022, at which this evaluation and recommendations will be submitted. PolyMet Mining, Inc. has submitted a CWA Section 404 permit application for its NorthMet mine project in northeastern Minnesota dredge and fill operations with the potential to impact approximately 928 acres of wetlands either directly or through fragmentation and other associated dredge and fill operations related to the mine. The proposed NorthMet project ("NorthMet project") includes a new open pit mine, temporary and permanent waste rock disposal areas, recommissioning of an existing processing plant and tailings basin, and refurbishment of an existing seven-mile railroad and utilities corridor between the mine and plant sites. Pursuant to CWA Section 401(a)(1), PolyMet received certification from the Minnesota Pollution Control Agency (MPCA) that the discharge from "the construction or operation of facilities" requiring a CWA Section 404 permit "will comply with the applicable provisions of [the CWA]" on December 20, 2018.¹ The Band contends that secondary impacts of the dredge and fill activities authorized by the CWA Section 404 permit include impacts to the Band's downstream water quality, as well as impacts to the hydrology of an unspecified and as yet unknown quantity of adjacent wetlands and streams.²

Basis for EPA's Evaluation and Recommendations:

In developing EPA's evaluation and recommendations with respect to the Band's Objection and pursuant to CWA Section 401(a)(2), EPA reviewed the Band's CWA Section 401(a)(2) notification of objection, hearing request, and "will affect" determination (which together constitute the Band's Objection), as well as other supporting and relevant information supplied by the Band.

In addition to reviewing information supplied by the Band, EPA also reviewed other pertinent information, including PolyMet's CWA Section 404 application to the Corps, MPCA's CWA Section 401 certification with respect to the CWA Section 404 permit, and other supporting and relevant information supplied by PolyMet and Minnesota. EPA also considered the Corps'

¹ MPCA, Final PolyMet 401 Certification, December 20, 2018, [hereafter MPCA's CWA Section 401 certification] <u>https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51hh.pdf</u> (last visited April 26, 2022); Background on the certification request is found in MPCA's Clean Water Act Section 401 Water Quality Certification Program Fact Sheet, <u>https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51jj.pdf</u> (last visited April 26, 2022). ² Fond du Lac Notification of Objection to NorthMet project, U.S. Army Corps Proposed Permit MVP-1999-05528Record of Decision pertaining to the Final Environmental Impact Statement (FEIS)³ and the CWA Section 404 permit issued and suspended by the Corps. Where other permits (e.g., CWA Section 402 permits) are referenced in the CWA Section 404 and CWA Section 401 documentation, EPA reviewed the relevant permitting records pertaining to mercury and specific conductance. See Appendix A *References* for a list of key information sources that EPA reviewed for this evaluation and recommendations.⁴

To further inform EPA's evaluation and recommendations, EPA requested and obtained a scientific review from EPA Office of Research and Development, Center for Computational Toxicology and Exposure, Great Lakes Toxicology and Ecology Division (ORD GLTED) of potential impacts from mercury as described by the Band in its objection. To evaluate potential impacts regarding the Band's Objection regarding specific conductance, EPA requested and obtained a scientific review from EPA's ORD, Center for Environmental Measurement and Modeling, Watershed and Ecosystem Characterization Division (ORD CEMM-WEDC).

Through EPA's evaluation of the Band's Objection, EPA identified several points of uncertainty and reasonably foreseeable discharges of mercury and dissolved ions contributing to specific conductance with respect to the NorthMet project and the CWA Section 404 permitted activities. These include significant uncertainty regarding the full acreage of secondary impacts to wetlands from the anticipated drawdown of groundwater from mine construction and operation. EPA also notes that there is uncertainty in the mercury present in and the fate and transport of such mercury from wetlands subject to secondary impacts from the anticipated drawdown of groundwater from mine construction and operation and uncertainty regarding the extent to which mercury methylation would increase in the St. Louis River watershed due to direct and secondary impacts to wetlands from mine construction and operation. EPA further identified uncertainty regarding the quantity of total mercury and dissolved ions (contributing to elevated specific conductance) discharged during mine construction, the quantity of total mercury and dissolved ions (contributing to elevated specific conductance) discharged via seepage, and unknown reduction in dilution capacity contributing to elevated specific conductance.

Summary of EPA's Evaluation regarding mercury discharges:

In EPA's evaluation of the Band's Objection to the CWA Section 404 permit based on projected exceedances of its water quality requirements for mercury, EPA considered projected discharges of mercury resulting from the NorthMet project's CWA Section 404 permitted activities, the potential for mercury discharges associated with MPCA's CWA Section 402 discharge permits for construction stormwater and process wastewater, and the extent to which MPCA's CWA

³ Department of the Army, St. Paul District Corps of Engineers Record of Decision for the Northmet Mine Project, <u>https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/NorthMet%20FEIS%20Record%20of%20De</u> <u>cision%20-%20Corps%20of%20Engineers.pdf?ver=2019-03-22-084206-570</u>, [hereafter Corps' ROD] (last visited April 27, 2022).

⁴ Although this list represents the documents and sources of information specifically referenced in or reviewed for this document, it may not be an exhaustive list of the information before EPA and is not necessarily the same list of documents that would represent EPA's administrative record in litigation.

Section 401 water quality certification for the CWA Section 404 permit would prohibit or limit mercury discharges.

The Band's waters downstream of the CWA Section 404 permitted activities are already impaired due to excess mercury. In addition, the documentation prepared regarding the CWA Section 404 permit application; suspended CWA Section 404 permit and MPCA's CWA Section 402 permits (permit suite); as well as MPCA's CWA Section 401 certification, acknowledge the potential for hydrologic disturbance of the wetlands surrounding the NorthMet project to lead to the loss of wetland value and function, including the sequestration of mercury. Significantly, Corps', PolyMet's, and MPCA's analyses do not encompass wetlands' function as environmental reservoirs of mercury, the impacts of hydrologic modifications of those wetlands due to CWA Section 404 permitted dredge and fill activities on those mercury reservoirs, or the predictable impacts of mercury release through hydrologic alteration on the Band's already mercury-impaired waters.

The efforts of PolyMet to quantify the scope of hydrologic impacts resulting from the NorthMet project are cursory and insufficient to assess the full impacts of the permitted activities or to provide a basis to properly condition the permit. Understanding the scope of the anticipated impacts due to changes to wetland hydrologic regimes resulting from the CWA Section 404 permitted activities is essential to determining an accurate estimate of the quantities of mercury that may be subject to mercury methylation, mobilization, and export downstream to the Band's already impaired waters. The available data and analyses supporting the CWA Section 404 permit and CWA Section 401 certification are insufficient to fully evaluate the mercury impacts in terms of area of wetlands affected and effects on the Band's water quality. Based on EPA's review of the information, EPA's evaluation is that that the CWA Section 404 permit and MPCA's CWA Section 401 certification lack conditions sufficient to protect from mercury mobilization, methylation, and export at levels that would exceed the Band's water quality requirements. Further, given these significant uncertainties, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for mercury for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

Summary of EPA's Evaluation regarding Specific Conductance:

Based on EPA's review of available data on specific conductance, the CWA Section 404 application and Corps' suspended CWA Section 404 permit, as proposed, would result in activities that would contribute additional mineral loadings to the St. Louis River and decrease the specific conductance dilution capacity currently provided by the existing, undisturbed forested wetland mine site. It is uncertain what the cumulative mineral loadings would be that contribute to specific conductance downstream of the NorthMet project, and there are no corrective actions specified in the permits that would reverse trends showing that specific conductance is increasing. However, any additional mineral loadings and loss of dilution capacity would likely increase specific conductance in the St. Louis River watershed. Based on the information EPA reviewed, even relatively small increases in specific conductance loading–and/or decreases in dilution capacity–would result in violations of the Band's water quality

requirements pertaining to specific conductance and antidegradation. EPA also notes that the CWA Section 404 permit application, MPCA's CWA Section 401 certification, Corps' ROD, and permit suite all predate adoption of the Band's numeric specific conductance criterion and therefore do not consider the potential for violations of the Band's water quality requirements for specific conductance.⁵ The CWA Section 404 permit and CWA Section 401 certification do not include conditions that would ensure compliance with the Band's water quality requirements. Based on this review, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's specific conductance for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

Summary of EPA's Recommendations:

EPA recommends the Corps not reinstate the suspended CWA Section 404 permit for the NorthMet project, as currently proposed and given current project design and discharges outside the CWA Section 404 permitted activities. The Band's waters downstream of the proposed NorthMet project are already impaired due to an excess of mercury and elevated specific conductance. EPA's evaluation has identified both significant uncertainties related to the extent of the potential discharge and release of mercury and the potential for additional mineral loadings contributing to elevated specific conductance from the CWA Section 404 permitted activities. These uncertainties include the scale of wetland dewatering that would contribute methylmercury to the system, net loading from all the discharges of mercury and mineral loadings in the watershed, and loss of dilution capacity that will contribute to elevated specific conductance. Given these uncertainties, in addition to the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are unaccounted for in the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities. Accordingly, EPA recommends that the Corps not reinstate the suspended permit, as currently proposed. EPA's recommendations do not foreclose any future modifications to the permit application or the NorthMet project design. Any future modifications should include meaningful involvement of the Band and Minnesota to ensure compliance with both tribal and state water quality requirements.

⁵ U.S. EPA, *EPA's Review of Revisions to the Fond du Lac Band of Lake Superior Chippewa's Water Quality Standards Under Section 303(c) of the Clean Water Act*, WQSTS # TR2018-1280, http://www.fdlrez.com/rm/downloads/WQSEPADecisionDocument10-5-2020.pdf (last visited April 15, 2022).

II. Background

A. NorthMet Project and Project Area Description

PolyMet has proposed developing a mine and processing plant to extract copper, nickel, and precious metals, including platinum, palladium, gold, and silver from the NorthMet Deposit in northeastern Minnesota. The proposed NorthMet project site is located about six miles south of Babbitt, Minnesota and one mile south of the existing Northshore (iron ore) Mine. Processing of the ore would take place at the former LTV taconite plant near Hoyt Lakes, Minnesota. The proposed NorthMet project includes a new open pit mine, temporary and permanent waste rock disposal areas, recommissioning of an existing processing plant and tailings basin, and refurbishment of an existing seven-mile railroad and utilities corridor between the mine and plant sites.⁶ The NorthMet deposit site totals approximately 4,300 acres and the former LTV facility proposed for reuse by PolyMet (Plant Site), including the existing tailings basin and a wastewater treatment plant, covers approximately 12,400 acres.⁷

The NorthMet project is located within the Embarrass River and Partridge River Watersheds, both of which are within the headwaters of the St. Louis River and are tributaries to the St. Louis River, which flows into Lake Superior. The NorthMet project site is upstream of both Wisconsin and the Fond du Lac Reservation by way of the St. Louis River and its tributaries. While the Plant Site, including the existing tailings basin have been disturbed by the former LTV taconite plant, the NorthMet deposit site (mine pit area) consists largely of currently undisturbed forested and bog wetlands and forested uplands.

The NorthMet project requires numerous state and federal permits, including a Corps' CWA Section 404 permit, and state CWA Section 402 permits, as well as a state-issued CWA Section 401 water quality certification for the CWA Section 404 permit. For more information on the history of the NorthMet project's permitting, please see Section C.2 of this Background.

The CWA Section 404 permit would authorize impacts to 928.16 acres of wetlands directly or through fragmentation and other associated dredge and fill operations related to the mine. The CWA Section 404 permit also recognizes the potential for secondary impacts to an unknown quantity of wetlands near the NorthMet project due to groundwater drawdown at the site and accounts for this with permit conditions requiring wetland monitoring, adaptive management, and potential compensatory mitigation for those impacts, if and when they occur.⁸

⁷ PolyMet Mining Corp. Annual Information Form for the year ended December 31, 2021, Submittal to the Securities and Exchange Commission, March 17, 2022,

https://www.sec.gov/Archives/edgar/data/0000866028/000106299322008047/exhibit99-1.htm (last visited April 19, 2022).

⁸ U.S. Army Corps of Engineers, PolyMet Mining, Inc. Permit No. MVP-1999-05528-TJH, <u>https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/NorthMet%20Permit%20-</u> <u>%20Corps%20of%20Engineers.pdf?ver=2019-03-22-091358-997</u> (last visited April 27, 2022). The Corps subsequently suspended this permit. *See* Letter from Colonel Karl D. Jansen, District Engineer, U.S. Army Corps of Engineers, to Christie Kearney, PolyMet Mining, Inc., March 17, 2021,

⁶ MPCA, PolyMet's NorthMet mining project, <u>https://www.pca.state.mn.us/regulations/polymets-northmet-mining-project</u> (last visited April 8, 2022).

B. Neighboring Jurisdictions

The NorthMet project site is located in the headwaters of the St. Louis River watershed, and EPA identified the Band and the State of Wisconsin as neighboring jurisdictions whose water quality may be affected by discharges from the NorthMet project's CWA Section 404 permitted activity. This permitted activity includes discharges to the Partridge River and the Embarrass River watersheds, both of which are tributaries to the St. Louis River. The Fond du Lac Band is approximately 100 miles downstream from the NorthMet project site and the St. Louis River forms a portion of the Band's boundary.⁹ Wisconsin is approximately 140 miles downstream from the NorthMet project site. Both the Band and Wisconsin have water quality requirements that apply in the St. Louis River and thus have waters potentially impacted by this project's CWA Section 404 permitted activity, including federally approved water quality standards.

The Band received "Treatment in a similar manner as State" and has authority under the CWA to set water quality standards for the Band's reservation. The water quality standards adopted by the Band, and approved by EPA, protect the Band's designated uses, including protection of aquatic dependent resources and the protection of culturally important designated uses. In its objection, the Band asserts that discharges from the CWA Section 404 permitted activities will adversely affect the Band's water quality. The Band states that the St. Louis River Watershed has unique importance to the Band because the Band retains the right to hunt, fish, and gather within the territory ceded under the Treaty of 1854, 10 Stat. 1109, which includes the St. Louis River Watershed.¹⁰ The Band also asserts that the NorthMet project will adversely impact the Band culturally, socially, economically, and ecologically, including threatening the Band's treaty rights to use and harvest resources. The Band emphasizes that the protection of its downstream waters is integral to protection of the Chippewa-Ojibwe tribes' treaty rights to water-dependent resources.¹¹

C. CWA Section 401(a)(2)

1. Description of the 401(a)(2) Process

CWA Section 401(a)(2) establishes a process for "neighboring jurisdictions" to participate in the federal licensing or permitting process in circumstances where EPA has determined that a discharge from an activity subject to CWA Section 401 certification from another jurisdiction

¹¹ See also, U.S. EPA, Application of Region 5's CWA 401(a)(2) "May Affect" Screening Analysis for PolyMet's NorthMet Mining Project, June 4, 2021, https://www.epa.gov/sites/default/files/2021-

https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/1999-05528-TJH 20210317 Polymet Suspension Letter.pdf?ver=MRtiztWwBXu8eHe208VOzw%3d%3d (last visited April 8,

^{2022).}

⁹ Treaty with the Chippewa, 1854, <u>https://glifwc.org/TreatyRights/TreatyChippewa09301854Web.pdf</u> (last visited March 28, 2022); Fond du Lac Objection at 33-34.

¹⁰ Fond du Lac Notification of Objection to NorthMet project, U.S. Army Corps Proposed Permit MVP-1999-05528-TJH, August 3, 2021, <u>https://www.epa.gov/mn/documents-submitted-epa-fond-du-lac-band</u>, Section V, Paragraphs 1-4, pp. 33-34 [hereafter Fond du Lac Objection]., (last visited April 28, 2022).

<u>06/documents/polymet-401a2-analysis-document-20210604-15pp.pdf</u> [hereafter EPA Screening Analysis]. (last visited April 28, 2022).

"may affect" their water quality. Neighboring jurisdictions include states and tribes that have received "treatment in a similar manner as a state." See 33 U.S.C. § 1377(e).

To initiate the CWA Section 401(a)(2) process, a federal licensing or permitting agency must "immediately" notify EPA when it receives a license or permit application and a CWA Section 401 certification. 33 U.S.C. § 1341(a)(2). EPA then has 30 days from the date EPA receives that notification to determine whether a discharge from the licensed or permitted activity may affect the water quality of a neighboring jurisdiction and, if so, to notify that neighboring jurisdiction, the licensing or permitting agency, and the project applicant. *Id*.

After receiving notice from EPA, the neighboring jurisdiction has 60 days to determine whether the discharge "will affect" its water quality so as to violate its water quality requirements, and, if so, object in writing to the issuance of the license or permit and request that the licensing or permitting agency conduct a hearing on its objections. *Id*. When the licensing or permitting agency conducts a hearing under CWA Section 401(a)(2), EPA must submit to the licensing or permitting agency an evaluation and recommendations regarding the objections of the neighboring jurisdiction. *Id*. In turn, CWA Section 401(a)(2) requires the licensing or permitting agency to condition the relevant license or permit "as may be necessary to insure compliance with applicable water quality requirements," based upon the recommendations of the neighboring jurisdiction and EPA, and any additional evidence presented at the hearing. If "the imposition of conditions cannot insure such compliance," the licensing or permitting agency shall not issue the license or permit.

2. History of this Action

In this case, EPA received notice from the Corps of PolyMet's CWA Section 404 permit application and MPCA's CWA Section 401 certification on December 20, 2018.¹² At that time, EPA did not notify other jurisdictions, including the Band, pursuant to CWA Section 401(a)(2) within 30 days of receipt of the Corps' notification. The Corps then issued the CWA Section 404 permit to PolyMet on March 22, 2019. The Band sued EPA and the Corps regarding, among other things, the lack of notice from EPA under CWA Section 401(a)(2). In its Order of February 16, 2021, the U.S. District Court for the District of Minnesota ruled that EPA had a non-discretionary duty to make a "may affect" determination pursuant to CWA Section 401(a)(2) in this matter.¹³ EPA voluntarily sought remand to reconsider whether to provide notice to the Band under CWA Section 401(a)(2). On March 8, 2021, the District Court granted EPA's request.¹⁴

¹² U.S. EPA, EPA in Minnesota, PolyMet NorthMet Mine, EPA CWA 401(a)(2) "May Affect" Notification for PolyMet's NorthMet Mine, <u>https://www.epa.gov/sites/default/files/2021-06/documents/fond-du-lac-polymet-section-401a2-letter-20210604-2pp.pdf</u> (last visited April 15, 2022).

¹³ Fond du Lac Band of Lake Superior Chippewa v. EPA, 519 F.Supp.3d 549, 567 (D. Minn. 2021).

¹⁴ Fond du Lac Band of Lake Superior Chippewa v. EPA, No. 19-cv-2489-PJS-LIB, slip op. at 2 (D. Minn., March 8, 2021).

In response to a March 4, 2021 letter from EPA,¹⁵ the Corps suspended the PolyMet CWA Section 404 permit on March 17, 2021 to allow for EPA to complete EPA's CWA Section 401(a)(2) review. EPA completed EPA's review under CWA Section 401(a)(2) and made a "may affect" determination and notified both the Band and Wisconsin on June 4, 2021.

On August 2, 2021, Wisconsin notified EPA and the Corps that it did not object to the issuance of the CWA Section 404 permit.¹⁶ On August 3, 2021, the Band notified EPA and the Corps that discharges from the NorthMet project would affect the quality of the Band's waters so as to violate water quality requirements and that the Band objected to issuance of the permit and requested that the Corps hold a public hearing in accordance with CWA Section 401(a)(2).¹⁷

The Band's Objection includes an analysis of potential water quality effects from the proposed NorthMet project, including those potential effects associated with the CWA Section 404 permitted activities, and concludes that the NorthMet project, as proposed, would violate the Band's water quality requirements for mercury and specific conductance, specifically resulting in irreparable injury to the Band's water quality and rights-protected aquatic-dependent resources, as well as disproportionate environmental justice-based injuries to the Band, its population, its water quality, and its aquatic-dependent resources.

3. EPA's Approach to this Evaluation and Recommendations

In developing this evaluation and recommendations with respect to the Band's Objection, EPA reviewed the Band's Objection, documentation provided by the Band with its objection (including its "will affect" determination), as well as relevant documents from the permitting record for the permit suite and MPCA's CWA Section 401 certification. Where other permits (e.g., CWA Section 402 permits) are referenced in the CWA Section 404 and CWA Section 401 documentation, EPA reviewed the relevant permitting records pertaining to mercury and specific conductance. See Appendix A *References* for a list of key information sources EPA reviewed for this evaluation and recommendations.¹⁸

EPA requested the technical support of mercury and specific conductance subject matter experts in EPA's ORD to evaluate potential downstream project impacts for both mercury and specific conductance. As a result of its analyses, ORD produced two memoranda documenting its review: "Request for Scientific Support Regarding Potential Downstream Impacts of the NorthMet Mine" ("ORD's Mercury Memo"), which is a scientific analysis of the potential mercury impacts

¹⁵ Letter from Colonel Karl D. Jansen, District Engineer, U.S. Army Corps of Engineers, to Christie Kearney, PolyMet Mining, Inc., March 17, 2021, <u>https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/1999-05528-TJH_20210317_Polymet_Suspension_Letter.pdf?ver=MRtiztWwBXu8eHe208VOzw%3d%3d</u> (last visited April 8, 2022).

¹⁶ Letter from David R. Siebert, Administrator, External Services Division, Wisconsin Department of Natural Resources, to Tera Fong and Chad Konickson, Chief, Regulatory Branch, Corps, August 2, 2022.
¹⁷ Fond du Lac Objection.

¹⁸ Although this list represents the documents and sources of information specifically referenced in or reviewed for this document, it may not be an exhaustive list of the information before EPA and is not necessarily the same list of documents that would represent EPA's administrative record in litigation.

that would result from the NorthMet project; and "Assessment of effects of increased ion concentrations in the St. Louis River Watershed with special attention to potential mining influence and the jurisdiction of the Fond du Lac Band of Lake Superior Chippewa" (ORD's Specific Conductance Memo), which is a scientific analysis of the potential impacts from increased specific conductance that would result from the proposed project. These memoranda are attached at Appendices B and C.

