

Environment and Natural Resources Trust Fund

Research Addendum for Peer Review

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1. Abstract

Over a century of iron mining in Northeastern Minnesota has left numerous stockpiles, open pits, and tailings basins that appear to be the dominant sources of sulfate (SO_4) to the St. Louis River. This SO_4 has recently become an environmental concern owing to the possibility of bacterial SO_4 reduction in reducing environments located downstream from the mining operations. Methylmercury, the type of mercury that accumulates in fish, is a possible byproduct of SO_4 reduction and many water bodies are already considered impaired with respect to mercury in fish. This project will evaluate sources and fate of SO_4 in the St. Louis River Basin, relying heavily on $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in dissolved SO_4 . The overall goal is to determine the degree to which SO_4 can be controlled and also to evaluate the degree of control that is needed to have positive environmental effects on the St. Louis River.

This study will advance along three fronts: (1) identification and mapping of current SO_4 sources (stockpiles, tailings basins, water-filled pits) using $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in dissolved SO_4 , (2) evaluation of the impacts of seasonally controlled SO_4 releases on chemical processes occurring in the St. Louis River Estuary, and (3) providing an objective assessment of mitigation and treatment options, including heretofore untried (in Minnesota) in-pit SO_4 reduction. Previous DNR research has focused on the St. Louis River north of Cloquet and these results will be used to guide sampling efforts and interpretations for the present study. The results of the overall research will be a comprehensive series of supporting documents and recommendations that state agencies, industry, and other stake holders can use to determine how best to manage SO_4 releases from mining to the St. Louis River.

2. Background

The St. Louis River basin is well known for its vast mineral resources. The Biwabik Iron Formation, which lies along the northern fringe of the basin (Fig. 1), supports a world class mining district that has supplied iron to the US continuously since the 1890s and could continue to do so for another century or more. Along the eastern edge of the St. Louis River watershed lies a series of undeveloped Cu-Ni sulfide/ precious metal deposits that, although relatively low in grade, are sufficiently large to be considered an important future US mineral resource.

It has long been known that SO_4 concentrations are elevated in the St. Louis River (Moyle and Kenyon, 1947; Maderak, 1963). Recent data suggest that SO_4 loading to the river is seasonal, increasing from approximately 25 tons/day under relatively dry conditions to more than 200 tons/day under relatively wet conditions (Berndt and Bavin, 2009). SO_4 concentrations are also seasonally variable, highest during dry times and lowest when water flow in the river is elevated. It is clear that under both dry and wet conditions, however, that most of the SO_4 in the river is delivered by tributaries that drain from the regions where iron mining has occurred (Fig. 2).

While SO_4 is typically not toxic to aquatic organisms, a growing body of research supports a link between bacterial SO_4 reduction and conversion of mercury (Hg) to methylmercury (MeHg) (Gilmour, 1992; Benoit et al., 1999). MeHg is the type of Hg that accumulates in fish and high Hg concentrations in fish are the leading cause of fish consumption advisories throughout the state, including the St. Louis River. As a result, the MPCA has recently issued guidance that is to be used for permitting SO_4 discharges into the environment

(MPCA, 2006). This guidance attempts to eliminate or reduce SO₄ discharge to environments that may bring SO₄ into contact with labile organic matter and Hg under reducing conditions, especially when SO₄ concentration is the limiting factor for SO₄ reduction.

The MPCA's new guidance presents a serious issue for the mining industry as well as to other industries in the state that discharge SO₄. As a result of this new guidance, the Minnesota DNR began studying SO₄ and Hg behavior in the St. Louis River in 2007 (Berndt and Bavin, 2009). Data collected during this study suggested that MeHg concentrations in the St. Louis River upstream from Cloquet are derived primarily from wetlands in each of its component watersheds and not produced within the river itself (Figure 3). With the greater density of wetlands in non-mining areas compared to mining regions, a relatively high percentage of the MeHg in the St. Louis River is derived from non-mining impacted watersheds. Further studies are being conducted in FY 2010 and 2011, closer to the mining districts, to determine if MeHg production in wetlands that directly receive SO₄ from mining sources is enhanced compared to MeHg production in areas that do not receive SO₄ from mining.

The study proposed here focuses on obtaining a more systematic and specific understanding of SO₄ release in the source regions and evaluating potential methods and costs of treatment and mitigation options. It is also a goal to determine how SO₄ loading affects the chemistry of waters and sediments in the St. Louis River estuary. In effect, the project will provide critical data needed for making a cost and benefit assessment of possible control of SO₄ from mining regions in the St. Louis River basin.

3. Hypotheses -

Sulfide minerals are present in the rocks and other materials that have been placed in stockpiles during more than a century of underground and open-pit mining of the Biwabik Iron formation. Where exposed to oxygen, these sulfide minerals oxidize and contribute SO₄ to pits and nearby streams that feed into the St. Louis River and eventually into its estuary on Lake Superior. We hypothesize that $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in dissolved SO₄ provides a means to monitor and track SO₄ released from mining and to help quantify the amount of sulfate reduction that is taking place in the environment. In-pit treatment of SO₄ in mine pits may provide a means to limit much of this release.

4. Methodology –

This research will use an integrated team approach to evaluate source and fate of SO₄ and potential methods of treatment to avoid negative environmental impacts. The LCCMR project is multifaceted and will involve projects in three areas: (1) systematic collection and analysis of rock and water samples in the St. Louis River Basin to assess specific loading sources and help quantify where near-source SO₄ reduction processes are taking place, (2) collection and analysis of sediment cores from the Lake Superior estuary to evaluate SO₄ reduction processes and effects on pore water geochemistry in a region that has previously been ignored, and (3) performance of experiments to begin evaluation of *in-Pit* SO₄ reduction to help limit SO₄ release to the environment. Each of these studies will be conducted separately, but by members of a team that will be in full communication with each other. The first study will be conducted by combined efforts of DNR scientists and professors and students from the University of Minnesota - Duluth Geology Department. The second study will be conducted primarily by the University of Minnesota – Duluth Civil Engineering Water Resources Department. The third study will be conducted by Dr. Berndt in the DNR's geochemical research lab located in Hibbing, MN.

The following outline provides a brief description of the approach and methods used in each of these studies during the first year of the study. At that point, a progress report will be issued updating status of research in each of these areas and a determination will be made on where greater emphasis is needed in the second year.

4.1. Rock and Water Survey of the St. Louis River Watershed

Isotopic measurements often provide a useful tool for identifying source and fate relationships for the targeted species in relatively complex geochemical systems. Isotopes of SO_4 are potentially useful in this regard because both sulfur and oxygen are common in the environment, have considerable isotopic variation among the various reservoirs (air, liquid, solids), and can fractionate during many chemical processes (Van Stempvoort and Krouse, 1994; Taylor and Wheeler, 1994; Eimers, et al., 2004; 2007). Thus, this study will rely heavily on isotopes to evaluate the linkage between sulfide minerals in rocks that are undergoing weathering and the SO_4 found in waters of the St. Louis River basin.

