

A Review of the NorthMet Draft Environmental
Impact Statement and Selected Supporting Documents
Related to the Effects of Sulfate Discharge on the
Production of Methylmercury and the Effect of Mercury
Air Emissions on Air and Water Resources

Review Conducted for
Minnesota Center for Environmental Advocacy and
Friends of the Boundary Waters Wilderness

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I. Introduction

My review of the NorthMet Project Draft Environmental Impact Statement (“DEIS”) is based on more than 20 years of research experience on the fate and transport of mercury as an environmental pollutant. I have authored or co-authored more than 25 peer-reviewed journal articles on mercury emissions, atmospheric deposition, and biogeochemical cycling in terrestrial and aquatic systems. Several of these publications (Fitzgerald et al. 1998; Swain et al. 1992) are among the most highly cited papers in this scientific field. I have served on numerous national and international panels dealing with mercury science and policy and have conducted mercury-related research throughout the Great Lakes region, New England, southern Florida, arctic and southeast Alaska, Newfoundland, and most intensively here in Minnesota. Of particular relevance to this review is a whole-ecosystem experiment on the role of atmospheric sulfate in stimulating mercury methylation in boreal wetlands (Jeremiason et al. 2006), which I have directed for almost ten years. Sulfate release and its potential effects on mercury cycling are among the most serious concerns raised by the sulfide-metal mining proposed for northern Minnesota.

The focus of my review is two-fold: (1) possible effects of sulfate discharges from the NorthMet Project on the production of methylmercury, and (2) the risk of mercury releases to air and water from mining and ore processing. The aquatic releases of mercury and sulfate are closely linked to hydrologic changes that will accompany the project. While there appears to be substantial uncertainty in the DEIS model-estimates of groundwater and surface flows, this review does not evaluate model reliability and simply takes hydrologic estimates at face value. The discharge and possible biotic effects of heavy metals other than mercury, and the potential for acid-mine drainage from oxidation of sulfide minerals are likewise not considered in this review.

II. Background: Mercury in the Environment

The primary concerns regarding mercury release to the environment are based on a solid understanding of the bioaccumulative nature of this potent neurotoxin and its effects on human health as well as that of certain wildlife species (Mergler et al. 2007; Scheuhammer et al. 2007). The primary route of human mercury exposure is dietary through consumption of mercury-contaminated fish (Mergler et al. 2007). Wildlife that consume fish and the fish themselves may be exposed to mercury levels that reduce survival or lead to sub-lethal effects on reproduction (Drevnick and Sandheinrich 2003; Hammerschmidt et al. 2002; Scheuhammer et al. 2007). A solid body of research has demonstrated conclusively that increased loading of mercury to surface waters, either from atmospheric deposition or direct industrial discharge will result in a corresponding rise in mercury levels at the top of the food chain (Harris et al. 2007b; Munthe et al. 2007; Orihel et al. 2006). A portion of the mercury in our air and water is of natural origin (volcanism, rock weathering, and surface evasion), but emissions from industrial sources (mining, coal combustion, and intentional use and disposal of mercury in products) have increased atmospheric concentrations and fluxes by a factor of three since the industrial revolution (Lindberg et al. 2007; Mason et al. 1994; Mason and Sheu 2002).

Inorganic mercury itself, though toxic, is not bioaccumulative, but rather must be converted to an organic form, monomethylmercury (or more commonly, methylmercury, MeHg) in order to be bio-concentrated. Mercury (Hg) levels in piscivorous fish at the top of the aquatic food chain are commonly more than one million times that in the water itself and more than 95% of that mercury is in the methyl form (MeHg) (Wiener et al. 2003). While mercury loading rates are a primary determinant of fish-mercury levels, factors that contribute to the formation of methylmercury also strongly influence resulting fish concentrations (Munthe et al. 2007). Mercury methylation is primarily a microbial process (though abiotic methylation does occur) involving bacteria that live in anoxic environments such as lake sediments, the bottom waters of stratified lakes, and wetland peat deposits. The most important group of these microbial methylators utilize sulfate as a terminal electron acceptor in the decomposition of organic matter for energy (Compeau and Bartha 1985). Known as sulfate reducing bacteria (SRB), these microbes inadvertently (for unknown adaptive reasons) intracellularly convert inorganic mercury to its methyl form. In addition to an anoxic environment and a supply of sulfate, the methylation process depends on a supply of labile organic matter and reactive inorganic mercury (Munthe et al. 2007). Not all mercury in the natural environment is readily methylated; a large portion is bound to high molecular-weight organic compounds (humic matter) that will not pass through the cellular membrane (Miller et al. 2007; Morel et al. 1998; Munthe et al. 2007). Likewise, charged mercury-sulfide species are also not readily methylated, such that methylation may be inhibited under high-sulfide conditions (Benoit et al. 2001; King et al. 2001).

