From: Axelrad, Don
To: Gilmour, Cindy
Subject: RE: adding polysulfides to lakes and coastal waters
Date: Tuesday, March 24, 2009 6:57:47 PM

Cindy,

I want to keep this simple; I am not writing this assessment for S biogeochemists.

Does any of the following offend your sensibilities?

Don

Assessment of proposal:

6. I contacted one of the co-authors of the paper Mr. Rowzee provided as evidence that methylmercury remediation via application of polysulfides to waterbodies was feasible (Dr. Cynthia Gilmour, Smithsonian Institution). See ATTACHMENT 2.

7. In essence, it is not at all certain that that methylmercury remediation of coastal waters or lakes via application of polysulfides is feasible.

8. Polysulfides are unstable and it would be difficult to obtain them.

9. Application of polysulfides to aerated surface waters could oxidize them and prevent polysulfides from reaching sediments where mercury methylation occurs.

10. Depending on water and sediment porewater chemistry, sulfur addition could either promote or repress mercury methylation.

11. Even if such a method of remediation was effective, the frequency of treatment (polysulfide) application is unknown.

12. Effective polysulfide application rate is unknown.

13. The effect of polysulfides on aquatic and marine life is unknown.

14. The Department already has an approach to methylmercury remediation - TMDLs - which assuming mercury sources can be reduced, has a high probability of reducing methylmercury levels in waterbodies and fish.

Office: (850) 245-8072
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From: Gilmour, Cindy [mailto:gilmourc@si.edu]
Sent: Tuesday, March 24, 2009 5:13 PM
To: Axelrad, Don
Subject: RE: adding polysulfides to lakes and coastal waters

Don –

You asked for a comment on the idea that polysulfides might be added to surficial freshwaters and coastal waters as way to reduce MeHg formation and bioaccumulation.

In natural environmental systems, "polysulfides" are generally defined as small polymers that contain sulfide and elemental sulfur. They commonly form at the interface between oxic and anoxic (sulfidic) zones – say at the surface of a tidal marsh or marine sediment, or in low oxygen waters. They commonly form in nature via the oxidation of sulfide that forms in anoxic environments. Polysulfide formation can be mediated by bacteria, or chemically (by metals or other oxidants). Polysulfides probably do not exist as isolated compounds in the environment, but rather form complexes with metals and perhaps organic matter. These are highly reactive species, and readily decompose in the presence of oxygen (or many other oxidants).

We studied how these natural polysulfides (chains of elemental sulfur and sulfide) might affect Hg complexation and methylation. Jenny Jay was a graduate student at the time and led the work. I sat on her committee and helped her with the microbial side of things. Jenny first studied the complexation of Hg with polysulfides (Jay et al. 2000) and showed that Hg forms complexes with sulfide that are mainly charged. Then we studied how the formation of these charged Hg(Sx) species affect Hg uptake and methylation by a pure culture of a specific Hg-methylating bacteria (Jay et al. 2002). The chemistry is complex. If you read the paper carefully, you will see that worked in sulfidic cultures, and in the presence of solid HgS (cinnabar). These defined conditions allowed us to numerically model the reactions we were studying. We added elemental S polymer (S8) to the sulfidic bacterial cultures in order to form polysulfides. The overall rate of methylation by the bacteria DID NOT CHANGE when S8 was added to cultures. However the polysulfides increased the dissolved concentration of Hg significantly, as predicted by Jenny's earlier work. We then used those data to predict that in natural sediment and soils porewaters where cinnabar is not at saturation, polysulfides should shift the speciation of Hg to charged forms that are less available to Hg-methylation bacteria for uptake.

However, the term "polysulfide" is used differently in the industrial world - to refer to organic-S polymers – like the vulcanization process in rubber, or in adhesives, where elemental S used to is crosslink the organic polymers. Sulfur polymers with cationic metals or alkaline earths are also sometimes referred to as polysulfides.

So… it's not clear from the emails you sent what exactly was meant by "polysulfides" in the proposal. But many natural polysulfides are highly reactive species that wouldn't stick around too long in aerated waters.

I found this paragraph in the email you sent interesting:
"Hydrophilic species of mercury are changed into hydrophobic methylmercury by microorganisms, particularly sulfate-reducing bacteria. Attempts at preventing or

remediating methylmercury by adding hydrophilic sulfur to their environment have not worked. **Adding polysulfide does work because polysulfide is amphiphilic. In the presence of polysulfide, sulfate-reducing bacteria either produce less methylmercury or the methylmercury produced by them is changed back into mercury sulfide."**

Addition of elemental sulfur (I assume this is the "hydrophilic S" referred to here) could have a host of effects on Hg methylation, although I don't know of any published studies of elemental S as a remediation technique for Hg methylation. Sulfur is reactive in the environment, cycling rapidly through microbial and chemical oxidation and reduction. Depending on the concentration of sulfur added, and the biogeochemistry of the system being remediated, sulfur additions at lower levels could stimulate sulfate reduction and enhance methylation, or at higher levels could lead to sulfide production and reduce MeHg production. Field data from sediments and soils in many ecosystems show that sulfide is often the dominant biogeochemical control on MeHg production. I can provide refs if you like.

