

# **Report for 2003WI45B: Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior**

There are no reported publications resulting from this project.

Report Follows

## **Project Summary**

**Title:** Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior  
(WR02R002)

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This investigation was conducted to explore the role of the hyporheic zone in the production and transport of methyl mercury into surface waters. We selected a field site where total Hg and methyl Hg concentrations could be measured along hydrologic flowpaths. Our investigation focused on 1) the temporal and spatial distribution of total Hg and methyl Hg in ground waters, hyporheic zone waters and sediments, and waters of surface streams, and 2) the relation of temporal and spatial patterns of total Hg and methyl Hg concentrations to environmental factors and processes potentially important in controlling transport and fate for mercury.

We selected sub-watersheds of the Trout Lake watershed the field site for investigation of hyporheic zones processes. This site, located in Vilas County, Wis., is also within the investigation areas for the UW-Madison NSF Long Term Ecosystem Research program and the USGS Water, Energy, and Biogeochemical Budgets program. This enabled collaboration with scientists from these groups and use of USGS background information and groundwater sampling sites installed at the site. We compared hyporheic zones at two sites within the Allequash Creek watershed, upper springs and middle wetland, to nearby sites at North Creek and Stevenson Creek, all within the greater Trout Lake watershed. Sampling was conducted in 2003 and 2004.

Surface stream water concentrations ranged from 0.56 to 4.44ng/L for total Hg and 0.07 to 0.73 ng/L for methyl Hg. In general, highest total Hg concentrations coincided with the spring melt period, while highest methyl Hg concentrations were observed in August and June. The proportional level of methyl Hg in stream water was highly variable, ranging from 2.3 to 51.4% of total Hg.

Total Hg concentrations in ground waters were similar to those in surface stream waters. Transects at the two in the Allequash Creek watershed sites showed that mercury (as total Hg) was present at moderate concentrations in all groundwater samples, ranging from 0.36 to 8.78 ng/L at the middle wetlands site and 0.26 to 10.76 ng/L at the upper springs site. Concentrations varied temporally, tending to be lower in October than in April, June, or August. Concentrations also varied spatially, both with depth at a given site and along the transects. However, there was not a clear distinction between concentrations in deeper ground waters beneath upland hill slopes and shallow groundwater in the riparian zones. In contrast, methyl Hg concentrations in ground waters were generally low in comparison to concentrations in surface waters, < 0.03 to 0.52 ng/L, with the exception of two sites where concentrations of 1.1 ng/L were detected, one in April and the other in June.

In pore waters within hyporheic zones, concentrations of total Hg tended to be higher than concentrations in either surface waters or ground waters, averaging about 6 ng/L, and there was not a clear trend with depth at a given site. Similarly, concentrations of methyl Hg were

typically also higher in hyporheic waters (averaging about 0.4 ng/L) than in either ground waters or surface waters.

Two hyporheic zone sites provided a contrast between upwelling and downwelling groundwater and the influence on methyl mercury concentrations. At a groundwater upwelling site (Allequash middle wetland), methyl Hg concentrations decreased with depth below the sediment water interface, while at a groundwater upwelling site (Stevenson Creek), concentrations were relatively constant with depth. Similarly, the percent of total Hg present as methyl Hg decreased with depth at the upwelling site, with typical values of about 10 % in the upper 5 cm as compared to 5% or less in the 10-15 cm region. In contrast, at the downwelling site, methyl Hg was a more constant proportion of total Hg with depth, typically around 5%. These trends indicate that net methylation rates are highest near the sediment-water interface. Furthermore, since upwelling rates of groundwater are high, net methylation rates must be high in order to maintain the relatively high methyl mercury concentrations. These results indicated that upwelling ground waters in the hyporheic zone are an important source of methyl Hg to stream waters.

Concentrations of total and methyl Hg in sediment cores were also measured. At the middle wetland site, concentrations of total Hg were relatively constant over the upper eight cm, ranging between 81 and 105 ng/gdw and similar for cores taken at two different times. However, methyl Hg concentrations varied with time. Concentrations in an August, 2003 core increased from about 1.6 ng/gdw at 8 cm to about 7 ng/gdw in the upper 3 cm, corresponding to an increase of percent methyl Hg from < 2% at 8 cm to 9 % near the surface. However, a second core taken in October 2003 showed lower and relatively uniform methyl Hg concentrations and percentages over the 8 cm depth. Cores taken in August 2003 at other hyporheic zone sites showed increases in both the concentration and proportion of methyl Hg near the sediment water interface.

The results of this investigation show that the hyporheic zone is a region of mercury accumulation, providing a reservoir of inorganic Hg(II) for methylation. High concentrations of methyl Hg in the hyporheic zone are more likely a result of production within the hyporheic zone rather than transport to the hyporheic zone by upgradient ground water. Methylation rates are often sufficiently high to maintain high methyl Hg concentrations in rapidly upwelling ground waters, providing a source of methyl Hg to stream waters. The temporal and spatial variation in both concentrations and proportions of methyl Hg likely reflect corresponding variations in the activity of sulfate-reducing bacteria believed to be responsible for the production of methyl Hg or in the bioavailability of Hg(II) for methylation. Methylation rates may be influenced by the availability of organic substrates for microbial respiration, the concentration of sulfate available to serve as an electron acceptor for sulfate reducers, the formation of organic and sulfide complexes of Hg(II) which reduce the bioavailability of Hg(II) for methylation, and high concentrations of Fe(II) in anoxic pore waters in this region which may influence sulfide concentrations and the concentration of Hg(II) sulfide neutral complexes believed to be important species of Hg(II) for methylation.