Eimers et al. (2004) found that $\delta^{34}\text{S}_{\text{SO}_4}$ in surface waters sampled during a study conducted in central Ontario was dominated by oxidation and mobilization of sulfide minerals present in the rocks undergoing weathering. However, wetlands were often found to be net sinks for SO_4 owing to bacterial SO_4 reduction trapping of the resultant sulfide. It has also been found, that some of the sulfide formed and stored in wetlands by SO_4 reduction processes can be exposed to oxidizing conditions during drought periods and, thus, remobilized into streams during wet periods (Eimers et al., 2007). SO_4 reducing bacteria, responsible for immobilization of SO_4 in wetlands, metabolize the isotopically lighter SO_4 molecules (e.g., containing ^{16}O and ^{32}S as opposed to ^{18}O or ^{34}S) and thereby generate a positive shift in both $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ for residual dissolved SO_4 when SO_4 reduction occurs.

Thus, seasonal variation of $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ due to SO_4 reduction and re-oxidation processes can overprint and add to the complexity of simple SO_4 release to the basin. It is believed, however, that with further study, $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in dissolved SO_4 can be used as a powerful tool to help identify specifically which sources are generating most of the SO_4 in tributaries of the St. Louis River and the degree to which SO_4 reduction and re-oxidation occurs in each of the individual watersheds.

4.1.1. Sampling of geologic materials for sulfide minerals

A petrologic and isotopic study will be conducted on sulfide minerals in rocks and materials undergoing oxidation in the St. Louis River watershed. Limited previous $\delta^{34}\text{S}$ values are available for sulfide minerals from the Biwabik Iron formation and overlying Virginia Formation, but considerably more data are available from the stratigraphically equivalent Gunflint and Rove Formations (Johnston et al., 2006). $\delta^{34}\text{S}$ values for three samples from the Upper Slaty member of the Biwabik Iron Formation ranged from 3.26 to 9.83 ‰. $\delta^{34}\text{S}_{\text{SO}_4}$ values for samples collected from locations stratigraphically higher in the iron formation had a larger range than this, and extended to $\delta^{34}\text{S}$ values above 20 ‰ for many of the samples. The highest $\delta^{34}\text{S}_{\text{SO}_4}$ samples were all from sulfide minerals collected from the Rove Formation. From this source, it is difficult to establish the values expected for material in stock piles of Biwabik Iron Formation, except that $\delta^{34}\text{S}_{\text{SO}_4}$ could be higher for waters derived by oxidation of sulfide minerals in the Virginia Formation compared to those derived from the Biwabik Iron Formation.

The present study will contribute greatly to our understanding of sulfide distribution in the Biwabik Iron Formation. Samples containing sulfide minerals will be collected, described, and analyzed by a graduate student in the Geology Department at the University of Minnesota - Duluth under the direction of Dr. James Miller (UMD). This graduate student will work with local geologists familiar with the geology in the region to locate drill core and rock sections that contain locally high concentration of sulfide minerals. The occurrences will be sampled *in-place* within the formations or from drill core for which locations and stratigraphy are well known. Thin sections will be produced to determine textural relationships that are useful in evaluating paragenesis, origin, and, thus, likely lateral and vertical extent of the sulfide mineralization. Special emphasis will be placed on distinguishing sulfide distributions that are controlled by primary sedimentary features as opposed to metamorphism and hydrothermal alteration. Those samples thought to represent the dominant sources of sulfide to the St. Louis River will be further analyzed for sulfur isotopes in the laboratory of Dr. Ed Ripley at Indiana University, in Bloomington, IN.

4.1.2. Stream Sampling and Analyses:

When sulfide minerals oxidize to SO₄, the resulting dissolved SO₄ typically has a $\delta^{34}\text{S}_{\text{SO}_4}$ value equal to that of the sulfide minerals being oxidized (Taylor and Wheeler, 1994). The $\delta^{18}\text{O}_{\text{SO}_4}$ for SO₄, meanwhile, reflects the environment in which oxidation occurs (Van Stempvoort and Krouse, 1994). The sulfur and oxygen isotope ratios can be used to distinguish SO₄ derived from specific mining sources (individual ore horizons and operations) from that contributed by other sources such as precipitation, energy production, waste water treatment, and natural oxidation of sulfide in glacial tills.

Berndt and Bavin (2009) measured $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ for SO₄ twice in the St. Louis River and many of its tributaries to determine if sufficient variation was present to warrant possible use as a means to identify SO₄ sources in watershed. In addition, the DNR also began encouraging mining companies to measure $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in selected waters as a part of their environmental impact studies, particularly in situations where SO₄ release was identified as a potentially important environmental concern (Mesabi Nugget, Polymet). The $\delta^{34}\text{S}_{\text{SO}_4}$ values and $\delta^{18}\text{O}_{\text{SO}_4}$ for stream samples that have been measured and reported so far reveal considerable variation, ranging from: +3 to +20 ‰ for $\delta^{34}\text{S}_{\text{SO}_4}$ and -11 to +8 for $\delta^{18}\text{O}_{\text{SO}_4}$ (Figure 4). These ranges are consistent with values expected for oxidation of sulfide minerals in the iron formation as modified by some SO₄ reduction and reoxidation within the watersheds.

A primary goal of the present study will be to combine systematic sampling of water chemistry, including isotopes, with flow measurements from specific rivers to provide seasonal geochemical “snapshots” of SO₄ concentration and isotopic distributions in the St. Louis River watershed. The “snapshot” approach affords the ability to directly compare tributary sources across a range of hydrologic conditions. These sampling periods will be carefully selected to represent (1) winter base-flow, (2) peak spring run-off, (3) summer low-flow, and (4) summer high-flow conditions. This sampling will include full chemical analysis of major cations and anions including SO₄, oxygen and sulfur analysis for dissolved SO₄, and other field parameters needed to conduct chemical speciation (Temperature, Eh, pH). Full chemistry combined with isotopic variability will permit us to evaluate primary SO₄ source regions as well as the chemical processes associated with SO₄ release and transport from the mining region.

In addition, samples will be collected weekly at the Scanlon Dam near Cloquet, which lies well downstream from all of the tributaries from the mining region. These samples will be

analyzed for full chemistry and isotopic composition as well. The USGS continuously monitors flow at this site and so by combining flow measurements with water chemistry, including SO_4 isotopes, a relatively complete picture can be obtained regarding the total fluxes of SO_4 from specific sources identified upstream, but on a weekly rather than quarterly time scale. The hope is that by combining the quarterly geochemical snapshots with the continuous data at a site that collects SO_4 from the entire watershed, a full picture will emerge on watershed SO_4 loading characteristics for the entire year.

Because MeHg is often connected to SO_4 reduction, limited sampling will also be conducted to establish mercury transport relationships in areas where data and field evidence suggest SO_4 reduction is occurring. This additional sampling will involve measurement of DOC and mercury speciation. The Minnesota DNR has worked for several years with Dr. Lian Liang Cebam Analytical (Seattle, WA) to develop methods to speciate mercury in river water samples, including THg, MeHg, reactive Hg (AHg) and unreactive (SHg) in dissolved and particulate fractions of the water. AHg is the non-methylated fraction of Hg that can be directly ethylated in the laboratory environment without pre-digestion (Liang et al., 2009). SHg is determined by subtracting AHg and MeHg from THg. It is thought that the AHg fraction consists of loosely bound, charged Hg species that are much more bio-available than the SHg fraction, which is tightly bound to organic thio-species (Liang et al., 2009). In practice, it has been found that AHg and THg are highest in the St. Louis River head waters during periods of high flow, as is MeHg. However, the MeHg component is closely tied to DOC.

