



LIBRARIES

UNIVERSITY OF WISCONSIN-MADISON

Importance of groundwater in production and transport of methylmercury in Lake Superior tributaries. 2002

Stoor, R. W. (Richard W.) et al.

Madison, Wisconsin: University of Wisconsin Water Resources Institute, 2002

<https://digital.library.wisc.edu/1711.dl/IIX4BSJKR6U6X8R>

<http://rightsstatements.org/vocab/InC/1.0/>

For information on re-use see:

<http://digital.library.wisc.edu/1711.dl/Copyright>

The libraries provide public access to a wide range of material, including online exhibits, digitized collections, archival finding aids, our catalog, online articles, and a growing range of materials in many media.

When possible, we provide rights information in catalog records, finding aids, and other metadata that accompanies collections or items. However, it is always the user's obligation to evaluate copyright and rights issues in light of their own use.

**Importance of Groundwater in Production and Transport of Methylmercury
in Lake Superior Tributaries**

**R. W. Stoor
David E. Armstrong
Kristofer Rolfhus
Lisa Cleckner
David P. Krabbenhoft**

2002

Project Completion Report

“Importance of Groundwater in Production and Transport of Methylmercury in Lake Superior Tributaries”

Wisconsin Groundwater Research Project R/UW-GSI-001

Submitted by

**R.W. Stoor, D.E. Armstrong¹, K. Rolfhus², and L. Cleckner³
Water Science & Engineering Laboratory and
Environmental Chemistry & Technology Program
University of Wisconsin-Madison**

And

**David P. Krabbenhoft
U.S. Geological Survey
Middleton, Wisconsin**

September, 2002

¹Also Department of Civil & Environmental Engineering, UW-Madison

²Now Chemistry Department, University of Wisconsin-LaCrosse

This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

Table of Contents

Title Page	page 1
Table of Contents	page 2
List of Figures and Tables	page 3
Project Summary	page 4
Introduction	page 6
Procedures and Methods	page 6
Results and Discussion	page 8
Conclusions and Recommendations	page 13
References	page 14

List of Figures

- Figure 1.** General locations of wells, lysimeter pits, and water level recorders (Ecotones) at the Tahquamenon Mouth and East Creek sites.
- Figure 2.** Groundwater and stream water level data collected from the Ecotones during 2001. Precipitation during the same period was obtained from the NCDC's Record of Climatological Observations
- Figure 3.** Tahquamenon River hydrograph for January 2000 to December 2001.
- Figure 4.** Groundwater Hg concentrations in wells at the East Creek and the Tahquamenon Mouth sites.

List of Tables

- Table 1.** Methylmercury concentrations (ng/L) in porewater of East Creek sediments.

PROJECT SUMMARY

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

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

Investigators: D.E. Armstrong, Professor, Department of Civil & Environmental Engineering, UW-Madison; Principal Investigator

R.W. Stoor, Graduate Student, Environmental Chemistry & Technology Program, UW-Madison; Research Assistant

D. P. Krabbenhoft, Research Scientist, U.S. Geological Survey, Middleton, WI; Co-Investigator

K. Rolfhus, Research Associate, Water Science & Engineering Laboratory, UW-Madison; Co-Investigator

L. Cleckner, Associate Researcher, Water Science & Engineering Laboratory, UW-Madison; Co-Investigator

Project Period: March 1, 2002 to June 30, 2002

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

Funding: Wisconsin Groundwater Research Program; US Geological Survey.