To inform EPA's evaluation of the Band's Objection, EPA reviewed the baseline water quality of the affected watershed and the impacts expected to result from the NorthMet project's discharges from permitted activities if the following permits remain as currently drafted: (1) The CWA Section 404 permit application and Corps suspended permit¹⁹; (2) MPCA's CWA Section 401 certification²⁰ of the CWA Section 404 permit; (3) MPCA's CWA Section 402 NPDES discharge permit for the NorthMet project²¹; and (4) MPCA's CWA Section 402 NPDES General Stormwater Construction Permit for the proposed project.²² EPA's review of these permits is described below.

EPA's evaluation was also informed by engagement with PolyMet and the Band both prior to and following EPA's "may affect" determination. Because of the unique history of this matter, prior to making a "may affect" determination, EPA held listening sessions for PolyMet and the Band. Following the "may affect" determination, EPA held a consultation with the Band on January 25, 2022, to ensure meaningful communication with the Band regarding concerns it raised regarding the NorthMet project.²³ Additionally, during the consultation process for this matter, EPA held meetings on March 17, 2022, and April 8, 2022, with Band representatives to

¹⁹ U.S. Army Corps of Engineers, PolyMet Mining, Inc. Permit No. MVP-1999-05528-TJH, https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/NorthMet%20Permit%20-%20Corps%20of%20Engineers.pdf?ver=2019-03-22-091358-997 (last visited April 8, 2022).

²⁰ MPCA 401 Water Quality Certification. Minnesota Pollution Control Agency, (December 20, 2018) CWA Section 401 Certification,

https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/Northmet%20Encl%20C%20401%20WQ%2 0Cert.pdf?ver=2019-03-22-091249-043 (last visited April 28, 2022).

²¹ NPDES Permit MN0071013, <u>https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51ff.pdf</u> (last visited April 27, 2022).

²² General Permit MNR100001: <u>https://www.pca.state.mn.us/sites/default/files/wq-strm2-80a.pdf</u> and Notices of Coverage: <u>https://webapp.pca.state.mn.us/csw/permits/C00053251;</u>

https://webapp.pca.state.mn.us/csw/permits/C00053252; https://webapp.pca.state.mn.us/csw/permits/C00053253; https://webapp.pca.state.mn.us/csw/permits/C00053254 (last visited April 27, 2022).

²³ The EPA Policy on Consultation and Coordination with Indian Tribes establishes clear EPA standards for the consultation process. It defines when and how consultation takes place, designates EPA consultation contacts to promote consistency and coordination of the process, and establishes management oversight and reporting to ensure accountability and transparency. The Policy sets a broad standard for when EPA should consider consulting with federally recognized tribal governments based on Executive Order 13175 and the 1984 EPA Policy for the Administration of Environmental Programs on Indian Reservations. *See*

https://www.epa.gov/sites/default/files/2013-08/documents/cons-and-coord-with-indian-tribes-policy.pdf (last visited April 26, 2022).

provide an opportunity for the Band to further communicate its concerns to EPA.²⁴ EPA's records of these meetings are attached at Appendix D.

4. Structure of this Document

This document is divided into three main sections including Background on this matter, EPA's Evaluation of the Band's Objection, and EPA's Recommendations based on the Band's Objections and the record before EPA. EPA's evaluation is divided into the following three subsections:

- Mercury/Methylmercury (at page 16),
- Specific Conductance (at page 30), and
- Additional topics (at page 37).

EPA's recommendations section discusses the information EPA reviewed in considering whether conditions for the CWA Section 404 permit that can ensure compliance with the Band's water quality requirements.

5. Conclusion from Evaluation and Recommendations

EPA has evaluated the Band's Objection. There is significant uncertainty regarding the water quality impacts under baseline conditions. Accordingly, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for mercury and specific conductance for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

Specifically, EPA has identified several points of uncertainty with respect to the NorthMet project, including the following examples:

- Neither the CWA Section 404 permit application, suspended CWA Section 404 permit, nor MPCA's CWA Section 401 certification adequately address the significant uncertainty regarding the full acreage of secondary impacts to wetlands from the anticipated drawdown of groundwater from mine construction and operation;
- The wetting, drying, and rewetting peat has been identified as a process that increases methylation of mercury, but the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the project do not address mercury methylation or releases of mercury into the St. Louis River system resulting from drying and rewetting of the wetlands surrounding the pits;
- An unknown and wholly uncontrolled quantity of total mercury and dissolved ions (contributing to elevated specific conductance) is expected to be released from discharges covered by the MPCA CWA Section 402 construction stormwater general permit that are related to mine construction activities, but the CWA Section 404 permit application and suspended permit, MPCA's CWA

²⁴ U.S. EPA, Consultation Notes, January 25, 2022; U.S. EPA Meeting Notes, March 17, 2022; U.S. EPA Meeting Notes, April 7, 2022.

Section 401 certification, and MPCA's CWA Section 402 permits, including the general permit for stormwater discharges from construction activity,²⁵ do not contain any controls or monitoring requirements that would ensure compliance with the Band's water quality standards for mercury and specific conductance; and

 Peat from the mine site is expected to contain mercury from decades of air deposition, and excavated peat is a known source of mercury, methylmercury and sulfate, but the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification and MPCA's CWA Section 402 permits for the project do not account for seepage from site features.²⁶

Given these uncertainties and the reasonably foreseeable discharges that are currently unaccounted for in the CWA Section 404 permit application, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for reservation waters, given current project design and discharges outside the Corps' authority. Accordingly, EPA recommends that the Corps not reinstate the suspended permit, as currently proposed.

III. EPA's Evaluation

A. Impacts on the Band's waters–Mercury and Methylmercury1. Introduction

With respect to mercury, the Band objects to the issuance of a CWA Section 404 permit for the proposed NorthMet mine and asserts that permitted activities will contribute to ongoing violations of the Band's water quality requirements for mercury.

The Band's Objection and supporting materials describe how the construction and operation of the NorthMet mine will alter the hydrology of some 6000 acres of wetlands, in addition to the approximately 939 acres of direct and fragmentation impacts. These wetland alterations, in addition to the loading of sulfates from the construction and operation of the NorthMet project, will both enhance methylation of mercury already present in the wetlands affected by the proposed mine and mobilize both total and methylmercury in those same wetlands. The mercury mobilized as a result of these wetland alterations will be exported from the NorthMet project site via the streams adjacent to the affected wetlands at the NorthMet project site and be transported downstream to the Fond du Lac Reservation. This mercury will further exacerbate ongoing exceedances of the Band's mercury criterion of 0.77 ng/L and ongoing nonattainment of the Band's designated uses.²⁷

²⁵ Polymet Mining Corp. NorthMet Project Water Management Plan – Mine (December 2017), <u>https://files.dnr.state.mn.us/lands_minerals/northmet/permit_to_mine/appendix_11_2_dec17.pdf</u> (last visited April 27, 22), p. 6: "Runoff from construction areas where the majority of the material being excavated is Unsaturated Overburden or Peat will be managed as construction stormwater."

²⁶ NPDES Permit MN0071013, pp. 3, 5.

²⁷ Fond du Lac Notification of Objection, beginning on p. 11.

Specific violations of water quality requirements that will result from the proposed project as identified by the Band include the following (specific language and citations to the Band's water quality standards are provided in Appendix E- Applicable Water Quality Standards)²⁸:

- The Band's antidegradation policies for surface waters requiring protection of existing uses and prohibiting new or increased discharges that would impact an existing use (wetlands and non-wetlands)²⁹;
- the Band's ambient numeric water quality criterion for mercury to protect wildlife, human health and aquatic life due to direct loads of mercury and methylmercury as well as due to enhanced methylation of mercury due to increased loads of sulfate to waters of the Band³⁰;
- the Band's narrative criteria prohibiting objectionable deposits and prohibiting water quality alterations that "may limit the growth and propagation of, or otherwise cause or contribute to adverse effect to wild rice and other flora and fauna of cultural importance to the Band"³¹; and
- the Band's Wildlife, Warmwater Fisheries, and Subsistence Fishing for nonwetlands and wetland designated uses.³²

In contrast, PolyMet's CWA Section 404 permit application and associated documentation focus on a mass balance of mercury for the NorthMet project and conclude that:

...most of the mercury input to the process will be sent to the Flotation Tailings Basin (FTB) and Hydrometallurgical Residue Facility and sequestered from the general environment. There will be a small amount of mercury (approximately 4.6 pounds per year) released to air and to surface water.³³

PolyMet considers mercury released into the air and direct discharges into water from the wastewater treatment plant and the discharge from the West Pit lake after closure, as the primary sources of mercury to the environment resulting from the NorthMet Project. PolyMet's mercury analysis, however, does not consider the way secondary impacts from the NorthMet Project on adjacent wetlands that are not directly filled and/or excavated but are subject to drawdown and flooding might affect mercury that has built up in these wetlands over time and consequently does not consider this source of mercury in its evaluations. PolyMet estimates that the NorthMet project is expected to impact only 939 acres of wetlands, with impacts

²⁸ Fond du Lac Notification of Objection, pp. 28-33.

²⁹ Fond du Lac Band of Lake Superior Chippewa, Water Quality Standards of the Fond du Lac Reservation, Ordinance #12/98, as amended through July 8, 2020 [hereafter FDL WQS] at Section 105, Antidegradation Policy and Implementation, <u>http://www.fdlrez.com/government/ords/12-98WaterQualityStandard2020.07.pdf</u> (last visited April 15, 2022).

³⁰ FDL WQS at Appendix 1, Standards Specific to Designated Use.

³¹ FDL WQS at Section 301.n.

³² FDL WQS at Sections 302.B, 302.C.2, and 302.C.3; Sections 701–703.

³³ Mercury Overview: A summary of potential mercury releases from the NorthMet Project and potential effects on the environment. Barr for PolyMet Mining Inc, March 2015,

https://www.pca.state.mn.us/sites/default/files/Mercury%20Overview.pdf, p. vi. (last visited April 27, 2022).

limited to excavation, filling, and fragmentation. The difference between the Band's and PolyMet's estimates of wetland impacts resulting from the project is due to PolyMet's view, as expressed in the CWA Section 404 permit application, that the vertical seepage of water in the wetlands at the mine site is "relatively weak" based on a 30-day pumping test at the mine site:

> The degree of hydraulic connection between the wetland areas and adjacent unconsolidated deposits and bedrock at the Mine Site is expected to be variable, depending on the characteristics of the wetlands and the localized hydraulic conductivity and degree of bedrock fracturing. The hydraulic conductivity of the bedrock and surficial deposits have been estimated at the Mine Site by a variety of methods, including conducting aquifer tests and using grain-size distribution data from soil borings and ranges over several orders of magnitude. Data collected during a 30-day pumping test at the Mine Site showed a small amount of drawdown in the deep wetland piezometer nearest the pumping well, but no detectable drawdown at other water table or deep wetland piezometers, indicating that the connection between the bedrock, unconsolidated deposits, and wetlands may be relatively weak. Virtually all water movement in peat wetlands occurs horizontally in the upper layers of peat. The deeper, more decomposed peat soils limit vertical seepage because of the low hydraulic conductivities (~0.0028 feet/day) and the wetland hydrology is simply perched on the relatively impermeable peat layer. Vertical seepage losses from wetlands without peat soils will only have the potential to occur in isolated areas of contiguous, high hydraulic conductivity bedrock faults and fracture zones located under isolated areas of high hydraulic conductivity glacial till and aligned with wetlands containing high hydraulic conductivity soils.³⁴

The CWA Section 404 application identifies wetland impacts as either "direct" (defined as filling or excavation within the boundaries of a wetland), or "indirect" (defined as "fragmentation" of wetlands by features of the NorthMet project such as open pits, stockpiles, haulroads, etc.).³⁵ The CWA Section 404 application describes wetlands impacts at the mine site as follows:

There are 59 directly impacted or fragmented wetlands located in the Mine Site covering approximately 758 acres (Large Table 2; Large Figure 9). The total directly impacted wetlands include fill (39%), excavation (24%), or both fill and excavation (37%). Thirty-seven percent of the directly impacted wetlands are also impacted by wetland fragmentation. Three wetland types comprise 90% of the proposed wetland impacts in the Mine Site and include 529 acres of coniferous bog (67%), 101 acres of shrub swamp (13%), and 72 acres of coniferous swamp (9%). In addition, 38 acres of sedge/wet meadow (5%), 23 acres of shallow marsh

³⁴ NorthMet Revised Permit Application, PolyMet Mining, August 19, 2013 [hereafter NorthMet Revised Permit Application],

https://www.pca.state.mn.us/sites/default/files/Wetland%20Permit%20Application%20v2%20AUG2013%20w%20 application.pdf (last visited April 28, 2022), p. 45.

³⁵ NorthMet Revised Permit Application, p. 52.

(3%), 13 acres of hardwood swamp (2%), 8 acres of open bog (1%), and 0.1 acre of deep marsh (less than 1%) will also be impacted.³⁶

The Corps, in its ROD and in the suspended CWA Section 404 permit, acknowledges the potential for changes in wetland hydrology due to the dewatering of the mine pit and includes several permit conditions (Nos. 16-29) that are intended to identify indirect adverse effects to wetlands, including changes to hydrology. Permit conditions 31-33 require PolyMet to obtain additional compensatory mitigation for wetland indirect effects that are identified during the life of the NorthMet project. However, this additional wetland mitigation (e.g., purchasing mitigation bank credits) would not account for any additional mobilization of mercury or increased methylmercury load caused by the changes in wetland hydrology. The ROD does consider mercury but focuses on mercury present in the discharge from the wastewater treatment plant and water released from the pit lakes and concludes that because these discharges will be at or below 1.3 ng/L, that the NorthMet project is, "not expected to add to any potential exceedance of the Fond du Lac mercury water quality standard of 0.77 ng/L within the Reservation."³⁷

The permit suite does not consider water quality impacts arising from changes in hydrology of wetlands due to the dewatering of the mine pit and that will result in the methylation of mercury and mobilization of mercury from the impacted wetlands. A summary of the requirements and conditions follows.

- **CWA Section 404 Permit and CWA Section 401 Certification**: The conditions included in the CWA Section 404 permit and MPCA's Section 401 certification are limited to monitoring and adaptive management only. PolyMet would report monitoring data to MPCA, who would use that data to determine whether adaptive management measures should be triggered. Should monitoring data indicate a violation of Minnesota's water quality standards, PolyMet is to report the violation to MPCA, along with an adaptive management plan to "monitor and remedy the cause of the violation."³⁸ The conditions do not control mercury discharges but rely on detecting and correcting water quality requirement violations after they occur with the expectation that violations will be corrected as identified. The conditions do not consider the Band's water quality requirements.
- **CWA Section 402 General Stormwater Permit**: The general stormwater permit for construction of the mine does not contain any limits on the discharge of mercury.
- **CWA Section 402 Individual Permit**: The individual CWA Section 402 permit does not contain numeric water quality-based effluent limitations for mercury. MPCA's permit fact sheet³⁹ explains that MPCA did not find that there was a reasonable potential to

³⁶ NorthMet Revised Permit Application, p. 53.

³⁷ Corps' ROD]

³⁸ MPCA's CWA Section 401 Certification, p. 6.

³⁹ MPCA, National Pollutant Discharge Elimination System/State Disposal System (NPDES/SDS) Permit Program Fact Sheet, MN0071013, Prepared for public comment period beginning January 31, 2018, https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51gg.pdf (last visited April 22, 2022).

exceed applicable water quality standards. Instead of water quality-based effluent limits, the permit includes "operating limits" on mercury. The CWA Section 402 individual permit includes an operating limit at an internal monitoring station that is set to Minnesota's water quality standard of 1.3 ng/L. The permit also contains technology-based effluent limitations on mercury at 1,000 ng/L as a monthly average and 2,000 ng/L as a daily maximum.⁴⁰

2. Impacts of Mercury on the St. Louis River Watershed

The proposed NorthMet mine is located in the Mesabi Iron Range near Hoyt Lake, St. Louis County, Minnesota. The NorthMet project proposes to reuse and expand an existing taconite tailings basin and ore processing site. There are numerous historic, active and planned mines, tailings basins and ore processing facilities in the St. Louis River watershed. Mercury levels in the St. Louis River and its associated watershed tend to be elevated compared to other similar waters. The Band's Objection notes that anthropogenic activities since the mid-1800s have resulted in large quantities of inorganic mercury being released to the atmosphere, increasing deposition to ecosystems by 200% to 500%.⁴¹ In low-oxygen aquatic environments such as lake sediments, slow-moving rivers and streams and wetlands (especially peatlands) in which sulfate-reducing bacteria are active, mercury can be converted to methylmercury. Methylmercury is a highly bioaccumulative toxin that biomagnifies up the trophic levels of the food chain, impacting human and wildlife consumers of fish and aquatic life.⁴² Mercury bioaccumulation in fish is a public health concern in northeast Minnesota, including the St. Louis River as it passes through the Band's reservation.⁴³ As noted in the ORD Mercury Memo:

Mercury bioaccumulation in fish is a public health concern in northeast Minnesota. Atmospheric mercury emissions to the St. Louis River watershed are relatively high for the region (10-100 g/km2/yr; Cohen et al., 2004) and total mercury (THg) in surface waters of the St. Louis River is among the highest in Minnesota (Monson, 2013). The State of Minnesota has posted a fish consumption advisory for fish in the St. Louis River related to the high mercury concentrations found in fish tissues; for example, St. Louis River walleye have mercury concentrations higher than the regional background (Monson, 2012). Newborns tested from the Minnesota portion of the Lake Superior basin have a relatively high blood mercury concentration, and the data pattern suggests that exposure through fish consumption is a likely factor (McCann, 2011).⁴⁴

⁴⁰ NPDES Permit MN0071013, technology limits, p. 352, operating limit p. 426.

⁴¹ Fond du Lac Objection, p. 9.

⁴² EPA ORD Review: Request for Scientific Support Regarding Potential Downstream Impacts of the NorthMet Mine, p. 9.

⁴³ EPA ORD Review: Request for Scientific Support Regarding Potential Downstream Impacts of the NorthMet Mine, p. 2.

⁴⁴ EPA ORD Review: Request for Scientific Support Regarding Potential Downstream Impacts of the NorthMet Mine, p. 2.

3. Baseline Water Quality Conditions and Impacts

EPA reviewed the baseline water quality conditions and impacts associated with mercury expected to result from the NorthMet project's discharges, as proposed and as if each of the permits in the permit suite remain as currently drafted. The baseline impacts in turn inform whether the NorthMet project's permits, as currently drafted, will ensure that any discharge from the NorthMet project will comply with the Band's water quality requirements.

Baseline water quality conditions

Atmospheric mercury emissions to the St. Louis River watershed are relatively high for the region, and total mercury (THg) in surface waters of the St. Louis River as it passes through the Band's reservation is among the highest in Minnesota.⁴⁵

The Barr Engineering report⁴⁶ provided to PolyMet reports background THg and methylmercury (MeHg) in precipitation, water seeping from the existing LTV tailings basin, various streams, and monitoring stations. All the values reported here are greater than 0.77ng/L, with concentrations in the St. Louis River among the greatest observed (7.8 ng/L at River Mile 179 (the headwaters of the St. Louis River); and 4.2 ng/L at Cloquet (immediately downstream of the Fond du Lac Reservation)).

The ORD Mercury Memo includes an assessment of the percent MeHg in the waters affected by the NorthMet project as an indicator of the potential for inorganic mercury to be converted to MeHg in these waters. The ORD Mercury Memo concludes:

On average, rivers have %MeHg of 4%, lakes are 8%, whereas wetlands, which have high methylation potential, are 15% (Krabbenhoft et al., 1999; Kelly et al., 1995), similar to what is observed in the Partridge River (the watershed in which the mine pit will be located).⁴⁷

In Table 2-1 of the *Mercury Overview*, PolyMet reports baseline percent MeHg for streams in the NorthMet project area 13.1 - 20.4%.

Minnesota has a water quality standard for mercury of 1.3 ng/L, while the Band has a water quality standard for mercury of 0.77 ng/L. EPA also observes that the St. Louis River is already impaired for mercury and most St. Louis River segments between the NorthMet project site and the Fond du Lac Reservation have been listed since 1998 on Minnesota's CWA Section 303(d) Impaired Waters List.

⁴⁵ Appendix B ORD Mercury Memo, p. 2.

⁴⁶ Mercury Overview: A summary of potential mercury releases from the NorthMet Project and potential effects on the environment, Barr for PolyMet Mining Inc, March 2015, Table 2-1, "Baseline Concentrations of Total Mercury, Methylmercury and Sulfate in Precipitation and Selected Surface Waters Evaluated for Potential Effects from the Project," <u>https://www.pca.state.mn.us/sites/default/files/Mercury%20Overview.pdf</u> (last visited April, 272022).

⁴⁷ Appendix B ORD Mercury Memo, p. 8.

MPCA acknowledges that the receiving waters that will be affected by the mine demonstrate exceedances of Minnesota's water quality criterion of 1.3 ng/L for mercury:

All projected surface discharge locations for the project have no surface water assimilative capacity and thus no flow dilution is allowed when considering protection of water quality standards.⁴⁸

EPA also notes that Minnesota has issued fish consumption advisories for fish from the St. Louis River due to elevated fish tissue concentrations of mercury.⁴⁹ Moreover, MPCA has been engaged in a more-than decade-long process for developing a total maximum daily load for mercury for the St. Louis River to restore the uses of the river that are impaired due to mercury contamination.⁵⁰

The Band's Objection letter provides the following description of the existing water quality conditions related to mercury on the Band's Reservation:

Mercury concentrations in the St. Louis River have exceeded the Band's chronic human health standard (0.77 ng/L) for more than a decade. Consumption of fish contaminated by methylmercury is the primary exposure pathway for Band members and wildlife, and existing monitoring data indicate levels are already elevated in many species that are consumed as food [citations omitted].

Because the St. Louis River is already impaired for mercury, the St. Louis River and its associated watershed lack assimilative capacity that would ameliorate any adverse impacts of additional mercury loading from the NorthMet project on downstream waters.

