

August 10, 2017

To: US Forest Service

From: Dr. Daniel R. Engstrom
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Science Museum of Minnesota
St. Paul and Marine on St. Croix, MN

Re: Northern Minnesota Federal Mineral Withdrawal EIS #50938

As one of the lead scientists studying the effects of sulfate on mercury cycling, wild rice, and sulfur biogeochemistry in Minnesota, I wish to enter into the public record my professional concerns regarding the risks posed by the operation of metal-sulfide mining within the Rainy River Watershed, including waters of the Boundary Waters Canoe Area Wilderness. The information summarized below is referenced primarily to a series of recent peer-reviewed scientific publications regarding the biogeochemical effects of sulfate loading to surface waters (wetlands, streams, and lakes) on mercury methylation, wild-rice growth and survival, and aquatic chemistry. The comments mostly pertain to sulfate, with or without the added impacts of lowered pH (acid drainage), and also to the relative sensitivity of the receiving waters to potential sulfate discharges. Although the studies on which these comments are based were carried out as part of my professional employment, the views expressed herein are my own and do not represent any formal position taken on this subject by my employer, the Science Museum of Minnesota.

Background / Standing

I am a Ph.D. research scientist with the Science Museum of Minnesota, where I serve as Director of the St. Croix Watershed Research Station, the Museum's environmental research center. I've held this position for 18 years and in that capacity supervise a team of research scientists with expertise in hydrology, biogeochemistry, environmental engineering, and aquatic biology. I also hold appointments as Adjunct Professor in the Department of Earth Sciences and the Water Resources Science Program at the University of Minnesota. I've worked specifically in the field of mercury fate and transport for three decades and have authored more than 35 journal articles and book chapters on the subject – several among the most highly cited in the field (Swain et al. 1992, Fitzgerald et al. 1998, Lindberg et al. 2007). This research has been heavily focused on boreal ecosystems, but also includes work in Arctic and southeast Alaska, the Canadian Maritimes, and the tropics (Florida, South America, East Africa). I've served on numerous scientific panels tasked with advancing understanding of human impacts on mercury cycling and contamination.

Specific to the issues surrounding sulfide-metal mining, I directed a multi-institution, 9-year ecosystem scale experiment on the effects of atmospheric sulfate deposition on mercury methylation in a boreal peatland at the Marcell Experimental Forest (USFS Northern Research Station) (Jeremiason et al. 2006, Coleman Wasik et al. 2012, Coleman Wasik et al. 2015, Strickman et al. 2016). These efforts were followed by a multi-year study, coordinated by the

Minnesota DNR, on the biogeochemical consequences of sulfate pollution from iron mining activities in the St. Louis River watershed of northern Minnesota (Berndt and Bavin 2011, 2012, Berndt et al. 2016, Jeremiason et al. 2016, Johnson et al. 2016, Bailey et al. 2017). This investigation also focused on the effects of sulfate on mercury cycling and methylation, but in systems of contrasting and highly elevated sulfate concentrations (as compared to the Marcell wetland). Finally, I participated in a Minnesota Pollution Control Agency (MPCA) investigation of the effects of sulfate on the growth and survival of wild rice (*Zizania palustris*) (Myrbo et al. 2017a, Myrbo et al. 2017b, Pastor et al. 2017, Pollman et al. 2017). The purpose of the study was to evaluate Minnesota's existing 10-mg/L sulfate standard for the protection of wild rice waters through a combination of field, laboratory, and experimental mesocosm approaches.

Biogeochemical Cascade

Sulfate serves a key biogeochemical role in aquatic environments where the availability of oxygen often limits the bacterial decomposition of organic matter. Under anoxic conditions that frequently prevail in sediments and stratified bottom waters, sulfate acts as a terminal electron acceptor (TEA) and is reduced to sulfide during microbial respiration. Because dissolved sulfate concentrations are often low in continental surface water (as compared to marine systems), the biogeochemical significance of microbial sulfate reduction (MSR) in freshwaters is often underappreciated (e.g., Capone and Kiene 1988). However, considerable evidence has accumulated that even slightly elevated sulfate concentrations can greatly enhance MSR and cause a cascade of effects including the stoichiometric release of dissolved C, N, and P, the build-up of toxic concentrations of sulfide in sediment porewaters, and increased mobility and internal loading of P to surface waters (Myrbo et al. 2017b). MSR is also a primary process leading to the formation of bioaccumulative methylmercury (see below).