Introduction

Concerns over the human health effects from consumption of fish containing high levels of methylmercury (MeHg) have led to issuance of fish consumption advisories by 40 states. The problem arises in part from atmospheric transport of mercury to the land surface, methylation of mercury within the watershed, and accumulation of MeHg in the foodwebs of streams and lakes. Methylation is apparently carried out by sulfate-reducing bacteria in anoxic environments. Thus, environments such as wetlands, groundwaters, and the sediments of streams and lakes are likely sites for MeHg production. Factors such as land use and surficial geology influence the speciation, bioavailability, and transport of mercury (Hg) species in watersheds (Hurley et al. 2000; St. Louis et al. 1994; Babiarz et al. 1998). Yet, little is known about the subsurface behavior of Hg and its transport to surface waters. In particular, little information is available on the production of MeHg in groundwater or the environmental factors that govern its fate and transport (Krabbenhoft and Babiarz 1992; Branfireun et al. 1996). The goal of this investigation was to obtain information on the importance of groundwater systems as a source of MeHg to northern temperate streams. We determined the spatial and temporal patterns in concentrations of MeHg in groundwaters and the hyporheic zone at two contrasting sites and examined relationships to land cover, biogeochemical conditions, and local hydrology.

Procedures and Methods

We compared two groundwater sites within the watershed of the Tahquamenon River, a tributary to Lake Superior that discharges to Whitefish Bay near Paradise, Mich. (Stoor 2002). One site was located near the headwaters of the Tahquamenon, in a deciduous forest near East Creek (a tributary of the Tahquamenon). The other site, located in a coniferous forest, was near the mouth of the Tahquamenon (Figure 1). Two Teflon wells for groundwater sampling and a lysimeter pit were installed at each site. In the spring of 2000, Ecotoneä 40 capacitance water level monitoring wells were placed near the sampling wells to monitor fluctuations in the water table in the area. In addition, mini-piezometers were installed at three sites along East Creek to sample subsurface waters within the near-stream hyporheic zone. Samples were collected at selected intervals from spring 2000 through fall 2001.

All sampling, sample processing, and analysis for mercury followed accepted clean protocols and techniques to minimize contamination (USEPA 1996b; Olson et al. 1997; Cleckner et al. 1998; Hurley et al. 1998). Water samples were filtered in-line through 0.45 μm membrane capsule filters (Meissner Filtrations Products, Inc.). After field collection, samples were transported to the UW Water Science & Engineering Laboratory and stored in refrigerators or freezers until analysis. Subsequent analyses were conducted using clean techniques under HEPA-filtered laminar flow hoods in dedicated trace metal clean rooms.

Samples for total mercury (Hg_T) were oxidized with BrCl and analyzed using the cold vapor atomic fluorescence spectroscopy (CVAFS) technique (Gill and Fitzgerald 1987; USEPA 1996a; Olson et al. 1997; Hurley et al. 1998). Methylmercury (MeHg) was analyzed by ethylation, gas chromatographic separation, pyrolysis, and CVAFS detection (Horvat et al. 1993; Liang et al. 1994; Olson et al. 1997; Hurley et al. 1998).