Both experimental and empirical studies suggest an optimal level of ambient sulfate for stimulation of SRB activity and hence mercury methylation, typically in the range of 2 to 60 mg/L – too little sulfate and no methylation, and too much sulfate and sulfide-inhibition of methylation (Munthe et al. 2007). Moreover, under conditions where sulfate levels are ample, other reactants (organic matter, reactive mercury) may become limiting, and additional sulfate may have little stimulatory effect (Mitchell et al. 2008b). However, conditions in the immediate environment of the SRB community may be very different from that of inflowing or overlying waters owing to uptake of sulfate (and other reactants) in the sediments or peat where methylation is occurring. Thus surface-water sulfate concentrations are often only weakly correlated with those of methylmercury (e.g., Bavin and Berndt 2008). However, such lack of correlation does not mean that sulfate has little influence on methylmercury production. On the contrary, there is strong evidence from laboratory, field-scale, and whole-ecosystem studies that sulfate additions will increase the production of methylmercury, that the effects are chronic (persistently higher methylmercury under higher sulfate loads) and that the added sulfate will result in enhanced methylation somewhere in the system (Branfireun et al. 2001; Branfireun et al. 1999; Gilmour et al. 1992; Gilmour et al. 1998; Jeremiason et al. 2006; King et al. 2000; Mitchell et al. 2008b).

Finally, it is important to note that in wetland-rich landscapes such as northern Minnesota, bogs and fens are the dominant source of methylmercury to lakes and rivers. While in-lake methylation (in sediments, bottom waters) can be an important input in some settings, the extent of hydrologically connected wetlands is one of the strongest predictors of fish-mercury levels in Minnesota lakes (Wiener et al. 2006). Hydrologic effects including water-table fluctuations and wetland outflows are critical determinants of wetland export of methylmercury to lakes and streams, such that mercury levels, especially in rivers, show high temporal variability (Balogh et

al. 2004; Balogh et al. 2006). Hence, a meaningful assessment of methylmercury production and the possible influence of mine-land drainage on a watershed scale require an intensive and well-constructed sampling program. A few spot samples taken infrequently over a short period of time can easily lead to erroneous conclusions.

III. Summary Evaluation of the DEIS

Of principal concern in this review of the NorthMet project is the possible enhancement of methylmercury production and the potential for significant mercury releases to air and water. Regarding mercury methylation, the relevant factors are the amount and location of predicted sulfate discharges, whether there are methylating environments along the flow path, ambient levels of sulfate in the receiving waters, and seasonal hydrologic fluctuations that could alter the redox (oxic vs. anoxic) conditions where SRB occur. The DEIS provides a reasonably balanced overview of the potential for sulfate to increase mercury methylation and concludes that seepage from the tailings basin and pit overflows, "...would introduce elevated sulfate concentrations to a high risk situation for mercury methylation." (4.1-127, 4.5-21). However, it also tends to downplay this concern by suggesting that sulfate levels may not be limiting mercury methylation where legacy sulfate releases (from former LTV operations) have already raised sulfate concentrations to high levels (4.5-21). While this may be true in a limited sense (those locations and sampling dates), it ignores the complexity of the landscape and hydrologic variability which could produce a different outcome (increased methylation) in other locations or at other times.

My overall assessment is that the NorthMet DEIS is deficient in its evaluation of the risks of increased mercury methylation and the development of contingency plans for adaptive management should unforeseen problems arise. The principal deficiencies are as follows:

1. There is a striking lack of useful data or supporting information on which to base predictions of methylation risk. As detailed below, mercury and methylmercury sampling of area streams, wetlands, and lakes are inadequate for assessment purposes. The samples are too few and data quality for total mercury is poor.
2. The water chemistry of area lakes and streams represents a legacy of past iron mining activity with many surface waters enriched with sulfate leaking from old mine pits and tailings basins. A proper sampling of this system could have provided a powerful analog for predicting the methylation effects of additional sulfate discharges. But again, only minimum sampling was done, and nothing conclusive can be drawn from the results.
3. The assessment of mercury methylation risks (supporting documents HG01 and HG02) by PolyMet's consultant, Barr Engineering, are scientifically biased and rely on inappropriate models and incorrect assumptions. Rebuttal memos by DNR and PCA staff scientists sharply criticize these documents, and as a result few if any of Barr's conclusions are included in the DEIS. The lack of a balanced and unvarnished assessment of methylation risk in supporting documents weakens the DEIS.
4. The DEIS does not fully consider the methylation risks posed by sulfate discharges to several key locations: the St. Louis River estuary, the wetland complex north of the tailings basin,

hypolimnetic (bottom) waters of the Embarrass chain of lakes, and beaver impoundments along the upper Partridge River. All of these locations represent high-risk situations for sulfate-enhanced mercury methylation.

5. There is little in the DEIS that would mitigate the effects of sulfate discharge on mercury methylation potential. A tailings-basin alternative that would intercept groundwater discharge to a wetland complex along the Embarrass River is likely to be essential, though the flow would ultimately be redirected to the Partridge River, rather than being eliminated. No consideration is given to sulfate-removal alternatives that might reduce sulfate concentrations in discharges to something approaching background (natural) levels.