Isotopic ratios for sulfur and oxygen in dissolved SO_4 will be analyzed at the University of Waterloo Environmental Isotope Laboratory in Ontario, Canada. Two methods may be used for sample preparation: direct BaSO_4 precipitation and column concentration preceding BaSO_4 precipitation. The method of choice will be determined by the analytical facility. An Element Analyzer will be used for the analysis. A total of 1000 mL will be sampled and shipped to the laboratory which should permit SO_4 isotope composition to be determined for solutions containing 5 mg/L SO_4 or more. Because dissolved SO_4 ions are considered stable in oxidizing waters, no preservation is required.

For cation and anion analysis, 60 mL samples for each will be filtered in the field. A portable vacuum pump will be used to pull the sample through acid washed, 0.45 μm Nalgene filters. The cation samples will be preserved with nitric acid and shipped cold for analyses by the University of Minnesota Geology department in Minneapolis, Minnesota. This lab uses inductively coupled plasma (ICP) atomic emission spectrometry for cation analysis and ion-chromatography to analyze anions.

The DOC samples are preserved with sulfuric acid and shipped to the Minnesota Department of Health (St. Paul, MN) where they are analyzed using a non dispersive-infrared analyzer (reference method SM 5310c).

Samples for mercury speciation will be analyzed by Dr. Lian Liang, Cebam, Inc.. in Seattle, Washington. AHg and MeHg are determined using ethylation, Tenax trap collection, GC separation, and cold vapor fluorescent atomic spectrometry (CVAFS) detection (modified EPA 1630). THg is oxidized with BrCl then analyzed by SnCl_2 reduction, gold trap collection, and CVAFS detection (modified EPA 1631).

4.2. Sediment core sampling and analysis in the St. Louis River estuary

SO₄ reducing bacteria commonly populate anaerobic environments in sediments such as those found in the St. Louis River estuary and it has also been found that biological SO₄ reduction in sediments is a primary driving mechanism for the production of MeHg. However, what is not known is the degree to which SO₄ reduction occurs within this estuary and how it impacts sediment and water chemistry. For this work, the DNR will enlist the assistance of Dr. Nathan Johnson at UMD and a graduate assistant in his department. The objective of this part of the proposed study is to investigate the role that sulfate plays in driving bacterial processes, including mercury methylation, in the surficial sediment of the St. Louis Estuary. The results will help to determine the influence of mining-related sulfate loads on mercury methylation in the sediment of the Estuary. Dr. Johnson proposed the following approach for this study and has submitted it, along with a proposed match from the Minnesota Department of Natural Resources, to another funding source (University of Minnesota Water Resources and USGS program). However, if Dr. Johnson's project is not funded, then it will be the DNR's goal to fund a similar reduced project using combine LCCMR and other funding resources.

Field sampling efforts will be conducted with the support of the National Lacustrine Core Respository (LacCore), a University of Minnesota-affiliated facility funded by the NSF and UMN Limnological Research Center. LacCore provides very low cost support to help facilitate the collection and study of lake sediment cores. Dr. Johnson has initiated a dialogue with LacCore about this project and received a preliminary quote for the cost of their services. Samples will be collected in duplicate or triplicate from five locations within the estuary in order to capture spatial variations. An initial sampling expedition to obtain sediment cores and grab samples from a subset of locations (2-3) will provide information to test analytical techniques and guide subsequent efforts. The main sampling initiative will take place in the winter, through ice on the river, with the experienced support of the LacCore staff to ensure safety. Cores of at least 18" depth will be collected in ~2.75" diameter polycarbonate tubes and stored with overlying water during transport back to the lab. Grab samples will be collected into 5 gallon buckets. The local USACE office will be contacted and to the extent possible, samples will be collected from locations undisturbed by recent dredging activities. Either on the boat or back in the lab, cores will be cut to a length that can be easily transferred to an anaerobic glovebox. Core processing will take place in the Civil Engineering building on the UMD campus.

The location of dominant bacterial zones in sediment can be characterized by measuring the products and biproducts of microbial metabolism (Luther et al. 1998). Different bacterial populations convert oxygen to water, Fe³⁺ to Fe²⁺, and SO₄ to sulfide at sequential depths in the sediment. In order to locate the depth at which active biological SO₄ reduction occurs, vertical profiles of the oxidized and reduced forms of iron and sulfur will be measured using a variety of analytical techniques. The depth at which active SO₄ reduction occurs will be identified and characterized by a buildup in reduced sulfur species (dissolved sulfide and solid phase iron-sulfides) and a reduction in SO₄. Other measurements, including the depletion of oxygen and reduced (ferrous) iron, will provide information on the location of other dominant biogeochemical zones that control the depth at which SO₄ reduction occurs. Methyl mercury concentrations will be analyzed on a subset of samples to identify the influence of SO₄ reduction in driving methylation in St. Louis River sediment.

In order to quantify the location and extent of sulfate reduction, the following criteria will be used: (1) A rapid depletion of oxygen is expected in the top few millimeters and this zone will be assumed to be dominated by aerobic bacteria. (2) An increase in ferrous iron (both

dissolved and solid phase) without an increase in FeS will be used in identifying a zone dominated by iron reducing bacteria. (3) A buildup of FeS with a concomitant decrease in porewater ferrous iron will be indicative of the activity of SO₄ reducing bacteria. The depth at which solid and dissolved sulfide is observed will be assumed to be the depth at which active SO₄ reduction begins to occur. Porewater SO₄ concentrations will also provide information on the location of active SO₄ reduction. If SO₄ concentrations remain constant with increasing depth, this will indicate that little SO₄ is being consumed in the surficial sediment. If SO₄ concentrations decrease with depth, it can be assumed that active SO₄ reduction is occurring in the sediment. Total carbon, iron, and sulfur will be analyzed on a subset of the cores and sections in order to characterize variability from site to site and the bulk geochemical characteristics of the estuary.

Laboratory analysis will take place at the UMD Civil Engineering Department and the Large Lakes Observatory (LLO). Upon arrival back in the lab, cores will first be analyzed for depth profiles of dissolved constituents including oxygen, pH, and dissolved sulfide, using microelectrodes and an automated micromanipulator. UMD Civil Engineering owns the necessary electrochemical equipment for making these measurements. Electrodes will be purchased from a well-known and trusted manufacturer of microelectrodes specifically for environmental research with which Dr. Johnson has worked before.

Once microelectrode profiles in the cores have been completed, cores will be transferred to an anaerobic glove box for sectioning and further processing. Sectioning of the cores in an oxygen-free environment is essential to maintaining the integrity of the redox-sensitive iron and sulfur constituents in the sediment and porewater. Cores will be extruded and sliced into sections to measure the depth profiles of iron and sulfur species. Solid-phase analysis will utilize standard extraction procedures include total reduced (ferrous) iron, iron sulfide (acid volatile sulfides – AVS), and organic carbon. Porewater concentrations of SO₄ constituents for which microelectrode measurements are not available (Fe²⁺ and SO₄²⁻) will be measured by spectrophotometry and ion chromatography following centrifugation and filtration of wet sediment. Aliquots of solid material will be placed in mercury-free Teflon-lined borosilicate glass vials and stored at -20°C. A subset of these samples will be chosen based on geochemical observations and shipped to a commercial lab for methyl mercury extraction and analysis.