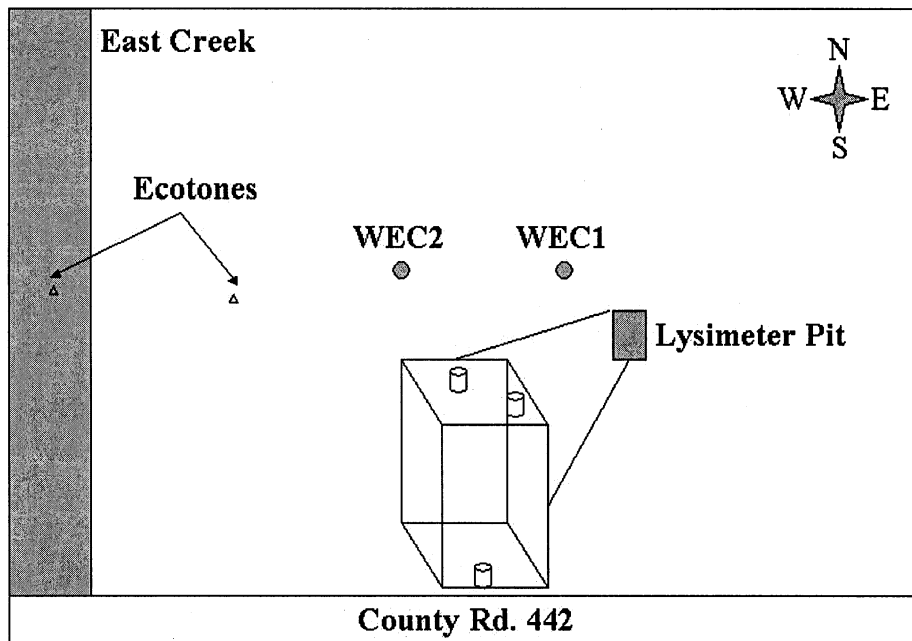
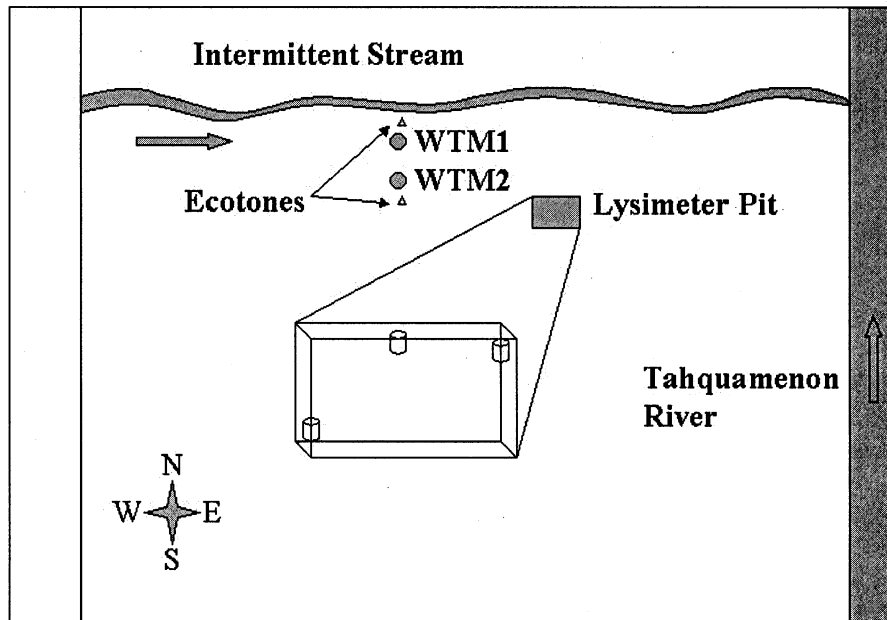


Figure 1. General locations of wells, lysimeter pits and water level recorders (Ecotones) at the Tahquamenon Mouth and East Creek sites