IV. Adequacy of Mercury Sampling and Analysis

Although the relationship between sulfate loading and mercury methylation is complex and difficult to model quantitatively, prior mining activity at the NorthMet site and nearby taconite operations have left a legacy of leaking mine pits and tailings basins that could provide a useful analog for predicting effects of future sulfate discharges on mercury methylation. The DEIS and supporting technical memo (HG01) report results from a modest sampling program conducted over a two year period (2006-2007) at 10 sites on the Partridge and Embarrass Rivers and smaller tributaries. Unfortunately this data set is grossly inadequate to assess sulfate effects on methylmercury levels in area surface waters. There are far too few sites to spatially characterize this large and complex drainage system, sampling frequency is too low to properly assess the effects of changing stream discharge on methylmercury and sulfate levels, and the analytical results for total mercury concentrations are nearly useless because of poor (high) detection limits and other analytical problems. Fully half of the 53 samples reported in Table 2 of Technical Memo HG01 report total-mercury levels below detection, which itself varies between 2 and 8 ng/L. Standard and widely used analytical procedures for total-mercury in water provide detection limits in the range of 0.5-1.0 ng/L, which is well below normal surface water concentrations.

The lack of reliable numbers for total-mercury means that the %MeHg (the proportion of total-mercury present as methyl) cannot be calculated. %MeHg is a widely accepted and useful metric for the methylation efficiency of the environment, which allows for comparison across sites where total-mercury and other water chemistry variables may range widely (see MPCA response to HG01). The DEIS points out that methylmercury concentrations in the upper Embarrass River are greater in low-sulfate waters above the LTV tailings basin than they are at a downstream site that receives tailings-basin drainage and has higher sulfate (4.1-126, 4.1-133). However, the difference in methylmercury between the two sites is not statistically significant and furthermore cannot be expressed as %MeHg for lack of reliable total-mercury data. Moreover, some of the highest methylmercury concentrations (and %MeHg) are reported from Second Creek, which also has very high sulfate levels from mine drainage (4.1-169, see also DNR response to HG01). But basically, the data set for the NorthMet site is far too sparsely populated with reliable numbers to allow for any statistically robust assessment of possible mine-drainage effects on methylmercury levels. In all fairness, the DEIS does point out that additional sampling of area waters is currently being conducted, which may help address the effects of legacy mining and sulfate loading on mercury methylation (4.1-113, 4.1-161, 4.5-1).

One final note on mercury monitoring of surface waters is that a sampling plan that focuses solely on water samples is likely to be uninformative (Harris et al. 2007a; Mason et al. 2005). This is because water samples provide only an instantaneous snapshot of environmental conditions, especially in flowing waters where concentrations and fluxes can change quickly. Most mercury monitoring programs today include, and indeed focus on, biotic indicators of ecosystem mercury exposure. Forage-fish, zooplankton, and aquatic insects integrate mercury exposure over meaningful periods of time, yet if properly selected, represent discrete food-web (trophic) positions that are comparable across sample sites and through time. These lower-trophic indicators are also highly correlated with, and predictive of, mercury levels in game-fish and hence of human mercury-exposure risk.

V. Potential Effects of Sulfate Discharges on Mercury Methylation

Embarrass River Wetlands

The DEIS predicts substantially increased groundwater leakage from the proposed NorthMet tailings basin largely in the direction of the Embarrass River to the north (4.1-65). This leakage would occur as a result of increased head gradients and is expected to discharge through an area of extensive wetlands located between the basin and the Embarrass River. Because leakage rates are expected to greatly exceed the flux capacity of the surficial aquifer, upwelling and surface ponding and drainage is expected to increase. According to the DEIS classification (4.2-3), most of these wetlands (72%) are ombrotrophic bogs (though a review by P. Glaser indicates that most are poor fens). Indeed, the DEIS concludes that legacy leakage from the existing LTV tailings basins is currently impacting portions of this wetland complex – though the actual extent of impact appears to be poorly known because of a lack of on-the-ground observation and sampling. Groundwater discharge through these wetlands and toward the Embarrass River is expected to increase from a current estimated rate of 1800 gpm to 3800 gpm by year-20 of operation (4.1-65). A tailings basin alternative in which ground-water seepage would be intercepted by a series of wells and returned to the plant operations as make-up water (or partially discharged to the Partridge River) is included in the DEIS (4.1-147). These operations, if implemented, would cease upon closure, and the tailings-basin leakage would revert to the Embarrass River wetlands (4.1-65).

