

## **Project Report**

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

**By**

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## 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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**Project Period:** 7-1-02 to 6-30-04

**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 MINIPPOINT sampler), and sediments (extruded and sliced cores). Sampling times were selected to provide comparisons of seasons and hydrologic events. Sampling and subsequent measurements of  $Hg_T$  and MeHg were made using clean techniques.

**Results and Discussion:** In surface waters, appreciable concentrations of both filtered total mercury ( $Hg_T$ ) and filtered methyl mercury (MeHg) were observed -- ranging from 0.6 to 4.4  $ng\ L^{-1}$  for  $Hg_T$  and 0.07 to 0.63  $ng\ L^{-1}$  for MeHg. Values for MeHg as a percent of  $Hg_T$  ranged between 2.8% and 51.4%. In groundwaters, moderately high concentrations of filtered  $Hg_T$  were observed -- typically in the range of 0.3 to 8  $ng\ L^{-1}$ . Groundwater  $Hg_T$  concentrations were generally higher than values in the associated surface water. However, MeHg concentrations in these groundwaters were usually very low, often  $< 0.03\ ng\ L^{-1}$ . 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  $ng\ L^{-1}$ . 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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## PROJECT REPORT

### INTRODUCTION

Production of methyl mercury (MeHg) in watersheds is of concern because accumulation of MeHg through the foodweb poses a health threat to consumers of fish in many lakes of Wisconsin, and the United States (U.S. EPA, 1998). New information on mercury sources and fluxes in the environment continues to emerge (Rudd, 1995; Mason and Fitzgerald, 1996) but the contribution from many sources remains uncertain, including the hyporheic zone.

Transport from the surrounding watershed is an important source of MeHg to surface waters. Production of MeHg occurs in anoxic subsurface waters in association with sulfate reduction (Gilmour and Mitchell 1992). Consequently, hyporheic zones are important sources of MeHg because these sites provide an environment conducive to both methylation and potentially rapid transport to adjacent surface waters. Identification of major sources is an essential step in developing management strategies for MeHg.

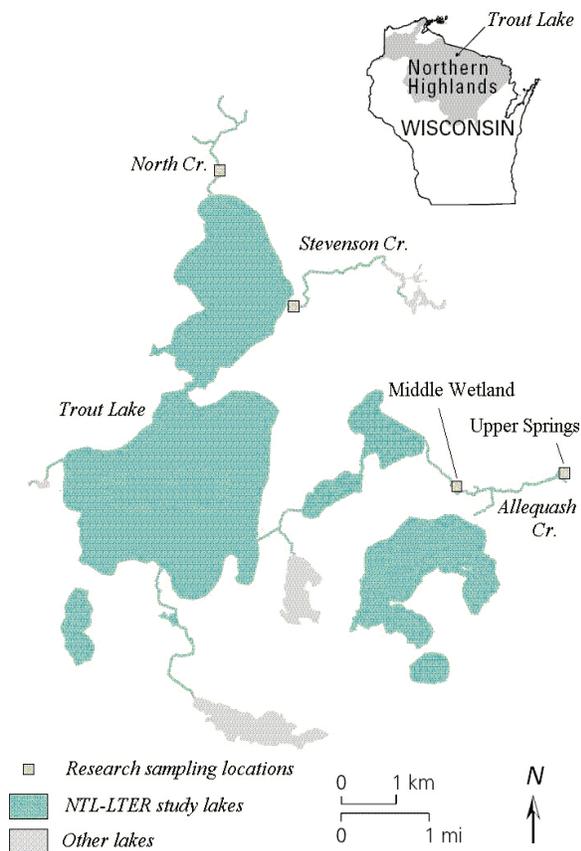
This investigation was conducted to explore the role of the hyporheic zone in the production and transport of MeHg into surface waters. We selected a field site where total Hg and methyl Hg concentrations could be measured along hydrologic flowpaths. Our investigation focused on two objectives: (1) To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

### PROCEDURES AND METHODS

**Study Sites:** This investigation was initially targeted for watersheds discharging into Lake Superior, but we moved our study sites to the Trout Lake Basin (Vilas County, WI) to take advantage of several important benefits. High among these benefits were the co-location of the UW-Madison Long Term Ecosystem Research (LTER) program and the U.S. Geological Survey (USGS) Water, Energy, and Biogeochemical Budgets (WEBB) program. This investigation benefited from collaboration with scientists in each group, and from the sampling infrastructure and long-term record on the groundwater sampling sites originally installed by the USGS.

