

Report for 2005WA119B: Oxygenation for the Management of Sediment Mercury Release from Aquatic Sediments

Publications

- Water Resources Research Institute Reports:
 - Beutel, Marc and Barry C. Moore. 2006. Oxygenation for the Management of Sediment Mercury Release from Aquatic Sediments. State of Washington Water Research Center, Washington State University, Pullman, Washington. State of Washington Water Research Center Report WRR-27. 14 pages.
- Conference Proceedings:
 - Leonard, Theo M. and Marc W. Beutel. 2006. Control of mercury release from profundal lake sediments using oxygenation. "in" Abstracts, Efficient Sustainability in a Dry Land, Sixth Annual Meeting of the American Ecological Engineering Society, Berkeley, California, April 13-14, 2006, p. 50.
http://aeesociety.org/annual_meeting/2006/AEES_Abstract_Booklet_Final.pdf

Report Follows

PROBLEM AND RESEARCH OBJECTIVES

Mercury bioaccumulation in aquatic food chains is of growing concern due to health effect in upper-trophic-level biota (e.g., humans, birds, fish). Bioaccumulation in the food chain is the result of microbial conversion of ionic mercury (Hg^{2+}) to methylmercury (CH_3Hg^+), which then accumulates in the mussel tissue of biota. For example, greater than 95% of the mercury found in fish is methylmercury. Thus, methylmercury production in aquatic systems is ultimately the cause of many mercury-related fish consumption advisories in the United States. The conversion of ionic mercury to methylmercury occurs in anoxic sediments in lakes and is facilitated by sulfate-reducing bacteria.

The objective of this research was to investigate how aerobic versus anaerobic conditions affect concentrations of mercury in water overlaying lake sediments. We hypothesize that the production and release of methylmercury at the sediment-water interface is partly regulated by the degree of oxygen penetration into surface sediments. Elevated dissolved oxygen levels should inhibit the production and subsequent release of methylmercury by: (1) decreasing the activity of sulfate-reducing bacteria at the sediment-water interface, and (2) promoting the oxidative de-methylation of methylmercury fluxing upwards from deeper sediments by heterotrophic bacteria. The intent of the research was to determine if lake oxygenation, a common lake management technique to improve water quality, could also be used to manage and control the release of methylmercury from anoxic sediments, thereby lowering mercury bioaccumulation in aquatic biota.

Although methylmercury was the target species of mercury for the experiments, budget constraints and technical limitations were such that we focused on total mercury. In addition, while we initially anticipated sending mercury samples outside of WSU for analysis, we instead developed and implemented in-house capabilities to measure mercury. Follow-up experiments will be conducted in the summer of 2006 that will include the evaluation of a number of mercury species in sediment-water interface samples collected from three sites (Deer, American, and Newman Lakes) of varying trophic status and management history.

METHODS

Study Site. The preliminary study site was Deer Lake, located north of Spokane. Based on a recent mercury study by the Washington State Department of Ecology (DOE), the lake has fairly low levels of mercury in sediments but high levels in fish. The maximum depth of Deer Lake is 75 feet while the mean depth is 52 feet. The lake encompasses 1,100 acres and has a volume of 57,000 acre-ft. Its drainage area is approximately 18 square miles. Various reports have labeled the lake as meso-oligotrophic due to its low occurrence of algal blooms and high clarity. The lake thermally stratifies during the summer and exhibits hypoxia (dissolved oxygen < 2 mg/l) in bottom waters in the late fall.

Sediment Collection. Sediment was initially collected with a 15 cm by 15 cm Eckman dredge. Sediment was soft enough to plug the jaws of the dredge, resulting in the collection of a minimally disturbed sediment surface with overlaying water. The dredge was brought to the surface, and a sediment-water interface sample was sub-sampled into a cylindrical Plexiglas chamber 1.8 liters in volume. The sub-sample was collected by slowly pushing the chamber top into the sediment and overlaying water captured in the dredge. A cap and gasket were then mated with the bottom of the chamber by hand while the chamber was still in the sediment. The capped chamber was pulled out

of the dredge and bolted onto a round Plexiglas base. Sediment-water interface samples consisted of a sediment core 4-8 cm thick with a surface area of 71 cm², and 100-300 ml of overlaying water. A total of four chamber samples were collected. After collection of the sediment-water interface sample, chambers were gently filled with bottom water and transported to the laboratory. We used “dirty hands/clean hands” techniques, conducted intensive pre-cleaning of apparatus used during the fieldwork, and took extra precautions to prevent metals contamination during fieldwork.

Incubations. Once in the laboratory, the four sediment cores were incubated in the dark at 10°C under oxic conditions (23 days), followed by anoxic conditions (27 days), followed by reaerated conditions (14 days). A control chamber was also incubated that included only de-ionized water. Oxic conditions in chamber water were maintained by bubbling with air and anoxic conditions were maintained by bubbling with nitrogen. Water overlaying the sediment was monitored every few days for a suite of compounds including DO, redox, pH, total mercury, iron, and manganese. DO, redox and pH in chamber water was measured with standard probes and meters inserted into an access port. Water samples for metals analyses were drawn from chambers with sterile syringes using pre-cleaned Teflon tubing and discharged into fluoropolymer bottles. After extraction of water samples, chambers were topped up with mercury-free reagent water to maintain a constant volume in each chamber of 1 L.