Impacts from current permits

CWA Section 404 permit and CWA Section 401 water quality certification conditions The Corps' currently suspended CWA Section 404 permit for this project does not include any discharge limitations on mercury. MPCA's CWA Section 401 certification on the CWA Section 404 permit includes two conditions on mercury:

• For wetlands: Conduct monthly (May to October) baseline THg and MeHg monitoring for at least two years and continue until the commencement of project mining operations. Monitoring will occur at 22 monitoring locations within the mine and plant sites. These monitoring wells are all located either within the mine site or on the immediate periphery of the mine site, limiting their value in detecting the kind of impacts identified by the Band.⁵¹

 ⁴⁸ Poly Met Mining, Inc. NPDES Antidegradation Review – Preliminary MPCA Determination, January 10, 2018.
 ⁴⁹ MN Department of Health Fish Consumption Guidance,

https://www.health.state.mn.us/communities/environment/fish/ (last visited April 22, 2022).

⁵⁰ St. Louis River Watershed mercury TMDL, Minnesota Pollution Control Agency, <u>https://www.pca.state.mn.us/water/st-louis-river-watershed-mercury-</u>

tmdl#:~:text=Because%20the%20main%20source%20of,93%20percent%20from%201990%20levels (last visited April 19, 2022).

⁵¹ MPCA's CWA Section 401 Certification, p. 2.

• For streams: Conduct quarterly THg and MeHg monitoring upon issuance of all state permits or upon commencement of project and continue through one year after cessation of mining operations. Monitoring to occur at five surface water monitoring locations.⁵²

The CWA Section 404 permit and CWA Section 401 certification include only monitoring requirements to identify any secondary impacts to wetlands surrounding the mine site due to hydrologic impacts arising from the construction and operation of the mine, relying on adaptive management efforts to respond to secondary impacts after they occur. The Band provides analysis and documentation in its objection that the wetlands surrounding the NorthMet project site are reservoirs of mercury. In EPA's evaluation, this analysis is supported by the available science. As noted in ORD's Mercury Memo:

The extensive contiguous acreage of wetlands and peatlands enhance the mercury bioaccumulation potential of the river because wetlands and peatlands are a source of mercury (i.e., a net sink of deposited mercury) to surface waters. Based on research in northern Minnesota peatland systems, most THg and [dissolved organic carbon] in streams adjacent to peatlands are derived from those peatlands compared to upland sources.⁵³

The Band states in its objection that approximately 6000 acres of wetlands are likely to be affected by hydrologic disturbance due to the construction of the mine and the ongoing dewatering of the mine that is necessary for the mine to operate. The ORD Mercury Memo considers this issue. Regarding the potential for hydrologic fluctuations to result in mobilization of mercury and sulfate, the ORD Mercury Memo states:

Coleman, Wasik et al. (2015) showed that in a boreal peatland, hydrologic fluctuations released increased concentrations of sulfate and total mercury over time, as well as a higher percent methylmercury as a result of drying. Thus, disturbing the wetlands via draining could result in the release of increased total mercury, methylmercury, and sulfates into downstream receiving waters.⁵⁴

The ORD Mercury Memo concludes:

Given the scientific community's understanding of the processes that would occur through drawdown of the wetlands, there is a potential with a strong likelihood that stored sulfate, organic matter, and THg with a high percent MeHg will be released over time (Krabbenhoft et al., 1999; Kelly et al., 1995; St. Louis et al., 2004; Coleman Wasik et al., 2012).⁵⁵

CWA Section 402 permits

⁵² MPCA's CWA Section 401 Certification, pp. 2-4.

⁵³ Appendix B ORD Mercury Memo, p. 7.

⁵⁴ Appendix B ORD Mercury Memo, p. 5.

⁵⁵ Appendix B ORD Mercury Memo, p. 5.

Minnesota has issued two permits for this project pursuant CWA Section 402, including a construction stormwater general permit and an individual permit for process wastewater discharge. Limitations of both permits are discussed below.

<u>Construction general permit</u>: MPCA issued coverage under its general permit for discharges of stormwater associated with construction activity⁵⁶ for the NorthMet project. The conditions in the general permit address pollutants such as sediments, that would typically be expected in stormwater runoff from construction site activity. The permit does not contain controls that would address dissolved parameters and does not contain any water quality monitoring requirements. There are no conditions in the general permit that are specific to mercury, but EPA acknowledges that controls implemented to control sediment would also control the fraction of total mercury that would be attached to that sediment.

<u>Individual permit</u>: MPCA issued permit number MN0071013 on December 20, 2018.⁵⁷ The permit contains three limitations on mercury discharges:

- *Numeric technology based effluent limitations* that are required by federal regulations at 40 C.F.R. 440:
 - \circ Mercury is limited at the final outfall to 1,000 ng/L as a monthly average and 2,000 ng/L as a daily maximum.⁵⁸
- *A numeric "operating limit"* of 1.3 ng/L, which is equivalent to Minnesota's water quality standard for mercury. This limit is applied at a monitoring station internal to the wastewater treatment plant.⁵⁹
- *Narrative water quality based effluent limits*, which provide:
 - The discharge of treated wastewater from the wastewater treatment system (WWTS) must not cause a violation of state water quality standards. [Minn. R. 7001.0170, Minn. Stat. ch. 115.03]⁶⁰; and
 - The MPCA may modify this permit, require corrective actions, or take other actions if it determines that a discharge authorized by this permit is causing or contributing to a violation of water quality standards. [Minn. R. 7001.0170, Minn. Stat. ch. 115.03].⁶¹

MPCA did not include numeric water quality-based effluent limits for the discharge covered by individual permit because it did not find that there was a reasonable potential for the state water quality standards to be exceeded for mercury. MPCA explains in its fact sheet for the individual CWA Section 402 permit:

⁵⁶ General Permit <u>MNR100001</u>: <u>https://www.pca.state.mn.us/sites/default/files/wq-strm2-80a.pdf and Notices of</u> <u>Coverage: https://webapp.pca.state.mn.us/csw/permits/C00053251;</u>

⁽https://webapp.pca.state.mn.us/csw/permits/C00053252; https://webapp.pca.state.mn.us/csw/permits/C00053253; https://webapp.pca.state.mn.us/csw/permits/C00053254 (last visited April 27, 2022).

⁵⁷ NPDES Permit MN0071013.

⁵⁸ NPDES Permit MN0071013.

⁵⁹ NPDES Permit MN0071013.

⁶⁰ NPDES Permit MN0071013.

⁶¹ NPDES Permit MN0071013.

The MPCA conducted a reasonable potential analysis for mercury as part of the permit application review. Based on its review, the Agency has determined there is no reasonable potential for concentrations of mercury in the WWTS effluent to cause or contribute to an exceedance of water quality standards. The MPCA expects no measurable change in mercury concentrations downstream in the St. Louis River at Forbes or below. However, to ensure the WWTS is removing mercury as expected, an Operating Limit of 1.3 ng/L total mercury applies at station WS074. The permit requires weekly monitoring of the WWTS effluent at stations WS074 and SD001 for total mercury using analytical method 1631 and clean-sampling method 1669. The applicable TBEL at station SD001 under the NSPS for mercury is a daily maximum of 0.002 mg/L and a monthly average of 0.001 mg/L.⁶²

MPCA's Fact Sheet explains that an operating limit was included for mercury because the influent mercury concentration to the wastewater treatment plant was predicted to be 1.0 ng/L, which is near Minnesota's applicable water quality standard.⁶³

MPCA also evaluated mercury in the context of its Antidegradation Preliminary Determination:

The only bioaccumulative chemical of concern in the effluent is mercury. The net loading of mercury will be prudently and feasibly minimized using the best available treatment technologies. The effluent from the wastewater treatment system is expected to be at or below the water quality standard of 1.3 ng/L and will not cause or contribute to any downstream mercury water quality exceedance. The receiving water wetlands and downstream creeks are not listed as impaired for mercury under Section 303(d) of the Clean Water Act; however, observed values in the downstream creeks are periodically in excess of applicable water quality standards (1.3 ng/L), primarily as a result of atmospheric deposition (Section 8.1 (pp. 83-84) of the Antidegradation Evaluation). Existing water quality with respect to mercury is discussed in Section 8.2 (pp. 84-85) of the Antidegradation Evaluation. Section 8.3 (pp. 85-93) of the Antidegradation Evaluation provides a comparison of existing and estimated water quality for mercury due to the project. All downstream waters are expected to show no measurable increase in estimated mercury concentrations or loading as compared to existing conditions. Additionally, because of flow (and resulting mercury loading) reductions to the Partridge River from the project upstream of the confluence with Second Creek, the overall loading of mercury to the Partridge River (and to the St. Louis River) downstream of Second Creek is estimated to decrease from current conditions. Because of the net decrease, all downstream OIRWs and ORVWs, including Lake Superior, will be protected.⁶⁴

⁶⁴ MPCA Antidegradation Preliminary Determination, January 10, 2018, p. 25, https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51n.pdf (last visited April 28, 2022).

⁶² MPCA, National Pollutant Discharge Elimination System/State Disposal System (NPDES/SDS) Permit Program Fact Sheet, MN0071013, Prepared for public comment period beginning January 31, 2018, p. 43.

⁶³ MPCA. National Pollutant Discharge Elimination System /State Disposal System (NPDES/SDS) Permit Program Fact Sheet, MN0071013, Prepared for public comment period beginning January 31, 2018, p. 43.

Not considered in the antidegradation preliminary determination is any release of mercury from adjacent wetlands as a result of secondary impact on those wetlands.

4. Data Limitations

As discussed previously, to estimate potential loadings of mercury, sulfate, and other solutes resulting from the proposed project, PolyMet relied on a mass-balance model that subsequently informed the suite of permitting documents and MPCA's CWA Section 401 certification. However, the Band has faulted the FEIS model as being too limited and that it specifically omits consideration of fate and transport of mercury present in the adjacent wetlands subject to secondary impacts, and that this significant loading of sulfate and mercury will lead to increased production of methylmercury.⁶⁵

The Band argues that the model:

- does not include major data parameters, including methylmercury;
- does not include error or uncertainty surrounding the data used to populate the model;
- does not quantify mercury inputs resulting from altering the hydrological and biogeochemical function of wetlands surrounding the mine site, including repeating cycles of drying and rewetting; and
- does not attempt to understand the fate and transport of mercury loads resulting from the NorthMet project and its indirect impacts on the surrounding wetlands.⁶⁶

EPA agrees with the Band that there are substantial limitations to the information presented in regard to estimates of mercury impacts based on the mass-balance model currently presented in the FEIS. Specifically, the ORD Mercury Memo states:

"At this time, the scientific information to predict the timing and magnitude of mercury concentration change in waters or fish downstream of the NorthMet mine is incomplete because the impact on regional wetlands and peatlands has not been sufficiently studied. To evaluate the effect of wetland impacts on methylmercury, as well as the additions of mercury and sulfate from treated, discharged waters, it is necessary to develop a processbased mass balance model of the system. Such an approach must incorporate wetlands and peatlands; surface, pore, and ground waters; and include future hydrologic changes owing to mine operations. While there are examples of such hydrologic models in the scientific literature (e.g., a Hydrologic Simulation Program FORTRAN, Berndt et al., 2016), no such model was applied to evaluate the NorthMet mine and processing facility impacts on area wetlands and peatlands with respect to changes in hydrology (whether direct or indirect). To apply such a model, it would first be necessary to characterize the current conditions at the proposed mine site and processing site, including mercury inventories and relevant water quality parameters such as sulfur and dissolved organic carbon concentrations in wetlands, surface waters, and ground waters, as well as measurements of surface and ground water flows. To address

⁶⁵ Fond du Lac Objection, Exhibits 24, 27, 30.

⁶⁶ Fond du Lac Objection, pp.11-18.

the timing and magnitude of mercury concentration change downstream and in fish, the model would be used to assess potential change in loading of mercury and methylmercury to the St. Louis River under varying mine operations and environmental conditions. Specifically, to address the CWA Section 401(a)(2) process, the model should also address fate and transport downstream of the mine site and processing facility to the Fond du Lac Reservation boundaries." (Emphasis added.)⁶⁷

These issues were raised to MPCA in the public comments on the proposed CWA Section 401 certification and the CWA Section 402 permit.⁶⁸ In its responses to comments regarding the limitations of the mass-balance presented in the FEIS, MPCA states that the mass-balance approach was appropriate "given the data available" and that the mass-balance "conceptual model used is more transparent and relies on fewer untested assumptions than a complex model incorporates."⁶⁹ Additionally, MPCA stated its belief that the drawdown in the wetlands surrounding the NorthMet project mine pits would not be significant, but added that if significant drawdown were to occur, the wetlands would essentially be converted to "upland" and thus would not become sources of methylmercury.⁷⁰ As discussed, the amount of drawdown and its effect on the hydrology and biogeochemistry of the wetlands surrounding the NorthMet project for the Band. The ORD Mercury Memo also concludes that there are fundamental data gaps related to mercury cycling and hydrology in the wetlands surrounding the NorthMet project.

During the CWA Section 401 certification process and in response to the Band's concerns, PolyMet published a report entitled "Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions."⁷¹ As the title of this report indicates, it was specifically developed to address the impacts of air/dust emissions from the NorthMet project. The analysis identified one "wetland of interest" (WOI) near the mine site that is anticipated to receive the highest loading of fugitive dust from the NorthMet project that contains sulfur and other metals and examined the impact of that deposition on mercury production in the wetland.

It should be noted that the WOI will not receive direct NPDES discharges as a result of the NorthMet project and will likely not be subject to drawdown based on the presence of a culvert. Based on analysis of the fugitive dust deposition to the WOI, the Cross-Media analysis

⁶⁸ MPCA's CWA Section 401 Certification Response to Comments,

⁶⁷ Appendix B ORD Mercury Memo, p. 3.

<u>https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-5100.pdf</u> (last visited April 27, 2022); MPCA 402 Permit Response to Comments, <u>https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51ll.pdf</u> (last visited April 27, 2022).

⁶⁹ MPCA Findings of Fact in the matter of the denial of contested case hearing requests and issuance of MPCA certification under Section 401 of the Clean Water Act for the proposed NorthMet project,

https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51kk.pdf, p. 29 (last visited April 27, 2022). ⁷⁰ MPCA Findings of Fact in the matter of the denial of contested case hearing requests and issuance of MPCA certification under Section 401 of the Clean Water Act for the proposed NorthMet project,

https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51kk.pdf, p. 19 (last visited April 27, 2022). ⁷¹ Cross-Media Analysis to Assess Potential Effects on Water Quality from the Project-Related Deposition of Sulfur and Metal Air Emissions, Barr, October 31, 2017, https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51i.pdf (last visited April 27, 2022), Appendix F.

determined that even with impacts from fugitive dust, the NorthMet project will still result in "non-measurable" changes to mercury and methylmercury concentrations at the St. Louis River at Cloquet. Although PolyMet does make some protective assumptions in its analysis, loadings from discharges from the NorthMet project are still assumed to meet the 1.3 ng/L mercury and 10 mg/L sulfate limit based on the analysis presented in the FEIS, and there is no indication of what happens in the event that these internal operating limits are not met.

As a result, EPA's evaluation is that the Cross Media analysis does not sufficiently address the concerns raised by the Band regarding the extent of wetland drawdown and fluctuations in water levels resulting from mine operations. Instead, the Cross Media analysis essentially extrapolated its analysis of the WOI to all wetlands surrounding the NorthMet project area based on major assumptions made that the WOI was representative of all wetlands near the project and that wetland export of sulfate and mercury will not change during mine operations versus current conditions.⁷² The Band states that this is a major flaw in the Cross Media analysis; EPA agrees. The Cross Media analysis is limited to the impact of air deposition on mercury cycling in one "wetland of interest" that does not receive direct NPDES discharges and is likely not subject to drawdown. Because of this limitation, it cannot be used to address the larger question of impacts on mine construction and operation on mercury cycling of wetlands in the surrounding landscape for the NorthMet project.

Informed largely by the Cross-Media Analysis, MPCA's CWA Section 401 certification is primarily focused on addressing impacts from air deposition resulting from the NorthMet project and does not sufficiently address alterations to wetland hydrology and biogeochemistry resulting from CWA Section 404 permitted activities for the NorthMet project. Although the CWA Section 401 certification states that 22 wetland sites must be monitored monthly during the ice-off period for Hg, MeHg, and sulfate, this monitoring is only required "for not less than 2 years and continue until the commencement of project mining operations."⁷³ After that MPCA states that follow-up monitoring will continue "as needed" with no indication of what might trigger further wetland monitoring.⁷⁴ The CWA Section 404 permit does contain triggers for adaptive management and compensatory mitigation, but they would not eliminate the hydrologic change that would result in discharges of methylmercury to the watershed. The Band asserts and EPA agrees that the CWA Section 401 certification's monitoring conditions will not be sufficient to determine whether discharges from CWA Section 404 permitted activities will result increases in methylmercury that could potentially affect the food web of the Saint Louis River Watershed.⁷⁵

⁷⁴ MPCA Findings of Fact in the matter of the denial of contested case hearing requests and issuance of MPCA certification under Section 401 of the Clean Water Act for the proposed NorthMet project,

⁷² Cross-Media Analysis to Assess Potential Effects on Water Quality from the Project-Related Deposition of Sulfur and Metal Air Emissions, Barr, October 31, 2017, Appendix F.

⁷³ MPCA's CWA Section 401 Certification.

https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51kk.pdf (last visited April 27, 2022) (last visited April 27, 2022), p. 113.

⁷⁵ Fond du Lac Objection, Exhibit 25.

In summary, EPA recognizes the limitations of the mercury mass-balance model presented in the FEIS and the lack of analysis addressing the potential impacts of altering the hydrology and biogeochemistry of large areas of peat-based wetlands surrounding the NorthMet project site.

5. Conclusion

As discussed above, mercury concentrations in the St. Louis River as it passes through the Fond du Lac Reservation already exceed the water quality criteria established by the Band to ensure that the Band's designated uses are protected and fish and aquatic life are safe for human consumption. Because the St. Louis River is already impaired for mercury, the St. Louis River and its associated watershed lack assimilative capacity that would ameliorate any adverse impacts of additional mercury loading from discharges from CWA Section 404 permitted activities on downstream waters.

The Band provides analysis and documentation in its objection that the wetlands surrounding the NorthMet project site are reservoirs of mercury and that project activities will result in the mobilization of mercury and sulfate. EPA agrees and notes that changes in hydrology are likely to result in mobilization of mercury and sulfate and that disturbing the wetlands via draining could result in mobilization of methylmercury downstream.⁷⁶ As a result, EPA's evaluation is that altering the hydrology of the wetlands surrounding the NorthMet project site has a strong likelihood to contribute to THg and MeHg downstream in the St. Louis River and within the Band's waters.

However, the documentation supporting the permit suite and the CWA Section 401 certification do not consider the function of wetlands as environmental reservoirs of mercury and the impacts of hydrologic modifications on those mercury reservoirs and fail to include conditions that ensure that mercury is not mobilized, methylated, and exported. With respect to the CWA Section 404 permit, minimal water quality monitoring is required in the suspended permit, and adaptive management for secondary impacts to wetlands would be required only after a hydrologic effect has occurred and mercury has been mobilized, leading to, in some circumstances, irreversible damage.

The CWA Section 402 individual permit authorizes continued exceedance of the Band's water quality standards for mercury because it allows a discharge from the wastewater treatment plant in excess of the Band's water quality standards for mercury of 0.77 ng/L and the receiving waters to this discharge within the headwaters of the St. Louis River already exceed the Band's water quality standard for mercury.⁷⁷ EPA's evaluation pursuant to CWA Section 401(a)(2) must consider whether the Band's more stringent water quality requirements and water quality criteria will be achieved at the point where water, including discharges from the proposed project, would enter the Band's downstream jurisdiction. Because all streams from the mine site to the mouth of the St. Louis River already exceed the Band's water quality standards for mercury, there is no assimilative capacity or dilution within this watershed that will result in dilution of the mercury concentration from 1.3 ng/L (as authorized by the current permit suite) such that water quality

⁷⁶ Appendix B, ORD Mercury Memo.

⁷⁷ NPDES Permit MN0071013.

downstream from the NorthMet project will comply with Band's more stringent criterion of 0.77 ng/L.

The efforts of PolyMet to quantify scope of the hydrologic impacts resulting from the discharges from CWA Section 404 permitted activities are extremely cursory, as detailed above in Section III.A.1. As a result, as noted in the ORD Mercury Memo, the available data and analyses supporting the CWA Section 404 permit and CWA Section 401 certification are insufficient to fully evaluate the mercury impacts in terms of area of wetlands affected and effects on the Band's water quality. Given these uncertainties, in addition to the reasonably foreseeable discharges that are unaccounted for in the CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for mercury for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

B. Impacts on the Band's waters–Specific Conductance

1. Introduction

With respect to specific conductance, the Band objects to the issuance of a CWA Section 404 permit for the NorthMet project due to the Band's determination that discharges from the permitted activity will violate its water quality standards for specific conductance due to the contributions of mineral loadings (dissolved ions contributing to specific conductance) to the St. Louis River watershed. In particular, the Band outlines that discharges of dissolved ions (increased mineral loadings leading to higher specific conductance) would both:

- violate the Band's numeric water quality standard for specific conductance of 300 $\mu\text{S/cm};$ and
- adversely affect aquatic life within the St. Louis River watershed and within streams and wetlands on the Fond du Lac Reservation.⁷⁸

Based on the Band's analysis, those impacts to aquatic life (e.g., benthic aquatic insects and sturgeon) would violate the Band's antidegradation standard within wetlands and streams on the Fond du Lac Reservation, which are tied to the Band's narrative standards and designated uses.⁷⁹ Specific violations of water quality requirements identified by the Band in its objection include the following:

- The Band's antidegradation policies for surface waters requiring protection of existing uses and prohibiting new or increased discharges that would impact an existing use (wetlands and non-wetlands);
- the Band's ambient numeric water quality criterion for specific conductance for the protection of aquatic biota;
- the Band's narrative criteria prohibiting objectionable deposits and prohibiting conditions that, "may limit the growth and propagation of, or otherwise cause or contribute to

⁷⁸ Fond du Lac Objection, beginning on p. 28.