4.3. In-situ treatment of sulfate in pit waters

Many studies and reports are available involving methods to treat SO₄ in waters before releasing them to the environment (ultra-filtration, nano-filtration, chemical precipitation, and wetland treatment) or to mitigate waste rock piles to prevent release of SO₄ into pits, lakes, and streams (covers, sub-aqueous disposal, encapsulation). Many of these processes are used in mining operations today. However, for the large amounts of water found in previously mined pits, it may be too late or too expensive to control SO₄ already or soon-to-be overflowing from them into nearby waters of the state. However, one relatively new method that is receiving recent attention elsewhere (e.g., Park, 2008), but which has not been used on the Iron Range, involves *in situ* treatment of SO₄ in mine pits. This method involves addition of organic carbon and iron to promote biological reduction of SO₄ to sulfide and subsequent precipitation as iron-sulfide.

There are several reasons why this method of treatment may be preferred for controlling SO₄ in mine pits. First, waste rock piles that may or may not contain sulfide minerals are typically found near the edges of mine pits. As a result, the mine pits are often the primary

receiving bodies for constituents released from waste rock piles. Second, depth profiles of two high-SO₄ pits on the Iron Range have revealed a strong chemical stratification with anoxic, high SO₄ waters at depth (hypolimnion or monimolimnion) and oxidized low-SO₄ waters near the surface (epilimnion or mixolimnion). The anoxic deep layers are often sealed for extensive periods from the atmosphere and can thereby serve as ideal locations for promoting biologic sulfate reduction. And, finally, an advantage of *in situ* SO₄ reduction is that it treats the water closest to its mining source (wall rock and stockpile sources within the pit's catchment) and prior to release into streams. Although there are numerous potential advantages to using in-pit sulfate reduction to manage sulfate release, the DNR and MPCA have no experience with this method and is highly unlikely to permit it without considerable evaluation specific to pits on the Iron Range.

A principal difficulty for application of this method on the Iron Range relates to the complexity of sulfide oxidation in waste rock piles under high P_{CO2} conditions and in the presence of magnesium rich carbonates (magnesio-siderite and ankerite) (Bavin and Berndt, 2009). The Mg-rich chemistry of the carbonate minerals in the Biwabik Iron Formation (Mg-Ca-siderite and ankerite) imparts an initially high Mg/Ca ratio on high-SO₄ waters flowing into the pits. This high Mg/Ca ratio can be increased further when CO₂ degasses and causes carbonate minerals to precipitate. This is because precipitation of Ca-rich carbonates is favored compared to Mg-rich carbonates owing to kinetic constraints (Berndt and Seyfried, 1999; Deelman, 2003). The resulting fluid can be highly supersaturated with respect to Mg-carbonate minerals and, consequently, the high SO₄ mine waters may need to be treated for hardness (owing to high Mg) as well as SO₄.

The DNR will conduct experiments to examine kinetics of SO₄ reduction, Fe-sulfide deposition, and carbonate precipitation from such waters. Primary variables to be tested are likely to include Ca/Mg ratio of the initial pit water, efficacy of different hydrocarbon and nutrient sources to promote SO₄ reduction in the water column, and the relationships between Fe addition methods (e.g., suspended fine Fe(OH)₃, dissolved Fe(HCO₃)₂, Fe-acetate, or FeCl₃) and Fe-sulfide precipitation. These experiments will begin with one- to four-week closed cell experiments, using sterile plastic cells, initially at vacuum (e.g., vacutainers), and filled with high P_{CO2} waters and chemistry similar to those found currently in deep pit waters. Constituents (hydrocarbons, nutrients, and iron source) will be added to promote SO₄ reduction and carbonate precipitation on a very small scale and the tubes will be refrigerated at typical hypolimnion temperatures (6 to 10 C) for one to four weeks. The advantage of this technique is that many experiments can be completed in a short amount of time, and those processes resulting in precipitation can be determined by close inspection of the constituents and verification by subsequent chemical analysis.

The most promising methods identified in small-scale experiments will be further tested on a larger scale using refrigerated columns designed specifically for this purpose. Columns will be constructed of clear two-inch plastic tubing and fitted with opaque covers to prevent photosynthesis (and production of O₂). The covers can be removed to allow periodic visual inspection of settling particles if and when SO₄ reduction and mineral precipitation occurs. Small sampling ports will be added to allow both injection of constituents and sampling of fluids. The experiments will be conducted in the DNR's laboratory in Hibbing, MN under the direction of Dr. Berndt. Starting fluids used in the experiments will be collected from depth in existing mine pits to simulate aqueous solutions found in some of the highest SO₄ pits known on the Iron Range today (about 1000 to 3000 ppm SO₄).

Methods to be used for chemical analysis are the same as those used in the field sampling studies with the exception that sample dilution may be required for some types of chemical analysis.

4.4. Citations

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Van Stempvoort, D. R., and Krouse, H. R., (1994) Controls of $\delta^{18}\text{O}$ in Sulfate: Review of Experimental Data and Application to Specific Environments. In Alpers, C. N., and Blowes, D. W., *Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series 550. p. 446-480.

4.5. Figures

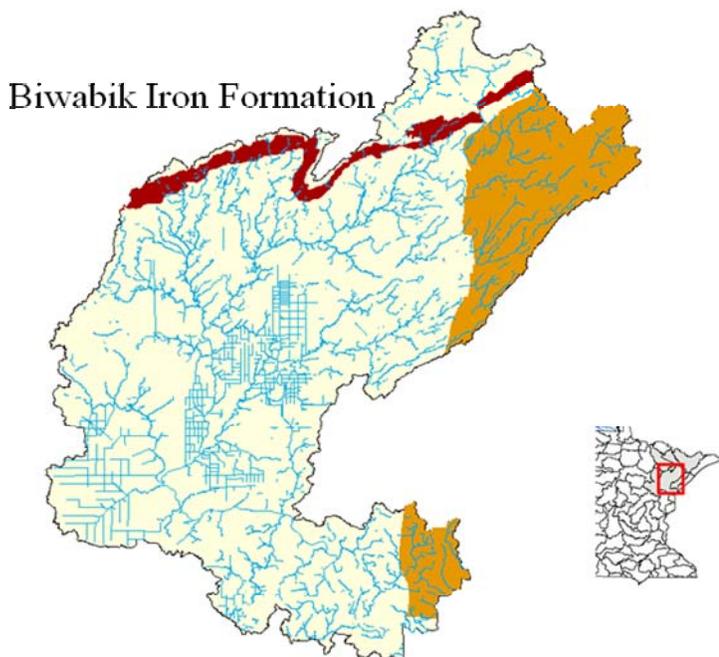


Figure 1. Location of St. Louis River basin and Biwabik Iron Formation in Minnesota.

