MPCA Strategy to Address Indirect Effects of Elevated Sulfate on Methylmercury Production and Phosphorus Availability

Summary: Although there is evidence that elevated sulfate loading can increase methylmercury production and phosphorus mobilization, it is premature to develop specific sulfate concentration limits or other regulatory responses based on these effects. The deleterious effects of sulfate may be restricted to certain areas of the state, certain background sulfate concentrations, or other environmental controlling factors. These factors will be explored in a multi-year data collection effort combined with ongoing data analysis. It is anticipated that sensitive areas of the state will be identified and appropriate controls on sulfate discharges will be developed if necessary. The primary focus of the strategy is to pursue research to further understand impacts from sulfate on methylmercury production and phosphorus mobilization and to use the research to guide the future need for additional requirements or controls in environmental review and NPDES permits. This strategy was approved by the MPCA Risk Managers on August 28, 2006 and the MPCA WQ Policy Forum on October 19, 2006.

Problem Statement: Research indicates a correlation between sulfate loading and methylmercury (MeHg) production and phosphorus (P) mobilization under certain conditions. Many waters of the state are impaired as a result of MeHg in fish tissues and excess nutrients. MPCA staff need to better understand the relationship between sulfate concentration and MeHg production/P mobilization so that appropriate responses, if necessary, can be developed. Sulfate is a common constituent in domestic and industrial wastewaters. Additional information is needed so that the MPCA can develop a permitting strategy for existing, expanding and new domestic and industrial process wastewater discharges. The strategy must reflect varying MeHg production and P availability under differing environmental conditions.

MPCA Actions to Monitor & Evaluate Sulfate Impacts

MPCA staff will evaluate the following hypotheses over three to five years.

1) Elevated sulfate discharge into low-sulfate receiving waters significantly increases MeHg concentrations (as percent of total mercury) and P concentrations.
2) Elevated sulfate discharge into high-sulfate receiving waters has no significant effect on MeHg concentrations (as percent of total mercury) and P concentrations.
3) Elevated sulfate discharge into low-sulfate waters has greater effect on P concentrations when the iron to P ratio is low in the sediments of the receiving water.

Environmental Analysis and Outcomes Division will coordinate the following activities to evaluate the above hypotheses and support eventual changes in the environmental review and permitting practices:

1) Continued research at Wetland 6 in the Marcell Experimental Forest north of Grand Rapids;
2) Milestone Monitoring – permanently add sulfate, TOC, total mercury, and MeHg to the MPCA's ambient water quality monitoring sites; (In FY07 Milestones did include THg, MeHg, sulfate, and TOC, through use of the Mercury Trends allotment).

3) Continue to track and participate in the research of national / international work groups;
4) Compile and map existing surface water sulfate concentration data in Minnesota;
5) Compile and map existing effluent sulfate concentration data in Minnesota;
6) Compile and map existing stormwater sulfate concentration data in Minnesota (if few data have been collected, consider obtaining representative data);
7) Fish Consumption Advisory Monitoring - Work with DNR and MDH to collect fish for mercury analysis of fish tissue at a subset of sites where environmental data is being collected on water or sediments;
8) Implement the Environmental Review and NPDES Permitting actions (below) Regional, Municipal and Industrial Divisions will lead as appropriate; and
9) Compile data from the above activities and complete an evaluation of the hypotheses.

Environmental Review and NPDES Permitting

While research shows a relationship between sulfate concentration and MeHg production/P mobilization, there is currently insufficient information to reach firm conclusions on whether specific point source (non-stormwater) discharges containing sulfate may impact water quality or cause/contribute to water quality impairments. The following information will guide the development of programmatic direction and procedures to address sulfate discharges. This approach includes 1) further characterization of the problem, 2) development of interim permitting and environmental review procedures, 3) research of sulfate impacts from point source dischargers, and 4) annual incorporation of new knowledge into the permitting and environmental review procedures. Prior to development of the interim procedures, NPDES permit writers and environmental review staff will need to manage projects on a case-by-case basis. They will use the current knowledge (as outlined below and in Appendix A) and work with the program supervisor and Ed Swain to assess and respond to the environmental risk from sulfate discharges.