⁷⁹ Appendix E Applicable Water Quality Standards, Fond du Lac Objection, beginning on p. 24.

adverse effect to wild rice and other flora and fauna of cultural importance to the Band"; and

• the Band's Wildlife, Warmwater Fisheries, and Subsistence Fishing for non-wetlands and wetland designated uses.⁸⁰

The record for the CWA Section 404 permit application and MPCA's CWA Section 401 certification do not speak directly to how the proposed NorthMet project will meet the Band's numeric specific conductance standard, which post-dates these permitting documents,⁸¹ nor the Band's narrative or antidegradation standards. The Corps' ROD, informed by the FEIS, describes how engineering controls, a wastewater treatment plant, and state permit conditions (within the permit suite) will generally minimize and manage the NorthMet project's potential effects to downstream water quality. While the ROD does not specifically reference the Band's specific conductance or narrative standards, the ROD does indicate that reusing the LTV tailings facility will mitigate for existing discharges of total dissolved solids (TDS) and hardness, which directly relate to specific conductance. EPA also notes that the CWA Section 404 permit application, MPCA's CWA Section 401 certification, Corps' ROD, and permit suite all predate adoption of the Band's numeric specific conductance criterion and therefore do not consider the potential for violations of the Band's water quality requirements for specific conductance.⁸²

2. Impacts of Elevated Specific Conductance on the St. Louis Watershed Unimpacted forested and wetland areas within the St. Louis River watershed provide dilution for St. Louis River watershed tributaries that contain elevated levels of specific conductance after receiving discharges from the iron range mining operations. See ORD's Specific Conductance Memo. Both lake sturgeon and brook trout, as well as the benthic invertebrates upon which they feed, require low specific conductance water for naturally sustained populations. Even at a specific conductance threshold below 300 μ S/cm, EPA determined that there would be declines in abundance in aquatic microinvertebrates, and lower thresholds may be needed to be protective of highly salt-intolerant species. As such, elevated specific conductance in wetlands and streams within the St. Louis River watershed would have adverse effects on macroinvertebrate communities as well as higher trophic fish and animal communities throughout, including in the Band's waters.⁸³

EPA's evaluation of the effects to the Band's water quality standards with respect to specific conductance is made in the context of a cumulative loadings and background, which includes both:

⁸⁰ Fond du Lac Objection, beginning on p. 28.

⁸¹ EPA approved the Band's water quality standards that included specific conductance on October 5, 2020. U.S. EPA, EPA's Review of Revisions to the Fond du Lac Band of Lake Superior Chippewa's Water Quality Standards Under Section 303(c) of the Clean Water Act, WQSTS # TR2018-1280,

http://www.fdlrez.com/rm/downloads/WQSEPADecisionDocument10-5-2020.pdf (last visited April 15, 2022). ⁸² U.S. EPA, EPA's Review of Revisions to the Fond du Lac Band of Lake Superior Chippewa's Water Quality Standards Under Section 303(c) of the Clean Water Act, WQSTS # TR2018-1280.

⁸³ EPA ORD Review: Assessment of effects of increased ion concentrations in the St. Louis River Watershed with special attention to potential mining influence and the jurisdiction of the Fond du Lac Band of Lake Superior Chippewa, March 15, 2022 [hereafter ORD Specific Conductance Memo].

- natural specific conductance levels within the St. Louis River, referred to in the ORD Specific Conductance Memo as "least disturbed background [specific conductance] SC," and
- existing sources of specific conductance in the St. Louis River watershed.⁸⁴

To evaluate the potential for the NorthMet project to violate the Band's water quality standard for specific conductance and antidegradation, EPA reviewed the predicted contributions of mineral loadings from the permitted activities (dissolved ions contributing to specific conductance) to the St. Louis River watershed, including:

- Discharges from construction of transportation corridors, tailing basin expansion, wastewater treatment system, and mine site infrastructure;
- Discharges from the tailings basin water treatment plant during operation;
- Discharges from the mine site, including pits, tailings piles, and peat storage during operation;
- Discharges from transportation corridors during operation (e.g., rail spillage);
- Air deposition, as described in the MPCA Multimedia Analysis; and
- Disturbances to unimpacted forested and wetland areas, removing the specific conductance dilution from those subwatersheds (e.g., much of the upper Partridge River), would contribute to higher specific conductance concentrations downstream in the St. Louis River.⁸⁵

3. Baseline Water Quality Conditions and Impacts

EPA reviewed the baseline water quality conditions and impacts associated with specific conductance expected to result from the NorthMet project's discharges, as proposed and as if each of the permits in the permit suite remain as currently drafted. The baseline impacts in turn inform whether the NorthMet project's permits, as currently drafted, will ensure that any discharge from the NorthMet project will comply with the Band's water quality requirements.

Baseline water quality conditions

ORD's Specific Conductance Memo evaluates the existing condition for specific conductance in the St. Louis River watershed. In particular, EPA ORD's analysis of the available data shows that the Partridge River watershed, which includes the proposed mine site, currently has low background specific conductance levels due to undisturbed vegetation and soils. Whereas several small tributaries to the St. Louis River receive high specific conductance discharges from the existing LTV Tailings Basin (proposed NorthMet project tailings basin facility and wastewater treatment plant) through First Creek, the low specific conductance water in the Partridge River draining from the currently undisturbed area of the proposed mine site dilutes the discharge from First Creek but not back to natural background levels.⁸⁶ As water flows downstream along the St. Louis River, specific conductance increases again with inputs from Mesabi Range watersheds until diluted by tributaries entering the St. Louis River mainstem nearer to the reservation.

⁸⁴ Appendix C ORD Specific Conductance Memo.

⁸⁵ Appendix C ORD Specific Conductance Memo.

⁸⁶ Appendix C ORD Specific Conductance Memo.

Existing anthropogenic sources of elevated specific conductance within the St. Louis River watershed include mining in the Mesabi range, wastewater treatment systems, agricultural runoff, unpaved roads, waste sites, and road salt application especially near highways and urban areas. Due to discharges containing specific conductance from many sources in the St. Louis River watershed, data collected in the St. Louis River mainstem shows that the river has been exceeding the Band's numeric water quality criterion of 300 μ S/cm as an annual average, in some recent years.⁸⁷

Impacts from current permits

CWA Section 404 Permit Conditions

The suspended Corps' CWA Section 404 permit⁸⁸ does not contain conditions that apply specifically to specific conductance. Instead, the Corps relies on MPCA's CWA Section 401 certification (along with the accompanying MPCA record) to evaluate whether the proposed project would violate water quality standards and to add water quality monitoring conditions (the certification conditions generally focus on parameters regulated by Minnesota's water quality standards, i.e., not specific conductance). See the *CWA Section 401 Certification Conditions* discussion below. One exception to this is CWA Section 404 Permit Condition No. 14, which is intended to minimize indirect effects to wetlands and streams by requiring erosion control and slope stabilization during construction.⁸⁹ This condition would result in decreasing some contribution of mineral loadings (which would otherwise result in increased specific conductance). Erosion control best management practices (BMPs), as required by CWA Section 404 Permit Condition No. 14, would assist in minimizing the discharge of sediments downstream of the construction, but BMPs alone cannot eliminate the discharges contributing to increased specific conductance downstream.

Additionally, while the suspended CWA Section 404 permit requires compensatory mitigation (in the form of bank credits) for direct and some secondary wetland impacts, it does not account for the loss of dilution capacity provided by the existing undisturbed forested and wetland mine site, which likely would increase specific conductance in the St. Louis River watershed and contribute to violations of the Band's numeric, narrative, and antidegradation water quality standards.

The suspended CWA Section 404 permit also includes a reporting condition as part of an annual Environmental Review Meeting (ERM), in which PolyMet must submit to the Corps "A summary of water quality data required by and reported to the Minnesota Department of Natural Resources (MDNR) and MPCA."⁹⁰ There are provisions of the ERM data reporting that may

⁸⁹ U.S. Army Corps of Engineers, PolyMet Mining, Inc. Permit No. MVP-1999-05528-TJH, March 22, 2019.
 ⁹⁰ U.S. Army Corps of Engineers, PolyMet Mining, Inc. Permit No. MVP-1999-05528-TJH, March 22, 2019, at Condition 34.e.

⁸⁷ Appendix C ORD Specific Conductance Memo, Part 4.

⁸⁸ U.S. Army Corps of Engineers, PolyMet Mining, Inc. Permit No. MVP-1999-05528-TJH, March 22, 2019, <u>https://www.mvp.usace.army.mil/Portals/57/docs/regulatory/PolyMet/NorthMet%20Permit%20-</u> %20Corps%20of%20Engineers.pdf?ver=2019-03-22-091358-997 (last visited April 28, 2022).

show instances of increased mineral loadings at a particular monitoring location (provided as total dissolved solids (TDS) or hardness). However, the suspended CWA Section 404 permit does not require PolyMet to take any action in response to this data, including any action to prevent discharges contributing to elevated specific conductance in the St. Louis River if the data identify any sediment discharge.

When describing the model results to demonstrate that the NorthMet project will not violate applicable water quality standards, the Corps' ROD refers to the Gold Sim Model,⁹¹ which uses probabilistic simulations that take into account uncertainty of the model inputs. The Corps concludes that the water quality model predicts that the NorthMet project would not cause any significant water quality impacts. However, the FEIS referenced surface water evaluation criterion for TDS at 500 or 700 mg/LTDS can be related to SC, and depending on the exact ionic mixture, 500-700 mg/L. TDS criterion would translate to approximately 800 μ S/cm-1200 μ S/cm specific conductance, which far exceeds the Band's numeric criterion of 300 μ S/cm.⁹²

CWA Section 401 Certification Conditions

MPCA's CWA Section 401 certification⁹³ includes wetland monitoring for several parameters, including specific conductance, only "[t]o provide data regarding methylmercury concentrations" related to air deposition.⁹⁴ This includes two years of monthly baseline monitoring from May to October at 22 wetland locations until mining operations commence.⁹⁵ MPCA's CWA Section 401 certification includes other conditions that do not pertain to specific conductance, such as requirements for annual reporting and adaptive management, if reported concentrations exceed some baseline or state water quality standards. However, Minnesota's water quality standards lack a specific conductance criterion to protect aquatic life that would be equivalent to the Band's numeric criterion, and the baseline threshold for action is not yet specified.

CWA Section 402 and Other State Authorizations

MPCA has issued coverage under its CWA Section 402 general permit to authorize discharge of stormwater associated with construction activity for construction of the mine and an individual permit for discharges of process wastewater from the mine, which includes conditions to minimize discharges associated with construction. However, conditions included in the general permit would not eliminate discharges of minerals (or any dissolved parameters).

http://www.fdlrez.com/rm/downloads/WQSEPADecisionDocument10-5-2020.pdf (last visited April 15, 2022). ⁹³ MPCA's CWA Section 401 Certification, Condition 1.

⁹¹ FEIS Section 5.2.2.1.

⁹² U.S. EPA, *EPA*'s Review of Revisions to the Fond du Lac Band of Lake Superior Chippewa's Water Quality Standards Under Section 303(c) of the Clean Water Act, WQSTS # TR2018-1280,

⁹⁴ MPCA's CWA Section 401 Certification, Condition 1.

⁹⁵ MPCA's CWA Section 401 Certification, Condition 1.

The MPCA's individual CWA Section 402 permit contains monitoring requirements for specific conductance, but no conditions that would limit the discharge of dissolved ions contributing to elevated specific conductance to a level that would ensure compliance with the Band's water quality standards. The wastewater treatment system, as designed would remove dissolved ions from the wastewater. However, minerals (granular calcite via the limestone contactor)⁹⁶ will be added to the treated water for effluent stabilization purposes, adding dissolved ions to the discharge. The permit requires monitoring of some parameters related to specific conductance (e.g., sulfate, TDS, hardness), but there is no water quality based effluent limit for specific conductance on the effluent. It is uncertain what the mineral content of the effluent would be. Further, Minnesota does not have a comparable water quality standard for specific conductance to the Band's water quality standards, and the Band's numeric water quality standard of 300 μ S/cm was not yet approved by EPA when the CWA Section 402 permit was issued.

MPCA's CWA Section 401 Certification relied on the CWA Section 402 permit to determine that there would be a net improvement in the "salty parameters" due to PolyMet's plan to manage seeps from the existing LTV Tailings Basin.⁹⁷ PolyMet is proposing to improve upon an existing seepage capture and return system at the tailings basin. The seepage capture system would collect and return seepage to the tailings basin, most of which currently flows to wetlands and small tributaries north and west of the Plant Site that flow towards the Embarrass River⁹⁸. MPCA predicts that the overall result of the seepage capture and return system to be an improvement in water quality parameters including specific conductance downstream of the tailings basin. However, it is not clear from 2017 NPDES Antidegradation Assessment that all loading contributing to elevated specific conductance were considered when the conclusion of net improvement was made. The FEIS model (960 μ S /cm) and CWA Section 402 permit (design model estimate of 334 μ S /cm) estimates of specific conductance within permitted discharges exceed the Band's standard and do not account for all potential sources of specific conductance.

4. Conclusion

Due to discharges containing mineral loadings from many sources in the St. Louis River watershed, data collected in the St. Louis River mainstem shows that the River has been exceeding the Band's numeric water quality criterion of 300 μ S/cm as an annual average, in some recent years. The NorthMet project, as proposed, includes discharges of mineral loadings contributing to specific conductance, removal of dilution from the mine development area, but also reduction of the current loading of dissolved minerals that contribute to specific conductance from the existing unpermitted seepage of pollutants from the existing tailings basin.

Additional inputs from the NorthMet project, as proposed, along with the elimination of some of the available dilution to the system will result in the criterion being exceeded more frequently. EPA recognizes that PolyMet proposes to decrease loadings (including dissolved minerals

 ⁹⁶ MPCA, National Pollutant Discharge Elimination System/State Disposal System (NPDES/SDS) Permit Program Fact Sheet, MN0071013, Prepared for public comment period beginning January 31, 2018, p. 38.
 ⁹⁷ MPCA's 401 Antidegradation Assessment, December 20, 2018,

https://www.pca.state.mn.us/sites/default/files/wq-wwprm1-51ii.pdf (last visited April 27, 2022). 98 FEIS Ch. 5, pp. 183-193.

contributing to SC) from the existing tailings basins by capturing existing seeps and constructing a new wastewater treatment system. However, without a quantification of total mineral loadings within the tailings basin and mine site sub-watersheds, EPA is not able to confirm that there would be a decrease in specific conductance as a result of the NorthMet project, as proposed.

Furthermore, as explained in the ORD Specific Conductance Memo, even the smallest amount of increase in specific conductance would result in violations of the Band's numeric water quality standards. The EPA ORD Specific Conductance Memo describes that an increase of the St. Louis River's annual average specific conductance levels of $3.4 \,\mu$ S/cm upstream from the Fond du Lac Reservation would violate the Band's water quality criterion of $300 \,\mu$ S/cm more frequently with concomitant impacts to aquatic life.⁹⁹ It is uncertain what the cumulative mineral loadings would be that contribute to specific conductance downstream of the NorthMet project, and there are no corrective actions specified in the permits that would reverse trends showing that specific conductance is increasing.

With respect to the suspended CWA Section 404 permit, EPA's evaluation is that, if issued, the permit would authorize activities that would contribute additional mineral loadings to the St. Louis River and decrease the dilution capacity provided by the existing undisturbed forested and wetland mine site, which likely would increase specific conductance in the St. Louis River watershed and contribute to violations of the Band's numeric, narrative, and antidegradation water quality standards. As detailed above, the suspended CWA Section 404 permit and the CWA Section 401 certification do not sufficiently address the Band's water quality requirements with respect to specific conductance. EPA also notes that the CWA Section 404 permit application, MPCA's CWA Section 401 certification, Corps' ROD, and permit suite all predate adoption of the Band's numeric specific conductance criterion and therefore do not consider the potential for violations of the Band's water quality requirements for specific conductance.¹⁰⁰ With respect to the CWA Section 401 certification conditions, EPA's evaluation is that the certification conditions would not ensure compliance with the Band's water quality requirements pertaining to specific conductance and antidegradation because it does not contain sufficient monitoring or action thresholds for specific conductance. With respect to the individual MPCA CWA Section 402 permit, although the permit requires instream water quality monitoring to demonstrate whether water quality improvements occur, there is no specific target or requirement to limit the discharge of dissolved ions contributing to elevated specific conductance that would comply with the Band's water quality standards. MPCA's coverage under its CWA Section 402 general permit to authorize discharge of stormwater associated with construction activity includes conditions to minimize discharges associated with construction. However, conditions included in the general permit would not eliminate discharges of minerals (or any dissolved parameters).

⁹⁹ EPA ORD Specific Conductance Memo, p. 2, Highlight No.1.

¹⁰⁰ U.S. EPA, EPA's Review of Revisions to the Fond du Lac Band of Lake Superior Chippewa's Water Quality Standards Under Section 303(c) of the Clean Water Act, WQSTS # TR2018-1280, http://www.fdlrez.com/rm/downloads/WQSEPADecisionDocument10-5-2020.pdf (last visited April 15, 2022).

As noted above, unimpacted forested and wetland areas within the St. Louis River watershed provide dilution for St. Louis River watershed tributaries that contain elevated levels of specific conductance after receiving discharges from the iron range mining operations. The increase in loadings from the NorthMet project and the decrease in dilution from the loss of the wetlands and forested areas will result in increased specific conductance concentrations in the Band's waters as a result of the discharges from the CWA Section 404 permitted activities, as proposed. Because even relatively small increases in mineral loading–and/or decreases in dilution capacity–would likely result in violations of the Band's water quality requirements pertaining to specific conductance and antidegradation, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for specific conductance for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

C. Other Topics

1. Introduction

The Band's Objection describes other concerns pertaining to specific design aspects of the NorthMet project, including the risk that the dam for the new tailing basin dam will fail and the possibility of future dam expansion. EPA did not include a comprehensive evaluation of these concerns as part of this CWA Section 401(a)(2) evaluation. However, EPA is providing observations regarding these aspects of the objection.

Additionally, the Band's Objection describes other concerns related to treaty rights and environmental justice concerns. As discussed below, EPA believes EPA's evaluation and recommendations are consistent with EPA's tribal treaty and rights obligations and commitment to addressing environmental justice issues.

2. Risk of Tailings Basin Failure

The Band's Objection discusses its concerns with the new tailing basins dam. According to the Band, because the dam will be built using the upstream construction methods using materials from existing LTV tailings basin, there is a high chance of failure.¹⁰¹ That failure would in turn cause discharges that would impact the Band's waters.

While EPA recognizes that a failure of the tailings basin, if it occurred, would likely constitute an unpermitted discharge of pollutants into the St. Louis River watershed, potentially contributing to a violation of the Band's water quality standards, EPA defers to the Corps' conclusion in the ROD that the "design of the tailings basin impoundment dam complies with industry standards for stability and safety."¹⁰²

¹⁰¹ Fond du Lac Objection, p. 11.

¹⁰² Corps' ROD, Decision Summary, p. 47 of 89.

3. Future Mine Expansion

According to the Band's Objection, there is a potential for PolyMet to need to expand the NorthMet project for it to be economically feasible, which would increase the adverse impacts described by the Band.¹⁰³

EPA acknowledges this concern and the resulting potential increases in adverse impacts from such an expansion. However, EPA defers to the Corps' response to this concern included in the Corps' ROD that at this time further expansion is speculative and, if proposed, would require additional environmental review and would need to meet appropriate regulatory requirements, including applicable water quality requirements.¹⁰⁴

4. Treaty Rights

The Band's Objection describes the unique importance that the St. Louis River watershed has to the Band because the Band retains judicially affirmed rights to hunt, fish, and gather within the territory ceded under the Treaty of 1854 (10 Stat. 1109), which includes the NorthMet project site.¹⁰⁵ Significantly, the St. Louis River forms part of the Band's reservation boundary.¹⁰⁶ The Band received "treatment in a similar manner as a state" in 1996 and has authority to set water quality standards for its reservation, including in the St. Louis River. The water quality standards adopted by the Band protect tribally designated uses, including protection of aquatic dependent resources and the protection of culturally important designated uses which are integral to protecting the health and welfare of Band members. The Band asserts that the NorthMet project will adversely impact the Band culturally, socially, economically, and ecologically, including threatening treaty reserved rights to use and harvest resources, as well as adversely impacting the health of Band members who consume fish and other aquatic dependent resources that will be adversely impacted by discharges from CWA Section 404 permitted activity. In addition, the Band states that the protection of its downstream waters is integral to protection of fish and other aquatic-dependent resources within the Band's reservation, which the Band's water quality requirements are designed to support.¹⁰⁷

EPA is committed to consulting and coordinating with federally recognized Indian tribes, as expressed in EPA's Policy on Consultation and Coordination with Indian Tribes and EPA's Policy on Consultation and Coordination with Indian Tribes: Guidance for Discussing Tribal Treaty Rights.¹⁰⁸ The Policy sets a broad standard for when EPA should consider consulting with

¹⁰⁸ EPA, Policy on Consultation and Coordination with Indian Tribes (May 4, 2011), <u>https://www.epa.gov/sites/default/files/2013-08/documents/cons-and-coord-with-indian-tribes-policy.pdf</u> (last visited April 27, 2022); EPA Policy on Consultation and Coordination with Indian Tribes: Guidance for Discussing Tribal Treaty Rights (February 19, 2016), <u>https://www.epa.gov/sites/default/files/2016-</u>

¹⁰³ Fond du Lac Objection, p. 5.

¹⁰⁴ Corps' ROD, Decision Summary, pp. 19-20 of 89.

 ¹⁰⁵ Fond du Lac Objection, pp. 33-34; *Minnesota v. Mille Lacs Band of Chippewa Indians*, 526 U.S. 172 (1999) and, *inter alia, Fond du Lac Band of Chippewa Indians v. Carlson*, No. 5–92–159 (D. Minn. Mar. 18, 1996).
 ¹⁰⁶ Treaty with the Chippewa, 1854, <u>https://glifwc.org/TreatyRights/TreatyChippewa09301854Web.pdf</u> (last visited

March 28, 2022); Fond du Lac Objection, pp. 33-34.

¹⁰⁷ Fond du Lac Objection at 33-34; see also U.S. EPA, Application of Region 5's CWA 401(a)(2) "May Affect" Screening Analysis for PolyMet's NorthMet Mining Project (June 4, 2021).

^{02/}documents/tribal treaty rights guidance for discussing tribal treaty rights.pdf (last visited April 27, 2022).

federally recognized tribal governments based on Executive Order 13175¹⁰⁹ and EPA's 1984 Policy for the Administration of Environmental Programs on Indian Reservations.¹¹⁰ These policies are amplified in the January 26, 2021 *Memorandum on Tribal Consultation and Strengthening Nation-to-Nation Relationships*,¹¹¹ which charges all executive departments and agencies with engaging in regular, meaningful, and robust consultation with Tribal officials in the development of Federal policies that have Tribal implications. EPA and the Department of the Army, together with other executive departments and agencies, are also signatories to the 2021 Memorandum of Understanding Regarding Interagency Coordination and Collaboration for the Protection of Tribal Treaty and Reserved Rights¹¹² (2021 MOU).