Our primary study sites were two areas within the Allequash Creek watershed (Figure 1). The Upper Springs area serves as the headwaters for Allequash Creek and consists of several groundwater point discharges at the base of a dominating hillslope forested by a mixture of deciduous and coniferous species. The Middle Wetland area is defined by a 3-m wide riparian zone located on both sides of the main creek channel. A culvert at the discharge of the wetland restricts and slows the flow of the creek in this area. The hillslopes are similar to those in the Upper Springs, although the steepness of the terrain is greater at the Middle Wetland. The geology of this area consists of 30 to 50 m of sandy outwash deposits overlying Precambrian igneous and metamorphic bedrock (Krabbenhoft et al., 1995).

Our secondary study sites were North Creek and Stevenson Creek, two sub-watersheds within the Trout Lake Basin. These areas are overgrown with tussocks sedge, leatherleaf, black spruce, sphagnum moss and tag alders, and are generally lacking in relief.



**Figure 1:** Sampling locations within the greater Trout Lake Watershed in Vilas County, WI (From Meyer, 2005, as modified from USGS, 2000)

**Methods:** Groundwater samples were collected from wells and piezometers, previously installed by the USGS WEBB project. Hyporheic pore-water samples were collected using a differential in-situ porewater sampler (DIPS) modeled after the MINIPPOINT sampler of Duff et al. (1998). Flow rates between 0.3 and 4.0 mL min<sup>-1</sup> were found to cause no disruption to the established gradient. The sampler operated at 1.0 and 2.0 mL min<sup>-1</sup> -- a rate well below the observed discharge of upwelling porewaters at the piezometers nests (~10.7 mL min<sup>-1</sup>). The observed superficial velocity was 1 cm/sec.

Hyporheic sediment cores were obtained by pushing acid cleaned acrylic tubes into the sediment to a depth of 15 to 20 cm. The cores were extruded and sliced at 1 cm intervals and collected in sample containers for subsequent freeze-drying and analysis (Meyer 2005).

Surface waters were collected by using a peristaltic pump to draw the water and a Teflon weight to submerge the end of the sample tubing under the water surface.

Total mercury (Hg<sub>T</sub>) and methyl mercury (MeHg) were analyzed using established procedures based on US EPA Methods 1630 and 1631. For MeHg, the procedure included distillation, ethylation, chromatographic separation, pyrolytic conversion to Hg<sup>0</sup>, and measurement by cold vapor atomic fluorescence spectroscopy (CVAFS). Hg<sub>T</sub> was measured by bromine monochloride oxidation, reduction with stannous chloride, and detection by CVAFS (Bloom, 1989; Liang *et al.*, 1994; Babiarez *et al.*, 1998). Sediment samples for Hg<sub>T</sub> analysis were pre-digested using a nitric acid/sulfuric acid reagent prior to BrCl oxidation (Gill and Fitzgerald, 1987).

## RESULTS

**Surface Waters:** Concentrations of both filtered total mercury (Hg<sub>T</sub>) and filtered methyl mercury (MeHg) in Allequash Creek, North Creek, and Stevenson Creek varied among sites and sampling times (Table 1). Values for Hg<sub>T</sub> ranged from 0.6 to 4.4 ng L<sup>-1</sup>, while the MeHg values ranged from 0.07 to 0.63 ng L<sup>-1</sup>. These ranges are comparable to those observed in a previous

**Table 1:** Surface water concentrations of filtered Hg<sub>T</sub> and MeHg at watershed study sites (Meyer, 2005)

| Concentrations<br>(ng L <sup>-1</sup> ) |                 | Allequash<br>Creek Middle<br>Wetland<br>(AQMW) | Allequash<br>Creek Upper<br>Springs<br>(AQU S) | North Creek<br>(NC) | Stevenson<br>Creek<br>(SC) |
|---|-----------------|--|--|---------------------|----------------------------|
| Mar-03                                  | Hg <sub>T</sub> | 0.59   | 1.34   | 0.56                |                            |
|   | MeHg            | 0.10   | 0.10   | 0.29                |                            |
|   | % MeHg          | 17.1%  | 7.3%   | 51.4%               |                            |
| Jul-03                                  | Hg <sub>T</sub> |  |  |                     |                            |
|   | MeHg            |  | 0.18   |                     |                            |
|   | % MeHg          |  |  |                     |                            |
| Aug-03                                  | Hg <sub>T</sub> |  |  | 1.82                |                            |
|   | MeHg            | 0.58   | 0.63   | 0.60                |                            |
|   | % MeHg          |  |  | 33.0%               |                            |
| Oct-03                                  | Hg <sub>T</sub> | 3.02   | 1.21   |                     |                            |
|   | MeHg            | 0.08   | 0.15   |                     |                            |
|   | % MeHg          | 2.8%   | 12.2%  |                     |                            |
| Apr-04                                  | Hg <sub>T</sub> | 1.42   | 1.97   | 2.75                | 4.44                       |
|   | MeHg            | 0.07   | 0.19   | 0.30                | 0.14                       |
|   | % MeHg          | 4.9%   | 9.6%   | 10.9%               | 3.2%                       |
| Jun-04                                  | Hg <sub>T</sub> | 0.99   | 1.20   | 2.44                |                            |
|   | MeHg            | 0.20   | 0.39   | 0.57                | 0.17                       |
|   | % MeHg          | 20.2%  | 32.5%  | 23.4%               |                            |