Environmental Review

If a new or expanding domestic or industrial process wastewater discharge triggers environmental review for a wastewater-related threshold (not a non-wastewater related threshold) or if wet air controls that contribute sulfate to a wastewater stream are proposed the impact from sulfate must be evaluated in the environmental review document. The environmental review should include available data on projected effluent design flow rate, sulfate concentration, and sulfate load as well as best estimates of receiving water flow rate (7Q10 and other statistics) and concentrations of sulfate, mercury, MeHg, iron, ortho-P, total P, and, as a measure of organic matter in the water, TOC and/or DOC. If receiving water flow was measured concurrently with water sampling, flow data should also be included. The environmental review must also include available data on the organic matter, mercury, iron, and P content of the sediments of receiving waters and lakes or impoundments downstream. It is understood that available data may be limited. To the extent possible, qualitative discussion of downstream conditions and mitigative options should also be included.

NPDES Permitting

If a new, expanding or existing domestic or industrial wastewater discharge for "high risk" situations is encountered, 1) the need for effluent and/or receiving water monitoring for sulfate, mercury, MeHg, iron, ortho-P and/or total P should be considered; and 2) if research or other information supports a likely impact from sulfate in a specific situation an evaluation of the treatment technologies and pollution prevention opportunities should be included with the permit application. Existing discharges will be addressed at the time of reissuance. A guidance for project proposers and NPDES permit writers will be developed by June 2007 to explain the procedures for addressing sulfate discharges. In the interim, permit writers will work with the program supervisor and Ed Swain to assess and respond to the environmental risk from sulfate discharges.

Currently, high-risk situations may include:

- Discharge of elevated sulfate concentrations into high-organic aquatic environments (e.g., wetlands that drain to fisheries, lakes with organic sediment, rivers with slow-moving back waters, ponds where rising water might inundate vegetation).
- Discharge of elevated sulfate into low-sulfate waters (< 40 ppm or so) where sulfate may be a limiting factor in the activity of sulfate-reducing bacteria (SRB).
- Discharge of elevated sulfate into streams with fluctuating water levels and bordering wetlands. Rising water levels would introduce sulfate into the high-organic wetland matrix, followed by falling water levels that hydraulically deliver elevated MeHg and/or phosphate to the stream.
- Discharge of elevated sulfate to waters that flow to a lake or impoundment downstream that may thermally stratify even temporarily in the summer or be cut off from the atmosphere from ice cover in the winter. Either stratification or ice cover can produce anoxic water, in which sulfate can be converted to sulfide, potentially enhancing both mercury methylation and phosphate release.

<u>Conditions that decrease the risk that elevated sulfate loading may enhance mercury methylation:</u>

- Discharge of elevated sulfate to waters with high background sulfate (>100 ppm or so), including downstream waters.
- Discharge of elevated sulfate to highly oxygenated, turbulent waters with low-organic sediment and no adjacent riparian or lacustrine wetlands, and none downstream.

Research Impacts of Sulfate from Domestic and Industrial Process Wastewater Discharges

MPCA staff will pursue funding to study specific impacts from domestic and industrial process wastewater discharges of sulfate on MeHg production and P availability in receiving waters. The study (or series of smaller studies) will include site-specific evaluations at facilities representing the various high risk situations identified in "Environmental Review and NPDES Permitting" above. This work may include effluent and receiving water monitoring for sulfate, mercury, MeHg, iron, ortho-P, total P, and supporting parameters that may reveal biogeochemical mechanisms, such as DOC, pH, oxygen, nitrate, and potassium. The work will include an evaluation of the data to determine whether domestic and industrial process wastewater discharges are impacting receiving waters during any time of the year with a particular focus on the summer months. Some of the study work may need to be contracted out to a research entity (i.e. UMD, NRRI, U of M St. Anthony, U of Toronto). Funding sources may include Legislative Initiative, CW Legacy Act, GLNPO, salary savings, or other related project savings.