EPA recognizes the importance of treaty rights and EPA's obligation to honor those rights. EPA's Guidance for Discussing Tribal Treaty Rights during consultation specifically provides that that:

during consultation with federally recognized tribes (tribes), EPA will seek information and recommendations on tribal treaty rights in accordance with [its] Guidance. EPA will subsequently consider all relevant information obtained to help ensure that EPA's actions do not conflict with treaty rights, and to help ensure that EPA is fully informed when it seeks to implement its programs and to further protect treaty rights and resources when it has discretion to do so.¹¹³

EPA held government-to-government consultation with the Band on January 25, 2022, to listen to the Band's concerns detailed in its Objection. Additionally, as part of the consultation process for this matter, EPA held meetings on March 17, 2022, and on April 8, 2022, with Band representatives to provide an opportunity for the Band to further communicate its concerns to EPA.¹¹⁴

EPA notes that the Corps, as the CWA Section 404 permit issuing authority, and as a signatory to the 2021 MOU, has an independent obligation to consider impacts the Band's treaty rights in making its decision regarding permit issuance. EPA further notes that the Corps' ROD for the NorthMet project contains little information regarding the consideration of treaty rights and, further, that the Corps concludes that the co-lead agencies were able to learn "little specific information concerning recent-historic subsistence use and [identified] no information regarding contemporary subsistence activity at the Mine Site, Transportation and Utility Corridor, or Plant

¹¹³ EPA's Guidance for Discussing Tribal Treaty Rights, <u>https://www.epa.gov/sites/default/files/2016-</u>

¹⁰⁹ Executive Order 13175, Consultation and Coordination with Indian Tribal Governments (November 9, 2000), <u>https://www.govinfo.gov/content/pkg/FR-2000-11-09/pdf/00-29003.pdf</u> (last visited April 27, 2022).

 ¹¹⁰ EPA, Policy for the Administration of Environmental Programs on Indian Reservations (November 8, 1984), <u>https://www.epa.gov/sites/default/files/2015-04/documents/indian-policy-84.pdf</u> (last visited April 27, 2022).
 ¹¹¹ EPA's Guidance for Discussing Tribal Treaty Rights <u>https://www.whitehouse.gov/briefing-room/presidential-actions/2021/01/26/memorandum-on-tribal-consultation-and-strengthening-nation-to-nation-relationships/.
</u>

¹¹² Memorandum Of Understanding Regarding Interagency Coordination and Collaboration for the Protection of Tribal Treaty Rights and Reserved Rights, November 2021, <u>https://www.epa.gov/sites/default/files/2017-</u>02/documents/mou_treat_rights_12-01-16_final.pdf (last visited April 25, 2022).

<u>02/documents/tribal_treaty_rights_guidance_for_discussing_tribal_treaty_rights.pdf</u> (last visited March 31, 2022). ¹¹⁴ Appendix D, U.S. EPA, Notes from January 25, 2022 Consultation Call; U.S. EPA, Notes from March 17, 2022 Lawyers' Call; U.S. EPA, Notes from April 8, 2022 Consultation Call.

Site."¹¹⁵ Aside from this lack of information gathering, EPA does not observe that there was an attempt to understand resource use within the Fond du Lac Reservation where the Band's water quality requirements specifically protect the Band's designated uses of reservation waters, including the protection of fish and aquatic dependent species upon which Band members rely for subsistence, but also because of the Band's commitment to protect these resources for their ecological and cultural values. EPA also does not observe that there was an attempt to understand how increased mercury impacts from the CWA Section 404 permitted activities would specifically impact and bioaccumulate in those species upon which Band members rely.¹¹⁶ Despite this lack of information, the Corps concludes:

Construction and operation of the Project is not likely to significantly reduce overall availability of 1854 Treaty resources that are typically part of subsistence activities in the 1854 Ceded Territory. Some individuals and localized populations may be affected, but overall species populations are expected to remain available. The sulfate released from the NorthMet waste rock and tailings is especially important because there are waters supporting the production of wild rice downstream from both the Mine Site and Tailings Basin. Research indicates that elevated sulfate concentrations can affect the growth and viability of wild rice. The MPCA has established a 10 mg/L sulfate water quality standard for waterbodies designated as waters used for production of wild rice. Effluent from the WWTS would be discharged at a water quality based effluent limit concentration that protects the sulfate standard for waters used for production of wild rice (10 mg/L). The Corps has determined the Project would have minor adverse impacts on cultural resources.¹¹⁷

The Corps also notes that the NorthMet project is unlikely to present a "statistically measurable" change to methylmercury concentrations and thus there is "no expected change in fish mercury concentrations, and no subsequent change in human health risks related to fish consumption [citation to FEIS omitted]."¹¹⁸ The Band raised issue with these conclusions in the Band's Objection and during consultation between EPA and the Band regarding the Band's concerns about increased mercury concentrations in fish within its reservation waters. EPA notes that the

¹¹⁵ Corps' ROD, pp. 63-64.

¹¹⁶ EPA notes that the Great Lakes Water Quality Guidance defines a bioaccumulative chemical of concern (BCC) as: "any chemical that has the potential to cause adverse effects which, upon entering the surface waters, by itself or as its toxic transformation product, accumulates in aquatic organisms by a human health bioaccumulation factor greater than 1000." For comparison, the bioaccumulation factors for mercury are 27,900 for trophic level three fish and 140,000 for trophic level 4 fish. EPA, *Great Lakes Water Quality Initiative Criteria Documents for the Protection of Human Health* (1995), p. 50, <u>https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=2000GYZK.txt</u> (last visited April 27, 2022). The Great Lakes Water Quality Guidance defines a bioaccumulative chemical of concern (BCC) as: "any chemical that has the potential to cause adverse effects which, upon entering the surface waters, by itself or as its toxic transformation product, accumulates in aquatic organisms by a human health bioaccumulation factor greater than 1000." For comparison, the bioaccumulation factors for mercury are 27,900 for trophic level 4 fish.

¹¹⁷ Corps' ROD, p. 64.

¹¹⁸ Corps' ROD, pp. 73-74.

Band's population harvests and consumes a higher per capita amount of fish than the general population.¹¹⁹ The Band specifically states in its Objection:

As the Band indicated in its March 6, 2012, letter to the St. Paul District of the Army Corps of Engineers, Attachment 2, Ex. 3, mercury and specifically methylmercury in Reservation waters and wetlands are the principal health concerns of the Band. Mercury concentrations in the St. Louis River have exceeded the Band's chronic human health standard (0.77 ng/L) for more than a decade. Consumption of fish contaminated by methylmercury is the primary exposure pathway for Band members and wildlife, and existing monitoring data indicate levels are already elevated in many species that are consumed as food [citation omitted]. The Band continues to be especially concerned about any new or expanded discharges to the St. Louis River system upstream of the Reservation that will contribute to cumulative increases in mercury and sulfate loadings, enhance mercury methylation, and increase methylmercury bioaccumulation in fish and wetland dependent wildlife. The discharges from the Project will increase the loading of mercury, manganese. [citation omitted] and sulfate in the St. Louis River [citation omitted]. Both the Embarrass and Partridge Rivers are listed by the Minnesota Department of Natural Resources as impaired waters, from their headwaters to their confluence with the St. Louis River. The St. Louis River is listed as impaired for methylmercury in fish tissue where it forms the northern and eastern boundaries of the Reservation. There have been and continue to be fish consumption advisories for the St. Louis River that greatly affect the Band's members by inhibiting the traditional and safe consumption of fish.¹²⁰

The Band has repeatedly voiced concerns that its members are at risk from elevated mercury levels in fish and have further raised concerns regarding mercury impacts to fish and aquatic-dependent resources within reservation waters. EPA does not observe that these concerns have been either acknowledged or addressed. Therefore, with respect to the protection of the Band's water quality requirements that ensure the protection of the Band's rights to fish and to harvest and consume other aquatic dependent species—and in light of the uncertainties discussed herein regarding pollutant discharges from permitted activities and the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are unaccounted for in the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project—EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for the protection of fish and other

¹¹⁹ Fond du Lac Objection, pp. 6, 8-9, 21-22, 33-34; EPA, Appendix D, Notes from Consultation, January 26, 2022. Because mercury is so highly bioaccumulative, fish consumption rate has a significant effect on the magnitude of water quality criteria to protect human health. Minnesota's criterion for mercury to protect human health are based on a fish consumption rate of 30 g/D, resulting in a human health criterion of 0.00153 μ g/L. The Band's criterion for mercury is based on a fish consumption rate of 60 g/D and results in a criterion of 0.00077 μ g/L to protect human health. Minnesota also has a wildlife criterion of 0.0013 μ g/L to protect wildlife which is more stringent than its human health criterion and is the criterion that is the basis for the operating limits contained in the CWA Section 402 permit for the NorthMet wastewater treatment facility.

¹²⁰ Fond du Lac Objection, pp. 8-9; *see also id.* pp. 6, 21-22, 33-34.

aquatic-dependent resources in reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

5. Environmental Justice

The Band asserts that NorthMet project impacts will disproportionately fall on Band members and that the Corps' review of the PolyMet CWA Section 404 permit application did not adequately consider environmental justice equities. The Band states in its Objection:

Band members rely on aquatic resources harvested from these freshwater ecosystems for subsistence foods and as part of their traditional fishing activities that are essential for maintaining and protecting culture. In addition to the deleterious impacts of methylmercury on human health (summarized below), studies for other indigenous groups have shown substantial social costs associated with restricted traditional hunting and fishing due to environmental contaminants including increases in depression, suicide, and addiction (Van Oostdam et al., 2005). As noted herein, hunting and fishing activities have already been limited due to environmental pollution within the Band's Reservation (and its Ceded Territory). Any further increase in pollution poses unacceptable risks to the Band's traditional lifestyle, culture, and health and violates environmental justice considerations.¹²¹

The Band asserts that EPA has an obligation to implement environmental justice principles in carrying out EPA's evaluation and recommendations pursuant to CWA Section 401(a)(2); and that the Corps has a parallel obligation to apply environmental justice principles in carrying out its permitting responsibilities under CWA Sections 401(a)(2) and 404.¹²²

EPA recognizes the importance of meaningful community engagement in and consideration of the impacts of federal actions through EPA's *Policy on Environmental Justice for Working with Federally Recognized Tribes and Indigenous Peoples* (July 2014). The policy affirms EPA's commitment to exercise and ensure fair treatment and meaningful involvement for federally-recognized tribes and indigenous peoples in all areas of the United States for all EPA matters that may affect their health or environment.¹²³ The Corps, as the CWA Section 404 permit issuing authority, has an obligation to consider environmental justice in making its permitting decisions. EPA notes that the Corps undertook an environmental justice analysis as part of its ROD for this project.¹²⁴ Based on this, the Corps concludes:

As described in Section 10.8, Band members' use of the Project area is not well-defined and did not emerge during interviews. Without private landowner permission, there is minimal opportunity for the Bands to exercise usufructuary rights (hunting, fishing, and gathering) on this property. Construction and operation of the Project is not likely to

¹²¹ Fond du Lac Objection, p. 22.

¹²² Fond du Lac Objection, pp. 33-34.

¹²³ EPA, Policy on Environmental Justice for Working with Federally Recognized Tribes and Indigenous Peoples (2016), <u>https://www.epa.gov/sites/default/files/2017-10/documents/ej-indigenous-policy.pdf</u> (last visited April 19, 2022), p. 1; see also U.S. EPA, EJ 2020 Action Agenda: EPA's Environmental Justice Strategy,"

https://www.epa.gov/sites/default/files/2016-05/documents/052216_ej_2020_strategic_plan_final_0.pdf (last visited April 19, 2022).

¹²⁴ Corps' ROD, p. 88 of 89.

significantly reduce overall availability of 1854 Treaty resources that are typically part of subsistence activities in the 1854 Ceded Territory. Effects on 1854 Treaty resources are difficult to quantify when the effects are within environmental standards, yet above current baseline conditions. Some individuals and localized populations may be affected, but overall species populations are expected to remain available. Effects on the environment, including any from increased mercury, are expected to meet the standards and regulations set forth by the appropriate state or federal agency or program. These laws are intended to protect important natural and cultural resources and include, but are not limited to the ESA, CWA, and CAA. In conclusion, the Project would not have a disproportionately high and adverse human health or environmental effect on minority populations and low-income populations. The proposed action is in compliance with Title VI of the Civil Rights Act and Executive Order 12898 [Emphasis added].¹²⁵

Available Census data shows that for the past 12 months, more than 20% of all persons living on the Fond du Lac Reservation and off-reservation trust lands are living at or below the poverty level, with some 31% of American Indian/Alaska Native *alone* living at or below the poverty level.¹²⁶ The Band, in its objection and elsewhere, has repeatedly stated that its members rely upon fish and other aquatic-dependent species for subsistence food and for the ecological and cultural significance of these species. The Band also notes the disproportionate impact of mercury consumption in children and in more vulnerable members of a population: Even without projected discharges from CWA Section 404 permitted activities from this project, the Band states that "[t]he remaining fish [in the St. Louis River watershed] are now so high in mercury that the Band members cannot safely feed the fish to their children."¹²⁷ In light of the Band's significant and documented reliance on fish and other aquatic dependent species, the Corps' ROD conclusion that "[s]ome individuals and localized populations may be affected [by activities permitted under the CWA 404 permit]" appears to discount environmental justice concerns.

With respect to the consideration of the Band's statements regarding the disproportionate impact the project is likely to have on Band members-specifically because of tribal members' particular reliance upon the fish and other aquatic-dependent species that are likely to be impacted within

¹²⁵ Corps' ROD, p. 88 of 89.

¹²⁶ United States Census Bureau, American Community Survey, 5-year estimates, 2020, Table ID B17001, Fond du Lac Reservation and Off-Reservation Trust Land, Poverty Status in the Past 12 Months by Sex by Age, https://data.census.gov/cedsci/table?q=fond%20du%20lac%20reservation&tid=ACSDT5YAIAN2015.B17001 (last visited April 29, 2022); United States Census Bureau, American Community Survey, 5-year estimates, 2020, Table ID B17001C, Fond du Lac Reservation and Off-Reservation Trust Land, Poverty Status in the Past 12 Months by Sex and Age (American Indian and Alaska Native Alone),

https://data.census.gov/cedsci/table?q=B17001C%3A%20POVERTY%20STATUS%20IN%20THE%20PAST%20 12%20MONTHS%20BY%20SEX%20BY%20AGE%20%28AMERICAN%20INDIAN%20AND%20ALASKA%2 0NATIVE%20ALONE%29&g=2800000US271125&tid=ACSDT5Y2020.B17001C (last visited April 28, 2022).

¹²⁷ Fond du Lac Objection at 34; *see also id.* pp. 6 and 22. Additionally, the Band states: "The Band presently has fish consumption guidelines in place to protect public health, including a recommendation to limit consumption for women who are or may become pregnant and for all children under 15 years old. *See* Attachment 4 (Geyaabi Go Onishi Brochure)." *Id.* p. 6.

the Band's reservation-and given uncertainties discussed throughout EPA's Evaluation regarding pollutant discharges from permitted activities, in addition to the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are unaccounted for in the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements that protect the Band's particular reliance on fish and aquatic species in reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

IV. EPA's Recommendations

The following recommendations are pursuant to the requirements of EPA outlined in the CWA Section 401(a)(2):

The Administrator shall at such hearing submit his evaluation and recommendations with respect to any such objection to the licensing or permitting agency.

The Corps then must consider the recommendations, and other relevant information in its CWA Section 404 permit decision, consistent with the subsequent statement, as follows:

Such agency, based upon the recommendations of such State, the Administrator, and upon any additional evidence, if any, presented to the agency at the hearing, shall condition such license or permit in such manner as may be necessary to insure compliance with applicable water quality requirements. If the imposition of conditions cannot insure such compliance such agency shall not issue such license or permit.¹²⁸

EPA recommends the Corps not reinstate the suspended CWA Section 404 permit for the NorthMet project, as currently proposed, because EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

This recommendation accounts for the current mercury impairment of the Band's waters, with the St. Louis River exceeding the Band's chronic human health standard for mercury (0.77 ng/L). Likewise, this recommendation accounts for the current condition of the Band's waters with regard to specific conductance. In some years, the St. Louis River where it in intersects the Fond du Lac Reservation also exceeds the Band's numeric standard for specific conductance (300 μ S/cm). The Fond du Lac Reservation is directly downstream of the NorthMet project. Thus, the discharges from CWA Section 404 permitted activities contributing to mercury/methylmercury and mineral loadings to the St. Louis River watershed would contribute to the total loadings that impact the Band's waters and violate the Band's water quality requirements.

¹²⁸ 33 U.S.C. § 1341(a)(2).

Further, the Band's water quality standard for mercury is more stringent than Minnesota's water quality standard (0.77 ng/L and 1.3 ng/L respectively), on which MPCA's CWA Section 401 certification is based. Similarly, Minnesota does not have a comparable numeric water quality standard to the Band's specific conductance standard of 300 μ S/cm, and MPCA did not adequately consider specific conductance in its CWA Section 401 certification.

As detailed in Sections III A.3 and III B.3 of this document, to assess whether and under what conditions, if any, the CWA Section 404 permit could be issued that would ensure compliance with the Band's water quality requirements, EPA reviewed the baseline water quality conditions and impacts associated with mercury and specific conductance expected to result from the NorthMet project's discharges, as proposed and as if each of the permits in the permit suite remain as currently drafted. For both mercury and specific conductance, EPA reviewed the suspended CWA Section 404 permit, MPCA's CWA Section 401 certification, and CWA Section 402 permits to evaluate permitted discharges contributing to elevated mercury and specific conductance as well as any permit conditions that may address the cumulative mercury and specific conductance contributions from the NorthMet project.

Through EPA's evaluation of the Band's Objection, EPA identified several points of uncertainty and reasonably foreseeable discharges of mercury and dissolved ions contributing to specific conductance with respect to the NorthMet project and CWA Section 404 permitted activities, including the following examples:

- Significant uncertainty regarding the full acreage of secondary impacts to wetlands from the anticipated drawdown of groundwater from mine construction and operation;
- Uncertainty in the mercury present in and the fate and transport of such mercury from wetlands subject to secondary impacts from the anticipated drawdown of groundwater from mine construction and operation;
- Uncertainty regarding the extent to which mercury methylation would increase in the St. Louis River watershed due to direct and secondary impacts to wetlands from mine construction and operation;
- An unknown quantity of total mercury and dissolved ions (contributing to elevated specific conductance) discharged during mine construction;
- An unknown quantity of total mercury and dissolved ions (contributing to elevated specific conductance) discharged via seepage; and
- An unknown reduction in dilution capacity contributing to elevated specific conductance.

In developing EPA's recommendation, EPA took these uncertainties into account, along with the baseline water quality conditions and water quality impacts as permitted and conditioned in each permit within the permit suite and the reasonably foreseeable downstream water quality effects from the discharges from the CWA Section 404 permitted activities.

In preparing recommendations, EPA considered whether conditions to the CWA Section 404 permit (e.g., monitoring, planning and adaptive management, and mitigation or remediation)

could be developed that would ensure compliance with the Band's water quality requirements (both pertaining to mercury and specific conductance). Such CWA Section 404 permit conditions would need to be implementable and enforceable by the Corps, meaning that they would contain measurable water quality-based limits/thresholds with required actions that would prevent the violation of a neighboring jurisdiction's water quality requirement (e.g., adaptive management, mitigation, remediation). Such water quality-based limits/thresholds are impractical in light of the previously discussed limitations on the available data and permit conditions. Because EPA cannot recommend a CWA Section 404 permit condition that would ensure the NorthMet project complies with the Band's water quality requirements on the reservation, EPA recommends the Corps not reinstate the suspended permit, as currently proposed.

The ORD Mercury Memo analysis contains recommendations to include additional modeling and monitoring of wetland dewatering and other mercury sources to create a process-based mass balance model for mercury contributions to the St. Louis River. EPA anticipates that the additional mercury/methylmercury load analysis could assist PolyMet to develop measures to minimize, adapt, and mitigate for the increased mercury/methylmercury. However, because the St. Louis River is already exceeding the Band's water quality standard for mercury and not meeting designated uses, any addition of mercury from the NorthMet project could contribute mercury at a concentration greater than the Band's water quality criterion of 0.77 ng/L and thereby violate the Band's water quality requirements. As mentioned, eliminating all releases of mercury is not feasible under the current mine design given pit dewatering and CWA Section 402 permitted discharges.

The ORD Specific Conductance Memo provides a potential path forward with respect to specific conductance, which consists of quantifying potential sources of increased specific conductance (including CWA Section 402 permitted discharges and loss of dilution due to land use change) and identifying specific conductance criteria for species of concern in the St. Louis River (e.g., brook trout and lake sturgeon). Once that analysis is complete, a subwatershed cumulative mineral loadings assessment may suggest engineering controls to balance changes in loadings due to the development of the proposed mine. However, as the CWA Section 404 permit is currently proposed, it is untenable to fit the ORD Specific Conductance Memo recommendations into a Corps CWA Section 404 permit condition because the outcome of the subwatershed total maximum daily load for specific conductance and the scale of wetland dewatering are unknown. The scale of loadings and dewatering are necessary information to develop implementable, enforceable, and meaningful conditions for adequate engineering controls to ensure the NorthMet project would comply with the Band's specific conductance and narrative water quality standards.

Given uncertainties regarding pollutant discharges from permitted activities, in addition to the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are unaccounted for in the CWA Section 404 permit application and suspended permit, MPCA's CWA Section 401 certification, and MPCA's CWA Section 402 permits for the NorthMet project, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for reservation waters,

given current project design and discharges outside the CWA Section 404 permitted activities. EPA's recommendations do not foreclose any future modifications to the permit application or the NorthMet project design. Any future modifications should include meaningful involvement of the Band and Minnesota to ensure compliance with both tribal and state water quality requirements.

