PROJECT SUMMARY

Title:	**Mercury Speciation Along A Groundwater Flowpath**
Project I.D.:	05-CTP-01, WR04R001
Principal Investigators:	D.E. Armstrong, Professor Emeritus, and C.L Babiarz, Assistant Scientist
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Project Period:	July 1, 2004 to June 30, 2006

Objectives: Our investigation focused on the cycling of mercury in wetlands within the Trout Lake Basin in Vilas County, Wisconsin. The three main objectives were:

1. To characterize the levels of total Hg and methyl mercury (MeHg) carried in stream waters flowing through the wetlands;
2. To characterize hyporheic zones within these wetlands regarding (a) concentrations of aqueous total Hg and MeHg, (b) factors influencing MeHg levels, and (c) the importance of hyporheic zones in controlling MeHg in stream waters;
3. To probe the forms of inorganic Hg(II) and MeHg in hyporheic zone waters and examine the implications of speciation on transport and on the bioavailability of Hg(II) for methylation.

Methods: This investigation was conducted in the Trout Lake Basin (Vilas County, WI). Our primary study sites were located near Allequash Creek and Stevenson Creek. We collected samples of ground water, hyporheic-zone pore waters, and surface stream waters. Seasonal measurements were made of total Hg, MeHg, and constituents or parameters related to biogeochemical processes, including Fe, S (total S and sulfide), dissolved organic carbon (DOC), NH_4 and pH. Speciation of inorganic Hg(II) and MeHg was investigated by experimental and modeling approaches. Modeling involved equilibrium calculations based on reported stability constants for the respective mercury complexes, pH, and measured concentrations of important ligands – especially dissolved organic matter (DOM), and sulfide. In addition, association of MeHg and Hg(II) with both DOM and sulfide was probed by an experimental technique involving measurements of retention by an anion exchange resin.

Results and Discussion: Concentrations of total Hg and MeHg in streams exhibited considerable temporal variation. Highest concentrations were observed from late winter through spring and early summer, reaching over 4 ng/L for total Hg and 0.2 ng/L for MeHg. Overall, the spring melt period contributed high concentrations, loadings, and proportions of MeHg in the wetland streams.

Production of MeHg was indicated by high concentrations of MeHg in hyporheic zones, where favorable conditions for production of MeHg were also observed. Decreasing concentrations of sulfate and increasing concentrations of sulfide with depth were indicative of both sulfate reduction and the activity of sulfate-reducing bacteria (believed to be largely responsible for

methylation of inorganic Hg(II) in reducing environments). Surface waters were the main source of sulfate to drive sulfate reduction in hyporheic zones, as evidenced by the high concentrations of sulfate in stream waters as compared to ground waters. Elevated concentrations of DOM, contributing to microbial activity in hyporheic zones, were attributed to diagenesis of plant material. Relationships between MeHg and Fe indicated the importance of hyporheic zones as a source of both Fe and MeHg to stream waters.

Speciation modeling predicted that HgS^0 was the dominant species of Hg(II) in sufidic (hyporheic) waters, while HgDOM complexes should be dominant in the absence of sulfide. In contrast, both $MeHgS^0$ and MeHg-DOM complexes were predicted to be important in the presence of sulfide. However, experimental measurements indicated HgDOM complexes were predominant in both sulfidic and non-sulfidic waters. These results raise important questions about factors controlling the bioavailability of Hg(II) for methylation.

Conclusions/Implications/Recommendations: Hyporheic zones are important sites for MeHg production and transport to surface waters. High DOC concentrations combined with sulfate (introduced mainly from surface water) promote the activity of sulfate-reducing bacteria (SRB). Inorganic Hg(II), partly from groundwater, is converted to MeHg, apparently by SRB, and transported into surface waters. Speciation modeling indicates that HgS^0 is dominant in these sulfidic waters. HgS^0 should facilitate methylation because neutral species of Hg(II) are presumed to be more available for uptake by SRB. However, experimental data indicate Hg(II) is bound mainly by dissolved organic matter (DOM) in sulfidic waters, indicating bioavailability of Hg(II) to SRB may be impeded by binding to DOM. Further investigations should explore the factors and conditions controlling methylation rates in hyporheic zones to facilitate new practices in wetland management that might limit MeHg production.

Related Publications and Presentations:

Chadwick, S.P., C.L. Babiarz, J.P. Hurley, D.E. Armstrong. 2006. Evaluation of the Role of Dissolved Organic Matter in the Speciation of Mercury and Methylmercury in a Lacustrine Watershed Using Diethylaminoethyl Resin. Abstracts, Conference on Mercury as a Global Pollutant, Madison, WI.

Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract. – Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.

Shafer, M., S. Kerr, J. Overdier, and D.E. Armstrong. 2005. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract – Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

Key Words: Mercury, methyl mercury, groundwater, hyporheic zones, stream waters.

Funding: UWS