Project Report

"Mercury Speciation Along A Groundwater Flowpath"
(05-CTP-01, WR04R001)

By

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PROJECT SUMMARY

Title:	**Mercury Speciation Along A Groundwater Flowpath**
Project I.D.:	05-CTP-01, WR04R001
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Affiliated Investigators:	M.M. Shafer, Associate Scientist; S.C. Kerr and S.P. Chadwick, Research Assistants
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Project Period:	July 1, 2004 to June 30, 2006

Objectives: Our investigation focused on the cycling of mercury in wetlands within the Trout Lake Basin in Vilas County, Wisconsin. The three main objectives were:

1. To characterize the levels of total Hg and methyl mercury (MeHg) carried in stream waters flowing through the wetlands;
2. To characterize hyporheic zones within these wetlands regarding (a) concentrations of aqueous total Hg and MeHg, (b) factors influencing MeHg levels, and (c) the importance of hyporheic zones in controlling MeHg in stream waters;
3. To probe the forms of inorganic Hg(II) and MeHg in hyporheic zone waters and examine the implications of speciation on transport and on the bioavailability of Hg(II) for methylation.

Methods: This investigation was conducted in the Trout Lake Basin (Vilas County, WI). Our primary study sites were located near Allequash Creek and Stevenson Creek. We collected samples of ground water, hyporheic-zone pore waters, and surface stream waters. Seasonal measurements were made of total Hg, MeHg, and constituents or parameters related to biogeochemical processes, including Fe, S (total S and sulfide), dissolved organic carbon (DOC), NH_4 and pH. Speciation of inorganic Hg(II) and MeHg was investigated by experimental and modeling approaches. Modeling involved equilibrium calculations based on reported stability constants for the respective mercury complexes, pH, and measured concentrations of important ligands – especially dissolved organic matter (DOM), and sulfide. In addition, association of MeHg and Hg(II) with both DOM and sulfide was probed by an experimental technique involving measurements of retention by an anion exchange resin.

Results and Discussion: Concentrations of total Hg and MeHg in streams exhibited considerable temporal variation. Highest concentrations were observed from late winter through spring and early summer, reaching over 4 ng/L for total Hg and 0.2 ng/L for MeHg. Overall, the spring melt period contributed high concentrations, loadings, and proportions of MeHg in the wetland streams.

Production of MeHg was indicated by high concentrations of MeHg in hyporheic zones, where favorable conditions for production of MeHg were also observed. Decreasing concentrations of sulfate and increasing concentrations of sulfide with depth were indicative of both sulfate reduction and the activity of sulfate-reducing bacteria (believed to be largely responsible for methylation of inorganic Hg(II) in reducing environments). Surface waters were the main source of sulfate to drive sulfate reduction in hyporheic zones, as evidenced by the high concentrations of sulfate in stream waters as compared to ground waters. Elevated concentrations of DOM, contributing to microbial activity in hyporheic zones, were attributed to diagenesis of plant material. Relationships between MeHg and Fe indicated the importance of hyporheic zones as a source of both Fe and MeHg to stream waters.

Speciation modeling predicted that HgS^0 was the dominant species of Hg(II) in sufidic (hyporheic) waters, while HgDOM complexes should be dominant in the absence of sulfide. In contrast, both $MeHgS^0$ and MeHg-DOM complexes were predicted to be important in the presence of sulfide. However, experimental measurements indicated HgDOM complexes were predominant in both sulfidic and non-sulfidic waters. These results raise important questions about factors controlling the bioavailability of Hg(II) for methylation.

Conclusions/Implications/Recommendations: Hyporheic zones are important sites for MeHg production and transport to surface waters. High DOC concentrations combined with sulfate (introduced mainly from surface water) promote the activity of sulfate-reducing bacteria (SRB). Inorganic Hg(II), partly from groundwater, is converted to MeHg, apparently by SRB, and transported into surface waters. Speciation modeling indicates that HgS^0 is dominant in these sulfidic waters. HgS^0 should facilitate methylation because neutral species of Hg(II) are presumed to be more available for uptake by SRB. However, experimental data indicate Hg(II) is bound mainly by dissolved organic matter (DOM) in sulfidic waters, indicating bioavailability of Hg(II) to SRB may be impeded by binding to DOM. Further investigations should explore the factors and conditions controlling methylation rates in hyporheic zones to facilitate new practices in wetland management that might limit MeHg production.