In my view this tailings-basin leakage poses the project's greatest risk of increasing mercury methylation and methylmercury export to downstream aquatic environments. As pointed out in the DEIS, wetlands are important sites for mercury methylation, and the aerial extent of hydrologically connected wetlands is one of the strongest predictors of fish-mercury levels in area lakes and streams (St. Louis et al. 1996; Wiener et al. 2006). Mercury methylation rates are strongly sulfate-limited in bogs (and poor fens), so that addition of sulfate from atmospheric deposition or groundwater discharge would be expected to stimulate methylmercury production (Branfireun et al. 2001; Branfireun et al. 1999; Jeremiason et al. 2006). The configuration of the Embarrass River wetland complex makes it especially susceptible to sulfate-enhanced mercury methylation. Not only would these bogs/poor fens be sulfate limited (and hence sensitive to additional sulfate), but the anticipated discharge would upwell through a mercury and carbon-rich, anoxic environment ideal for SRB. Such groundwater discharge at the upland-wetland margin has been identified as creating sites of intense mercury methylation – “methylation hot

spots” where methylmercury concentrations (or %MeHg) are exceptionally high relative to other wetland areas (Mitchell et al. 2008a). The increased ground-water and surface discharge toward the Embarrass River would also increase mercury transport from sites of methylation to the river itself where the methylmercury load could then impact downstream aquatic systems.

It is one of the unfortunate outcomes of Barr’s stream sampling scheme that no water samples were apparently collected within the wetland complex north of the tailings basin (except locally at its toe). Such sampling would have provided a picture of current (legacy) groundwater discharge and associated sulfate and mercury levels by which a better understanding of the effects of increased groundwater discharge might be derived.

Perhaps the best analogue for what might be expected from discharge of sulfate-rich groundwater through the Embarrass River wetlands is provided by the Everglades ecosystem of south Florida where agricultural drainage of sulfate-rich surface waters has greatly increased mercury methylation and mercury levels at all levels of the food chain (Gilmour et al. 1998). More recent reductions in sulfate discharge to the Everglades are closely associated with marked declines in mercury levels in fish and fish-eating wildlife (Atkeson et al. 2003; Frederick et al. 2001).

Partridge River

A portion of the groundwater leakage from the tailings basin is predicted to occur toward the Partridge River during operations (4.1-63). If the tailings-basin alternative is implemented, some portion of the recovered groundwater seepage that would have gone to the Embarrass River could also be redirected in discharge to the Partridge River (4.1-155,156). Following closure additional sulfate loading to the upper reaches of this river will occur via overflow from the West mine pit and to the lower reaches (below Colby Lake) as discharge from the tailings basin through Second Creek (4.1-88). While the DEIS recognizes that these hydrologic inputs will increase sulfate loading to the Partridge River, the risk of sulfate-enhanced mercury methylation is downplayed because (1) sulfate levels are already high in the lower river (below the confluence with Second Creek, which drains former LTV Pits 1 and 6 on the proposed Mesabi Nugget site) (4.1-39), and (2) there are reportedly few wetlands along the Partridge River where mercury methylation might be enhanced. In-stream production of methylmercury is generally considered to be of minor importance relative to other watershed sources. However, elsewhere in the DEIS (4.1-23) the Partridge River is described as having “a very well-developed floodplain along most of its reaches with “...many beaver dams along the entire length ... which create wide pools.” Recent studies have shown that beaver impoundments provide conditions suitable for active mercury methylation and represent net sources for methylmercury in riverine systems (Roy et al. 2009). It thus seems likely that the risk of enhanced methylation from sulfate discharge to the Partridge River may be greater than is concluded in the DEIS.

Two lakes located in the Partridge River watershed, Colby and the Whitewater Reservoir, could also see increases in mercury methylation as a consequence of the proposed action. Colby Lake is predicted to see a modest increase in sulfate loading from the Partridge River (increasing lake concentrations from 10 mg/L to 15 mg/L) (4.1-116), and the Whitewater Reservoir is expected to see a larger range of water level fluctuations (to maintain water levels in Colby

Lake) than currently occurs (4.1-105). Fluctuating water levels are known to increase mercury methylation – principally through redox cycling of sulfate in littoral sediments during drying and rewetting (Munthe et al. 2007; Sorensen et al. 2005). The DEIS incorrectly concludes that this will not be a problem in the Whitewater Reservoir because it does not receive inflows from the Partridge River under normal flow conditions (4.1-127). This conclusion presupposes that additional sulfate inputs from the Partridge River would be necessary for water-level fluctuations to induce mercury methylation. However, it should be expected that current sulfate inputs to the Whitewater Reservoir (e.g. from other inflows including the City of Hoyt Lakes WWTP) would be sufficient to stimulate microbial sulfate reduction (and mercury methylation) during water level fluctuations.

The Embarrass River Chain of Lakes

Four lakes located along the Embarrass River downstream of the NorthMet project (Sabin, Wynne, Embarrass, and Esquagama) are potential high-risk sites for sulfate-enhanced mercury methylation. The four lakes are also 303d-listed for mercury in fish tissue impairment (4.1-40). There are no water quality data for these lakes in the DEIS or supporting documents, but monitoring results from an upstream site on the Embarrass River (PM13) show elevated sulfate levels (mean = 36 mg/L), a consequence of legacy mine drainage from LTV Pit 5NW (4.1-41, 4.1-122). The fish mercury levels in these lakes are in the high range for northeastern Minnesota, though a comparison with other regional (non mine-impacted) lakes in the Barr Technical Memo (HG02) was biased and not useful as an objective evaluation (see MPCA and DNR responses to HG02). Nonetheless, the question remains as to whether fish-mercury levels are currently elevated in the Embarrass lakes because of legacy sulfate discharge (sulfate-enhanced methylation) or because of other factors known to contribute to high fish-mercury – in particular the presence of extensive contributing wetlands and high DOC (dissolved organic carbon) levels in the upper Embarrass River (4.1-125).