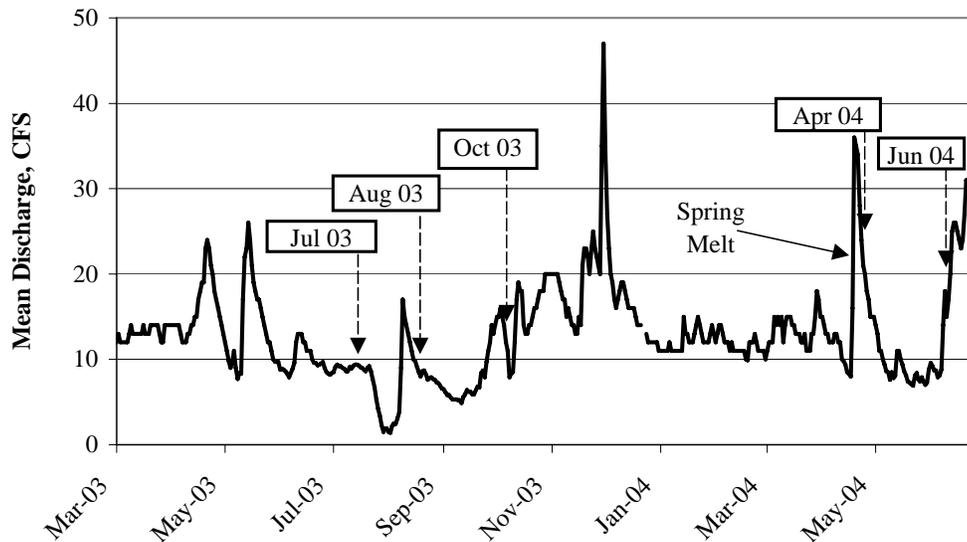


denotes no sample taken or analyzed

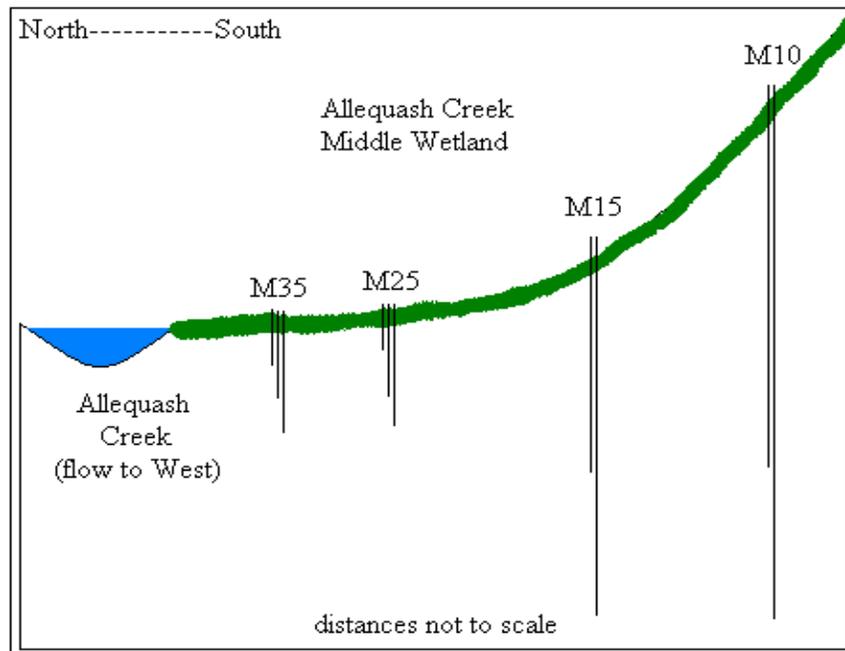
study of the Allequash Creek Watershed (Krabbenhoft et al, 1995). Concentrations of Hg<sub>T</sub> were highest at three of the four sampling sites during April of 2004, coinciding with the spring melt identified on the hydrograph (Figure 2). The highest concentrations of MeHg, ranging from 0.58 – 0.63 ng L<sup>-1</sup>, were observed in August of 2003 for the Allequash and North Creek sites (Stevenson was not sampled in August of 2003). Values for MeHg as a percent of Hg<sub>T</sub> ranged between 2.8% and 51.4%, with values in April and June 2004 averaging: 7.2% (range: 3.2% to 10.9%) and 25.4% (range: 20.2% to 32.5%), respectively.