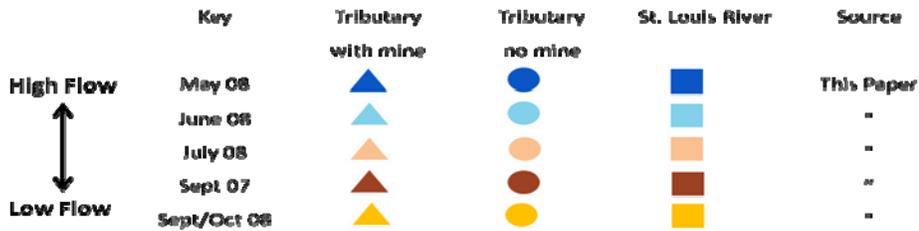
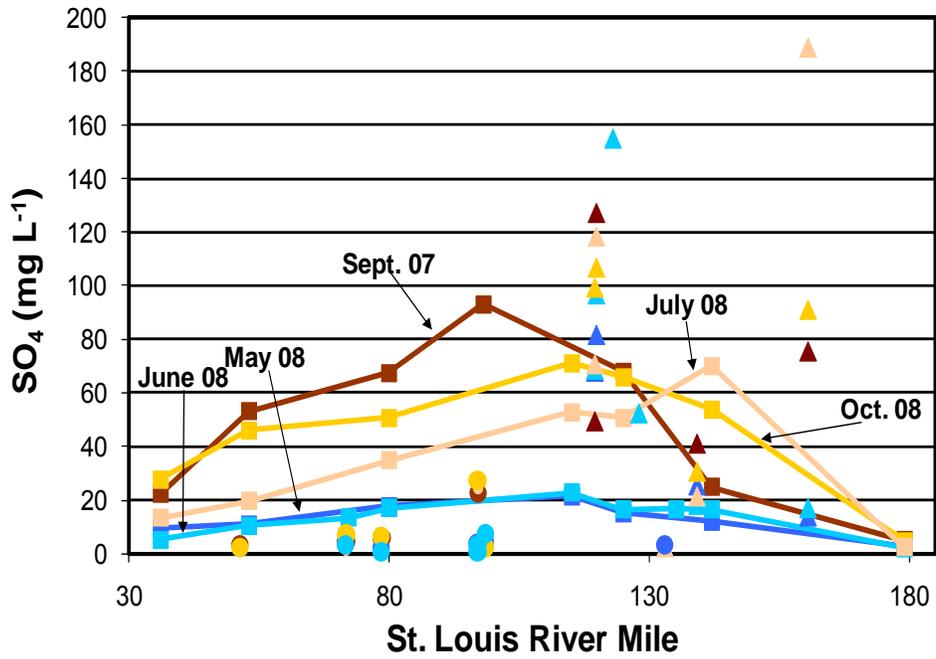


Figure 2. Sulfate concentrations for the St. Louis River and its tributaries as a function of St. Louis River mile (0 at mouth, 180 at headwaters). The blue colors represent samples collected under relatively high flow conditions, while tan, brown and orange represent samples collected under moderate to low flow conditions. Figure is from Berndt and Bavin (2009).

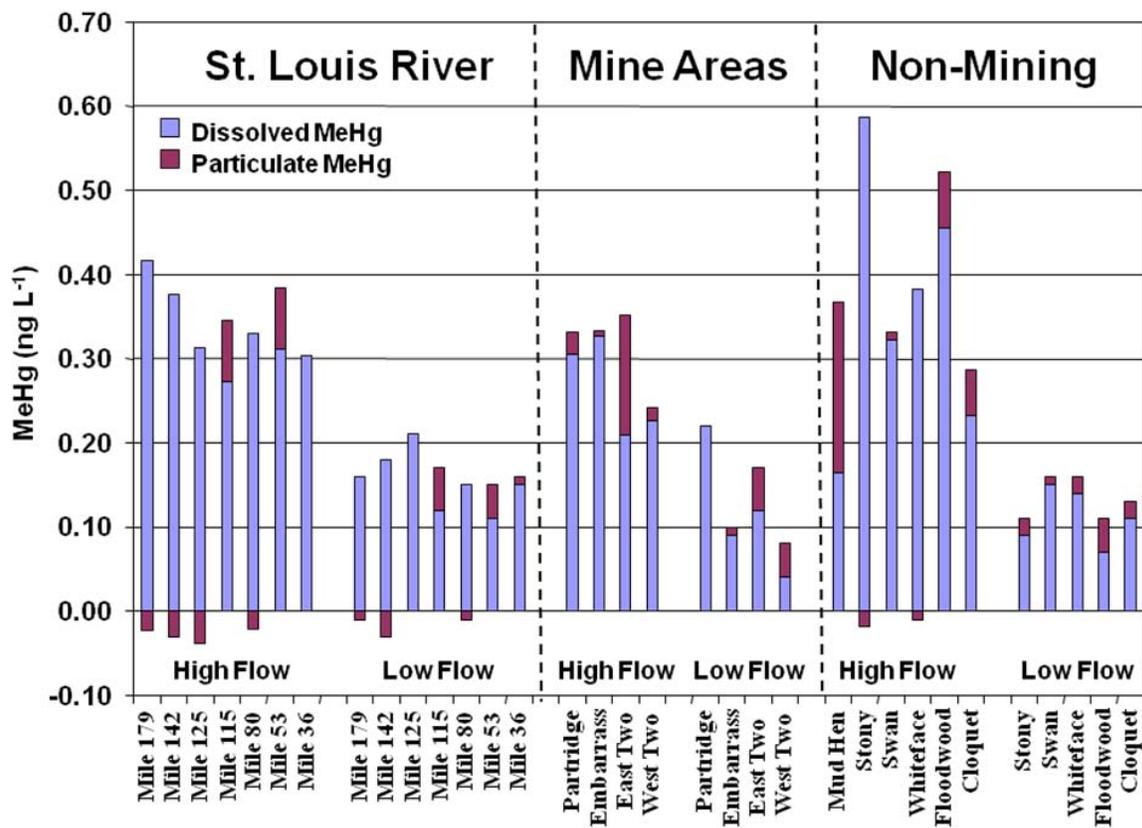


Figure 3. Dissolved and particulate MeHg concentrations for samples collected from the St. Louis River and its tributaries during May and September/October 2008. Negative values for particulate MeHg indicates samples where the MeHg concentration measured in filtered samples was slightly higher than that in unfiltered samples. Figure is from Berndt and Bavin (2009).