Related Publications and Presentations:

Chadwick, S.P., C.L. Babiarz, J.P. Hurley, D.E. Armstrong. 2006. Evaluation of the Role of Dissolved Organic Matter in the Speciation of Mercury and Methylmercury in a Lacustrine Watershed Using Diethylaminoethyl Resin. Abstracts, Conference on Mercury as a Global Pollutant, Madison, WI.

Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract. – Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.

Shafer, M., S. Kerr, J. Overdier, and D.E. Armstrong. 2005. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract – Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

Key Words: Mercury, methyl mercury, groundwater, hyporheic zones, stream waters.

Funding: UWS

INTRODUCTION

The accumulation of methyl mercury (MeHg), the most toxic form of Hg, in aquatic foodwebs is a major problem in freshwaters across the United States. Production of MeHg occurs through methylation of inorganic Hg(II) by bacteria in anoxic environments such as wetlands (Benoit et al., 1999; Hammerschmidt et al., 2004). Groundwater is partly responsible for movement of Hg(II) into these environments (Meyer, 2005; Stoor et al., 2006). Although information is emerging, the factors and mechanisms controlling MeHg production are not well understood. Our investigation was designed to provide information on the importance of hyporheic zones as a site for MeHg formation and transport into surface waters. We also investigated the forms of inorganic Hg(II) and MeHg in the hyporheic zones, and examined the influence of speciation on both Hg(II) bioavailability for methylation, and MeHg transport into surface waters and foodwebs.

Our investigation focused on the cycling of mercury in wetlands within the Trout Lake Basin in Vilas County, Wisconsin. The three main objectives were:

1. To characterize the levels of total Hg and MeHg carried in stream waters flowing through the wetlands;
2. To characterize hyporheic zones within these wetlands regarding (a) concentrations of aqueous total Hg and MeHg, (b) factors influencing MeHg levels, and (c) the importance of hyporheic zones in controlling MeHg in stream waters;
3. To probe the forms of inorganic Hg(II) and MeHg in hyporheic zone waters and examine the implications of speciation on transport and on the bioavailability of Hg(II) for methylation.

PROCEDURES AND METHODS

Study Sites: This investigation was conducted in the Trout Lake Basin (Vilas County, WI) to co-locate with 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 program and from the sampling infrastructure originally installed by the USGS.

Our primary study sites were two areas within the Allequash Creek watershed (Fig. 1). The *Upper Springs* are the headwaters for Allequash Creek and consists of several groundwater point discharges at the base of a dominating hillslope. The terrain is forested by a mixture of deciduous and coniferous species. The *Middle Wetland* is defined by a three-meter wide riparian zone located on both sides of the main 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.
Our secondary study sites were *North Creek* and *Stevenson Creek,* two sub-watersheds within the Trout Lake Basin. These areas are are generally lacking in relief, and are overgrown with tussocks sedge, leatherleaf, black spruce, sphagnum moss, and tag alders.