Action Items / Resource Needs

1) Risk Managers need to select an EAO Division representative to coordinate the overall Sulfate Strategy **by August 28, 2006**. Action Complete: Marvin Hora will be overall coordinator.

2) Sulfate Strategy Coordinator (Marvin Hora) will work with the appropriate managers to recommend staff team members to develop guidance documents described in the Environmental Review and NPDES Permitting action items below **by September 25, 2006**. Recommendation: Team should include Ed Swain, Jeff Stollenwerk, Deb Lindlief, Dana Vanderbosch, Bruce Wilson and a GIS specialist (see MPCA Actions 4 & 5 above).

3) Water Policy Team reviews and approves the Sulfate Strategy including staff assignments **by October 31, 2006**. Jeff Stollenwerk will coordinate.

4) EAO staff should develop funding requests, detailed plans and funding applications, RFPs and conduct study oversight necessary to complete research on impacts of sulfate from domestic and industrial process wastewater discharges. **Ed Swain - Ongoing.**

5) The Sulfate ER/NPDES Permitting staff team (from item 2 above) further defines and characterizes high-risk situations/criteria and develops interim procedures for environmental review and NPDES permitting activities. This action should be completed **by February 28, 2007**. Estimated time commitment – 40 to 80 hours for each team member.

6) The Sulfate ER/NPDES Permitting staff team (from item 2 above) develops brief guidance for project proposers and MPCA staff that provides background on the sulfate issue and factors that will need to be evaluated as part of the environmental review and/or permit process. Guidance should also address permitting projects that do not require environmental review. The team should develop procedure documents that will be included in the program manual for the environmental review and the NPDES Permit Writers' Manual. This document will provide background on the sulfate issue and issues that will need to be evaluated as part of the environmental review and/or permit process. These actions should be completed and presented to the WQ Policy Forum for review and approval **by June 29, 2007**. Estimated time commitment – 30 to 40 hours for each team member.

7) If necessary, revise the Illuminated EAW document and NPDES permit application to include background on the sulfate issue and issues that will need to be evaluated as part of the environmental review and NPDES permitting. These actions should be completed **by July 31, 2007.** ER Staff, Permit Staff and EAO staff – 10 hours each.

8) Complete technical review of environmental review submittals and NPDES permit applications. Develop responses to comments on specific projects. **Timeline is project-specific.** Environmental Review, Municipal/Industrial engineers and permit writers lead, and EAO staff support – workload could vary greatly.

9) Review research findings and if necessary incorporate into permitting and environmental review procedures. Sulfate ER/NPDES Permitting staff team (from item 2 above) 10 to 20 hours – **Annually.**

10) Provide technical assistance to permit writers regarding high-risk case-specific monitoring requirements and information protocols for targeted facilities or facility types. – EAO staff **as needed** – 40 to 80 hours per year.
11) Update agency managers on policy development needs, including needs to revise the sulfate standard - Strategy Coordinator **– Annually.**

Attachment A

MPCA Strategy to Address Indirect Effects of Elevated Sulfate on Methylmercury Production and Phosphorus Availability

Technical Background

Sulfur naturally cycles in aquatic systems between sulfate and sulfide, depending on multiple factors, including oxygen availability, hydrologic fluctuations, and organic matter degradation. Sulfate is a relatively inert chemical species, but its conversion to sulfide has a number of undesirable indirect effects that this strategy ultimately seeks to minimize. Under certain as-yet undefined environmental conditions, additional sulfate may enhance MeHg production and the availability of P for algal growth. The mechanisms associated with enhanced MeHg production and P availability are different, but are both associated with the tendency during decay of organic matter for natural bacteria to convert sulfate to sulfide after oxygen is depleted. This group of bacteria is called sulfate-reducing bacteria (SRB).