Mercury samples were preserved with bromine monochloride (BrCl), which oxidizes all forms of mercury to stable dissolved ionic mercury (Hg²⁺). Total mercury was measured in-house via cold-vapor atomic fluorescence spectrometry (CVAFS) on a Tekran mercury autoanalyzer. In this method stannous chloride (SnCl₂) is added to reduce preserved Hg²⁺ to volatile elemental mercury (Hg⁰). The Hg⁰ is sparged with nitrogen gas onto a gold trap, and then thermally desorbed into an atomic fluorescence spectrometer. Samples for iron and manganese analysis were preserved with nitric acid. Iron and manganese were measured via inductively coupled plasma mass spectrometry (ICP-MS) in the WSU Chemistry Department.

PRINCIPAL FINDINGS AND SIGNIFICANCE

A key outcome of this project was the development of in-house capabilities to analyze total mercury in aqueous samples. We purchased and operated a Tekran mercury auto-analyzer using CVAFS methodology. After much effort and persistence in the lab, we are able to consistently measure total mercury at the part per trillion (ppt) or nanogram per liter (ng/L) level. Our detection limit was around 0.3 ng/L. This summer we will be expanding our analytical capabilities to include methylmercury.

Mercury. Due to apparent contamination issues, the results of our preliminary incubation were inconclusive. When accounting for dilution as a result of sample removal and make-up water addition, chambers (including the control chamber) tended to accumulate mercury at a slow but steady rate during the initial aerated phase. A few days into the anoxic phase chambers showed a dramatic spike in mercury with concentrations rising from around 20 ng/L to around 200 ng/L. Since this spike was also observed in the control chamber with no sediment, it was the result of contamination. During the reaeration phase, mercury decreased rapidly in treatment chambers, dropping by around 100 ng/L. In contrast, mercury levels were steady in the control chamber.

The rapidity of mercury loss after reaeration suggests that the overriding mechanism was physical/chemical versus biological. It is possible that mercury was co-precipitated out of the water

column with iron and manganese oxides formed under reaerated conditions. As discussed below, under anoxic conditions sediments released reduced, dissolved iron and manganese into overlaying water. These metals decreased once oxygenated conditions were reestablished. This phenomena merits further research. Co-precipitation may be an important temporal component of the mercury mass balance in productive, stratified lakes.

These preliminary findings also suggest that treatment of lakes with alum (aluminum sulfate) or other metal salts (e.g., ferric chloride), which typically are used to impede phosphate release from anoxic lake sediments, could also be effective at controlling mercury. In fact, one of our future study sites, Newman Lake, has been treated with alum and oxygenated since the early 1990s. Results from the DOE mercury study show that older fish (8 years old) in Newman Lake have more mercury, normalized by length (ug/kg/meter), than younger fish (2 years old). This contradicts typically observations in aquatic systems that show younger fish bioaccumulate mercury more rapidly than older fish. Thus, recent active management of the lake may be reducing the level of mercury bioaccumulation in younger lake biota.

Iron and Manganese. During the first aerated phase, iron and manganese levels tended to decline in water overlaying sediments. The reestablishment of oxygenated conditions likely resulted in the oxidation and subsequent precipitation of the metals as iron and manganese oxides. During the subsequent anoxic phase, iron and manganese steadily increased to greater than 3 mg/L for both metals. Accumulation rates were on the order of 8 mg/m²/d for iron and 30 mg/m²/d for manganese. Metals accumulation was the result of the biological reduction of metal oxides in surface sediments by anaerobic microorganisms that utilize iron and manganese as terminal electron acceptors for anaerobic respiration. In some sediments under some conditions, hydrogen sulfide can also chemically reduce metal oxides. During the final reaeration phase iron and especially manganese concentrations decreased. As discussed above, this decrease in metals co-occurred with a rapid drop in mercury in chamber water.

Future Incubations. Three sets of subsequent incubations are planned for summer 2006 from Deer Lake and two additional Washington Lakes. The new sites include Newman Lake, a lake with a history of oxygenation and alum treatment. Intriguingly, as noted above the lake has relatively low levels of mercury in younger fish. The other new site is American Lake. The lake is very similar to Deer Lake in size and depth, but is more eutrophic. Based on lessons learned from the preliminary incubations reported herein, method modifications to minimize contamination will include:

- (1) Glass rather than Plexiglas chambers will be used. The use of glass will minimize the loss of mercury via sorption to chamber surfaces.
- (2) Make-up water will not be added to chamber incubations. Chambers will be initially filled with a maximum possible amount of overlaying water and sample volumes will be kept to a minimum.
- (3) Replicate chambers will be incubated in parallel (three chambers under oxic conditions and three chambers under anoxic conditions) rather than in aerated/anoxic phases. This will compress the duration of the incubations and minimize the volume of sample water removed from each chamber over the course of the incubation.

- (4) Gas will not be introduced to chambers. Instead oxic chambers will simply be kept open to the atmosphere while anoxic chambers will be closed airtight.
- (5) Probes will not be inserted into chambers. Instead any probe measurements will be made on samples first extracted from the chambers.