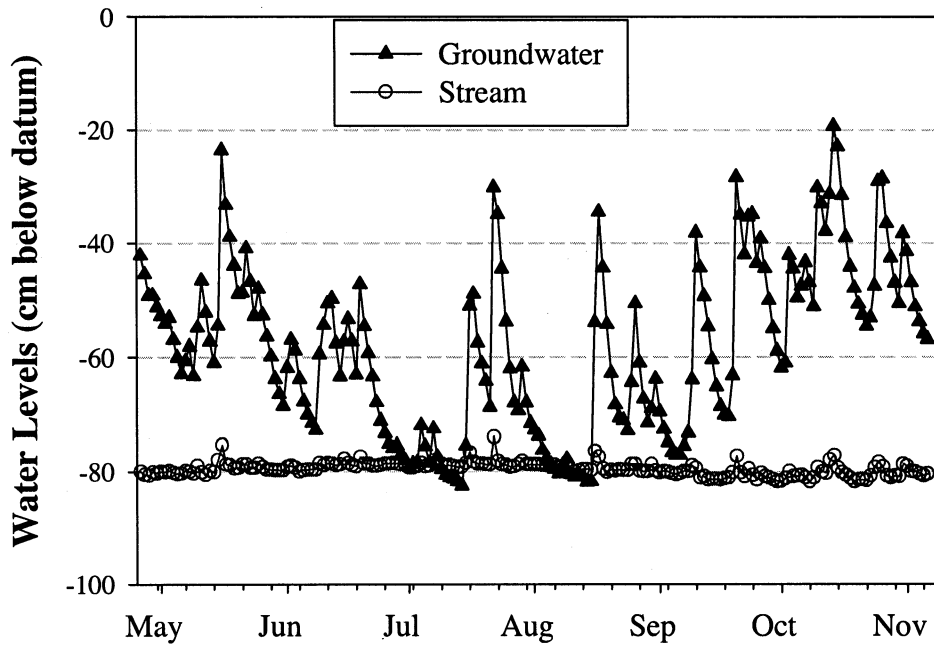
Results and Discussion

Data from the water level recorders showed differences in hydrogeology between the two sites (Figure. 2). At East Creek, large fluctuations in subsurface water levels of up to 50 cm occurred in response to precipitation events, while water levels in East Creek remained relatively constant throughout the summer, with a few small responses to heavy rainfall. A head difference between the creek and the groundwater was also maintained throughout the summer at East Creek, indicating flow of groundwater to the stream. At the Tahquamenon Mouth site, the response of the groundwater table to precipitation events was muted, with almost no fluctuation in water table levels after rain in the area but a gradual decline in the water table over the summer. Hydraulic conductivities were relatively high at both sites, typical of silty sands and fine sands, but higher at the Tahquamenon Mouth site. Apparently, infiltration to the shallow groundwater table is rapid at both sites, but the slower transport of groundwater at East Creek resulted in temporary increases in groundwater elevation in response to precipitation events. Rapid transport in the more conductive aquifer at Tahquamenon Mouth site apparently reduced the response of groundwater elevation to precipitation events.

During the summer of 2000, the area under investigation received very little rain, with little precipitation from June to mid-August. The hydrograph in Figure 3 indicates the effect on streams in the area. Discharge for the main stem of the Tahquamenon River at Paradise continually dropped throughout this period. Note that sampling dates for our subwatersheds are transposed on the hydrograph from the main stem of the Tahquamenon. Near the end of August, discharge gradually increased with the return of precipitation to the area. Data from the water level recorders began in the spring of 2001, so specific site water level data for January 2000 to May 2001 is not available, but assuming the river is in connection with the groundwater table, groundwater levels likely declined during the dry summer of 2000.

Groundwater at both sites contained moderate to relatively high concentrations of both Hg_T (0.1 to 15 ng/L) and MeHg (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 Hg_T and MeHg concentrations (Figure 4). Hg_T concentrations were higher at the East Creek sites, especially WEC2. In contrast, MeHg concentrations were higher at the Tahquamenon Mouth sites, and higher at one site (WTM1) than the other (WTM2). Temporal patterns in MeHg concentrations, especially at the Tahquamenon Mouth sites, appeared to be related to the hydrograph of the river (Figure 4). 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 MeHg in groundwater during periods of relatively low flow and flushing of MeHg-enriched groundwater 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 (see Stoor 2002). MeHg concentrations increased with the rise in the hydrograph during spring melt, reaching the highest concentration as the hydrograph began to fall.