Although numerous studies have explored these various processes individually, their collective effects were recently revealed in a comprehensive mesocosm-scale experiment reported by Myrbo et al (2017b). Here the surface waters in a replicated series of large wetland enclosures (stock tanks in which wild rice was grown) were emended with five different sulfate treatments (control, 50, 100, 150, and 300 mg/L) and sampled (for sediments, porewaters and surface waters) after 3 and 5 growing seasons. The sulfate additions increased the mineralization of organic matter, thereby increasing surface water concentrations of dissolved and inorganic carbon, phosphorus, nitrogen, and total mercury in proportion to cumulative sulfate reduction. Mercury methylation was also enhanced by the sulfate addition, but peaked at intermediate treatment levels because of sulfide suppression of methylation in the highest sulfate treatment.

These results clearly demonstrate the potential for increased sulfate loading to significantly alter the biogeochemical environment of aquatic ecosystems through a cascade of primary and secondary environmental changes. Consequences include increased nutrient (N & P) availability and associated trophic changes, higher porewater sulfide with toxic effects on benthic communities and rooted aquatic plants, elevated biotic exposure to methylmercury, and increased alkalinity and dissolved organic carbon (DOC), keystone variables in the chemistry and physics of freshwater.

Mercury Methylation

Mercury (Hg) released to the atmosphere and surface waters from human activities is a serious environmental problem, because even trace amounts can bioaccumulate to harmful levels in fish and upper levels of the aquatic food chain. Inorganic mercury is transformed into its bioaccumulative form, methylmercury (MeHg), by anaerobic bacteria in the metabolic breakdown of organic matter in lake and wetland sediments and the bottom waters of thermally stratified lakes. Sulfate reducing bacteria (SRBs) are the most widely studied group of methylators, although other groups are known to possess the genetic and metabolic machinery needed to methylate (Gilmour et al. 1992, Hsu-Kim et al. 2013, Podar et al. 2015).

A number of key studies, both laboratory and field-based, have demonstrated conclusively that the experimental addition of sulfate to low-sulfate waters can stimulate SRB activity and increase the production of MeHg (Gilmour et al. 1992, Branfireun et al. 1999, Branfireun et al. 2001). At the same time, sulfide build-up in sulfate enriched systems can limit the bioavailability of inorganic mercury through the formation of charged mercury-sulfide species, thereby inhibiting methylation (Benoit et al. 2003, Hsu-Kim et al. 2013). These dual processes produce what is known as a “goldilocks” effect where sulfate is stimulatory at low concentrations and inhibitory at high concentrations. The optimal sulfate levels for methylation vary among systems, depending on the availability of other mercury ligands (particularly DOC), labile organic matter to drive microbial metabolism, and dissolved iron, which can precipitate sulfide and limit its negative feedback on bacterial uptake of inorganic mercury (Orem et al. 2014, Bailey et al. 2017, Pollman et al. 2017).

These complex interactions are well illustrated for northern Minnesota ecosystems by a series of studies that examined sulfate-mercury interactions in natural systems low in sulfate and contaminated waters with highly elevated sulfate concentrations. The first of these was a decade-long whole-ecosystem experiment where atmospheric sulfate inputs to a small boreal peatland were first increased and then decreased to explore the *in situ* response of net MeHg production and sulfur cycling. Results showed a dramatic rise in MeHg in both porewater and solid-phase peat as well as aquatic insects living in the experimental treatment (Jeremiason et al. 2006, Coleman Wasik et al. 2012). The cessation of experimental sulfate addition produced an initially rapid recovery that was also strongly modulated by hydrologic variation over the course of the experiment (Coleman Wasik et al. 2012, Coleman Wasik et al. 2015). The experimental sulfate increases were rather modest (4x ambient deposition) but produced a pronounced biogeochemical reorganization of the system including the bacterial community itself (Strickman et al. 2016).

A subsequent set of studies involving mining-impacted lakes and wetlands on Minnesota's Iron Range further illustrates the complexity of sulfate-mercury interactions (Bailey et al. 2017) (Johnson et al. 2016). In this case, study sites chronically impacted by sulfate discharges from iron mining (~200-300 mg/L) were compared with sites with moderate to background sulfate concentrations (5-30 mg/L). A strong and significant relationship was observed between porewater and solid-phase MeHg and sulfide concentrations <0.65 mg/L, but not at higher levels (sulfide > 0.65 mg/L) where methylation appeared to be suppressed by complexation of inorganic mercury with porewater sulfide (Bailey et al. 2017). In the most heavily sulfate-impacted sites, high sulfide contributed to the depletion of porewater iron in a feedback loop that

further limited the availability of inorganic mercury to bacterial uptake and methylation. Although high sulfide appeared to suppress the production of MeHg, it also contributed to its increased solubility in sediment porewaters, potentially enhancing transfer to the water column and biological uptake.