The important point I wish to make here, and as noted in the DNR response to HG02, is the potential for enhanced mercury methylation in the hypolimnia of these lakes during summer stratification, should bottom waters become anoxic. The zone of active mercury methylation can move from bottom sediments into the water column as oxygen becomes depleted, and hypolimnetic methylation can be a very important in-lake source of methylmercury (Eckley et al. 2005; Munthe et al. 2007). Moreover, sulfate reduction, especially during periods of stratification, could consume much of the current sulfate load to the first lakes in the chain, thereby rendering lower lakes susceptible to increased sulfate inputs. My understanding is that PolyMet (Barr Engineering) is currently conducting water-chemistry sampling in the Embarrass chain of lakes (under advisement from MPCA and DNR staff) in order to assess the potential for in-lake methylmercury production.

St. Louis River Estuary

The DEIS points out that there are few wetlands or lakes on the middle St. Louis River where sulfate-enhanced mercury methylation would be a problem. However, the document only briefly considers the potential for mercury methylation in the St. Louis River estuary (4.1-196). Sulfate concentrations in the lower St. Louis River are relatively low, as compared to upper reaches

principally because of dilution from major (non-mining) tributaries such as the Cloquet (4.1-195). At lower concentrations, sulfate tends to be a limiting factor for mercury methylation by sulfate reducing bacteria, and increased sulfate inputs are more likely to stimulate SRB activity. We currently have little information regarding the methylating potential of the estuary, but its shallow and relatively productive waters suggest that it could be high (Munthe et al. 2007). This section of the river is state listed for fish-mercury levels as well as for mercury in water (4.1-194). Equally important, the estuary supports a rich recreational fishery and abundant wildlife, and is a critical cultural resource for the Fond du Lac Band of Lake Superior Chippewa. The failure of the DEIS to address mercury-exposure risks in the estuary associated with the NorthMet project is a serious oversight. Based on this near-complete lack of information it is difficult to see how the DEIS can conclude (4.1-196) that, "Overall, the Project is not expected to contribute significantly to cumulative effects on mercury or methylmercury in the St. Louis River."

VI. Other Issues

Sulfate removal

PolyMet proposes a wastewater treatment facility (WWTF) at the mine site which would treat process water and runoff from other site operations (4.1-67,68). The proposed treatment system would utilize chemical precipitation of drainage with elevated trace metals and/or low pH followed by nanofiltration to concentrate the circumneutral drainage with lower levels of trace metals. The nanofiltration would remove an unspecified amount of sulfate, yielding process water with a residual concentration of 250 mg/L, which would then be pumped to the tailings basin for reuse or to expended mine pits for flooding. Under a proposed mitigation option, the WWTF could be fitted with nanofiltration units in series to improve the removal of sulfate and other solutes. (4.1-167). Other discharges, including leakage from the tailings basin, would not be treated for sulfate removal, and surface waters would be impacted accordingly. There is no discussion of the expected efficacy of the WWTF mitigation option nor is there any consideration of alternatives (e.g. sulfide precipitation in the mine pits) that might reduce sulfate concentrations in discharges closer to background (natural) levels. The DEIS appears to accept the inevitability of high sulfate loading from the NorthMet Project to area surface waters, even as it recognizes cumulative effects of high sulfate from legacy mining and other proposed operations (e.g. Mesabi Nugget) (4.1-189).

Wetland treatment of process water

A constructed wetland in the filled East Pit of the NorthMet mine-site is proposed as a means of treating ("polishing") mine-site drainage following closure (4.1-112). Little information is provided regarding the nature of this wetland (water depth, vegetation, residence time, substrate), and it is very difficult to predict its efficacy in treating contaminated drainage waters (4.1-112, 4.1-123). However, another issue not addressed in the DEIS is the potential for mercury methylation in the constructed wetland. While natural wetlands are important methylation sites, the constructed wetland may function very differently, depending on whether there is an organic rich substrate supporting redox conditions suitable for sulfate reducing bacteria. If sulfate inputs to the wetland are very high (as expected), methylation could be inhibited by high sulfide levels

which favor charged mercury-sulfide species that are not readily methylated (Benoit et al. 1999). Again, it is very difficult to predict this outcome based on first principles. However, constructed wetlands at the nearby Dunka mine, which currently treat rock-stockpile seepage, would make a good a case study for evaluating mercury cycling and methylation under conditions at least approximate to those proposed for NorthMet.