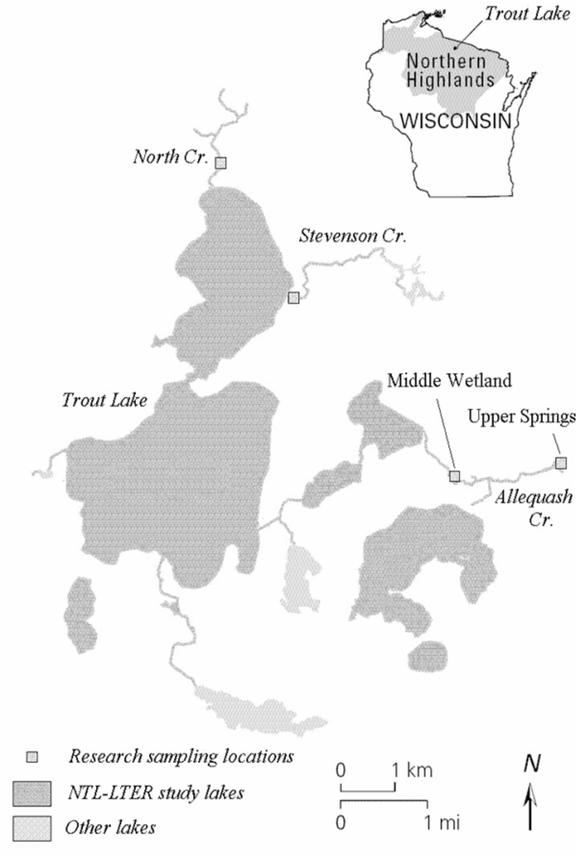

***Figure 1:** Sampling locations within the greater Trout Lake Watershed in Vilas County, WI (From Meyer, 2005, as modified from USGS, 2000)*

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 MINIPOINT sampler of Duff et al. (1998). The sampler operated at 1.0 and 2.0 mL min^{-1} - a rate well below the observed discharge of upwelling waters at piezometers nests (~10.7 mL min^{-1}).

Surface waters were collected using a peristaltic pump to draw water through an all-Teflon sampling line and weight submerged under the water surface. Surface water samples obtained between March 2004 and November 2005 were collected by collaborators at the USGS in Middleton, WI and analyzed for total and methyl mercury in their laboratories.

At the UW Environmental Chemistry Program, total Hg and MeHg were analyzed using established procedures based on US EPA Methods 1630 and 1631 (Babiarz et al., 1998). Hyporheic waters were also analyzed for pH, Fe, S, sulfide, NH_4, and DOC.

Speciation of MeHg and inorganic Hg(II) was calculated based on the concentrations of important ligands (especially sulfide and DOC) and their binding constants using the equilibrium speciation code MINEQL+ (Schecher and McAvoy, 1998).

RESULTS AND DISCUSSION

Data Sets

Stream waters were collected monthly from Allequash Creek and Stevenson Creek from April 2004 through April 2005 and analyzed for total and filterable Hg and MeHg at the USGS Mercury Laboratory in Middleton, WI. Some of these data are summarized here. Other constituents, including dissolved organic carbon, were measured in our laboratories.

Hyporheic zone waters were collected from Allequash Creek and Stevenson Creek from March 2003 through June 2004 and analyzed for total Hg and MeHg in filtered samples at the UW-

Madison Mercury Laboratory. Some of these data are summarized here and are also reported by Meyer (2005) and Armstrong et al. (2005). This data set was extended by collecting additional hyporheic zone samples in July, August, and October 2005.

In conjunction with a concurrent research project (Shafer and Armstrong, 2003), samples from hyporheic zones and rivulets were collected by Sara Kerr and Martin Shafer (UW-Madison, Environmental Chemistry Program) from June 2004 through September 2005 for characterization of biogeochemical processes influencing trace metal levels and transport in the hyporheic zone (Kerr et al., 2004; Shafer et al., 2005a, b). Some of these data, including selected profiles of sulfate, sulfide, iron, and DOC, are included in this report.

Mercury in Stream Waters

Concentrations of THg and MeHg in streams exhibited considerable temporal variation as shown by the example from Allequash Creek (Fig. 2). In general, highest concentrations were observed in the late winter through spring and early summer, reaching over 4 ng/L for total Hg and 0.2 ng/L for MeHg. Similarly, the amounts of total Hg and MeHg carried by the stream were highest from January to May due to a combination of high concentrations and stream flow. The proportion of MeHg varied from approximately 5 to 45 %, with highest values occurring in the late winter-spring period. Overall, the spring melt contributed high concentrations, loadings, and proportions of MeHg in the wetland streams.