The initial tasks of the strategy involve collecting and interpreting data so that defensible quantitative permitting limits on sulfate discharge can be established. For instance, aquatic systems that are naturally elevated in sulfate due to local geological sources may not be sensitive to moderate increases in sulfate concentration. Other environmental attributes may make some systems more or less sensitive to added sulfate, including existence of wetlands and background dissolved iron concentrations.

Elevated sulfate can enhance MeHg production because SRBs are known to convert inorganic mercury (which is widely available due to atmospheric pollution) to MeHg, the only form that accumulates in fish. When the availability of sulfate controls the activity of SRBs, then additional sulfate may cause additional fish contamination. Recent research (Jeremiason et al. 2006) has documented increased MeHg production through increased sulfate concentrations in a wetland environment. SRBs produce MeHg when certain environmental factors coincide: low oxygen and adequate levels of bioavailable inorganic mercury, sulfate, and decaying organic matter. High organic matter can, of course, cause low oxygen because other bacteria will consume available oxygen in the first phases of organic matter degradation. SRBs are most active in aquatic systems because water decreases atmospheric oxygen availability and maintains a moist environment in which bacteria can thrive. SRB production of MeHg can be constrained by low mercury, low sulfate, low organic matter, or high oxygen. There is also a hypothesis that continued production of sulfide by SRBs can produce negative feedback by reducing mercury availability through the formation of sulfide-mercury chemical bonds. However, it is not clear how to model such negative feedback, and the production of sulfide is not necessarily permanent, as sulfide can oxidize back to sulfate. So, at this point, trying to maintain high sulfide does not seem like a viable strategy. However, data collection will provide empirical information on this hypothesis.

Elevated sulfate can enhance P availability because of an indirect effect of sulfide production. When aquatic systems become anoxic (common in both hypolimnia and wetlands) there is a tendency for enhanced P release from sediment to the water. While anoxic, iron oxides become soluble, which causes the dissolution of phosphate that had co-precipitated with the iron during an oxygenated phase. The phosphate will largely re-precipitate with the iron when the water is oxygenated, unless the iron to phosphate ratio is too low. During anoxia, sulfide may be produced, which has the unfortunate ability to form a precipitate with the dissolved iron—unfortunate because elevated levels of sulfide can decrease the amount of iron that is available to co-precipitate the P. If the P is not precipitated upon oxygenation (either turnover of a lake or hydraulic movement in a wetland), then the additional P will likely stimulate algal growth above the historical range for that waterbody (Caraco et al. 1993).

Both of these indirect effects of elevated sulfate are difficult to model in a quantitative manner. One impediment is that the conversion to sulfide may be downstream from the site of sulfate discharge because the required combination of low oxygen and elevated organic matter may not occur immediately below the discharge. Sulfate conversion may occur when water flows laterally into adjacent wetlands or when the water reaches an impoundment or lake deep enough to have a hypolimnion. Enhanced loading of P and MeHg would occur when the anoxic water mixes back into surface water. This mixing would occur in a lake when the hypolimnion mixes with the epilimnion, and in rivers with lateral wetlands during a falling hydrograph.

Sulfate comes from a variety of sources. Generally, natural background sources result from marine rock and glacial till containing some marine rock such as limestone or shale. Surface water and ground water in the granitic Canadian Shield area is expected to have relatively low sulfate concentrations while waters in other parts of the state are expected to have relatively higher sulfate concentrations. Anthropogenic sources include air deposition (typically less than 1 mg/l) and domestic and industrial wastewater discharges. Wastewater sulfate concentrations can be elevated above surface water concentrations simply because of use of high-sulfate groundwater. In addition, sulfate may be elevated in wastewater by concentration through evaporation, capture of sulfur compounds by air pollution control equipment, or various industrial processes (e.g. lime addition in taconite production).

