

**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.

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## **Draft plan for combining DNR and MPCA resources for development of a Mercury TMDL for the St. Louis River and its estuary**

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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 H<sub>2</sub>S 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 SO<sub>4</sub> reduction in Fe-limited settings. Streams feeding this lake contain elevated SO<sub>4</sub> and nutrient levels, conducive for SO<sub>4</sub> reduction in bottom sediments. The sediments also lack Fe and so all of the SO<sub>4</sub> reduced to sulfide in sediments is released as H<sub>2</sub>S. Geochemical calculations for this and other sites have predicted that MeHg releases in this and other sites are linked to formation of H<sub>2</sub>S 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 SO<sub>4</sub> 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, SO<sub>4</sub>, 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 ( $\text{SO}_4^{2-}$ ) to nearby surface and ground waters. While it has long been known that  $\text{SO}_4^{2-}$  is released by iron mining in Northeastern Minnesota, proposed mining of the metal sulfides in the Duluth complex could contribute additional  $\text{SO}_4^{2-}$ . These  $\text{SO}_4^{2-}$  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  $\text{SO}_4$  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  $\text{SO}_4$  released from the mining regions and evaluating several means to reduce future  $\text{SO}_4$  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  $\text{SO}_4^{2-}$  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 SO<sub>4</sub> 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 SO<sub>4</sub> 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.