Stream and Groundwater levels at EC1



Groundwater levels at TM and Precipitation for Luce County

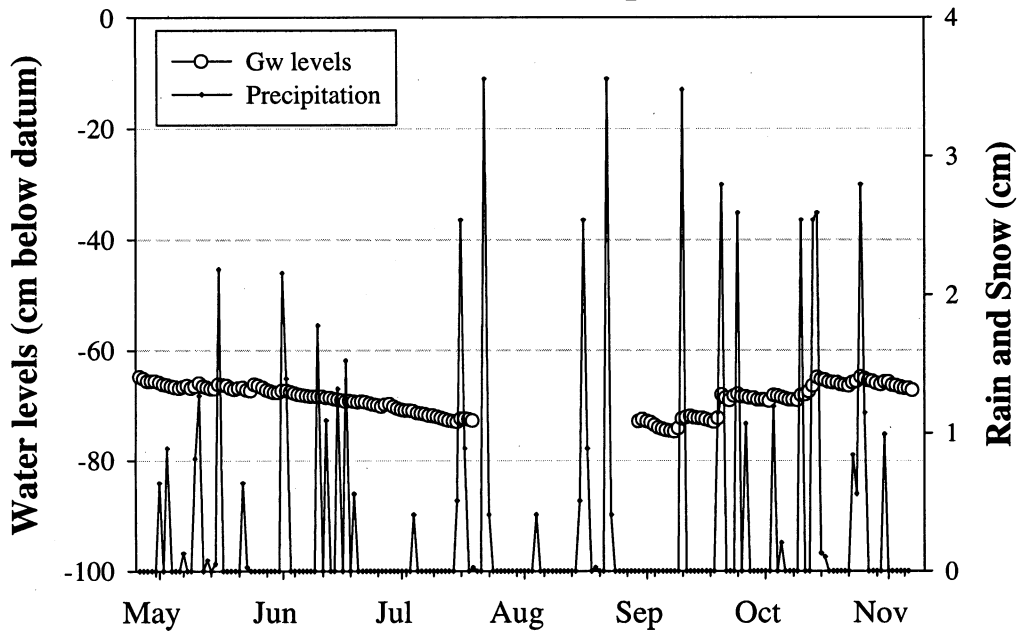


Figure 2. Groundwater and stream water level data collected from the Ecotones during 2001. Precipitation during the same period was obtained from the NCDC's Record of Climatological Observations.