Mercury releases to air and water

It is difficult to fully evaluate the potential for mercury releases to air and water from the proposed NorthMet project, but if DEIS estimates are even remotely correct, the numbers will be low relative to other mercury sources. Based on the observed performance of other tailings basins used for taconite processing (Berndt 2003), I would expect high retention of dissolved and particulate mercury and low concentrations in outflow waters – as documented in the DEIS (4.1-124).

A large area of wetland and forest soils will be cleared at the mine site, with the resulting stockpiles of peat representing a large potential source of mercury and methylmercury that could be mobilized with subsequent drying and oxidation (4.1-123). Drainage from these stockpiles would be captured and routed to the WWTF and from there to the tailings basin or later, the constructed wetland and flooded mine pits. Neither the WWTF nor the constructed wetland is expected to be effective at sequestering mercury. Thus mercury discharge from the Project will depend largely on the removal efficiency of the tailings basin or the mine pits. The mine pits are expected to be a fairly effective sink for mercury (through sedimentation), given their depth and hydraulic residence time. The DEIS does not consider the efficacy of the mine pits in removing methylmercury. Both methylmercury loss through photo-demethylation in surface waters and methylmercury production by SRB in anoxic bottom waters are likely to occur and should be evaluated in the DEIS.

Air emissions are more problematic, as autoclave and scrubber performance is not assured. Projected annual air emissions of 9 pounds is probably overly optimistic, and in any case would have to be mitigated through emission trading in order to meet targets for the mining sector of the statewide mercury TMDL (4.6-35). A comprehensive monitoring program for mercury releases needs to be implemented for this project should it be approved (4.1-172). That said, it is my professional opinion that direct mercury releases from the NorthMet project represent a much smaller risk of biotic mercury exposure than that posed by sulfate discharges and a resulting increase in mercury methylation in receiving waters of the St. Louis River and tributaries.

VII. Summary

The discharge of sulfate-laden waters from the mine site and tailings basins, either during operations or following closure is among the most serious environmental risks posed by the proposed NorthMet project. Based on a large body of experimental and observational evidence, it is my view that these discharges are likely to increase the microbial methylation of mercury somewhere in the watershed of the St. Louis River, either in wetlands or lakes proximal to the mining/processing operations or possibly downstream in its estuary with Lake Superior. This increase in methylmercury production will be transferred up the food chain to increased levels of

mercury in game fish, with the attendant increase in human and wildlife exposure. Lakes along the Embarrass River as well as the St. Louis River itself are currently state-listed as impaired (303d) for high mercury levels in fish, which raises important regulatory questions for proposed activities that might further increase methylmercury exposure.

To some extent, the DEIS downplays these risks by emphasizing legacy conditions of high sulfate levels from past mining activities in certain river sections and tributaries. While it is unlikely that additional sulfate inputs will stimulate methylation in some specific stream reaches (because sulfate may not limit SRB activity at high concentrations), it is probable that sulfate concentrations will fall into a more sensitive (lower) range further downstream as a result of dilution or sulfate uptake. The basic assumption here is that increased sulfate loads are likely to generate additional methylmercury somewhere along the flow path of the receiving waters. This point is briefly acknowledged in the DEIS (4.1-125).

It is also my view that the DEIS underrates our current scientific understanding of mercury biogeochemistry and the environmental factors controlling methylation rates (4.5-19). That is, there is less uncertainty that mercury methylation will be enhanced by sulfate discharge, than the document acknowledges. While it is still difficult to accurately predict the degree by which methylation will be increased or exactly where in the landscape it will occur, we now possess a solid conceptual framework from which to identify conditions that pose substantial risk.

In the final analysis it would be prudent for the state regulatory agencies to require additional on-site sampling and analysis of those sectors of the watershed that represent high-risk conditions for sulfate-induced mercury methylation. The DEIS is equivocal in its depiction of the risks of increased mercury methylation posed by the NorthMet project (4.5-21). Some of this uncertainty arises from the biogeochemical complexity of mercury cycling and methylation. However, firmer conclusions could have been reached had there been a better assessment of existing conditions, including the effects of legacy sulfate contamination from past mining activities. Such an assessment if properly structured could provide a more reliable picture of the project's likely effects on methylmercury levels in the St. Louis River and its headwaters.

VIII. Recommendations

- (1) The DEIS should provide a more realistic assessment of the mercury methylation risks posed by sulfate discharges to key sensitive areas (Embarrass River wetlands, Embarrass chain of lakes, Partridge River beaver impoundments, and the St. Louis River estuary).
- (2) There needs to be an evaluation of the potential for mercury methylation in the constructed treatment wetland. The nearby Dunka mine-site, where constructed wetlands are used to treat rock-stockpile seepage, provides a good analog for the NorthMet project. It should be monitored for mercury methylation as part of this evaluation.
- (3) The DEIS should incorporate new results from ongoing monitoring of area rivers and lakes, especially those receiving sulfate leakage from legacy mining operations.