It is important to minimize the effect of sulfate on MeHg and P because Minnesota's water quality is threatened by these chemicals state-wide. Federal NPDES permitting regulations prohibit the authorization of wastewater discharges that may cause or contribute to water quality impairments. Numerous water bodies in the state are listed as impaired because the MeHg concentrations in fish tissues make the fish unsuitable for frequent human consumption. Similarly, numerous water bodies are impaired because of excess P concentrations.

Treatment technologies for sulfate removal from wastewaters are limited. Reverse osmosis and evaporation are energy intensive and generally considered infeasible. A new treatment technology, submerged packed bed, has shown potential but there is an unevaluated risk of MeHg production within the treatment system. Land application or rapid infiltration basins may be effective but must be evaluated on a case-by-case basis.

While research indicates a strong correlation between sulfate loading and MeHg production in a sulfate-poor wetland, the factors that control MeHg production and P release in other surface waters are not documented. The research results do not, however, tell us how aquatic systems higher in sulfate react to increased sulfate loading. We have not reached a sufficient level of confidence with our understanding of the controlling factors such that firm effluent limitations based on these phenomena can be established. Therefore, a permitting strategy will need regulatory and study/monitoring components to reflect our varying levels of understanding of MeHg production under differing environmental scenarios. MeHg study and control is further complicated by the lack of a standard EPA analytical method and limited commercial laboratories that are prepared to conduct MeHg analyses. EPA has developed Draft Method 1630 (January 2001) for MeHg analyses. The draft method can be found at:

http://www.epa.gov/nerleerd/108Complete.pdf#search=%22mercury%20method%20methyl%201630%20site%3Aepa.gov%22
and
http://www.brooksrand.com/FileLib/1630.pdf

MPCA staff have used Frontier Geosciences in Seattle, WA for recent analyses. It is anticipated that the MDH lab, and possibly other labs in Minnesota, would gear-up to run Draft Method 1630 if demand for this work increased.

Notes: [since this note does not seem to be referred to anywhere, perhaps it should be moved up into the text.—otherwise, it is not contributing to the appendix]

1) As a general rule, the order of depletion of electron acceptors during bacterial metabolism in aquatic systems is O_2, NO_3, Fe_2O_3, MnO_2, then SO_4. SRBs are known to produce MeHg and it is thought that iron-reducing bacteria may also methylate mercury under certain conditions. In any given environmental setting, it is not easy to determine which bacteria are dominating degradation of organic matter. To achieve an understanding of biogeochemical mechanisms of the effects of elevated sulfate, it may be desirable to measure a number of parameters, including sulfate, total mercury, MeHg, iron, ortho-P, total P, and supporting parameters such as DOC, pH, oxygen, nitrate, and potassium (for an example of the utility of measuring this suite of parameters, see Balogh et al. 2004). For instance, elevated nitrate or oxidized iron could negate the effect of elevated sulfate because the bacterial community likely finds it energetically advantageous to consume either of those two chemicals as electron acceptors before consuming sulfate. Without information on nitrate and iron, the effect of elevated sulfate may appear to be inexplicably unpredictable. Potassium data may be useful in a different way—elevated potassium can be an indicator of a hydraulic source area in decaying organic matter such as a wetland. When potassium is correlated over time with DOC, MeHg, and P, then the weight of evidence tends toward wetlands as the source area for all of the materials.

Literature Cited:

Balogh, S.J., Y. Nollet, and E.B. Swain. 2004. Redox Chemistry in Minnesota Streams during Episodes of Increased Methylmercury Discharge. Environmental Science & Technology. 38:4921-4927.

Caraco, N.F., J. J. Cole, and G. E. Likens. Sulfate control of phosphorus availability in lakes. Hydrobiologia. 253:275-280.

Jeremiason et al. 2006. Sulfate addition increases methylmercury production in an experimental wetland. Environmental Science & Technology. 40:3800-3806.