A couple of key points in evaluating proposals for Hg remediation:

- Hg methylation occurs in anoxic sediments, soils and bottom waters. Amendments targeting reduction in MeHg production must be delivered to these zones of MeHg production.
- The effects of sulfur amendments (in any form) on ecosystems are complex. Sulfur can enhance or inhibit methylation depending on the natural and added concentrations, and the concentrations of ligands for sulfide- ie Fe and organic matter. Sulfur has a host of additional negative impacts in freshwater systems, including enhance release of P from soils, and potentially sulfide toxicity to plants and organisms.
- Most MeHg in natural surface waters is complexed in organic colloids (DOC). DOC is very effective at keeping Hg and MeHg in the aqueous phase, but Hg-DOC complexes do not seem to be highly available for uptake by organisms. Effective remediation strategies for MeHg would probably remove MeHg from solution.

Hope that helps… nothing is simple! Cindy

From: Axelrad, Don [mailto:Don.Axelrad@dep.state.fl.us]
Sent: Tuesday, March 24, 2009 3:57 PM
To: Gilmour, Cindy
Subject: adding polysulfides to lakes and coastal waters

Cindy,

See the two Emails below, and the attached Jay et al., 2002 paper that "Mike" provided me.

Mike's idea is to add polysulfides in liquid form to lakes and coastal waters to reduce mercury methylation rate and MeHg in fish.
(He obtained this idea from the attached paper)

He wishes to apply for a NOAA grant (http://www.nmfs.noaa.gov/habitat/restoration/) **to fund this and wants Florida to nominate several sites that he could remediate (of MeHg).**

As discussed, please comment as to feasibility.

Don Axelrad

850-245-8072
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From: mike@arrowscience.net [mailto:mike@arrowscience.net]
Sent: Wednesday, March 11, 2009 5:39 PM
To: Sole, Michael
Subject: Mercury Remediation

We are applying for a grant from the National Marine Fisheries Service (NFMS). We have developed an in situ process for safely remediating halogenated organic compounds (XOCs) and methylmercury from aquatic environments such as coastal shores, lakes, rivers, and streams. Would you be interested in our providing this service in your state as part of this grant? We would employ people from your state and most of the grant funds would be spent there. There would be no charge to you but we would ask that you provide an independent evaluation to NFMS.

Best regards,

Mike

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From: mike@arrowscience.net [mailto:mike@arrowscience.net]
Sent: Saturday, March 21, 2009 2:48 PM
To: Axelrad, Don
Subject: RE: remediating halogenated organic compounds (XOCs) and methylmercury from aquatic environments

Don,

Thank you for your phone call. I have attached the research paper I mentioned. The research paper explains what happens but doesn't explain why. The "why" explanation is the key to mercury remediation. Inorganic mercury is hydrophilic. Organic mercury and methylmercury are lipophilic, and methylmercury is hydrophobic. You should keep in mind, some compounds have more polarity than others, and the presence of other compounds in the environment can affect reactions.

Unfortunately, the solution to the methylmercury problem is not as simple as going to the middle of the lake and dumping in a bag of polysulfide. The concentration would be harmful to fish and other organisms. The polysulfide must be added as a highly-diluted, aqueous solution. Although polysulfide is amphiphilic, the presence of water can hinder reactions with mercury, particularly where other lipophiles are present. Adding a phase-transfer catalyst to an aqueous, decontaminating formulation is often essential where highly-diluted reactants are used and prompt reactions are desired.

I apologize for our late communication with you. The grant we are applying for was posted on March 6th, but must be turned in by April 6th. The grant is part of the economic-recovery effort intended to quickly add jobs and funds to the economy.

Expenses to the State can be funded by the grant. Florida would be a perfect environment for this grant because we could work year-round. Please let me know if you require additional information. If we will be working in Florida, I will need to know before we turn in our grant proposal on April 6th.

Mike

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The Department of Environmental Protection values your feedback as a customer. DEP Secretary Michael W. Sole is committed to continuously assessing and improving the level and quality of services provided to you. Please take a few minutes to comment on the quality of service you received. Simply click on this link to the DEP Customer Survey. Thank you in advance for completing the survey.