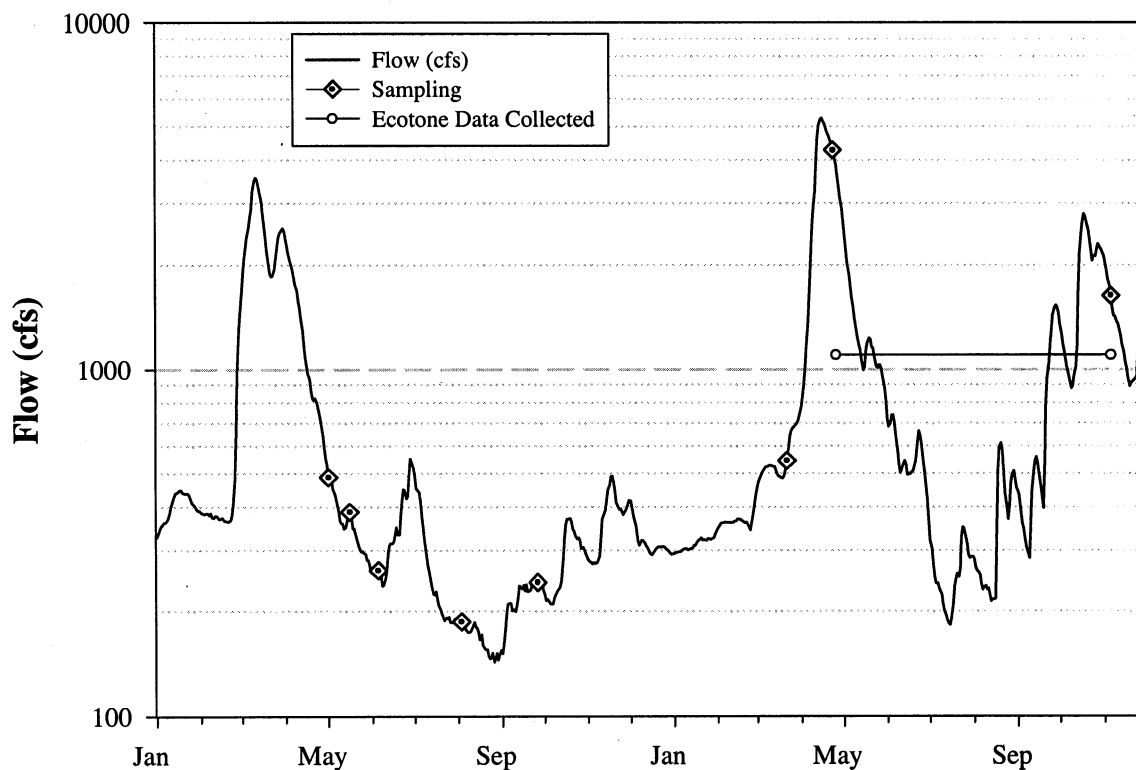


Figure 3. Tahquamenon River hydrograph for January 2000 to December 2001. Sampling dates for the subwatersheds (?) are indicated directly on the hydrograph for the Tahquamenon River. The time period where water level recorders were in operation is also indicated (o—o).

Differences between the Tahquamenon Mouth and East Creek sites may account for the differences in methylmercury concentrations. Appreciable concentrations of sulfide were detected at both sites, indicating that sulfate-reducing bacteria capable of producing methylmercury were present. The more stable groundwater table at the Tahquamenon Mouth may produce a more favorable environment for methylation by the sulfate-reducing bacteria (Benoit et al. 1999; Gilmour et al 1998). The land cover type differed between sites, consisting of coniferous forest at the Tahquamenon Mouth and deciduous forest at East Creek. Soils also differed, represented by spodosols at Tahquamenon Mouth and mollisols at East Creek. The surficial geology also differed, as reflected by higher Ca and Mg concentrations in the Tahquamenon Mouth groundwater. Other chemical data also indicate a difference in the subsurface solid phase composition between the two sites. High concentrations of Fe at Tahquamenon Mouth indicated the presence of iron oxides in the subsurface (e.g., Goethite, FeOOH), while higher Al levels in the East Creek are indicative of aluminum oxides (e.g., Gibbsite, Al(OH)₃). The high concentrations of Fe, Mn, and Al may also reflect the existence of reducing conditions in the subsurface during different times of the year.