Appendices

Appendix A- References Appendix B- ORD Mercury Memo Appendix C- ORD Specific Conductance Memo Appendix D- EPA Record of Meetings with the Band Appendix E- Applicable Fond du Lac Water Water Quality Standards

WaterLegacy Comments August 11, 2023 St. Louis River Watershed Mercury Total Maximum Daily Load

EXHIBIT 11

(Army Corps, Section 404 Permit Decision Memo for the PolyMet NorthMet Mine Project, June 7, 2023)

EXECUTIVE SUMMARY: Pursuant to Clean Water Act (CWA) Section 401(a)(2), 33 U.S.C. § 1341(a)(2), the U.S. Army Corps of Engineers, St. Paul District (Corps) prepared this CWA Section 404 permit decision document following the Corps' public hearing on the objection raised by the Fond du Lac Band of the Lake Superior Chippewa (Band) to the Corps' issuance of a CWA Section 404 permit for the proposed PolyMet Mining, Inc.¹ (PolyMet) NorthMet mine project in northeastern Minnesota (project). Following EPA's June 4, 2021 "may effect" determination, the Band submitted its "will affect" determination, objection letter, and hearing request to the U.S. Environmental Protection Agency (EPA) and the Corps on August 3, 2021 (Band's Objection). The Corps held a public hearing on the Band's Objection on May 3-5, 2022, at which EPA submitted its evaluation and recommendations. In addition, the Corps received information at the hearing from the Band and PolyMet, as well as over 22,500 comments from the public. The Band contends that the discharges from the project will violate the Band's water quality requirements for mercury and specific conductance. EPA agreed with the Band's determination and recommended that the Corps not reinstate the suspended CWA Section 404 permit as EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for Reservation waters. PolyMet disagrees with the Band and EPA's determinations and requests that the Corps reinstate the CWA Section 404 permit.

The Band claims that the project will contribute to ongoing violations of its water quality requirements for mercury. According to the Band, the construction and operation of the project will alter the hydrology of up to 6000 acres of wetlands, in addition to the approximately 939 acres of direct and fragmentation impacts. The Band contends that these wetland alterations, in addition to the loading of sulfates from the construction and operation of the NorthMet project, will both enhance methylation of mercury already present in the wetlands affected by the proposed mine and mobilize both total and methylmercury in those same wetlands. The Band claims that the mercury mobilized because of these wetland alterations will be exported from the NorthMet project site via the streams adjacent to the affected wetlands at the project site and be transported downstream to the Band's Reservation. The Band concluded that this mercury will further exacerbate ongoing exceedances of the Band's mercury criterion of 0.77 ng/L and ongoing nonattainment of the Band's designated uses.

In addition to the Band, EPA presented concerns at the hearing pertaining to the Band's water quality requirements for mercury. Minnesota has a water quality standard for mercury of 1.3 ng/L, which is higher than the Band's 0.77 ng/L mercury standard. EPA observed that the St. Louis River is already impaired for mercury and lacks assimilative capacity that would ameliorate any adverse impacts of additional mercury loading from the NorthMet project on downstream waters. EPA cited to gaps in data and expressed uncertainty about mercury methylation, mobilization, and discharges to downstream

¹ PolyMet Mining, Inc. is now known as NewRange Copper Nickel LLC, which is a 50:50 joint venture of PolyMet US, Inc. and Tech American Incorporated. This decision document will still refer to "PolyMet" throughout as "PolyMet Mining, Inc." is still the name of the entity listed on the suspended CWA Section 404 permit.

waters as a result of indirect effects to adjacent wetlands. EPA also determined that the project permit suite (consisting of various state and federal permits for the project) does not consider water quality impacts arising from changes in hydrology of wetlands due to the dewatering of the mine pit that will result in the methylation of mercury and mobilization of mercury from the impacted wetlands. EPA concluded that any addition of mercury from the NorthMet project could contribute mercury at a concentration greater than the Band's water quality criterion of 0.77 ng/L and thereby violate the Band's water quality requirements. Given these uncertainties, in addition to the reasonably foreseeable discharges that are unaccounted for in PolyMet's state and federal permits, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements for mercury for Reservation waters, given current project design and discharges outside the CWA Section 404 permitted activities.

Conversely, PolyMet claims that because the project will reduce sulfate loading, it will lower downstream methylmercury. PolyMet has a plan to capture and treat both seepage from the project's tailings basin and any water that contacts mine features. In addition, PolyMet claims that its water management and treatment will also reduce total mercury loading to the watershed and that the large reduction in sulfate should similarly reduce methylmercury in the St. Louis River watershed. PolyMet disagrees with the Band's determination that the project will cause a widespread wetland drawdown and analogizes to a similar project, the Peter Mitchell pit, which PolyMet states did not involve such drawdown. PolyMet claims that even if there is uncertainty about compliance with the Band's water quality requirements, its monitoring and adaptive management plans will ensure that the project's discharges will not violate the Band's requirements.

The Band claims that discharges from the project will violate the Band's water quality requirements for specific conductance due to the contributions of mineral loadings to the St. Louis River watershed. The Band's numeric water guality standard for specific conductance is 300 us/cm to protect sensitive macroinvertebrate species and the relatively high biodiversity in the Band's waters. Both the CWA Section 404 permit and Minnesota CWA Section 401 certification predate the Band's adoption of its numeric specific conductance water quality criterion. EPA states that the St. Louis River has been exceeding this numeric water quality criterion in recent years and that the Clean Water Act 404 permit would authorize activities that would contribute additional mineral loadings to the St. Louis River and decrease the specific conductance dilution capacity currently provided by the existing undisturbed forested wetland mine site. EPA concludes that even relatively small increases in specific conductance loadings and/or decreases in dilution capacity would result in violations of the Band's water guality requirements pertaining to specific conductance and anti-degradation requirements of the Band within wetlands and streams on the Band's Reservation. In contrast, PolyMet claims that its water management and treatment will lower specific conductance and that its activities at the mine site will not increase specific conductance downstream.

Following the hearing, the Corps spent a significant amount of time reviewing a voluminous amount of scientific information and analysis provided by EPA, the Band and PolyMet – as well as other relevant information provided to the Corps by the public at the hearing. As outlined above, the Band and EPA assert that project discharges both within and outside of the Corps' purview under CWA Section 404 will violate the Band's water quality requirements for mercury and specific conductance. Neither the Band nor EPA offered permit conditions that the Corps could attach to a modified CWA Section 404 permit for the project to ensure compliance with the Band's downstream water guality requirements. In addition, PolyMet offered no permit conditions that would ensure compliance with the Band's water quality requirements. The Corps can confirm it did not include any conditions on the CWA Section 404 permit to address potential mercury mobilization, methylation and export to downstream waters from adjacent wetlands. Further, the Corps can confirm that the Section 404 permit predates adoption of the Band's numeric specific conductance criterion and potential for violations of the Band's water quality requirements for specific conductance were not considered. The Corps acknowledges that EPA and the Band have CWA authority on water quality matters concerning the Band's Reservation. Accordingly, the Corps has determined that, given the Corps' jurisdiction under CWA Section 404, the Band and EPA's water quality authorities, and the absence of any necessary permit conditions to ensure compliance with the applicable downstream water quality requirements of the Band as required by CWA Section 401(a)(2), the Corps cannot reissue or modify the suspended permit. Consequently, the Corps must revoke the currently suspended CWA Section 404 permit. This decision does not preclude PolyMet from submitting a new CWA Section 404 permit application that will meet all applicable water quality requirements for its project.

I. BACKGROUND: On March 21, 2019, the Corps completed a Record of Decision and authorized under CWA Section 404 the discharge of dredged and fill material into 901 acres of wetlands and indirect impacts to 27 acres of wetlands in association with the construction and development of the NorthMet mine, located in Minnesota's St Louis County. The Corps determined that the NorthMet Project was compliant with all applicable federal laws and regulations. Under CWA Section 401, the Minnesota Pollution Control Agency issued its Water Quality Certification on December 20, 2018, for impacts to regulated waters in and around the NorthMet mine site within Minnesota.

The Corps suspended its Section 404 permit on March 17, 2021, in response to the EPA's request that it be allowed to consider the effects from the NorthMet Mine Project under CWA Section 401(a)(2) in response to a prior court ruling. Specifically, EPA determined that it needed to consider, under Section 401(a)(2), effects from the NorthMet Project to the water quality of downstream neighboring jurisdictions, which included the state of Wisconsin and the Band. EPA issued a "may affect" determination to the Band and the State of Wisconsin on June 4, 2021. EPA's determination provided each party 60 days to determine if the discharge associated with the Clean Water Act Section 404 permit at the mine site would affect the quality of its waters so as to violate any water quality

requirements. The state of Wisconsin did not object to the Section 404 Clean Water Act permit. The Band did submit an objection to the CWA Section 404 permit on August 3, 2021 and requested that the Corps hold a public hearing on its objection pursuant to CWA Section 401(a)(2). The Band is a federally-recognized tribe and Sovereign Nation and its Reservation is downstream of the NorthMet mine. The Band is recognized as a "state" for purposes of CWA Section 401(a)(2).

The Corps conducted a three-day public hearing from May 3-5, 2022, to collect information to inform its decision. At that hearing the Corps sought information on the Band's objection and whether there were any new conditions that could be added to a modified CWA Section 404 permit to ensure compliance with applicable water quality requirements of the Band. The Corps was required to consider all relevant information presented at the public hearing to inform its final decision to either revoke the currently suspended CWA Section 404 permit, reinstate the permit, or modify the permit with new conditions.

II. INFORMATION FROM PUBLIC HEARING: The following section summarizes what was presented at the public hearing.²

1. Hearing Day 1

Opening statements from the Band and Objection Overview:

The Band stated its objection to the Corps' issuance of the Section 404 CWA permit not because the Band is against mining, but because the project as planned will not protect the Band's Reservation waters and its treaty resources. (Transcript Day 1, page 18). The Band claims federal and state agencies have ignored the science that shows the project raises significant and negative impacts that will reach the Band's downstream Reservation waters. (Transcript Day 1, page 19).

The Band provided information on the reason it adopted water quality standards: to protect and restore all the natural resources essential to the Band's way of life, its culture and homeland. According to the Band, there are no conditions that can be put in place to ensure the NorthMet project will meet its standards. (Transcript Day 1, page 19). The Band issued a comprehensive determination supported by multiple experts that the proposed PolyMet project will result in discharges that will reach downstream Reservation waters and violate the Band's federally approved water quality standards. (Transcript Day 1, page 20).

The Band believes Section 401 of the CWA was enacted to ensure that before a project is permitted, steps are taken to ensure that the project will not pollute waters. It is not intended to merely address pollution caused by the project after the fact through actions

² The following summary was derived from the transcripts of oral statements provided on days 1-3 of the hearing. To the extent this attempted summary misstates, mischaracterizes or is otherwise in conflict with or inconsistent with the transcripts, the transcripts shall govern for accuracy purposes.

like adaptive management. The Band claims PolyMet would try to address violations after the violations have already occurred with no concrete plans on how the problems could ever be fixed. (Transcript Day 1, page 22).

The Band summarized its "will affect" analysis by stating the discharges from the proposed PolyMet project will flow downstream to the Band's Reservation and violate many of the Band's water quality standards, including its anti-degradation policies, its numeric standards for mercury, narrative standards for the protection of aquatic life and culturally-important flora and fauna as well as designated uses for wildlife, warm water fisheries, and subsistence fishing. (Transcript Day 1, pages 18-22).

EPA Overview of its Evaluation and Recommendations:

EPA provided an overview of its evaluation and recommendations. As the NorthMet project is currently designed, there are no conditions that EPA can provide to the Corps that would ensure that the discharges from the Clean Water Act Section 404 permitted activities would comply with the Band's water quality requirements. (Transcript Day 1, page 26.)

EPA's evaluation and recommendations were informed by the Band's objection letter providing its "will affect" determination and supporting documents; documents EPA received from PolyMet during EPA's CWA Section 401(a)(2) "may affect" process and related documents; input received from the Fond du Lac Band during government-to-government consultation with EPA; PolyMet's CWA Section 404 application to the Corps for the NorthMet project and supporting documents; the Minnesota Pollution Control Agency's 401 certification for the Corps' CWA Section 404 permit; the Corps' ROD and Final Environmental Impact Statement for the CWA Section 404 permit for the NorthMet Project (FEIS); the Minnesota Pollution Control Agency's CWA Section 402 permitting documentation, including a general construction stormwater permit and individual surface water discharge permit for the NorthMet project and additional scientific review that EPA Region 5 obtained from its Office of Research and Development. (Transcript Day 1, page 30).

EPA's evaluation identified uncertainty regarding the full acreage of secondary impact to wetlands from the anticipated drawdown of groundwater from mine construction and operation; uncertainty in the mercury present in, and the fate, and transport of, such mercury from wetlands subject to secondary impacts from the anticipated drawdown of groundwater from mine construction and operation; uncertainty regarding the quantity of total mercury and dissolved ions contributing to elevated specific conductance that would be discharged during mine construction; uncertainty regarding the quantity of total mercury and dissolved ions that would be discharged from the mine through seepage; and uncertainty regarding the reduction in dilution capacity of water bodies affected by the NorthMet project that would contribute to elevated specific conductance. (Transcript Day 1, pages 31-32).

With respect to mercury, EPA summarized that the Band's water quality criterion for mercury to protect human health is .77ng/L. This standard is not currently attained in waters within the Band's Reservation. According to EPA, mercury released from wetlands adjacent to the mine site because of changes in hydrology due to construction and operation of the NorthMet mine is a significant potential source of mercury to the St. Louis River watershed. Such mercury releases could exacerbate the ongoing exceedances of the Band's water quality requirements. (Transcript Day 1, page 32). In addition, EPA determined that the data and analysis supporting the CWA Section 404 permit and CWA Section 401 certification is insufficient to fully evaluate the mercury impacts from the NorthMet project in terms of the area of wetlands affected and the effects on the Band's water quality. (Transcript Day 1, page 33).

According to EPA, understanding the scope of the anticipated impacts from the NorthMet project due to changes in wetland hydrologic regimes resulting from the CWA Section 404 permitted activities is essential to estimating the quantities of mercury that may be subject to mercury methylation, mobilization, and export downstream to the Band's already impaired waters. EPA noted that the CWA Section 402 permit for construction of the project does not contain numeric water quality based effluent limitations for mercury that would ensure compliance with the Band's water guality requirement. (Transcript Day 1, page 33). The CWA Section 402 permit includes operating limits on mercury at an internal monitoring station set to Minnesota's water quality standard of 1.3 ng/L. However, this is not sufficient to ensure compliance with the Band's downstream water quality requirements. Technology based effluent limitations on mercury at 1,000 ng/L as a monthly average and 2,000 ng/L as a daily maximum are also not sufficient to ensure compliance with the Band's standards. (Transcript Day 1, pages 33-34). Based on this information, EPA concluded that the CWA Section 404 permit, 402 permit and 401 certification lack conditions sufficient to protect mercury mobilization, methylation and export at levels that would exceed the Band's water guality requirements given current project design and discharges outside of the CWA Section 404 permitted activities. (Transcript Day 1, page 34.).

Regarding specific conductance, EPA noted that the Band's numeric water quality standard for specific conductance is 300 us/cm. (Transcript Day 1, page 34). The CWA Section 404 permit and 401 certification predate the Band's adoption of its numeric specific conductance water quality criterion. Further, neither the CWA Section 404 permit nor the Section 401 certification account for the potential impact of increased specific conductance of the Band's water quality requirements. The St. Louis River has been exceeding this numeric water quality criterion in recent years. (Transcript Day 1, page 36). According to EPA, the CWA Section 404 permit would authorize activities that would contribute additional mineral loadings to the St. Louis River and decrease the specific conductance dilution capacity currently provided by the existing undisturbed forested wetland mine site. EPA also concluded that even relatively small increases in specific conductance loadings and/or decreases in dilution capacity would result in violations of the Band's water quality requirements pertaining to specific conductance and anti-degradation. (Transcript Day 1, page 35-36).

Based on its review, EPA is unaware of any CWA Section 404 permit conditions that the Corps could add to the NorthMet Section 404 permit to ensure compliance with the Band's water quality requirements for specific conductance, given the current project design and discharges outside the CWA Section 404 permitted activities. (Transcript Day 1, page 36). EPA recommends the Corps not reissue the permit for the project as currently proposed. (Transcript Day 1, page 39).

EPA also summarily addressed other issues raised by the Band pertaining to the risk of tailings basin failure, future mine expansion, treaty rights and environmental justice. (Transcript Day 1, pages 36-38). However, these considerations did not appear to play a role in EPA's conclusions on the CWA Section 404 permit based on CWA Section 401(a)(2) considerations. Ultimately, EPA determined that based on significant uncertainties related to the extent of potential discharge and release of mercury and the potential for additional mineral loadings contributing to specific conductance from the CWA Section 404 permitted activities related to the project, in addition to the reasonably foreseeable discharges of methylmercury, mercury, and mineral loadings contributing to specific conductance that are unaccounted for in the CWA Section 404 permit, 402 permits and 401 certification, EPA is unaware of any CWA Section 404 permit conditions that would ensure compliance with the Band's water quality requirements – given current project design and discharges outside the scope of the CWA Section 404 permitted activities. (Transcript Day 1, pages 38-39).

Views, Opinions and Recommendations from the Band:

The Band provided information on work its Resource Management Division does to care for the Band's way of life and what projects like NorthMet imperil in its current form as proposed. The Band shared information about history of the land, the ceded territories, connection of the Band to the land and its waters, the importance of plants and animals, and especially the importance of wild rice. (Transcript Day 1, pages 41-60).

The Band presented information on how it developed its water quality standards 25 years ago that were ultimately approved by EPA. (Transcript Day 1, pages 61-62). The Band's consideration for off-reservation impacts has evolved as it realized that some of the problems it was seeing through monitoring did not originate on the Reservation but rather were coming to the Band from upstream sources. (Transcript Day 1, page 62). The Band has tribally-specific designated uses that include such things as wild rice, cultural resources, and aesthetic resources. Numeric and narrative criteria were established to protect the Band's water resources so that it can continue to support and provide the kinds of resources that its community relies upon for subsistence. The Band's water quality requirements are not intended to simply provide a basement level of protection. Instead, the Band's requirements are in place to protect the qualities and conditions that allow for diversity, healthy and highly functioning ecosystems. (Transcript Day 1, page 64).

According to the Band, all of its Reservation waters are at least tier 2 or exceptional use waters. The Band's wild rice waters are tier 3, and no degree of degradation is permitted to occur in these waters. Based on 20+ years of monitoring, the only impairment the Band has determined that needs to be addressed for Reservation waters is mercury.

Mercury concentrations in the water and in fish are problematic. (Transcript Day 1, page 65). The Band stated its challenges with consuming contaminated fish while trying to balance the need for encouraging the practice of traditional life ways. (Transcript Day 1, page 75).

With respect to specific conductance, the Band is seeing elevated dissolved constituents contributing to specific conductance, or total hardness, of Reservation water on account of impacts from mining features upstream. (Transcript Day 1, page 79). The Band has measured upstream water chemistry inputs 79 miles downstream of where the impact may have originated. (Transcript Day 1, page 96). The Band is concerned that the rising level of specific conductance will thwart its investments in reestablishing a sustainable population of lake sturgeon. (Transcript Day 1, page 94). The Band also noted that its water quality standard for specific conductance, which was approved in 2020, is being exceeded 100 percent of the time. (Transcript Day 1, page 96).

During this session, the Band also provided an overview of the work the Great Lakes Indian Fish and Wildlife Commission (GLIFWC) has done since the project was first proposed, as well as recent mapping in support of Band's "will affect" determination. Information was presented to help characterize the effects of large-scale land use alterations on natural resources on which tribal members depend. The Band described different models that have been used to evaluate potential indirect effects to wetlands adjacent to the mining pits and contested the idea that wetlands at the project site are so disconnected from groundwater that no amount of drawdown can have an effect on the hydrology. (Transcript Day 1, pages 107-141).

Next, the Band provided an overview of the mercury cycle and its concerns with the formation of methylmercury. According to the Band, fish have about one million times more mercury than the water in which they live. (Transcript Day 1, page 150). The Band described methylmercury concentration in wetland soils and stated that even small amounts of additional sulfate can significantly increase methylmercury. (Transcript Day 1, page 156). However, there is a lack of background data in the project's EIS and permitting related to concentrations of inorganic mercury and methylmercury in sediments, water, and biota even though methylmercury presents the greatest risk to downstream resources and fish consumers and the St. Louis River has the right conditions for methylation. (Transcript Day 1, page 166).

The Band called attention to the exclusion of mercury from the Gold Sim model assessment due to PolyMet's belief that there was insufficient data to include it. The Band stated this further demonstrates insufficient baseline monitoring in the first place and that the mass balance model included no uncertainty and did not incorporate the interactions between sulfate, organic matter, and inorganic mercury through the biomethylation process. (Transcript Day 1, pages 174-176).

The Band stated there is no physical evidence that wetlands at the site are perched and not coupled to regional groundwater. (Transcript Day 1, pages 183, 204). The Band provided an overview of the University of Minnesota's study at the Marcell Experimental Forest. This study concluded that periods of extended drought released sulfate and inorganic mercury, up to 400% more inorganic mercury upon rewetting, and that the

enhanced production of methylmercury during rewetting happened because of the recycling of sulfate associated with the water table rising and falling. (Transcript Day 1, pages 143-186).

The Band asserts that there is potential for additional project impacts to riparian wetlands along the St. Louis River and to streams and wetlands along and within the Band's Reservation. (Transcript Day 1, page 206). The Band claims that the fish and wildlife resources that use the St. Louis River and its riparian wetlands and the streams and wetlands of the Reservation will be exposed to elevated levels of methylmercury. The Band asserts that the project discharges will affect biogeochemical functions of these impacted wetlands, which will in turn substantially affect ecological functions. (Transcript Day 1, pages 207-208). The Band asserts that the discharged waters from the mine and plant sites containing elevated levels of mercury and sulfate will interact with dissolved organic matter to generate methylmercury, which will be transported downriver to Reservation waters and wetlands, especially in the event of high flows and floods. (Transcript Day 1, pages 208-209). The Band concludes that these impacts will result in noncompliance with the Band's designated uses and antidegradation provisions of its water quality standards. (Transcript Day 1, pages 206-212).