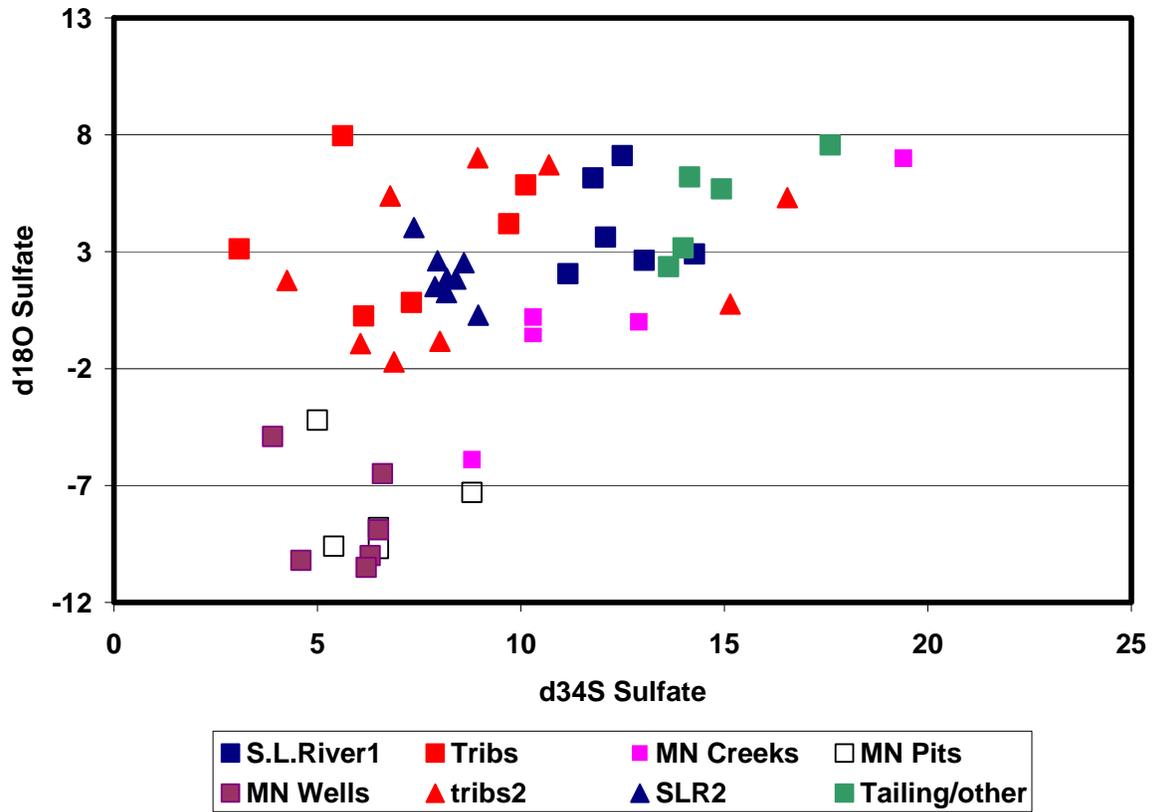


Figure 4: $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ for waters in the St. Louis River watershed. Data include published and unpublished data from DNR studies and from environmental studies conducted by mining companies. There is local and seasonal variation in the isotopic composition of dissolved SO_4 in the St. Louis River, but data needed for full interpretation of this variation is lacking.

5. Results and Deliverables –

There are, essentially, five separate deliverables in the proposed study. There are three independent studies that will be completed during the first year, followed by the production of an interim report that will be circulated to scientists and stakeholders as a means of gathering additional input. An interim report will be generated containing a brief update and the preliminary results for each of the three studies that comprise the overall project. This interim report is considered the first deliverable and will be used to inform stakeholders of the progress that has been made as well as to help to determine the relative emphasis needed in each subject area during the second year. Ultimately, a final report will be generated for each of the three project areas containing final data and interpretation by the end of the second year. These will be accompanied by a summary report linking the three studies together and providing overall interpretations regarding the controllability of SO₄ loading from mining (cost and effectiveness) and the likely impact such SO₄ controls would have on improving the environment.

6. Timetable –

Deliverable or Result	Begin	Complete
Sulfide Mineral and Stream Sampling Survey	July 1, 2010	June 30, 2012
St. Louis River Sediment Study	July 1, 2010	June 30, 2012
In-Pit Treatment Study	July 1, 2010	June 30, 2012
Interim Report	June 1, 2011	June 30, 2011
Final Reports	March 31, 2012	June 30, 2012

7. Budget –

This is a multi-component project involving a team of investigators and multiple sources of funding. For this research, Dr. Berndt will be assisted by research efforts of Dr. James Miller and Dr. Nathan Johnson at the University of Minnesota Duluth. The LCCMR funding will serve as core funding for an overall project that ties these research efforts together. Managing the research projects necessarily requires an adaptive approach whereby funding decisions for the second year are based partially on findings from the first year. However, most of the field and laboratory work and associated chemical analysis will be conducted during the first 1.5 years of the study. The last half year is reserved for consolidation of results, literature research, and writing of final reports.

A Research Scientist II, located at the Minnesota Department of Natural Resources and funded by LCCMR, will be dedicated to this project half-time during the first year to assist primarily with field and laboratory work. The other half of this researcher's employment will be provided by other research grants received by the DNR. This scientist's responsibility and funding during the second year of this project will be increased to full-time as he or she will be

expected to conduct up-to-date literature searches, consolidate findings from the new studies, and write reports that summarize the new data in the context of existing literature on the subject. A summer intern will also be employed to assist with sampling duties during the both summers. In addition, the project will require part-time assistance from a Chemist-1 or equivalent level field assistant. Dr. Berndt will contribute up to 40% of his time throughout the study at no cost to the project.

	Year 1	Year 2	Total (2 years)
Research Scientist II	\$35,000	\$70,000	\$105,000
Chemist 1	\$10,000	\$10,000	\$20,000
Student Summer Employment	\$2,500	\$2,500	\$5,000
UMD Contracts	\$35,000	30,000	\$65,000
Stream Gaging	\$5,000	\$5,000	\$10,000
Field Expense – Travel, meals, Lodging	\$2,500	\$2,500	\$5000
Chemical Analysis	\$37,500	\$12,500	\$50,000
Supplies	\$7,500	\$2,500	\$10,000
Total	\$135,000	\$135,000	\$270,000

8. Credentials –

8.1. Michael E. Berndt: Vita –November 2009

Research Interests:

Aqueous geochemistry, both low and high temperature. Economic geology as it relates to the origin of ore deposits and the distribution of minerals in the Earth's crust. Applying knowledge of mineral distributions and aqueous geochemistry to help evaluate environmental effects of mining in Northeastern Minnesota.

Education:

- 1980: BS Geology, University of Minnesota
BS Geophysics, University of Minnesota
- 1983: MS Geology, University of Wisconsin
- 1987: PhD Geology, University of Minnesota

Work Experience: (last position held at each employer)

2001-present: Research Scientist III at Minnesota Department of Natural Resources – Division of Lands and Minerals (DNR-LAM). Adjunct Faculty - University of Minnesota Department of Geology and Geophysics.

1987-2001: Senior Research Associate - University of Minnesota, Department of Geology and Geophysics.

Recent Reports and Publications (reverse chronological):

Bavin, T. K. and Berndt M. E. (2009) Chloride and Methylmercury Chemistry of the St. Louis River in NE Minnesota: A Report to the Minnesota Pollution Control Agency CFMS Contract No. B15507. 30 pages.

Berndt M. E. and Bavin T. K. (2009) Sulfate and Mercury Chemistry of the St. Louis River in Northeastern Minnesota: A Report to the Minerals Coordinating Committee. Minnesota Department of Natural Resources, Division of Lands and Minerals. St. Paul, MN. 83 pages, in review.

Lapakko, K. A. and Berndt, M. (2009). Laboratory dissolution of tailings under three different test conditions. *In Proc. Securing the Future and 8thICARD*, June 22-26, 2009, Skellefteå, Sweden (CD ROM). 11 p.

Bavin, T. K. and Berndt, M. E. (2008) Sources and fate of sulfate in NE Minnesota watersheds: A Minerals Coordinating Committee progress report. Minnesota Department of Natural Resources Division of Lands and Minerals, St. Paul, MN, 23p. plus figures, tables, and appendices.

Berndt, M. E. and Brice, W. (2008) The Origins of Public Concern with Taconite and Human Health: Reserve Mining and the Asbestos Case. *Regulatory Toxicology and Pharmacology*. 52, S31-S39.