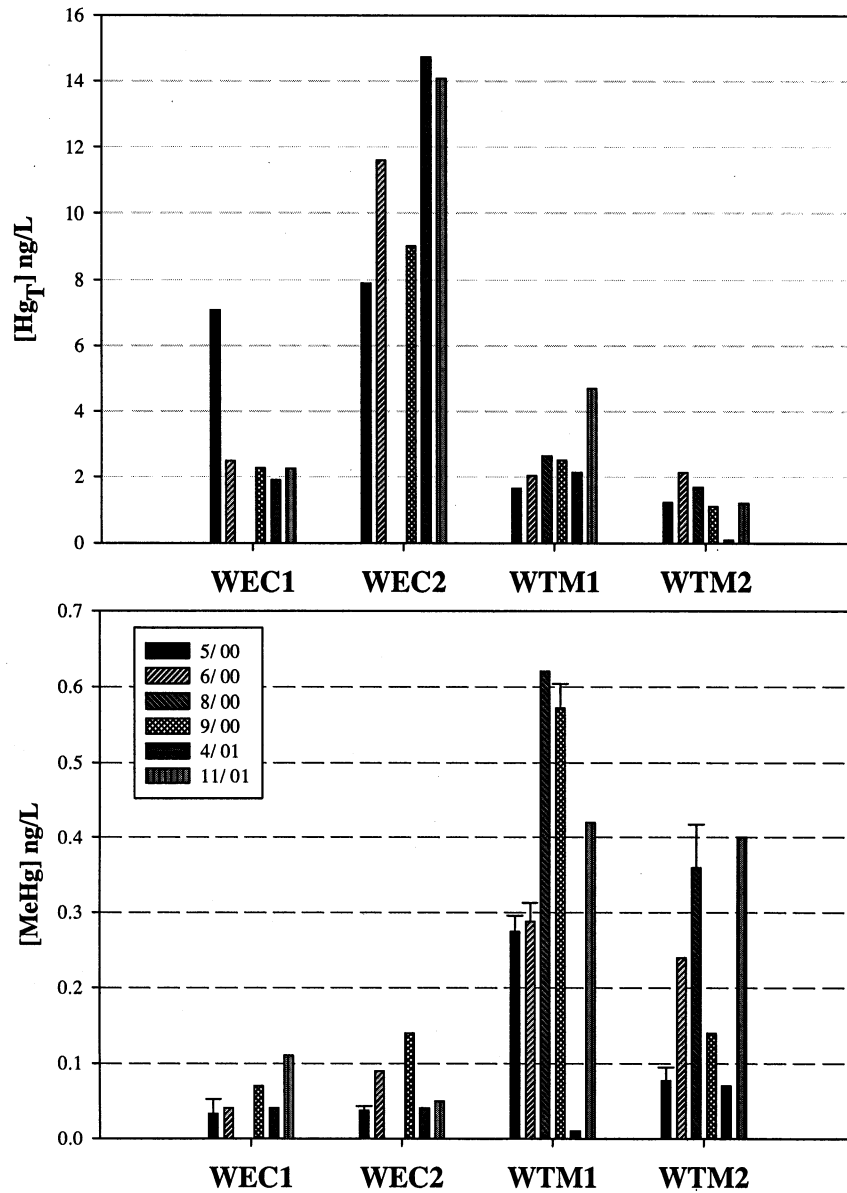


Figure 4. Groundwater Hg concentrations in wells at the East Creek and the Tahquamenon Mouth sites. WEC1 and WEC2 are East Creek, and WTM1 and WTM2 are Tahquamenon Mouth sites.

At three sites along East Creek, mini-piezometers were installed in close proximity to the creek to examine Hg_T and MeHg concentrations in the hyporheic zone. Two sites (EC1 and EC2) were located in a deciduous forest area and the other (EC3) in a wetland. The mini-piezometers were positioned to sample the saturated zone within a few meters of the creek and below the creek bed. MeHg concentrations were relatively low (non-detectable to 1.5 ng/L) in the subsurface zone adjacent (within a few meters) to the stream bank. However, concentrations were relatively high in porewaters beneath the creek (up to 12 ng/L), although highly variable both spatially and temporally (Table 1). Concentrations in porewaters were generally high relative to concentrations in East Creek, indicating that this region of the hyporheic zone could be an important source of MeHg to East Creek. Concentrations of MeHg in groundwater and porewaters were higher in the wetland site (EC3) than at the forested site (EC1, EC2), 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.

Table 1. MeHg concentrations (ng/L) in porewater of East Creek sediments.

Depth Below Sediment Surface (cm)	MeHg (ng/L)					
	June-00			Aug 00		
	<u>EC1</u>	<u>EC2</u>	<u>EC3</u>	<u>EC1</u>	<u>EC2</u>	<u>EC3</u>
5				0.76		
10	1.13	0.12	clogged	6.75	0.05	12.44
20				4.37		
Depth Below Sediment Surface (cm)	Sep-00			Apr-01		
	<u>EC1</u>	<u>EC2</u>	<u>EC3</u>	<u>EC1</u>	<u>EC2</u>	<u>EC3</u>
5	0.6			0	0.01	1.19
10	0.48	0.05	0.77	0.12	0.03	0.84
20	0.79			0.13	0.11	0.08

Conclusions and Recommendations

Moderately high concentrations of both total mercury (0.1 to 15 ng/L) and methylmercury (0.04 to 0.6 ng/L) in groundwaters in the Tahquamenon River watershed indicate that groundwater is a potentially important source of mercury to streams fed by groundwater in the region.

