# **PROJECT SUMMARY**

**Title:** Role of the Hyporheic Zone in Methyl Mercury Production and Transport to Lake Superior

## Project ID: WR02R002

#### **Investigators:**

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**Background:** Production of methyl mercury (MeHg) in watersheds is of concern because MeHg accumulates in aquatic foodwebs and poses a health threat to consumers of fish in many lakes. Production of MeHg occurs in anoxic subsurface zones in association with sulfate reduction. Consequently, hyporheic zones are potentially important sources of MeHg because these sites provide an environment conducive to both methylation and potentially rapid transport to adjacent surface waters.

**Objectives:** This investigation focused on two main objectives:

- (1) measure the temporal and spatial distribution of total Hg and methyl Hg in three distinct zones along a hydrologic flowpath: deep ground water, shallow hyporheic water (and sediments), and surface stream water
- (2) relate the temporal and spatial patterns of total Hg and methyl Hg concentrations to environmental factors and processes potentially important in controlling the transport and fate of mercury.

**Methods:** Hyporheic zones were investigated within three well-instrumented watersheds of the Trout Lake Basin in Vilas County, WI. The selected watersheds (Allequash Creek, North Creek, and Stevenson Creek) provided several contrasts among the hydrologic and biogeochemical features of hyporheic zones, including water direction (downflow versus upflow), and redox condition. Common to each watershed was a strong hydrologic communication between the groundwater, hyporheic zone and overlying surface water. Samples collected included groundwater (wells and piezometers), hyporheic zone porewaters (modified MINIPOINT sampler), and sediments (extruded and sliced cores). Sampling times were selected to provide comparisons of seasons and hydrologic events. Sampling and subsequent measurements of Hg<sub>T</sub> and MeHg were made using clean techniques.

**Results and Discussion:** In surface waters, appreciable concentrations of both filtered total mercury (Hg<sub>T</sub>) and filtered methyl mercury (MeHg) were observed -- ranging from 0.6 to 4.4 ng  $L^{-1}$  for Hg<sub>T</sub> and 0.07 to 0.63 ng  $L^{-1}$  for MeHg. Values for MeHg as a percent of Hg<sub>T</sub> ranged between 2.8% and 51.4%. In groundwaters, moderately high concentrations of filtered Hg<sub>T</sub> were observed -- typically in the range of 0.3 to 8 ng  $L^{-1}$ . Groundwater HgT concentrations were generally higher than values in the associated surface water. However, MeHg concentrations in these groundwaters were usually very low, often < 0.03 ng L<sup>-1</sup>. In hyporheic porewater, concentrations of  $Hg_T$  were usually higher than associated surface waters or ground waters, and ranged from 1.5 to 14.2 ng L<sup>-1</sup>. Concentrations of MeHg were also relatively high, and ranged from 0.2 to 1.2 ng  $L^{-1}$ . In hyporheic sediments, MeHg concentrations up to 7 ng/gdw were observed, but there was also considerable temporal and spatial variability. For example, average MeHg concentrations in hyporheic sediments at the Middle Wetland site were substantially higher in August (4.2 ng/L) than in October 2003 (1.4 ng/L). Concentration patterns versus depth for MeHg in porewaters differed between upflow and downflow sites. Variations appeared consistent with favorable conditions for sulfate reduction and associated production of MeHg, but factors such as the supply of organic substrates (for anaerobic respiration), alternative electron acceptors, demethylation rates, and speciation of Hg(II) are also expected to be important.

**Conclusions:** Hyporheic zones in the Trout Lake watershed are important sites for production of MeHg and transport into nearby surface waters. High MeHg concentrations in hyporheic porewater from both upwelling and downwelling sites show that the hyporheic zone is an important source of MeHg to surface waters and groundwater alike. Conversely, both ground water and surface water are sources of Hg(II) to hyporheic zone, providing a supply of Hg(II) for MeHg production. In this region, surface waters are a source of sulfate, enabling microbial sulfate reduction and associated production of MeHg. Future research should focus on: measurements of methylation and demethylation rates; the processes controlling these rates; and the links between Hg concentration and transport rates in order to couple chemical information with hydrologic models.

## **Related Publications:**

Meyer, M.H. 2005. Distributions of total and methyl mercury along flow paths in the Allequash, Creek Watershed area. M.S. Thesis (Environmental Chemistry & Technology), University of WI, Madison.

**Key Words:** hyporheic zone, mercury, methyl mercury, hydrology, groundwater, surface water,

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