Unlike the Marcell wetland experiments, these comparative studies do not allow us to conclude what may have happened to methylation rates as mining-related sulfate discharges initially began to rise. It seems likely that they would have increased, even if additional sulfate loads eventually suppressed net MeHg production. Indeed, a biomonitoring study of mercury levels in dragonfly larvae from mining-impacted and non-impacted streams of the St. Louis River system do not show particularly elevated Hg in the sulfate impacted tributaries (Jeremiason et al. 2016). Although one might conclude from this that chronic sulfate enrichment had no deleterious effects on biotic exposure to MeHg, that would be incorrect, as pre-impact conditions are unknown for the sulfate-enriched tributaries and furthermore, many of the non-impacted ones drain extensive peatlands, which are known methylating environments (Wiener et al. 2006); wetlands are largely absent from mining-impacted sub-watersheds.

Wild Rice

Minnesota is unique among U.S. states and Canadian provinces in having a water quality standard that regulates dissolved sulfate to protect wild rice, *Zizania palustris* (Minnesota Rules 5050.0224). The standard is based on the long-standing empirical observation that wild rice is largely restricted in Minnesota to surface waters of less than 10 mg/L sulfate (Moyle 1944, 1945, DNR 2008). Although the standard has seldom been enforced, increasing public pressure to do so in the mining-impacted St. Louis River and a resurgent interest in developing metal-sulfide mining in northern Minnesota prompted the state to undertake a comprehensive re-evaluation of the standard to determine its appropriateness (MPCA 2015b). This 6-year investigation, only recently completed, used a combination of experimental and empirical approaches to better understand the mechanisms by which sulfate might affect the growth and survival of wild rice.

In a laboratory-based study wild rice germination and seedling growth were examined in hydroponic experiments that showed no direct effects of sulfate (under oxic condition) on seed germination or seedling development (Pastor et al. 2017). However, sulfide generated by sulfate reduction under anoxic conditions greatly reduced juvenile seedling growth at concentrations exceeding 320 µg/L. At the same time, outdoor mesocosm experiments – in which wild rice was grown in large containers containing lake sediment and standing water over 5 field seasons – showed progressive declines in seedling emergence, seedling survival, biomass growth, and seed production with sulfate additions over the course of the experiment (Pastor et al. 2017). Wild rice became largely extinct at sulfate concentrations of 250 mg/L or greater in the overlying water. These experimental results were corroborated by an extensive field survey of chemical and physical attributes of wild-rice habitat in more than 100 lake and river sites across Minnesota (Myrbo et al. 2017a). This field study demonstrated that sulfide in sediment porewaters, generated by microbial reduction of sulfate, is the primary control of wild rice.

A syntheses of these results using structural equation modeling (SEM) showed that pore-water sulfide could be accurately predicted by a combination of three key variables, surface water sulfate and the concentrations of organic carbon and amorphous iron in the sediments (Pollman

et al. 2017). The inferred mechanism is that both sulfate and organic matter stimulate microbial reduction of sulfate to sulfide, with iron serving to precipitate FeS in a feedback loop that limits the build-up of dissolved sulfide. The state of Minnesota is now weighing whether to retain the existing 10 mg/L sulfate standard or replace it with one that is based on site-specific measurement of the three controlling variables. The working conclusion of these studies is that the existing 10 mg/L standard may be over- or under-protective of certain waters, but that overall it is well justified based on the improved understanding of how sulfate affects wild rice growth and survival (MPCA 2015a).

These Minnesota studies demonstrate clearly the toxic nature of sediment sulfide to rooted aquatic plants like wild rice. Such toxicity was first identified in paddy-grown white rice (*Oryza sativa*) in the 1950s (Pearsall 1950), but has only recently been recognized as a critical control on the distribution abundance of plant and animal communities in freshwater ecosystems (Lamers et al. 2013). Increases in surface water sulfate have been implicated in declines of sawgrass (*Cladium jamaicense*) in the Florida Everglades (Li et al. 2009). The historical extirpation of wild rice from Minnesota lakes and streams receiving high sulfate drainage from iron mining activities is also suspected (Vogt 2012). Although wild rice may be particularly sensitive to sulfide toxicity, there is good reason to expect that other rooted aquatic macrophytes would be similarly impacted by elevated inputs of sulfate. Indeed, wetlands currently receiving high sulfate loads from iron mining activities (leakage or pumping from mine pits and tailings basins) have an extremely depauperate flora, largely dominated by cattails (*Typha* spp.), which are able to survive in sulfide-rich waters either by translocation of oxygen into their roots or metabolic detoxification of sulfide (Li et al. 2009, Lamers et al. 2013).