Comparisons of hydrologic and chemical data indicate a pattern of buildup of methylmercury in groundwater during the summer, when groundwater flow is slow and conditions are anoxic, followed by flushing of methylmercury-enriched groundwater into streams during recharge events, especially spring melt. The hyporheic zone is also a potentially important source of methylmercury to surface waters. At sites along East Creek, a tributary to the Tahquamenon River, concentrations of methylmercury in hyporheic waters are relatively high (up to 12 ng/L), especially in pore waters beneath the stream. The hyporheic zone is probably an important source of methylmercury to East Creek.

Concentrations of total mercury and methylmercury in ground waters and hyporheic waters are highly variable, both temporally and spatially. Factors such as land cover, soil type, and hydrogeology likely influence variability, but local conditions influencing methylation and demethylation rates probably contribute to within-site spatial variability.

In assessments of methylmercury sources to surface waters, fluxes from groundwater and the hyporheic zone should be included. Measurements of mercury methylation and demethylation rates and transport rates in the hyporheic zone should be made to confirm the importance of this region in methylmercury production and transport into surface waters.

References

- Babiarz, C.L., J.P. Hurley, J.M. Benoit, M.M. Shafer, A.W. Andren, and D.A. Webb. 1998. Seasonal influences on partitioning and transport of total and methyl mercury in rivers from contrasting watersheds. *Biogeochim.*, 41:237-257.
- Benoit J.M., R.P. Mason, and C.C. Gilmour. 1999. Estimation of Mercury-Sulfide Speciation in Sediment Pore Waters Using Octanol-Water Partitioning and Implications for Availability to Methylating Bacteria. *Environmental Toxicology and Chemistry*, 18(10):2138-2141.
- Branfireun B.A., A. Heyes, and N.T. Roulet. 1996. The Hydrology and Methylmercury Dynamics of a Precambrian Shield Headwater Peatland. *Water Resources Research*, 32(6):1785-1794.
- Cleckner, L.B., P.J. Garrison, J.P. Hurley, M.L. Olson, and D.P. Krabbenhoft. 1998. Trophic transfer of methyl mercury in the northern Florida Everglades. *Biogeochim.*, 40:347-361.
- Gill, G.A. and W.F. Fitzgerald. 1987. Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. *Marine Chem.*, 20:227-243.
- Gilmour C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40(2-3):327-345.
- Horvat M., L. Linag, and N.S. Bloom. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II. *Anal. Chim. Acta.*, 282:153-168.
- Hurley, J.P., S.E. Cowell, M.M. Shafer, and P.E. Hughes. 1998 Partitioning and transport of total and methyl mercury in the lower Fox River. *Wisconsin. Environ. Sci. Technol.* 32:1424-1432.
- Hurley, J.P., L.B. Cleckner, M.M. Shafer, and R.C. Back. 2000. Watershed Influences of mercury transport to Lake Superior. *Verh. Internat. Verein. Limnol.* 27,1-4.
- Krabbenhoft D.P. and C.L. Babiarz. 1992. The Role of Groundwater Transport in Aquatic Mercury Cycling. *Water Resources Research* 28(12):3119-3128.
- Liang, L., N.S. Bloom, and M. Horvat. 1994. Simultaneous determination of mercury speciation in biological-materials by GC/CVAFS after ethylation and room-temperature precollection. *Clin. Chem.* 40:602-607.
- Olsen, M.L., L.B. Cleckner, J.P. Hurley, D.P. Krabbenhoft, and T.W. Heelan. 1997. Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades. *Fresenius J. Anal. Chem.* 358:392-396.

St Louis V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom, and R.J. Flett. 1994 Importance of Wetlands as Sources of Methyl Mercury to Boreal Forest Ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences* 51(5):1065-1076.

Stoor, R.W. 2000. Groundwater contributions of methylmercury to a Lake Superior watershed. M.S. Thesis, Environmental Chemistry & Technology, University of Wisconsin-Madison.

USEPA. 1996b. Method 1669: Method for sampling ambient water for determination of metals at EPA ambient criteria levels. EPA 821-R-96-011. U.S.EPA, Office of Water, Office of Science and Technology, Engineering and Science Division (4303), 401 M Street SW, Washington, DC 20460