- (4) There needs to be an evaluation of the potential for mercury demethylation and/or methylation in flooded mine pits.
- (5) A more complete evaluation of sulfate removal alternatives including the expected efficacy of enhanced nanofiltration as a mitigation alternative is needed. Other possible methodologies, such as enhanced sulfide precipitation in flooded mine pits, should be considered.
- (6) The DEIS needs to spell out a more comprehensive monitoring program to evaluate the effects of sulfate discharge from the NorthMet project. The program should include sampling of food-web organisms as well as surface waters and should be spatially and temporally intensive. High risk areas, as outlined in this review (and especially the Embarrass River wetlands), should be a priority for sampling. The program should be designed by mercury scientists with the MPCA and DNR and peer-reviewed by independent mercury experts to insure that results are meaningful.
- (7) The conclusion that there is little risk of sulfate-enhanced mercury methylation in the St. Louis River estuary (4.1-194) is unsubstantiated and should be modified or deleted.
- (8) Conclusions based on sulfate and methylmercury concentrations at sites along the Embarrass River (4.1-126, 4.5-21) rest on questionable data and should be modified or deleted.

References

- Atkeson T., Axelrad D., Pollman C.D. and Keeler G.J. 2003. Integrating Atmospheric Mercury Deposition and Aquatic Cycling in the Florida Everglades: an approach for conducting a Total Maximum Daily Load analysis for an atmospherically derived pollutant. Florida Department of Environmental Protection, Tallahassee, FL, 115 pp.
- Balogh S.J., Nollet Y.H. and Swain E.B. 2004. Redox chemistry in Minnesota streams during episodes of increased methylmercury discharge. *Environ. Sci. Technol.* 38: 4921-4927.
- Balogh S.J., Swain E.B. and Nollet Y.H. 2006. Elevated methylmercury concentrations and loadings during flooding in Minnesota rivers. *Sci. Tot. Environ.* 368: 138-148. (attached).
- Bavin T. and Berndt M.E. 2008. Sources and Fate of Sulfate in Northeast Minnesota Watersheds: A Minerals Coordinating Committee Progress Report. Minnesota Department of Natural Resources, St. Paul.
- Benoit J.M., Gilmour C.C. and Mason R.P. 2001. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). *Environ. Sci. Technol.* 35: 127-132.
- Benoit J.M., Gilmour C.C., Mason R.P. and Heyes A. 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* 33: 951-957.

- Berndt M.E. 2003. Mercury and Mining in Minnesota. Minerals Coordinating Committee Final Report. Minnesota Department of Natural Resources, St. Paul.
- Branfireun B.A., Bishop K., Roulet N.T., Granberg G. and Nilsson M. 2001. Mercury cycling in boreal ecosystems: the long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophys. Res. Lett.* 28: 1227-1230.
- Branfireun B.A., Roulet N.T., Kelly C.A. and 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. *Glob. Biogeochem. Cycles* 13: 743-750.
- Compeau G. and Bartha R. 1985. Sulphate-reducing bacteria: principle methylators of mercury in anoxic estuarine sediment. *Appl. Envir. Microbiol.* 50: 498-502.
- Drevnick P.E. and Sandheinrich M.B. 2003. Effects of dietary methylmercury on reproductive endocrinology of fathead minnows. *Environ. Sci. Technol.* 37: 4390-4396.
- Eckley C.S., Watras C.J., Hintelmann H., Morrison K., Kent A.D. and Regnell O. 2005. Mercury methylation in the hypolimnetic waters of lakes with and without connection to wetlands in northern Wisconsin. *Canadian Journal of Aquatic Science* 62: 400-411. (attached).
- Fitzgerald W.F., Engstrom D.R., Mason R.P. and Nater E.A. 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* 32: 1-7.
- Frederick P.C., Spaulding M.G. and Dusek R. 2001. Wading birds as bioindicators of mercury contamination in Florida: annual and geographic variation. *Environ. Toxicol. Chem.* 21: 262-264.
- Gilmour C.C., Henry E.A. and Mitchell R. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* 26: 2881-2887.
- Gilmour C.C., Riedel G.S., Ederington M.C., Bell J.T., Benoit J.M., Gill G.A. and Stordal M.C. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40: 327-345. (attached).
- Hammerschmidt C.R., Sandheinrich M.B., Wiener J.G. and Rada R.G. 2002. Effects of dietary methylmercury on reproduction of fathead minnows. *Environ. Sci. Technol.* 36: 877-883.
- Harris R., Krabbenhoft D.P., Mason R., Murray M.W., Reash R. and Salzman T. 2007a. *Ecosystem Responses to Mercury Contamination* CRC Press, Boca Raton.
- Harris R.C., Rudd J.W.M., Amyot M., Babiarz C.L., Beaty K.G., Blanchfield J., Bodaly R.A., Branfireun B.A., Gilmour C.C., Graydon J.A., Heyes A., Hintelmann H., Hurley J.P., Kelly C.A., Krabbenhoft D.P., Lindberg S.E., Mason R.P., Paterson M.J., Podemski C.L., Robinson A., Sandilands K.A., Southworth G.R., St. Louis V.L. and Tate M.T. 2007b. Whole-ecosystem study shows rapid fish mercury response to changes in mercury deposition. *PNAS* 104: 16586-16591.
- Jeremiason J.D., Engstrom D.R., Swain E.B., Nater E.A., Johnson B.M., Almendinger J.E., Monson B.A. and Kolka R.K. 2006. Sulfate addition increases methylmercury production in an experimental wetland. *Environ. Sci. Technol.* 40: 3800-3806. (attached).