Berndt, M. E. and Engesser, J. (2007) Mercury Transport in Taconite Processing Facilities: (III) Control Method Test Results. Iron Ore Cooperative Research Final Report. Minn. Dept. of Nat. Resources. 38 pages plus appendices.

Berndt, M. E. and Leibfried, R. (2007), A Geochemical Tracer Study of Minnesota's First In-Pit Disposal Facility for Taconite Tailings, Minn. Dept. Nat. Resources Reports, Div. of Minerals, St. Paul, MN. 36 p.

Berndt, M. E., Engesser, J., and Berquó, T. S. (2005) Mercury Chemistry and Mössbauer Spectroscopy of Iron Oxides During Taconite Processing on Minnesota's Iron Range. In Proceedings Air Quality V, International Conference on Mercury, Trace Elements, SO₃, and Particulate Matter. Washington, DC, Sept. 2005. 15 p.

Berndt, M. E. and Engesser, J. (2005) Mercury Transport in Taconite Processing Facilities: (I) Release and Capture During Induration. Iron Ore Cooperative Research Final Report. Minnesota Department of Natural Resources. 31 pages plus appendices.

Berndt, M. E. and Engesser, J. (2005) Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers. EPA: Great Lakes National Program Office Report. 32 pages.

Selected Other Publications/reports:

Berndt, M. E., Allen, D. E., and Seyfried, W. E., Jr. (1996) Reduction of CO₂ during serpentinization of olivine at 300C and 500 bars. *Geology* 24, 351-354.

Berndt, M. E., and Seyfried, W. E. Jr. (1999) Rates of aragonite conversion to calcite in dilute aqueous fluids at 50 to 100C: experimental calibration using Ca-isotope attenuation. *Geochim. Cosmochim. Acta.* 63, 373-382.

Berndt, M. E. and Seyfried, W. E., Jr., (1997) Calibration of Br/Cl fractionation during subcritical phase separation of seawater. *Geochim. Cosmochim. Acta.* 61, 2849-2854.

Berndt, M. E., Seyfried, W. E., and Person, M. A. (2001) SaltTherm- an integrated numerical (finite volume) flow model for predicting two phase flow near magma chambers at mid-ocean ridges. V. W. Goldschmidt Conference Proceedings, Warm Springs, Va.

Berndt, M. E., Seal, R. R., II., Shanks, W. C., III, and Seyfried, W. E., Jr. (1996) Hydrogen isotope systematics of phase separation in submarine hydrothermal systems: experimental calibration and theoretical models. *Geochim. Cosmochim. Acta.* 60, 1595-1604.

Berndt, M. E. and Soule, R. (2000) Minnesota Arsenic Study: Report on Geochemistry, in Messing, R. B. et al., The Minnesota Arsenic Study (MARS), Minnesota Department of Health, St. Paul, MN. 30 p.

Berndt, M. E., Soule, R. G., and Erickson, M. (2000) The Minnesota Arsenic Study (MARS). Possible Roll Front Mechanism to account for high arsenic in western Minnesota drinking water. Minnesota Groundwater Association Newsletter. 4p.

Foustoukos, D.I., James R.H., Berndt M.E. and Seyfried W.E.Jr. (2004) Lithium isotopic systematics of hydrothermal vent fluids at the Main Endeavour Field, Northern Juan de Fuca Ridge. *Chemical Geology* 212 (1-2), 17-26

Horita, J. K. and Berndt, M. E. (1999) Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science*, 285, 1055-1057.

Seyfried W.E.Jr., Seewald J.S., Berndt M.E., Ding K. and Foustoukos D.I. (2003) Chemistry of hydrothermal vent fluids from the Main Endeavour Field, Northern Juan de Fuca Ridge: Geochemical controls in the aftermath of June 1999 seismic events. *Journal of Geophysical Research* 108(B9).

8.2. Nathan W. Johnson: Vita-November, 2009

Department of Civil Engineering, University of Minnesota-Duluth

1305 Ordean Ct., 229 Voss-Kovach Hall, Duluth, MN 55812

nwjohnso@d.umn.edu; ofc: 218-726-8063; cell: 512-636-9779; fax: 218-726-8581

EDUCATION

PhD Civil Engineering (2009)

The University of Texas at Austin, Austin, TX

M.S. Environmental and Water Resources Engineering (2005)

The University of Texas at Austin, Austin, TX

B.S.E. Civil and Environmental Engineering (2003, Cum Laude)

Princeton University, Princeton, NJ

RESEARCH AREAS

Environmental biogeochemistry & aquatic chemistry

Mathematical modeling of complex environmental systems

Fate and transport of environmental contaminants in aquatic sediments

GIS, hydrologic, and water quality modeling

EXPERIENCE

08/09 – Present Assistant Professor, University of Minnesota Duluth

08/05 – 08/09 PhD Research, The University of Texas at Austin

Dissertation Topic: Mercury Biogeochemistry in Aquatic Sediments

09/07 – 11/07 Visiting Researcher, Norwegian Water Research Institute, Oslo, Norway

Research Topic: Mercury Methylation in Sandefjord, Norway

09/03 – 09/05 Master's Research, The University of Texas at Austin

Thesis Topic: ArcGIS and Hydrologic/Water Quality Modeling

PUBLICATIONS

A Model for Methyl Mercury-Related Biogeochemical Processes in Aquatic Sediments. N. W. Johnson, D. D. Reible, L. E. Katz, [in preparation] Research Paper.

- Biogeochemical Changes and Mercury Methylation beneath a Sediment Cap. N. W. Johnson, D. D. Reible, L. E. Katz, in review at Environ. Sci. Technol. Research Paper.
- Development of HSPF Interface Data Model for Regional Watershed Modeling. Y. C. Su, P. Zardo, T. Brink, N. W. Johnson, D. R. Maidment, GIS and Water Resources AWRA Spring Specialty Conference. Proceedings Paper. June 2006.
- The ArcGIS HSPF Preprocessing Methodology. N. W. Johnson, D. R. Maidment, Report to the San Antonio River Authority. Tools & Documentation. September 2005.

PRESENTATIONS

- Mercury Methylation beneath an in-situ Sediment Cap. N. W. Johnson, D. D. Reible, L. E. Katz, ACS Annual Meeting, Washington, DC. Platform Presentation. August 2009.
- Mercury Methylation beneath an in-situ Sediment Cap. N. W. Johnson, D. D. Reible, L. E. Katz, SETAC North American 21st Annual Meeting, Tampa Bay, FL. Platform Presentation. November 2008.
- Transport and transformation of mercury in forest–wetland–lake ecosystems. L. E. Katz, N. W. Johnson, TCEQ Mercury Impaired Waters Advisory Group. Invited Talk. November 2008.
- Availability of Organic and Inorganic Contaminants. N. W. Johnson, D. D. Reible, Y. S. Hong, D. Lampert, Geological Society of America Joint Meeting. Invited Talk. October 2008.
- Mercury Fate Beneath a Sediment Cap. N. W. Johnson, D. D. Reible, L. E. Katz J. Liu. BATTELLE Conference on Remediation of Contaminated Sediments. Platform Presentation. January 2007.
- ArcGIS to HSPF: A Practical Application to TMDLs of Texas Waterbodies. J. L. Watts, D. R. Maidment, ESRI 2005 GIS Hydro Preconference Seminar. Online Document and Presentation. June 2005. <http://www.crwr.utexas.edu/gis/gishydro05/>
- Considerations for Interacting with HSPF in ArcGIS. N. W. Johnson, D. R. Maidment, ESRI 2004 GIS Hydro Preconference Seminar. Online Document and Presentation. June 2004. <http://www.crwr.utexas.edu/gis/gishydro04/>