**Groundwaters:** Sampling of groundwater was structured to relate mercury concentration with position along the groundwater flowpath (for example, see the cross-section of the Allequash Creek Middle Wetland site in Figure 3).

Moderately high concentrations of  $Hg_T$  were found in groundwaters (Table 2). The  $Hg_T$  concentrations in groundwater wells and piezometers located at the Allequash Creek Middle Wetland (AQMW) ranged between a low of  $0.4 \text{ ng L}^{-1}$  at piezometer M35.4 in October 2003 to a high of  $8.8 \text{ ng L}^{-1}$  in June of 2004 at M10.1 (Table 2). All of the wells and piezometers at this sampling location showed elevated concentrations of  $Hg_T$  as compared to the surface water  $Hg_T$  of Allequash Creek for the April and June 2004 samples. For most sampling events, the concentration of  $Hg_T$  in groundwater increased as the depth approached the sediment-water interface. Piezometer M35.3 did not exhibit this characteristic and M25.1 had values greater than M25.02 on two of four sampling events.



**Figure 2:** Allequash Creek Hydrograph March 2003 thru June 2004 (Meyer, 2005)



**Figure 3:** Schematic of well and piezometer locations at the Allequash Creek Middle Wetland site (From Meyer 2005).

Concentrations of filterable Hg<sub>T</sub> in groundwater wells and piezometers located at the Allequash Creek Upper Springs ranged from 0.3 ng L<sup>-1</sup> Hg<sub>T</sub> at U10.2 in August 2004 to 10.8 ng L<sup>-1</sup> in April of 2004 at M10.1 (Table 2). While nearly all wells sampled in April and June of 2004 showed Hg<sub>T</sub> values higher than the corresponding surface water of Allequash Creek (Tables 1 and 2), the levels in October of 2003 were lower except for U10.2. Particularly high levels of 7.8 and 10.8 ng L<sup>-1</sup> Hg<sub>T</sub> were observed in April 2004 at the 225 cm depths of U40.2 and U50.2. These values were almost double and quadruple the values of the other nested depths (163 cm and 288 cm) at U40 and U50, respectively. The general pattern of increasing Hg<sub>T</sub> concentration at the Upper Springs was opposite that observed at the Middle Wetland, with concentrations increasing with depth below ground surface.

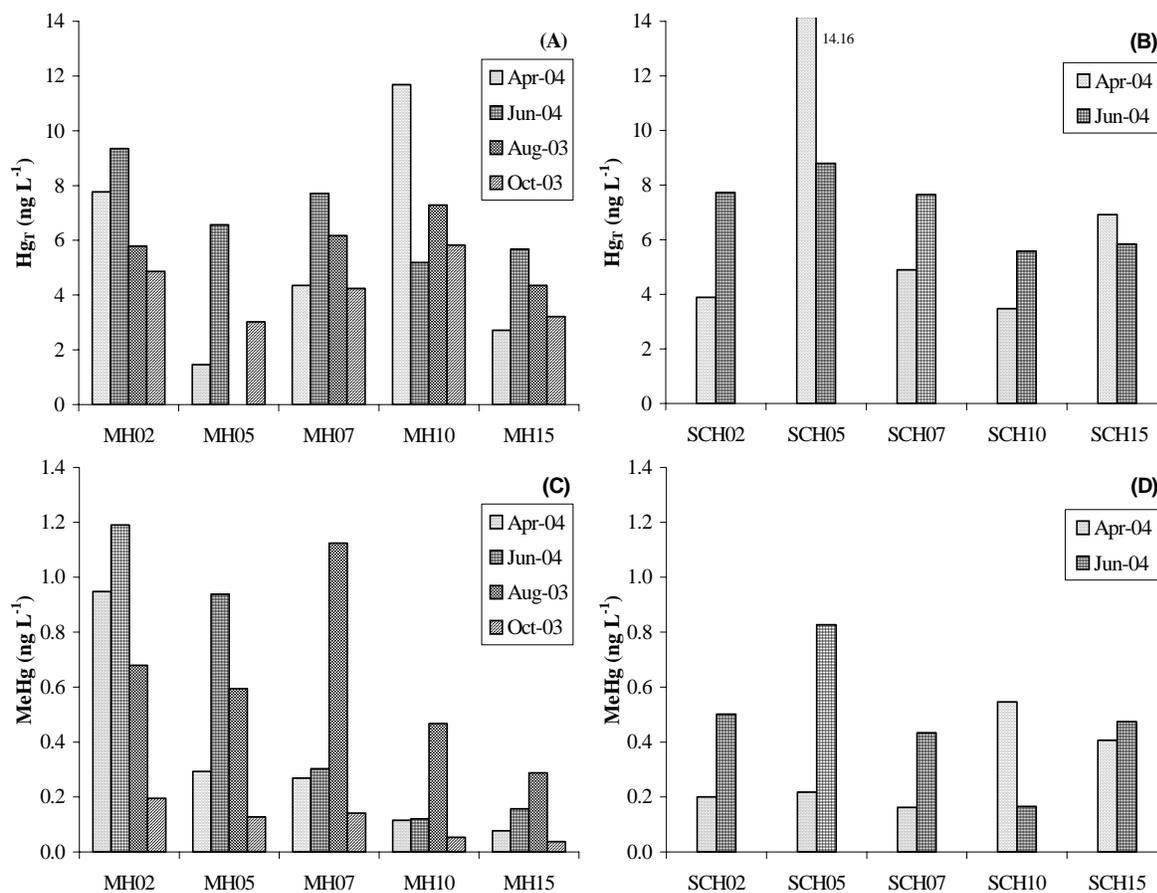
**Table 2:** Concentrations of filtered total mercury (Hg<sub>T</sub>) and methyl mercury (MeHg) in groundwater wells and piezometers along two transects, Allequash Creek Middle Wetland and Allequash Creek Upper Springs.