Implications for the BWCAW

The potential effects of sulfate release on the biogeochemistry of lakes and streams of the BWCAW and the Rainy River watershed depend on both the chemistry of the receiving waters and the magnitude of mining-related discharges. Although it is the position of mining interests that releases will not occur during active operations, there is substantial evidence that hydrological connections, either via groundwater or surface flow or from in-filling of existing mine pits will induce discharge from mine-impacted areas (mine pits, waste rock sites, processing basins) into nearby Birch Lake and the Kawishiwi River and thence into the heart of the BWCAW (Myers 2014, 2016a, b). Even if sulfate-impacted waters are contained during the period of active mining, perpetual treatment of drainage waters from abandoned mine operations will likely be needed following eventual mine-closure and site inactivation. Whether sufficient safeguards are ultimately put in place to ensure long-term protection of the Rainy River watershed is beyond the scope of these comments. However, it should be noted that sulfate-rich drainage from abandoned iron-mining operations currently discharge into Birch Lake, raising sulfate and trace-metal levels in the receiving waters (USEPA 1994). The full biogeochemical consequences of this historical contamination are presently unknown.

Surface waters of the BWCAW are likely to be among the most sensitive to elevated sulfate inputs of those in any of Minnesota's major watersheds. Located on crystalline bedrock of the Canadian Shield, most lakes and streams are ionically dilute, of circumneutral pH, and high in dissolved organic carbon (DOC). The MPCA's water quality database, EQUIS, contains some 7000 records of surface-water sulfate from Lake and St. Louis counties. Within this data set,

lakes and streams not impacted by existing iron-mining operations are invariably quite low in sulfate (3.3 ± 1.8 mg/L; mean \pm s.d.; $n = 2960$). The Kawishiwi River is only slightly higher (5.7 ± 2.8 , $n = 108$), while Birch Lake is significantly elevated (9.5 ± 3.4 , $n = 75$), presumably owing to leakage from waste rock at the nearby Dunka mine site. At these ambient levels, it is highly likely that an increase in sulfate loading will cause an increase in microbial sulfate reduction (MSR) and associated mercury methylation. That is, these waters are on the lower (rising) limb of the “goldilocks curve” under which sulfate will stimulate net methylation of mercury, rather than inhibit it. If sulfate discharges to the system are sufficiently large (c.f. the mining-impacted St. Louis River), sulfate contamination will progress downstream. Sulfate will be consumed through MSR in upstream lakes and a zone of enhanced methylation (goldilocks peak) will migrate downstream. Finally, there are abundant wetlands in the Birch Lake watershed near proposed sulfide-metal mining operations (e.g. Filson and Kelley creeks) (Geerts 2017), as well as further downstream, and boreal wetlands are known to be especially effective methylating environments (Wiener et al. 2006). Lakes and streams of the Rainy River watershed also support abundant and diverse plant communities, including wild rice, which are almost certain to be impacted by elevated inputs of sulfate from mining operations. Finally, the biogeochemical release of nutrients (P and N) from enhanced MSR could lead to increased algal production in surface waters and a wholesale change in trophic conditions in what are otherwise among the most pristine waters of the U.S.

The BWCAW is classified as “outstanding resource value water” under the Minnesota statutes (MAR 7050.0180), whereby: “The agency [MPCA] recognizes that the maintenance of existing high quality in some waters of outstanding resource value to the state is essential to their function as exceptional recreational, cultural, aesthetic, or scientific resources. To preserve the value of these special waters, the agency will prohibit or stringently control new or expanded discharges from either point or nonpoint sources to outstanding resource value waters.” (MAR 7050.0180 Subpart 1). Given the abundant evidence, summarized above, that sulfate releases from mining operations through the Kawishiwi watershed and into the BWCAW pose substantial environmental risk to these outstanding resource value waters, it is scientifically prudent that mining leases held by Twin Metals and other mining interests be withdrawn by the Secretary of the Interior for a 20-year term as requested by the US Forest Service.

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