PROJECT SUMMARY

Title: Importance of Groundwater in Production and Transport of Methylmercury in Lake Superior Tributaries

Project I.D. R/UW-GSI-001

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Background and Need: Methylmercury accumulation in food chains of streams and lakes presents a health hazard to wildlife and humans. Although production of methylmercury occurs in anoxic zones, little is known about production of methylmercury in groundwaters or the factors that govern its transport and fate.

Objectives: We determined the spatial and temporal patterns in mercury (Hg) and methylmercury concentrations in groundwaters and hyporheic zone waters at two contrasting sites and examined relationships to land cover, biogeochemical conditions, and local hydrology.

Procedures and Methods: We compared groundwaters at two sites, one near the headwaters of the Tahquamenon in a deciduous forest near East Creek, a tributary to the Tahquamenon, and the other in a coniferous forest near the mouth of the Tahquamenon. In addition, we sampled hyporheic zone waters at three sites along East Creek. Samples were collected at selected intervals from spring 2000 to late fall 2001 using mercury-clean techniques and analyzed using clean, sensitive methods. Water chemistry, groundwater elevation, and soil properties were also measured.

Results and Discussion: Groundwater at both sites contained moderate to relatively high concentrations of both total mercury (0.1 to 15 ng/L) and methylmercury (0.04 to 0.6 ng/L), indicating that groundwater may be a significant source of mercury to surface waters. Spatial differences were observed in both total mercury and methylmercury concentrations. Total mercury concentrations were higher at the East Creek sites. In contrast, methylmercury concentrations were higher at the Tahquamenon Mouth sites, and higher at one site than the other. Temporal patterns in methylmercury concentrations, especially at the Tahquamenon

Mouth sites, appeared to be related to the hydrography of the river. Concentrations tended to increase during the summer (May to September of 2001) and were also high in November 2001. However, concentrations were low in April 2001, following the spring melt period. We believe this pattern reflects a build up of methylmercury in groundwater during periods of relatively low flow and flushing of methylmercury-enriched ground water into surface waters during high recharge events, especially spring melt. This pattern is supported by the variations in MeHg observed in the Tahquamenon River during 1997. Concentrations increased with the rise in the hydrography during spring melt, reaching the highest concentration as the hydrography began to fall.

At three sites along East Creek, mini-piezometers were installed in close proximity to the creek to examine mercury concentrations in the hyporheic zone. The mini-piezometers were positioned to sample the saturated zone within a few meters of the creek and below the creek bed. Methylmercury concentrations were relatively low (nondetectable to 1.5 ng/L) in the subsurface zone adjacent to the stream, but concentrations were relatively high in porewaters beneath the creek (up to 12 ng/L), although highly variable both spatially and temporally. Concentrations in pore waters were generally high relative to concentrations in East Creek, indicating that this region of the hyporheic zone could be an important source of methylmercury to East Creek. Concentrations of methylmercury in groundwaters and pore waters were higher in the wetland site than at the forested site, consistent with observations that wetlands are important contributors of MeHg to surface waters. Concentrations of Fe and Mn were elevated in the hyporheic zone, indicative of anoxic conditions and a favorable environment for methylmercury formation.

Conclusions and Recommendations: Groundwater, containing up to 0.6 ng/L of methylmercury, is a potentially important source of methylmercury to streams in the Tahquamenon River watershed. Hydrologic and chemical data indicate a pattern of buildup of methylmercury in groundwater during low flow periods and flushing into streams during recharge events, especially spring melt. The hyporheic zone of East Creek, a tributary to the Tahquamenon River, is also a potentially important source of methylmercury. The porewaters below the stream contained up to 12 ng/L of methylmercury. Concentrations of methylmercury in both groundwaters and hyporheic zone waters are highly variable, both spatially and temporally. In assessments of methylmercury sources to surface waters, fluxes from groundwater and the hyporheic zone should be considered.

Related Publications:

Stoor, R.W. 2002. Groundwater contributions of methylmercury to a Lake Superior Watershed. M.S. Thesis, Environmental Chemistry and Technology Program, University of Wisconsin-Madison.

Key Words: groundwater, hyporheic zone, mercury, methylmercury

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