| Well                                       | Depth<br>(m) | Hg <sub>T</sub> (ng/L) |       |       |       | MeHg (ng/L) |        |        |        |
|--|--------------|------------------------|-------|-------|-------|-------------|--------|--------|--------|
|  |              | Apr04                  | Jun04 | Aug03 | Oct03 | Apr04       | Jun04  | Aug03  | Oct03  |
| <b>Allequash Creek Middle Wetland Site</b> |              |                        |       |       |       |             |        |        |        |
| M10.1                                      | 5.29         | 3.17                   | 8.78  | 2.23  | 1.26  | <0.028      | <0.028 | 0.17   | 0.09   |
| M10.2                                      | 9.29         | 1.81                   | 3.96  | 0.41  | 0.39  | NS          | NS     | <0.058 | <0.028 |
| M15.1                                      | 1.39         | 8.11                   | 5.72  | 1.52  | NS    | NS          | NS     | <0.058 | NS     |
| M25.02                                     | 0.61         | 1.88                   | 5.77  | 2.89  | 1.66  | 0.14        | 1.12   | 0.37   | 0.26   |
| M25.1                                      | 3.08         | 2.68                   | 3.64  | 3.94  | 0.46  | <0.028      | <0.028 | 0.1    | <0.028 |
| M25.3                                      | 4.3          | 1.28                   | 3.35  | 0.67  | 0.41  | <0.028      | <0.028 | 0.07   | <0.028 |
| M35.3                                      | 1.95         | 2.5                    | 3.27  | 6.27  | 0.71  | <0.028      | <0.028 | 0.12   | <0.028 |
| M35.4                                      | 2.32         | 3.64                   | NS    | 8.06  | 0.36  | NS          | NS     | 0.43   | <0.028 |
| M35.5                                      | 2.93         | 2.93                   | 3.23  | 4.29  | 0.68  | <0.028      | <0.028 | 0.43   | <0.028 |
| M35.6                                      | 3.54         | 1.77                   | NS    | 1.44  | 0.56  | NS          | NS     | <0.058 | <0.028 |
| <b>Allequash Creek Upper Springs Site</b>  |              |                        |       |       |       |             |        |        |        |
|  |              | Apr04                  | Jun04 | Aug03 | Oct03 |             | Jul03  | Aug03  | Oct03  |
| U10.1                                      | 2.95         | 1.84                   | NS    | 0.39  | NS    |             | <0.036 | <0.058 | NS     |
| U10.2                                      | 8.65         | 3.41                   | 3.2   | 0.26  | 1.22  |             | 0.14   | <0.058 | <0.028 |
| U15.2                                      | 4.3          | 2.54                   | 3.22  | 1.7   | 0.58  |             | <0.036 | 1.09   | <0.028 |
| U40.1                                      | 1.63         | 3.48                   | 3.16  | 2.46  | 1.04  |             | <0.036 | <0.058 | 0.022  |
| U40.2                                      | 2.24         | 7.87                   | NS    | 1.7   | 0.78  |             | 0.1    | <0.058 | <0.028 |
| U40.3                                      | 2.85         | 3.98                   | 2.95  | 4.75  | 0.95  |             | <0.036 | 0.19   | <0.028 |
| U50.1                                      | 1.66         | 2.36                   | 2.92  | 2.16  | NS    |             | 0.14   | <0.058 | NS     |
| U50.2                                      | 2.27         | 10.76                  | NS    | 2.98  | NS    |             | <0.036 | <0.058 | NS     |
| U50.3                                      | 2.88         | 2.17                   | 2.89  | 3.87  | NS    |             | <0.036 | 0.052  | NS     |