The Band asserts it "must be treated as an expert on its own water quality standards. Our experts have been clear and there are no permit conditions that can be applied or placed on the 404 permit that would ensure compliance with the Band's downstream water quality standards." (Transcript Day 1, page 228).

2. Hearing Day 2

PolyMet Views, Opinions and Recommendations:

PolyMet claims it will not violate the Band's water quality standards. First, because PolyMet is cleaning up a legacy brownfield site, which in turn will also clean up the St. Louis River. And second, because the project is located 116 river miles upstream from the Band's Reservation and the project discharges will only be about 0.5 percent of the flow at the Band's Reservation. (Transcript Day 2, page 5).

According to PolyMet, the Biden Administration has focused on transition to electric vehicles and renewable energy and has taken many steps over the last year to strengthen and boost the domestic supply chains of critical metals needed. In a June 2021 White House report, the NorthMet project is cited on page 99 as a fully permitted domestic nickel mine. (Transcript Day 2, pages 6-7).

PolyMet provided information on mercury at two locations: the Forbes USGS site 50 miles downstream of NorthMet and 66 miles upstream of the Band (average flow is 570 CFS); and the Cloquet River, 143 miles downstream from NorthMet and 5 miles downstream from the Band (average flow is 2300 CFS). For context, PolyMet provided the following information about flows from the mine site: 4 CFS of flow including storm water and runoff; plant site: 8 CFS of flow, with 1 CFS going to the Partridge and 7 CFS going to the Embarrass River from mainly wastewater treatment system discharge and some storm water. Downstream of NorthMet, a Partridge River location has 49 CFS of flow and an

Embarrass River location has 87 CFS of flow. (Transcript Day 2, pages 9-10).

Next, PolyMet presented on the brownfield site it plans to use for its plant. This site contains a legacy taconite mine that has water quality issues on-site. (Transcript Day 2, page 11). PolyMet has an appropriation permit to take water if needed to run the plant (brownfield) site from Colby Lake, which is high in mercury. Any water taken from Colby Lake will be treated prior to discharging back to the lake. (Transcript Day 2, page 12). The tailings basin holds over 800 million cubic yards of taconite tailings. These tailings are the cause of the legacy water quality problems downstream and around the project site. (Transcript Day 2, pages 12-13). The tailings basin is covered under a consent decree and is the source of several elevated constituents to downstream waters including sulfate and specific conductance. PolyMet's water management plan will account for these issues. However, this plan is omitted from the Band's "will affect" letter and descriptions of the project site. (Transcript Day 2, page 13).

PolyMet next described its proposed management of mine water and stormwater during project construction and operation, which includes seepage containment systems and a cut off wall tied into bedrock to stop further seepage from leaving the tailings basin. PolyMet referenced the Band's statement from Day 1 of the hearing where the Band stated it has seen cut-off walls only 50-60% effective. (Transcript Day 2, pages 16-17). According to PolyMet, these types of controls have been used for decades around the world in landfills, remediation sites and dams. (Transcript Day 2, page 17). Membrane treatment technology is used at Eagle Mine in Michigan. This mine is required to use a detection limit of 0.5 ng/L of mercury. However, the mine has been measuring nondetects in its discharge. (Transcript Day 2, pages 18-19). PolyMet ran a test pilot plan with 3 million gallons of water and showed it could meet the 10 mg/L sulfate standard, which PolyMet agreed to meet for a rice standard even though the stated federal drinking water standard is 250 mg/L. (Transcript Day 2, page 19). PolyMet has measured mercury in rainfall at the site at 11-12 ng/ and runoff at 3.5 to 6 ng/L. PolvMet says it will treat discharge to 1.3 ng/L and its brownfield cleanup will remove 100 grams of mercury from the St. Louis River over the life of the mine and 28 million kilograms of sulfate from the system. (Transcript Day 2, pages 19-21, initially cited as "billion" was later corrected to "million", see Transcript Day 2, page 77).

PolyMet provided information about mercury loading and stated the loading is driven by atmospheric processes, primarily precipitation (29.8 inches per year average). (Transcript Day 2, pages 26-27). The least significant source of natural mercury input into the St. Louis River watershed is the sub-watershed around the NorthMet project. Rather, the behavior of mercury in the St. Louis River near the Reservation is really driven by these other watersheds and what's occurring there naturally via precipitation. (Transcript Day 2, page 27). PolyMet asserts that sulfate is one of the constituents that drives methylmercury behavior. (Transcript Day 2, page 30). During project operation, water will be collected at the tailings basin through the seepage collection system. (Transcript Day 2, page 31). Therefore, methylmercury will be inhibited by a reduction of sulfate. (Transcript Day 2, page 34-35).

PolyMet addressed the Band not accounting for the project's water management and

treatment plans. According to PolyMet, non-mining watersheds, particularly the Cloquet River and Whiteface River watersheds, are primary contributors of methylmercury loading to the Lower St. Louis River that come in below the mining district and impact the Band's waters. (Transcript Day 2, page 44). Wetlands within the Partridge River are providing methylmercury load. PolyMet states that the project will not increase flows and it will not flush more organic matter carrying more mercury and methylmercury downstream, but rather the project will stay within existing conditions and water loading is not an issue. (Transcript Day 2, pages 44-56).

PolyMet next addressed the Band's drawdown claims (i.e., the Band's claims that massive drawdown will lead to methylmercury creation and transport to the St. Louis River). Drawdown scenarios as presented in the FEIS were based on an analog method from the nearby Canisteo Mine. This mine is in the Biwabik formation, which is permeable relative to the Duluth Complex and the Virginia formation, where the project would be developed. PolyMet contends that the analog method at NorthMet is conservative and overestimates drawdown. (Transcript Day 2, pages 62-63). But even considering an overestimated amount of drawdown, the project would still result in a net reduction in methylmercury creation. (Transcript Day 2, pages 63-64).

According to PolyMet, MODFLOW is a good tool for estimating groundwater inflow to a mine pit. (Transcript Day 2, page 66). However, PolyMet disputes that the model is a good predictor of wetland impacts for the project. (Transcript Day 2, pages 61, 69). MODFLOW contains some important limitations, which makes the model unusable for predicting directly what is happening in wetlands and how sulfate, mercury and wetland sediments may mobilize down gradient. (Transcript Day 2, page 70). Based on PolyMet's assessment, any sulfate, methylmercury, and mercury that's created in the pores of the wetland sediments, instead of reporting down to the Partridge River and downstream waters, is actually going to report to the mine, or otherwise, not go downstream and would be pumped over to the plant site where it would be treated by the reserve osmosis and membrane treatment system. (Transcript Day 2, page 71).

While the Band claims that there will be larger drawdown than claimed in the FEIS, which will increase oxidation and methylmercury production, PolyMet presented important mitigating factors that would tend to pull any increased sulfate, mercury, and methylmercury into the mine where it would be treated before discharge. (Transcript Day 2, pages 75-76). For instance, the hydraulic gradient will be reduced, therefore the driving force that would push groundwater to the Partridge River is reduced which will result in a lower load of water, of sulfate and other constituents to the Partridge River. (Transcript Day 2, pages 72-73). Further, during snowmelt and high flow events, there will likely be less wetland pore water discharging up into runoff and making it to the Partridge River and downstream waters. So, during high events, there will be greater infiltration, a greater balance of more infiltration and less discharge, less runoff and less sulfate and methylmercury making it into rivers. (Transcript Day 2, page 73). Third, there will be some vertical redistribution of methylmercury downward into the soil column once there is some drawdown underneath, which will effectively sequester some of the mercury into a deeper portion of the sediment column. (Transcript Day 2, pages 73-75). And finally, demethylation of mercury. (Transcript Day 2, page 75). In conclusion,

PolyMet asserts that sulfate, mercury, and methylmercury would decrease rather than increase on account of the project and that PolyMet's monitoring and adaptive management plan would ensure that this is the case. (Transcript Day 2, page 76).

PolyMet next provided an overview of its monitoring and adaptive management for the project. PolyMet will have 280 monitoring locations to include stream water quality, stream flow, groundwater guality, groundwater levels, wetland hydrology, wetland vegetation, wetland water guality, industrial water collection, treated water discharge, macroinvertebrate, and fish monitoring. Specifically, PolyMet has 66 locations to monitor mercury. (Transcript Day 2, pages 78-79). PolyMet has adaptive engineering controls that can be changed because of monitoring data or modeling data (e.g., water treatment plant is an engineering control that's designed to be modular so if PolyMet is seeing higher flows or higher loads, additional units can be added to it to be able to expand the engineering control in order to meet permit conditions). (Transcript Day 2, page 82). According to PolyMet, "speculation is not enough to show a violation of a water quality standard." (Transcript Day 2, page 83). Through reuse of existing infrastructure, PolyMet will be bringing the site up to modern standards and cleaning up legacy issues. The project is the only mining discharge in the state that will meet 10 mg/L wild rice standard for sulfate. (Transcript Day 2, pages 83-84). EPA gave the project's Supplemental Draft EIS a rating of EC-2, which is the highest rating a mining company in the United States has ever received. (Transcript Day 2, page 85).

Band's Rebuttal:

The Band opened its rebuttal by stating "[s]ignificantly, EPA agrees with the Band that its downstream [R]eservation water will be impacted by the proposal." (Transcript Day 2, page 87). PolyMet ignores there are already exceedances of numeric standards for mercury and specific conductance under existing conditions. PolyMet's assumption that Minnesota's standards will be met have nothing to do with the Band's downstream standards. (Transcript Day 2, page 87). PolyMet's studies are insufficient to show all hydrologic impact. The Band has not ignored PolyMet's assertions regarding reductions in mercury and sulfate due to project operations and its conclusions are not speculative. (Transcript Day 2, pages 87-88). The project's CWA Section 402 permit authorizes continued exceedance of the Band's water guality standards for mercury because it allows a discharge from the wastewater treatment plan in excess of the Band's water guality standards for mercury of .77 ng/L. (Transcript Day 2, page 90). While PolyMet claims it is subject to 7,000 permit conditions, importantly, not one of those conditions is keyed to the Band's downstream standards. (Transcript Day 2, page 91). The Band presented information on its government-to-government relationship with the United States, dam failure and environmental justice concerns. (Transcript Day 2, page 91). The Band concluded its opening rebuttal by stating EPA agrees with its conclusions, and that there are no conditions that could be placed on the suspended 404 permit that would ensure compliance with the Band's downstream water quality standards. (Transcript Day 2, page 92).

Next, the Band addressed concerns regarding the project's seepage capture system at the tailings basin. According to the Band, there is another taconite facility with a seepage

capture system a few miles away from the project site constructed 8-9 years ago and touted to have virtually a 100% capture rate. Instead, the system is performing at 50-60%. (Transcript Day 2, pages 95-96). At the U.S. Steel Minntac project, the cutoff wall was supposed to be keyed into bedrock to provide a no flow boundary. However, due to similar geology as the PolyMet site, the project was not able to key in its sheet piling to bedrock. (Transcript Day 2, page 96). In addition, there has been no accounting for wetlands just outside the tailings basin cutoff wall, north of the tailings basin, that are currently saturated with contaminated tailings water from past operations and will continue to impact the Embarrass River watershed. (Transcript Day 2, page 97-98). There will continue to be a northward migration of that plume of contaminants for years to come. (Transcript Day 2, page 98).

The Band responded to PolyMet's position that it did not account for water treatment at its plant and discussed concerns with the project's NPDES permit. (Transcript Day 2, pages 98-99). The crux of the Band's concern is not the sulfate or mercury loading from the project. Rather, it is the massive wetland destruction and disturbance to the watershed and the profound hydrologic changes the project will have that will contribute to or exacerbate existing exceedances of the Band's water quality standards and cause an increase in mercury methylation and subsequent bioaccumulation to the Band's detriment. (Transcript Day 2, pages 100-101).

Next, the Band provided its views of the differences between the Eagle Mine and the project. According to the Band, Eagle is a very small mine. Its surface footprint is a fraction of the NorthMet footprint, and the wetland fill for Eagle was under 10 acres. (Transcript Day 2, page 102). In addition, the Eagle Mine is completely underground and indirect impacts due to drawdown were not an issue. In short, this mine is not a comparable example to NorthMet. (Transcript Day 2, page 102).

The Band responded to statements that MODFLOW is not a good tool to assess hydrologic impacts to wetlands. The Band purports that MODFLOW can be and has been used throughout the country to assess impacts to wetlands, including the DeBeers Diamond mine to predict impacts to surface water features including wetlands. (Transcript Day 2, pages 102-103). The Band never suggested that MODFLOW should be the one tool used in a quantitative wetland assessment. (Transcript Day 2, page 103). The Band re-affirmed that GLIFWC's analog analysis and the USGS groundwater modeling results both support its contention that the FEIS underpredicts drawdown adjacent to the mine site. (Transcript Day 2, 103-104).

The Band provided some information on the impact of wetland removal and cumulative impacts. It is not so much the total distance between NorthMet and the Band's Reservation that matters according to the Band, but the fact that the mine site is inextricably linked to the Reservation via streams, wetlands, and the St. Louis River. (Transcript Day 2, page 104). The Band disregarded PolyMet's use of percentages as a way to trivialize the appearance of adverse impacts. Instead, absolute numbers, not percentages, are what matter. (Transcript Day 2, page 105). PolyMet's assertion that removal of wetlands from the project will be a benefit because it will reduce inputs of methylmercury, the Band claims, is "an absurd argument." (Transcript Day 2, page 105).

The Band responded to PolyMet's statements about the way mercury is delivered to the environment. According to the Band, mercury from rainfall is not the largest source of mercury to watersheds, but rather the primary source is atmospheric gaseous mercury taken up by plants which become part of the soil. Mercury that falls from the atmosphere is incorporated almost completely into soils and is slowly released from that pool to soil water, groundwater, and runoff. (Transcript Day 2, page 107). The large pool of mercury that exists in soils is the main source of mercury to surface waters and streams. (Transcript Day 2, page 108). The Band stated that while mercury in rainfall is decreasing, there's probably several hundred years of mercury still in the soils to continue to contribute to mercury exceedances in streams and lakes. PolyMet's emphasis on precipitation draws attention away from indirect project impacts on account of hydrologic changes and interactions with souls. (Transcript Day 2, pages 108-109).

The Band took issue with PolyMet's precise numbers for mercury despite the inherent uncertainty. It also highlighted areas where PolyMet's analysis did not take into consideration the changing environment and increasing frequency of wetting and drying extreme events and the potential for flushing events that exceed those which are currently experienced. (Transcript Day 2, pages 109-110).

The Band also addressed PolyMet's assertions regarding the fluctuation of the water table and the formation of methylmercury. According to the Band, water table fluctuation influences methylation, but methylation is driven more strongly by interactions with the catchment hydrology than the input of mercury from the atmosphere as suggested by PolyMet. (Transcript Day 2, pages 110-111). Underdrainage amplifies the natural fluctuation that is expected because of both annual variability and climate change induced increases in fluctuation variability. (Transcript Day 2, page 111).

In regard to demethylation, the Band claims that demethylation is not a process that is going to offset increases in methylation because the concentrations of methylmercury that are in the environment are actually the result of the competitive processes of methylation and demethylation that are happening all the time. (Transcript Day 2, page 112). The Band provided additional information on the methylation and demethylation process. Ultimately, demethylation will not remove mercury and methylmercury from the system and prevent export to downstream waters. (Transcript Day 2, pages 113-116).

The Band addressed how its findings are not "speculation". Speculation implies no scientific basis to findings. This is not true of the Band's findings. (Transcript Day 2, page 117). The Band's work is better described as a conceptual model or hypothesis that is based on knowledge and scientific understanding of the way the world works and that these measurable parameters could be evaluated for relative importance. (Transcript Day 2, page 118). PolyMet provided information on direct effects but did not cover indirect effects of wetlands and the processes of methylmercury and methylation in the environment in the proximal regions associated with the project. (Transcript Day 2, page 118).

Lastly, the Band summarized its rebuttal by addressing the federal government's responsibilities to tribes, treaty rights, environmental justice, and the importance of the wetlands at issue. (Transcript Day 2, pages 119-120).

PolyMet's Rebuttal:

PolyMet provided an overview of the major project changes between the Draft EIS and Supplemental Draft EIS, including adding a containment wall around the tailings basin to capture all the water around the tailings basin; membrane treatment plant to meet the 10 mg/L sulfate standard; and a plan to take all waste rock that could have potential acid rock drainage and backfill that into the pit so it will not be a concern long-term. (Transcript Day 2, pages 122-123). These changes resulted in PolyMet receiving an EC-2 rating from EPA, which was much higher than EPA's prior rating of EU-2 (environmentally unsatisfactory). (Transcript Day 2, page 123). EC-2 is the highest rating that a mining project has ever received in the United States and is the same rating as the St. Croix Bridge project and St. Paul to Minneapolis light rail project. (Transcript Day 2, page 123).

Next, PolyMet summarized statements EPA made in response to that Preliminary Final EIS. EPA concluded that the project contained extensive improvements and that the environmental review was clear and complete. EPA's extensive discussions with the colead and cooperating agencies for the EIS have helped to resolve virtually all of its previous comments. (Transcript Day 2, pages 124-125). In December 2015, EPA issued a letter resolving its comments pertaining to base flow and cumulative impacts, model calibration and contradictory information. According to PolyMet, the FEIS found no exceedances of the Band's mercury standard as the project would cause an overall reduction in mercury loadings to the downstream St. Louis River, upstream of the Band's Reservation boundary. (Transcript Day 2, page 125). This determination on overall reduction in mercury loadings was also present in the Corps' ROD for the CWA Section 404 permit. (Transcript Day 2, pages 125-126). PolyMet also addressed similar findings in its MPCA permits. (Transcript Day 2, pages 126-127).

PolyMet addressed concerns on its seepage containment system and provided information on the unique aspects of its design and function. (Transcript Day 2, pages 127-128). PolyMet's seepage containment system works differently from the Minntac cutoff wall that was alluded to by the Band. (Transcript Day 2, page 128). According to PolyMet, the NorthMet system will capture 93 percent or more of seepage. (Transcript Day 2, page 128). PolyMet provided information in a memo to the co-lead agencies on the degree of use of this type of system in the industry, and that it's been used around the world for decades. (Transcript Day 2, page 129). PolyMet's permit conditions require that it maintain a system of paired monitoring wells and piezometers so that it can make sure it maintains an inward gradient between the outside and inside of the cutoff wall. (Transcript Day 2, pages 129-130).

PolyMet then provided information on its membrane treatment system, which is its best available technology for water treatment. (Transcript Day 2, page 130). PolyMet plans to employ a reverse osmosis system like the one used at Eagle Mine and its mill for water treatment. Data from Eagle Mine shows over several years of operation. It is

successfully removing mercury, with one point above the detection limit of 0.5 ng/L, in 3.5 years of treatment, sampling and discharge. (Transcript Day 2, 130-131).

PolyMet addressed how its project compares to Eagle Mine and the water management and treatment that its project will entail. (Transcript Day 2, pages 132-135). The Eagle Mine tailings basin at its mill site contains a cutoff wall (slurry wall) that goes own about 75 feet and is keyed into bedrock. This wall holds back contaminated pit water from seeping into waters that drain to Escanaba River. The same type of technology that's being used at the Eagle Mine is being employed in the perimeter of the tailings basin. (Transcript Day 2, page 135). Water that is collected out of this treatment will be routed through a wastewater treatment plant, which contains membrane technology like reverse osmosis. (Transcript Day 2, page 136). PolyMet also explained how water at the mine site would be treated and reused to augment wetlands and streams around the perimeter of the tailings facility, (Transcript Day 2, pages 136-137), as well as project stormwater. (Transcript Day 2, page 138). PolyMet concluded this phase of its presentation with remarks on the benefit of its project due to the reduction of contaminate loading into the system and reductions in sulfate, mercury, and specific conductance. (Transcript Day 2, pages 137-140). According to PolyMet, NorthMet is really about a brownfield redevelopment effort. (Transcript Day 2, page 133).

PolyMet next provided additional information on project modeling and addressed concerns with the USGS model relied on for the GLIFWC analysis and the Crandon Method use of MODFLOW. (Transcript Day 2, pages 141-145). More information was also provided on the alleged drawdown impacts and the proposed mitigation steps to counteract this concern. (Transcript Day 2, pages 145-147).

Following this discussion, PolyMet presented on sulfate and methylmercury reduction. According to PolyMet, mass balance is informative in expanding watershed processes. (Transcript Day 2, page 149). A cross-media analysis was prepared to specifically address the Band's concerns about sulfide mineral dust adding sulfur to wetlands that would then create more methylmercury to be flushed downstream to the Reservation. (Transcript Day 2, page 150). Mass balance was used to predict what might happen during certain water flow events. (Transcript Day 2, page 150). The modeling confirmed that there would be a reduction in mercury, sulfate, and methylmercury. PolyMet's modeling also assessed that there would be no measurable change to fish tissue mercury in the Embarrass and Partridge River sites closest to the project. (Transcript Day 2, page 151). PolyMet purports, if there is no measurable change near the project, it would be very hard to ever see change in fish mercury down the St. Louis River. (Transcript Day 2, page 151).

More information was provided by PolyMet on adaptive water management, which has been recommended by EPA as a good way to react and respond to changes that occur in a project. PolyMet's state permits require an adaptive management plan. (Transcript Day 2, page 152). According to PolyMet, there is always uncertainty and natural systems are complex. (Transcript Day 2, pages 152-153). The models have been reviewed and accepted by the agencies as a conservative way to predict impacts. (Transcript Day 2, pages 153-154). Also, adaptive management will help identify a problem before it exists

and water quality issues can be addressed before violation occurs. (Transcript Day 2, page 154).

PolyMet's then provided its legal views on the Section 401(a)(2) hearing process and the Band's burden of persuasion. (Transcript Day 2, pages 154-158).

PolyMet concluded its rebuttal by analogizing this project to the Eagle Mine and the similar obstacles present in both situations. (Transcript Day 2, pages 158-161). PolyMet worked very hard to achieve its EC-2 rating from EPA on the EIS and the technology that will be implemented to protect water quality is proven. (Transcript Day 2, pages 161-162). PolyMet believes its project is important for strategic national reasons and that cleaning up the environmental and producing medals are not a mutually exclusive proposition. (Transcript Day 2, pages 162-165).