PROFESSIONAL AFFILIATIONS

- American Chemical Society (ACS)
- Society of Environmental Toxicology and Chemistry (SETAC)
- American Geophysical Union (AGU)

HONORS AND AWARDS

- Graduate Dean's Prestigious Fellowship Supplement, 2007-Present
- EPA STAR Graduate Research Fellow (US Environmental Protection Agency), 2006-Present
- THRUST 2000 Fellowship (The University of Texas at Austin), 2005-Present
- Honors at Graduation, Dept. of Civil and Environ. Eng. (Princeton University), 2003

Elected Sigma Xi (2003)

8.3. James Miller: Vita – November 2009

Department of Geological Sciences, University of Minnesota-Duluth
mille066@d.umn.edu; Phone: 218-726-6582 (UMD) 218-720-4355(NRRI)

EDUCATION

- PhD Geology (1986)
University of Minnesota-Twin Cities
- BS Geology (1977)
University of Illinois-Urbana Champaign

RESEARCH AREAS

- Bedrock geologic mapping of Precambrian terrains in northeastern Minnesota
- Petrologic and metallogenic studies of mafic layered intrusions of the Duluth Complex

PROFESSIONAL EXPERIENCE

- 1/08-pres. Department of Geological Sciences, University of Minnesota Duluth
Position: Associate Professor
- 6/06-pres. Precambrian Research Center, University of Minnesota Duluth
Position: Administrative Director
- 7/83-1/08 Minnesota Geological Survey, UM-TC
Positions: Senior Scientist (6/90-present)
Scientist (7/85 - 6/90)
Research Assistant (7/83 - 7/85)

SELECTED PUBLICATIONS

Journal Articles and Reports

- Miller, J.D., Jr. **1999**, Geochemical evaluation of platinum group element (PGE) mineralization in the Sonju Lake intrusion, Finland, Minnesota. Minnesota Geological Survey Information Circular 44, 32 p.
- Miller, J.D. Jr., Green, J.C., Severson, M.J., Chandler, V.W., Hauck, S.A., Peterson, D.E., and Wahl, T.E., **2002**, Geology and mineral potential of the Duluth Complex and related rocks of northeastern Minnesota. Minnesota Geological Survey Report of Investigations 58, 207p. w/ CD-ROM
- Park, Y-R., Ripley, E.M., Miller, J.D., Li, C., Mariga, J., and Shafer, P., **2004**, Stable isotopic constraints on fluid-rock interaction and Cu-PGE-S redistribution in the Sonju Lake Intrusion, Minnesota. *Economic Geology*, v. 99, no. 2, p. 325-338.
- Miller, J.D., Jr., **2004**, Petrology and PGE potential of the Greenwood Lake Intrusion, Central Duluth Complex, Lake County, Minnesota. Minnesota Geological Survey Report of Investigations 62, 93p.

- Jirsa, M.A., Miller, J.D., Jr., Severson, M.J., and Chandler, V.W., **2006**, Final report on the geology, geochemistry, and geophysical attributes of mafic to ultramafic intrusions in Minnesota, excluding the Duluth Complex. Minnesota Geological Survey Open-file Report OF-06-3; on-line report
- Li, C., Ripley, E.M., Oberthür, T., Miller, J.D., Jr., Gregory D. Joslin, G.D., **2007**, Textural, mineralogical and stable isotope studies of hydrothermal alteration in the main sulfide zone of the Great Dyke, Zimbabwe and the precious metals zone of the Sonju Lake Intrusion, Minnesota, USA. *Miner Deposita*, v. 42, in press.
- Jirsa, M.A., Miller, J.D., Jr., and Morey, G.B., **2008**, Geology of the Biwabik Iron Formation. *Regulatory Toxicology and Pharmacology* v. 52, p. S5-S10.

Geological Maps

- Miller, J.D., Jr. and Chandler, V.W., **1999**, Bedrock geologic map of the central Duluth Complex and western part of the Beaver Bay Complex, Lake and St. Louis Counties, Minnesota. Minnesota Geological Survey Miscellaneous Map Series, M-101, 1:100,000 scale.
- Miller, J.D., Jr., Green, J.C., Severson, M.J., Chandler, V.W., and Peterson, D.E., **2001**, Geologic map of the Duluth Complex and related rocks, northeastern Minnesota. Miscellaneous Map Series, M-119, scale 1:200,000, 2 sheets.
- Jirsa, M.A., and Miller, J.D., Jr., **2004**, Bedrock geology of the Ely and Basswood Lake 30' x 60' quadrangles, northeast Minnesota. Minnesota Geological Survey Miscellaneous Map M-148, scale 1:100,000.
- Severson, M.A. and Miller, J.D., Jr., **2005**, Bedrock geology of the Babbitt quadrangle, St. Louis County, Minnesota. Minnesota Geological Survey Miscellaneous Map M-159, scale 1:24,000.
- Miller, J.D., Jr., Severson, M.A. and Foose, M.P., **2005**, Bedrock geology of the Babbitt Northeast quadrangle, St. Louis and Lake Counties, Minnesota. Minnesota Geological Survey Miscellaneous Map M-160, scale 1:24,000.
- Miller, J.D., Jr. and Severson, M.A., **2005**, Bedrock geology of the Babbitt Southwest quadrangle, St. Louis County, Minnesota. Minnesota Geological Survey Miscellaneous Map M-161, scale 1:24,000.
- Miller, J.D., Jr., **2005**, Bedrock geology of the Babbitt Southeast quadrangle, St. Louis and Lake Counties, Minnesota. Minnesota Geological Survey Miscellaneous Map M-162, scale 1:24,000.
- Miller, J.D., Jr., Green, J.C., and Jerde, E.A., **2006**, Bedrock geology of the Little Marais quadrangle, Lake and Cook Counties, Minnesota. Minnesota Geological Survey Miscellaneous Map M-172, scale 1:24,000.
- Miller, J.D., Jr., and Green, J.C., **2008**, Bedrock geology of the Duluth Heights and eastern portion of the Adolph quadrangles, St. Louis County, Minnesota. Minnesota Geological Survey Miscellaneous Map M-181, scale 1:24,000.
- Green, J.C., and Miller, J.D., Jr., **2008**, Bedrock geology of the Duluth quadrangle, St. Louis County, Minnesota. Minnesota Geological Survey Miscellaneous Map M-182, scale 1:24,000.

Miller, J.D., Jr., and Green, J.C., 2008, Bedrock geology of the West Duluth and eastern portion of the Esko quadrangles, St. Louis County, Minnesota. Minnesota Geological Survey Miscellaneous Map M-183, scale 1:24,000.

9. Dissemination and Use –

All reports from the Minnesota Department of Natural Resources are public documents. The documents prepared in connection with this study will all be published as official DNR reports, available free to citizens in electronic form and, depending on the number of requests received, either free or at-cost in hard-copy forms.

12/18/08