Concentrations of MeHg in groundwater along the Middle Wetlands transect were usually below the concentrations in the surface water. Most other samples had values very near or below the analytical detection limits, with the exception of August 2003 M35.4 site which also exhibited

had a high value for Hg<sub>T</sub>. Concentrations of MeHg along the Upper Springs transect were also below the corresponding surface water values for nearly all samples and locations (Table 2).

**Hyporheic Zone Pore Waters:** Sampling of hyporheic pore waters was focused at the Middle Wetland and Stevenson Creek sites because they provided a contrast between upwelling (Middle Wetland) and downwelling (Stevenson Creek) waters. Concentrations of Hg<sub>T</sub> were greater than those observed for the associated surface water samples, but did not show consistent patterns with depth (Figure 4). The highest average Hg<sub>T</sub> concentration across the five sample depths was observed in June 2004, averaging 6.9 ng L<sup>-1</sup> at the Middle Wetlands and 7.1 ng L<sup>-1</sup> at Stevenson Creek.

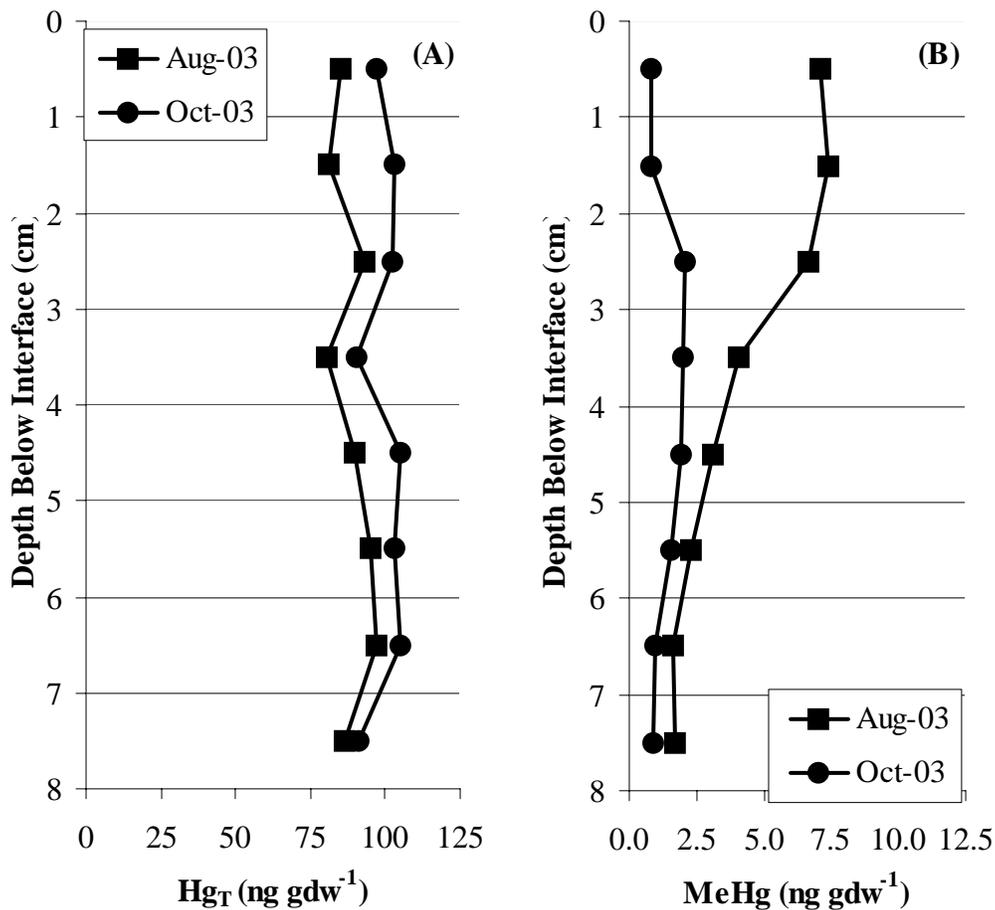


**Figure 4:** Concentrations of Hg<sub>T</sub> and MeHg in hyporheic porewaters for Allequash Creek Middle Wetland (MH) and Stevenson Creek (SCH). The numbers on the x-axis are depth below the sediment surface (cm). (Meyer, 2005)