3. Hearing Day 3

On Day three of the hearing, members of the public were given the opportunity to express their verbal comments to the Corps. Numerous commenters expressed statements of support both for and against reinstating the permit. Many comments expressed concern with the project's environmental impacts while others expressed the importance of permitting the project for both national and regional economic reasons.

4. Summary of Post-Hearing Public Comments

After the close of the hearing on day three, the public was provided until June 30, 2022, to submit written comments for Corps consideration. In total, over 22,500 public comments were received including written comment briefs from PolyMet and the Band. No comments were received by EPA during the public comment period.

The Band provided a comment letter, dated June 6, 2022. The Band claimed that the proposed project relies on flawed and misconceptualized modeling and that PolyMet's assertions regarding a new reduction in mercury are incorrect. The Band also took issue with PolyMet's assertions regarding a standard of proof for providing a violation under CWA Section 401(a)(2). According to the Band, no evidence was presented at the hearing that changed either the Band's or EPA's determination that the CWA Section 404 could not be re-issued. The Band also alleged other shortcomings involving the project's tailings basin dam and issues concerning treaty rights, environmental justice, and the Corps' Section 404(b)(1) analysis for the original permit issuance.

PolyMet also provided a comment letter, dated June 10, 2022. PolyMet emphasized that its project will capture and treat tailings basin seepage and wetland runoff that currently contributes sulfate, mercury, methylmercury, and specific conductance to the St. Louis River watershed, and that due to this treatment, the project will lower the amount of those pollutants in the St. Louis River. PolyMet claimed that its project will not violate the Band's water quality requirements due to wetland drawdown at the mine site. PolyMet emphasized the agencies in the EIS were right to reject the Band's claims

of widespread drawdown. PolyMet claimed that the USGS model the Band used at the hearing to predict drawdown is only a teaching tool consistent with USGS warnings about its use and that it was not developed or calibrated to make specific predictions for real-world mining projects. Moreover, PolyMet argued that to prevail on its objection. the Band must prove that the project's discharges will violate the Band's water quality requirements. PolyMet claimed that this has not been proven by the Band. PolyMet does not accept EPA's premise that simply showing an upstream pollutant discharge proves a downstream violation. A discharge 116 river miles away into watersheds that represents 0.5% of the St. Louis River flow at the Band's Reservation makes it hard - if not impossible - for the Band to prove an effect. According to PolyMet, the claim that a discharge from its project would exceed the Band's numeric standards is not enough to prevail under CWA Section 401(a)(2). In addition, uncertainty about violations of the Band's water quality requirements and downstream effects is not enough to revoke PolyMet's CWA Section 404 permit. Ultimately, PolyMet believes that adaptive management will ensure that its discharges will not violate the Band's water quality requirements and that adaptive management is inherently a proactive approach that accounts for uncertainty and variability by using flexible engineering controls that can respond to actual conditions. PolyMet further claimed that the Band's allegations concerning treaty rights and environmental justice are issues that are not within the scope of the hearing.

While many of the other comments received were form letters, the Corps did receive detailed letters supporting permit revocation from the Northern Lakes Scientific Advisory Panel, Clean Up the River Environment (CURE), a coalition of medical doctors, Public Employees for Environmental Responsibility, State Senator Mary Kunesh, the Sierra Club, Minnesota Environmental Partnership members, WaterLegacy and the Minnesota Center for Environmental Advocacy. Many of those comments largely raised issues regarding the project's insufficient engineering controls to protect water quality and wastewater; mine construction impacts to wetlands and water quality; and tailings basin fill among other concerns. Commenters also claimed that the mine project is not needed to support the "green economy", contrary to various assertions otherwise.

The Corps likewise received about 150 form letters in support of issuing the Section 404 CWA permit. More detailed letters of support were provided by Minnesota Power, Laborers' International Union of North America, City of Babbitt, Operating Engineers Local 49 and North Central States Regional Council of Carpenters, 19 of 37 Iron Range Mayors, Grand Rapids Area Chamber of Commerce, Mining Minnesota, ME Global, International Union of Operating Engineers, APEX, MN State Building and Construction Trades Council, Hibbing Area Chamber of Commerce, Range Association of Municipalities and Schools (RAMS), Jobs for Minnesotans, eight State House and Senate Members of the Iron Range Delegation, and the St. Louis County Commissioner.

Comments in support of the project provided examples of similar mines that are meeting success criteria for water quality and environmental protection. In addition, some comments raised concerns regarding economic disparity and human rights should the project not proceed. For instance, if the permit were rescinded, concern was expressed that the United States would need to import the metals from other countries and companies that have little regard for the environment and utilize child labor. Some comments raised concerns with EPA's analysis on "uncertainty" and that EPA was creating too high of a standard for projects going forward under CWA Section 401(a)(2).

No conditions were identified in any of the 22,500-plus public comments that the Corps could add to the CWA Section 404 permit for the project that would ensure compliance with the Band's water quality requirements.

III. Corps Assessment of CWA Section 404 Permit Conditions to Ensure Compliance with the Band's Water Quality Requirements

A. Both EPA and the Band expressed concerns about the project's permit suite failing to include conditions to ensure that mercury is not mobilized, methylated, and exported to the Band's waters. In the Corps assessment of information presented by the Band and EPA, and conversely presented by PolyMet, we acknowledge substantial disparity in the scientific views presented. For example, one major point of disagreement between the EPA and Band's views in comparison to PolyMet's centers on the full acreage of secondary impacts to wetlands from the anticipated drawdown of groundwater from mine construction and operations, as well as the uncertainty regarding the likely transport of such mercury from wetlands subject to secondary impacts from the anticipated drawdown of groundwater from the groundwater from the anticipated drawdown of groundwater from the ground

The Corps can confirm that there may be dewatering of wetlands adjacent to the mining pit and this issue was studied extensively throughout the EIS in coordination with EPA and other stakeholders. (See Corps ROD, pages 35-37). Because of the uncertainty related to the extent of potential dewatering, the Corps included CWA Section 404 permit conditions that PolyMet monitor for these secondary adverse effects and provide compensatory mitigation to offset any indirect loss of wetlands. (See CWA Section 404 Permit Condition Nos.16-21). No conditions to ensure mercury is not mobilized, methylated, and exported to downstream waters from adjacent wetlands were included in the CWA Section 404 permit for the project. These issues are largely outside of the Corps' regulatory authority under CWA Section 404. While PolyMet claims it will treat all water impacted by the Project and ensure compliance with downstream water quality requirements, the FEIS considered by the Corps in its 2019 Section 404 CWA permit and ROD do not appear to fully assess the potential for mercury methylation in adjacent wetlands, the fate of such methylmercury, or whether any mobilized methylmercury will effectively be treated by PolyMet's water treatment system in such a manner that will ensure compliance with the Band's downstream water guality standards.

We understand PolyMet claims to have completed new bounding calculations and that its approach was based on highly protective and unreasonable worst-case assumptions.

For instance, PolyMet concludes that even under a new calculation scenario based on the Band's assertion of a 6,000-acre drawdown around the mine, there will still be a net loss of sulfate, mercury and methylmercury to the pore waters and wetland sediments. (See Transcript Day 2, pages 64-69). Nevertheless, the rebuttal information that PolyMet has provided is not sufficient for the Corps to resolve the scientific differences of opinion that have been presented by the Band, EPA and other commenters on project discharges affecting the Band's water quality standards. The Corps was unable to find fault with either the Band or EPA related to their concerns about mobilization, methylation and export of mercury to the Band's waters. In addition, the Corps notes that EPA and the Band have determined that other non-CWA Section 404 discharges from the project, which are regulated under CWA Section 402, will also impact the Band's waters. Accordingly, the Corps gives great deference to EPA's and the Band's views and recommendations as the water quality authorities on matters affecting the Band's waters. As suggested by EPA, additional mercury/methylmercury load analysis could assist PolyMet in developing measures to minimize, adapt, and mitigate for increased mercury/methylmercury. The Corps also recognizes EPA's assertions regarding the limitations of the mercury mass-balance model used in the FEIS and the potential need for a process-based mass balance model of the system, and further PolyMet's concern that a process-based mass balance model would not be reasonable to carry out.

B. Both EPA and the Band expressed concerns with project discharges meeting the Band's requirements for specific conductance. EPA concluded that the project would contribute additional mineral loadings to the St. Louis River and decrease the specific conductance dilution capacity currently provided by the existing, undisturbed forested wetland mine site, and that there are no corrective actions specified in the permits that would reverse trends showing that specific conductance downstream of the project is increasing. According to EPA, the increase in loadings from the project and decrease in dilution from the loss of the wetlands and forested areas will result in increased specific conductance in the Band's waters as a result of the discharges from the CWA Section 404 permitted activities, as proposed. In addition, EPA determined that the project's CWA Section 402 permit does not contain any conditions that would limit the discharge of dissolved ions contributing to elevated specific conductance to a level that would ensure compliance with the Band's water quality standards. And even the smallest amount of increase in specific conductance would result in violations of the Band's numeric water quality standards. EPA notes that the Corps' CWA Section 404 Permit Condition No. 14 is intended to minimize indirect effects to wetlands and streams by requiring erosion control and slope stabilization during construction. While this condition would result in decreasing some contribution of mineral loadings (which would otherwise result in increased specific conductance), EPA determined that best management practices alone cannot eliminate the discharges contributing to increased specific conductance downstream. EPA also notes that the CWA Section 404 permit application, MPCA's CWA Section 401 certification, Corps' ROD, and permit suite all predate adoption of the Band's numeric specific conductance criterion and therefore do

not consider the potential for violations of the Band's water quality requirements for specific conductance.

Outside of CWA Section 404 permit condition #14, which is specific to erosion control measures, the Corps can confirm that the permit does not contain any conditions pertaining to specific conductance that would remedy concerns from either the Band or EPA for project discharges occurring under CWA Sections 404 and 402. In addition, the Corps can confirm that FEIS did not address whether the project would meet the Band's water quality standard for specific conductance of 300μ S/cm or the Band's narrative or antidegradation standards. PolyMet claims that activities at the mine site will not increase specific conductance downstream and all stormwater that touches mining-disturbed surfaces will be routed to lined basins for treatment. The Corps acknowledges this claim. However, for similar reasons stated above, the Corps is not able to resolve the scientific differences of opinion that have been presented by the Band, EPA and other commenters on this issue. The Corps is not aware of any conditions that could be added to the CWA Section 404 permit that would ensure compliance with the Band's requirements for specific conductance, particularly as some of the project discharges at issue are regulated under CWA Section 402.

C. Based on the information provided at the hearing, the Corps has determined that the existing permit conditions in the suspended CWA Section 404 permit are not sufficient to ensure that there will be no violation of the Band's downstream water quality requirements. The Corps understands from information offered throughout this process that PolyMet is committed to constructing and operating a responsible mine project in compliance with applicable water quality standards and also that neither the EPA nor the Band are opposed to responsible mining that would be done in a way that will comply with applicable water quality standards. Notwithstanding the preceding, the Corps finds the information provided by EPA and the Band to be compelling and determinative with respect to the impact that the project will have on the Band's waters. In addition, no new conditions were provided at the hearing that the Corps could add to the suspended CWA Section 404 permit that would ensure compliance with the Band's water quality requirements. Based on all information provided at the hearing, to include the absence of such conditions, the Corps is unable to issue a modified CWA Section 404 permit that would ensure at the hearing.

IV. Other Topics Raised at the Hearing

The Band presented on additional reasons to revoke the CWA Section 404 permit aside from water quality impacts. Those reasons included issues regarding the Corps' CWA Section 404(b)(1) analysis for the permit, the U.S. Government's treaty right obligations, tailings basin dam failure and environmental justice, among other concerns. Because the Corps has decided to revoke the CWA Section 404 permit for reasons concerning water quality under CWA Section 401(a)(2), those additional reasons that the Band presents for revocation are not germane to the Corps' decision and do not need to be addressed at this time.

V. CONCLUSION:

For the reasons discussed herein, the Corps is unable to include sufficient conditions in the CWA Section 404 permit that would ensure compliance with the applicable downstream water guality requirements of the Band as required by CWA Section 401(a)(2). In accordance with the procedures of CWA Section 401(a)(2), the Band and EPA have determined that discharges from the project would cause a violation of the Band's water quality requirements for mercury and specific conductance. Based on information submitted to the Corps during the public hearing process, the Corps was not able to identify conditions under CWA Section 404 that would ensure compliance with the Band's water quality requirements. Therefore, the Corps cannot reissue or modify the suspended CWA Section 404 permit and must revoke the permit. See CWA Section 401(a)(2); 40 C.F.R. § 230.10(b)(1). The permitting authority granted by regulations empower the District Engineer to suspend, modify and revoke DA permits when it is in the overall public interest to do so. See 33 CFR. § 325.7(a)-(e). With the finding that there are currently no conditions that can ensure compliance with the water guality requirements of the Fond du Lac Band of Lake Superior Chippewa, I have determined that revocation of the subject DA permit would be in the public interest. Further, consistent with the Corps public interest review process as described at 33 C.F.R. § 320.4(a)(1), the Corps cannot issue a permit if such permit would not comply with the EPA's 404(b)(1) Guidelines or with any other applicable guidelines or criteria.³ The discharges authorized by this permit do not comply with the applicable criteria of CWA Section 401(a)(2) because there are no conditions that can ensure compliance with the water quality requirements of the Fond du Lac Band of Lake Superior Chippewa. This failure to ensure compliance with the Band's appliable water guality standards also means it would not comply with EPA's 404(b)(1) Guidelines (see 40 C.F.R. § 230.10(b)(1)). Therefore, because the discharges authorized by the permit would not comply with the criteria established by CWA Section 401(a)(2) and would not comply with EPA's 404(b)(1) Guidelines, the Corps must revoke the permit.

The decision to revoke the CWA Section 404 permit will not have a significant effect on the human environment. While the permit was issued on March 21, 2019, no major construction has commenced due to the litigation filed against the project in both federal and state court and due to the Corp's decision to suspend the CWA Section 404 permit on March 17, 2021. The environmental consequences of the Corps' revocation decision are similar to the effects described as a part of the No Action Alternative in the project's FEIS and in paragraph 8 of the Corps' ROD.

The Corps received many comments from the public hearing from many people who were both against and in support of the project. The Corps acknowledges these comments but recognizes that its decision on the CWA Section 404 permit following the hearing must be based on water quality impacts consistent with the requirements of the CWA Section 401(a)(2) process. While the Corps is unable to reinstate the permit or

³ 33 C.F.R. § 320.4(a)(1) references §§ 320.2 and 320.3 as other applicable guidelines and criteria. Section 401 is the first law referenced in § 320.3.

modify the permit with new conditions, this decision does not preclude PolyMet from submitting a new CWA Section 404 permit application that will meet all applicable water quality requirements for its project.

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Eric R. Swenson Colonel, Corps of Engineers District Commander

APPENDIX A: References⁴

NewRange Copper Nickel LLC letter to Corps regarding name change from PolyMet Mining, Inc. to NewRange Copper Nickel LLC., March 9, 2023

Public comments submitted to Corps following the hearing during comment period that ended June 30, 2022

Corps Public Notice providing additional time for public comments, June 15, 2022

PolyMet Mining, Inc. submittal to Corps with attachments, June 10, 2022

Fond du Lac Band submittal to Corps with attachments, June 6, 2022

Day 1 Public Hearing Transcript May 3, 2022, Reported by Lisa Thorsgaard

Day 2 Public Hearing Transcript May 4, 2022, Reported by Lisa Thorsgaard

Day 3 Corps Public Hearing Transcript May 5, 2022, Reported by Brenda Foss

Information presented or submitted at Public Hearing May 3 and May 4:

- 1. Corps Public Hearing Presentation, May 3, 2022
- 2. From EPA:
 - a. U.S. Environmental Protection Agency Region 5 Clean Water Act Section 401(a)(2) Evaluation and Recommendations with respect to the Fond du Lac Band's Objection to the Proposed Clean Water Act Section 404 Permit for the NorthMet Mine Project, April 29, 2022 (with appendices)
 - b. Tera Fong, Overview of EPA's Clean Water Act Section 401(a)(2) Evaluation and Recommendations on Fond du Lac Band's Objection to the Proposed Clean Water Act Section 404 Permit for the NorthMet Mine Project, May 3, 2022.
- 3. From the Band:
 - a. Brian Branfireun, Effects of the PolyMet NorthMet Mine on Downstream Mercury in Water and Biota, May 3, 2022
 - b. Esteban Chiriboga, John Coleman and Scott Cardiff, Mapping of Wetlands Upstream of the Fond du Lac Reservation, May 3, 2022
 - c. Thomas Howes, Fond du Lac Resource Management presentation, May 3, 2022
 - d. Nancy Schuldt, Fond du Lac Office of Water Protection, Protecting Natural and Cultural Resources in the St Louis River watershed: Fond du Lac

⁴ Although this list represents the documents and sources of information specifically referenced in or reviewed for this decision memorandum, it may not be an exhaustive list of the information before the Corps and is not necessarily the same list of documents that would represent the Corps' administrative record in litigation.

Engagement in Environmental Review and Permitting of the PolyMet NorthMet copper-nickel mine project, May 3, 2022

- e. Matt Schweisberg, Wetland Strategies and Solutions, LLC, PolyMet Mining Inc.'s NorthMet Mine Project: Adverse Impacts to Wetlands & Other Aquatic Resources, especially on the Fond du Lac Reservation, May 3, 2022
- f. Brian Branfireun, Fond du Lac Rebuttal to PolyMet's Public Hearing Information, May 4, 2022
- 4. From PolyMet:
 - a. PolyMet Mining, 401(a)(2) Hearing Presentation, May 4, 2022
 - b. PolyMet Mining, Inc. Section 401(a)(2) Hearing Brief, May 3, 2022
 - c. NorthMet Project Comprehensive Water and Wetland Monitoring Plan, Version 1, April 2022
 - d. Cliff Twaroski memo, Barr Engineering, 401(a)(2) public hearing on PolyMet's NorthMet project Section 404 permit NorthMet Project supplemental evaluation of baseline wetland water levels, water chemistry (sulface, total mercury and methylmercury) and export to downstream waters, May 2, 2022
 - e. Steve Donohue et al, Foth, 401(a)(2) public hearing on PolyMet's NorthMet project Section 404 Permit: Mercury and Sulfate Loadings via Precipitation to the St Louis River Watershed upstream of the Fond du Lac Reservation in Comparison to the PolyMet NorthMet project, May 2, 2022
 - f. Steve Donohue, Foth, 401(a)(2) public hearing on PolyMet's NorthMet Project Section 404 Permit: review of Fond du Lac Band of Lake Superior Chippewa Claims that the NorthMet Mine Project Will Affect Water Quality on the Fond du Lac Reservation, May 2, 2022
 - g. Steve Donohue et al, Foth, 401(a)(2) Public Hearing on PolyMet's NorthMet Project Section 404 Permit: Methylmercury Formation and Release and the Role of Seasonal Wetland Water Table Fluctuations in Peat Environments at the NorthMet Project
 - h. Steve Donohue et al, Foth, 401(a)(2) Public Hearing on PolyMet's NorthMet Project Section 404 Permit: Project-related effects on Specific Conductance and Salinity in the St. Louis River at the Fond du Lac Reservation
 - Tetra Tech, Greg Council and Scott Simpson, 401(a)(2) Public Hearing on PolyMet's NorthMet Project Section 404 Permit Response to Fond du Lac Band's Concern Regarding Mine-Induced Drawdown Affecting Downstream Water Quality
 - j. PolyMet Mining, 401(a)(2) Hearing Rebuttal Presentation, May 4, 2022

Corps Public Notice announcing public hearing to be held May 3-5, 2022, issued March 31, 2022

Corps letter to Chairman Kevin Dupuis, Fond du Lac Band of Lake Superior Chippewa, offering information on public hearing logistics, December 2, 2021

Sonosky, Chambers, Sachse, Endreson & Perry, LLP letter on behalf of Fond du Lac Band, expressing the Band's views on the public hearing, December 27, 2021

Venable LLP letter on behalf of PolyMet Mining, Inc, expressing PolyMet's views on the public hearing, December 14, 2021

Wisconsin Department of Natural Resources letter to U.S. EPA and Corps, notifying it did not object to the issuance of the CWA Section 404 permit, August 2, 2021

Fond du Lac Band letter and attachments to U.S. EPA and Corps, providing notification of the Band's determination that impacts from the NorthMet CWA Section 404 permitted activities "will affect" the Fond du Lac Band's waters, August 3, 2021

U.S. EPA notification (with attachments) to the Band and State of Wisconsin that the NorthMet Project "may affect" the Band and the State of Wisconsin, June 4, 2021

Corps letter to PolyMet Mining, Inc., suspending the Clean Water Act 404 permit while the EPA reconsidered effects on downstream water quality from the proposal under Section 401(a)(2), March 17, 2021

Corps memorandum, Findings for Suspension of Permit – 1999-05528-TJH, March 17, 2021

U.S. EPA letter and attachments to the Corps asking the Corps to suspend the CWA Section 404 permit it had issued for the NorthMet project to allow EPA to complete its CWA Section 401(a)(2) review, March 4, 2021

U.S. District Court for the District of Minnesota's order granting Federal Defendants' motion for voluntary remand and stay, Fond du Lac Band of Lake Superior Chippewa v. EPA, No. 19-cv-2489-PJS-LIB, slip op. at 2 (D. Minn., March 8, 2021)

Federal Defendants' motion requesting a voluntary remand and stay to allow EPA to make the "may affect" determination required by Section 401(a)(2), March 4, 2021

U.S. District Court for the District of Minnesota's ruling on defendants' motions to dismiss. See Fond du Lac Band of Lake Superior Chippewa v. EPA, 519 F.Supp.3d 549 (D. Minn. 2021), February 16, 2021

Fond du Lac Band of Lake Superior Chippewa's complaint against EPA and the Corps in the United States District Court for the District of Minnesota, No. 19-cv-2489-PJS-LIB, September 10, 2019

U.S. Army Corps of Engineers, March 22, 2019, PolyMet Mining, Inc. Permit No. MVP-1999- 05528-TJH U.S. Army Corps of Engineers, March 22, 2019, Record of Decision for the NorthMet Mine Project

Final Environmental Impact Statement for NorthMet Mining Project and Land Exchange, November 2015