- King J.K., Kostka J.E., Frischer M.E. and Saunders F.M. 2000. Sulphate-reducing bacteria methylate mercury at variable rates in pure culture and in marine sediments. *Appl. Environ. Microbiol.* 66: 2430-2437.
- King J.K., Kostka J.E., Frischer M.E., Saunders F.M. and Jahnke R.A. 2001. Quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on the community composition and activity of sulfate-reducing bacteria. *Environ. Sci. Technol.* 35: 2491-2496.
- Lindberg S., Bullock R., Ebinghaus R., Engstrom D., Feng X., Fitzgerald W., Pirrone N., Prestbo E. and Seigneur C. 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* 36: 19-32.
- Mason R.P., Abbott M.L., Bodaly R.A., Bullock O.R., Jr., Driscoll C.T., Evers D., Lindberg S.E., Murray M. and Swain E.B. 2005. Monitoring the response to changing mercury deposition. *Environ. Sci. Technol.*: 15A-22A.
- Mason R.P., Fitzgerald W.F. and Morel F.M.M. 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* 58: 3191-3198.
- Mason R.P. and Sheu G.-R. 2002. Role of the ocean in the global mercury cycle. *Glob. Biogeochem. Cycles* 16: 1093,1010.1029/2001GB001440.
- Mergler D., Anderson H.A., Hing Man Chan L., Mahaffey K.R., Murray M., Sakamoto M. and Stern A.H. 2007. Methylmercury exposure and health effects in humans: A worldwide concern. *Ambio* 36: 3-11.
- Miller C.L., Mason R.P., Gilmour C.C. and Heyes A. 2007. Influence of dissolved organic matter on the complexation of mercury under sulfidic conditions. *Environ. Toxicol. Chem.* 26: 624-633.
- Mitchell C.P.J., Branfireun B.A. and Kolka R.K. 2008a. Spatial characteristics of net methylmercury production hot spots in peatlands. *Environ. Sci. Technol.* 42: 1010–1016. (attached).
- Mitchell C.P.J., Branfireun B.A. and Kolka R.K. 2008b. Assessing sulfate and carbon controls on net methylmercury production in peatlands: an in situ mesocosm approach. *Appl. Geochem.* 23: 503-518.
- Morel F.M.M., Kraepiel A.M.L. and Amyot M. 1998. The chemical cycle and bioaccumulation of mercury. *Ann. Rev. Ecol. Syst.* 29: 543-566.
- Munthe J., Bodaly R.A., Branfireun B.A., Driscoll C.T., Gilmour C.C., Harris R., Horvat M., Lucotte M. and Malm O. 2007. Recovery of mercury-contaminated fisheries. *Ambio* 36: 33-44. (attached).
- Orihel D.M., Paterson M.J., Gilmour C.C., Bodaly R.A., Blanchfield P.J., Hintelmann H., Harris R.C. and Rudd J.W.M. 2006. Effect of loading rate on the fate of mercury in littoral mesocosms. *Environ. Sci. Technol.* 40: 5992-6000.
- Roy V., Amyot M. and Carignan R. 2009. Beaver ponds increase methylmercury concentrations in Canadian Shield streams along vegetation and pond-age gradients. *Environ. Sci. Technol.* 43: 5605-5611.

- Scheuhammer A.M., Meyer M.W., Sandheinrich M.B. and Murray M.W. 2007. Effects of environmental methylmercury on the health of wild birds, mammals and fish. *Ambio* 36: 12-18.
- Sorensen J.A., Kallemeyn L.W. and Sydor M. 2005. Relationship between mercury accumulation in young-of-the-year yellow perch and water-level fluctuations. *Environ. Sci. Technol.* 39: 9237-9243.
- St. Louis V.L., Rudd J.W.M., Kelly C.A., Beaty K.G., Flett R.J. and Roulet N.T. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Technol.* 30: 2719-2729.
- Swain E.B., Engstrom D.R., Brigham M.E., Henning T.A. and Brezonik P.L. 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* 257: 784-787.
- Wiener J.G., Knights B.C., Sandheinrich M.B., Jeremiason J.D., Brigham M.E., Engstrom D.R., Woodruff L.G., Cannon W.F. and Balogh S.J. 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* 20: 6281-6286. (attached).
- Wiener J.G., Krabbenhoft D.P., Heinz G.H. and Scheuhammer A.M. 2003. Ecotoxicology of mercury. In: D. J. Hoffman, B. A. Rattner, G. A. Burton, Jr. and J. Cairns (eds.), *Handbook of Ecotoxicology* (2nd ed.). Lewis Publishers, Boca Raton, FL, pp. 409-463.