Concentrations of MeHg were considerably higher in hyporheic zone pore waters (Figure 4) than in groundwaters (Table 2; Note that the numbers on the x-axis are depth (cm) below the sediment-water interface). At the Middle Wetlands (upwelling) site, a general pattern of increasing concentration toward the sediment-water interface was observed. The temporal pattern varied with depth, but concentrations were lower in October than earlier in the summer or spring. For Stevenson Creek (downwelling), the pattern with depth varied with time. In April 2004, concentrations at the 10 and 15 cm depths were nearly double that of the three shallower depths (Figure 4). However, in June 2004, values were highest at the upper depths, 2 and 5 cm.

The percentage of  $Hg_T$  as MeHg in hyporheic pore waters was relatively high in comparison to other systems (Hurley et al., 1995). Values at the Middle Wetlands and Stevenson Creek sites ranged from  $< 5\%$  to over  $15\%$ . Values near  $25\%$  were found for some samples at the at the Upper Springs and North Creek sites (data not shown).

**Hyporheic Zone Sediments:** Sediment cores were obtained at the Allequash Creek Middle Wetland site in August and October of 2003. Concentration profiles of  $Hg_T$  in both cores were similar, ranging between  $81$  and  $105$   $ng\ gdw^{-1}$  (Figure 5). For MeHg, however, a significant difference was observed. In August, concentrations of MeHg in the upper  $3$  cm were near  $7$   $ng\ gdw^{-1}$ . However, in October the MeHg concentrations in surficial sediments were much lower. Similarly, the percentage of  $Hg_T$  present as MeHg in the sediment cores reflected the change in MeHg concentrations between August and October. The value peaked at  $9\%$  MeHg in the upper  $1-2$  cm of the August core and steadily declined to less than  $2\%$  below  $6$  cm. In October, the peak value was only  $2\%$  MeHg at  $3-4$  cm, and the lowest value was  $0.8\%$  at  $1-2$  cm.



**Figure 5:** Total and methyl mercury concentrations for Allequash Creek Middle Wetland (AQMW) sediment cores (Meyer, 2005)

## DISCUSSION

Elevated concentrations of MeHg observed in the hyporheic porewaters, as compared to the associated groundwaters and surface waters, provides compelling evidence of enhanced production and transport of MeHg in hyporheic zones in the Allequash Creek Watershed. These results are consistent with previous observations by Hurley et al. (1995), Branfireun et al. (1996) and St. Louis et al. (1996). When the hyporheic porewater concentrations of MeHg were very low in October 2003 at the Middle Wetland site (Figure 4), the corresponding surface water values for MeHg were also low, even though  $Hg_T$  concentrations had not decreased in either the porewaters or surface waters. In fact, the highest surface water value of  $Hg_T$  at the Middle Wetlands site was observed in October 2003 at  $3.0 \text{ ng L}^{-1}$ , over double any other sampled period. These variations observed in the surface water concentrations indicate that heterogeneity in local hydraulic and biogeochemical processes likely play a key role in the capacity of a particular hyporheic zone to serve as a source or sink of mercury and MeHg.

At the Middle Wetlands site, very low concentrations of MeHg were present in most groundwater samples below the hyporheic zone (Table 2). Similarly, the concentrations of MeHg in Allequash Creek surface water were also very low ( $<0.2 \text{ ng L}^{-1}$ ) for all samples except on August 2003 (Table 1). The hydrograph of Allequash Creek shows a significant increase and decline in the mean discharge just prior to this sampling period (Figure 2). The increase in surface water concentration may have been impacted by this discharge event. However, this flushing event could not account for the observed increase without MeHg production in the hyporheic zone, because MeHg concentrations in groundwater were low during this period. Therefore, the hyporheic zone likely contributed to the pool of MeHg flushed into the creek during this event. Apparently, conditions in the hyporheic zone are often conducive to microbial sulfate reduction and associated MeHg production (Gilmour and Mitchell 1992; Benoit et al. 1999). However, flushing of MeHg into surface waters was not evident during the spring melt event in April 2004 or after the October 2003 discharge event, perhaps due to flow dilution and possibly reduced production due to low biological activity as a result of cold temperatures.

Stevenson Creek was chosen to enable comparison of upwelling (Middle Wetlands) and downwelling (Stevenson Creek) conditions. In contrast to the Middle Wetlands site, MeHg concentration at Stevenson Creek peaked at a depth 7 to 10 cm below that observed at the Middle Wetlands (Figure 4). This suggests that residence time of waters in the hyporheic zone influences MeHg accumulation in hyporheic waters where conditions (especially sulfate reduction) are conducive to methylation. Furthermore, the higher concentrations of both  $Hg_T$  and MeHg in hyporheic waters as compared to overlying surface waters at Stevenson Creek (Figure 4) indicates that hyporheic zones can function as sites of methylation, regardless of whether water is supplied by groundwater (Middle Wetlands) or surface water (Stevenson Creek).

Although % MeHg values were variable, both temporal and spatial patterns indicated a tendency for association of higher MeHg concentrations with higher  $Hg_T$  concentrations. Sediment

characteristics conducive to  $Hg_T$  retention in the hyporheic zone (e.g., organic matter content) may also enhance sulfate reduction and MeHg formation.

The distributions of mercury in sediments showed that the hyporheic zone contains a large reservoir of  $Hg_T$  for potential MeHg production, possibly due to the binding of Hg (II) to natural organic matter (NOM) in the sediment (Barrow and Cox, 1992; Yin et al., 1996; Skyllberg et al., 2000). Similarly, during periods of high net methylation, substantial concentrations are associated with the solid phase in the hyporheic zone. The high concentrations of organic matter in the sediment and porewater may also enhance methylation (Hurley et al., 1995), possibly by providing a substrate for microbial growth, especially sulfate reducers. The sediment data also suggested that demethylation rates may be high in hyporheic zones. Thus, the large decrease in surficial sediment MeHg between August and October 2003 indicates this was a period of net demethylation, possibly due to either enhanced demethylation of reduced MeHg production during this period. The lower sediment MeHg levels in October were associated with a similar lower concentration of MeHg in the sediment pore waters (Figure 4), reflecting the expected coupling of sediment and porewater MeHg.

## CONCLUSIONS AND RECOMMENDATIONS

Hyporheic zones located near streambeds in the Trout Lake watershed are important sites for production of MeHg and its transport into nearby surface waters. The importance of the hyporheic zone is shown by concentrations of total and MeHg in groundwaters, surface waters, and pore waters of the hyporheic zone. Moderately high levels of total mercury are found in groundwaters, averaging about 1.6 ng/L, indicating that groundwaters provide a substantial source of mercury for potential methylation. However, concentrations of MeHg in groundwaters are typically low, often below a detection limit of 0.03 ng/L. The low MeHg concentrations in groundwaters indicate conditions in groundwater are often not conducive to methylation of mercury. Levels of readily available organic matter for heterotrophic bacteria may be low in these groundwaters, resulting in low activity of the sulfate reducing bacteria responsible for production of MeHg. However, as groundwaters or surface waters move into hyporheic zones, concentrations of total mercury and MeHg are markedly increased, averaging 6.0 and 0.50 ng/L, respectively. Thus, conditions for methylation are more favorable in the hyporheic zone than in groundwater, possible due to production of available organic matter by plants in the riparian zone and/or algae in the stream. Enhanced microbial respiration promotes sulfate reduction and associated methylation of inorganic mercury, Hg(II). High MeHg concentrations were found in both upwelling and downwelling hyporheic zones. The moderately high concentrations of total mercury (almost 100 ng/gdw) in sediments within a hyporheic zone influenced by upwelling groundwater shows that hyporheic sediments can accumulate Hg(II), providing a reservoir for potential methylation and transport of MeHg to surface waters. Large changes between August and October in MeHg concentrations in surficial sediments at this site indicate that MeHg concentrations may be influenced by rapid transport and/or changes in the balance between methylation and demethylation rates within the hyporheic zone. Future research should focus on measurements of methylation and demethylation rates, the processes controlling these rates, and the links between concentration and transport rates through coupling chemical information with hydrologic models.

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## **APPENDIX A. Publications and Presentations**

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

Meyer, MH. DE Armstrong. Role of the Hyporheic Zone in Methyl Mercury Production and Transport to Allequash Creek. 28<sup>th</sup> Annual Meeting of the Wisconsin Section of the American Water Resources Association, Wisconsin Rapids, Wisconsin, March 2004 (student presentation)

C Babiarez, J Hurley, D Krabbenhoft, R. Stoor, H. Manolopoulos, M. Meyer, and M. Shafer. Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management. Invited presentation: Fall Meeting of the American Geophysical Union, San Francisco, California, December 2004