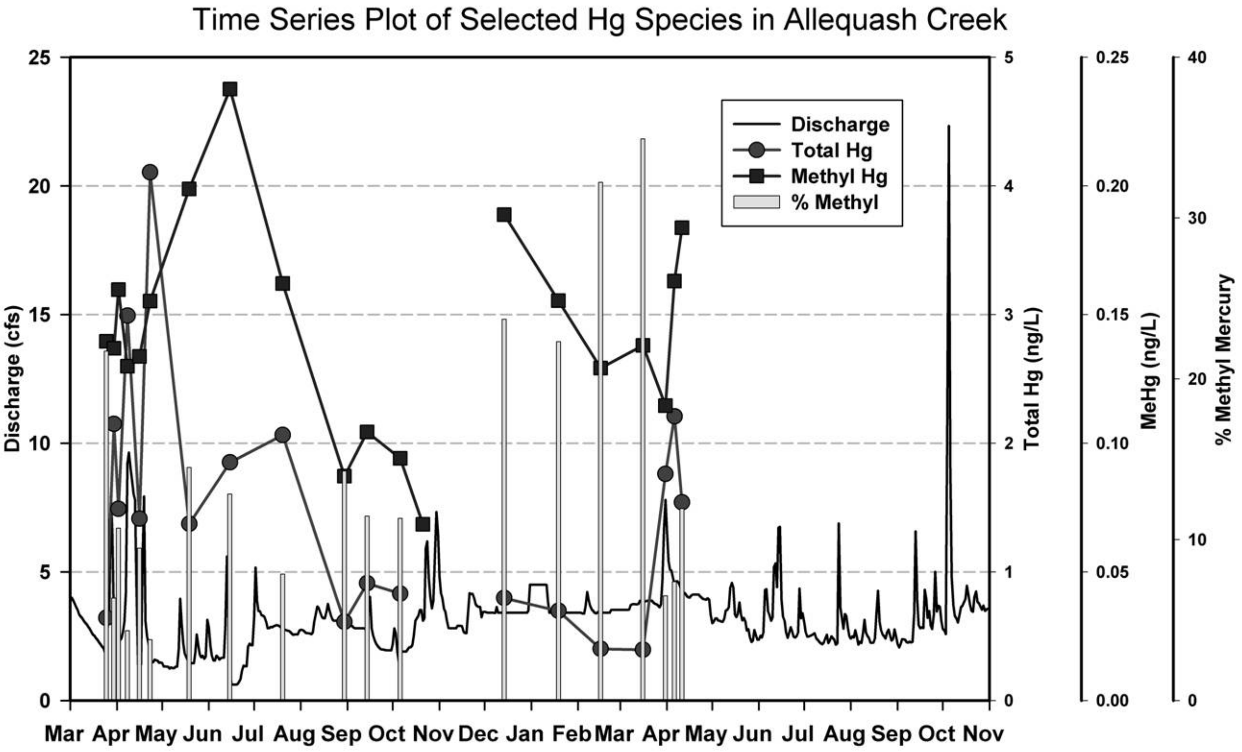

Figure 2. *Total and methyl mercury in Allequash Creek in 2005 (Shafer et al, 2005).*

Conditions in Hyporheic Zones

The wetland hyporheic zones showed favorable conditions for production of MeHg (see example in Fig 3). The decreasing concentrations of sulfate and increasing concentrations of sulfide with depth indicate sulfate reduction and the activity of sulfate-reducing bacteria. These bacteria are believed to be largely responsible for methylation of inorganic Hg(II) in reducing environments (Benoit et al., 1999; Hammerschmidt et al., 2004). Surface waters or recently infiltrated meteoric waters are the main source of sulfate to hyporheic zones, as evidenced by the high concentrations of sulfate (30 to 70 µM) in stream waters as compared to old ground waters (~ 1 µM). Even though groundwater flows upward (discharge) at the Allequash Creek site, mixing of ground water and surface water within the hyporheic zone is apparently sufficient to provide significant amounts of sulfate over the upper 15 cm. DOC concentrations in the hyporheic zones are higher than either surface water or ground water (Figure 3), indicating diagenesis of plant residues and/or peat. Profiles of NH_4 and Fe illustrate the influences of the hydrologic contrasts between the Allequash and Stevenson hyporheic zones (data not shown). At Stevenson (down flow), concentrations increased with depth, apparently reflecting production of NH_4 by organic matter diagensis and the enhancement of aqueous Fe by dissolution of Fe oxides. At the Allequash (up flow) site, concentrations exhibited subsurface maxima, apparently due to biogeochemical interactions influenced by the mixing of oxic surface water with oxygen-depleted ground water, producing a sub-oxic boundary created by bacterial oxidation of organic matter.

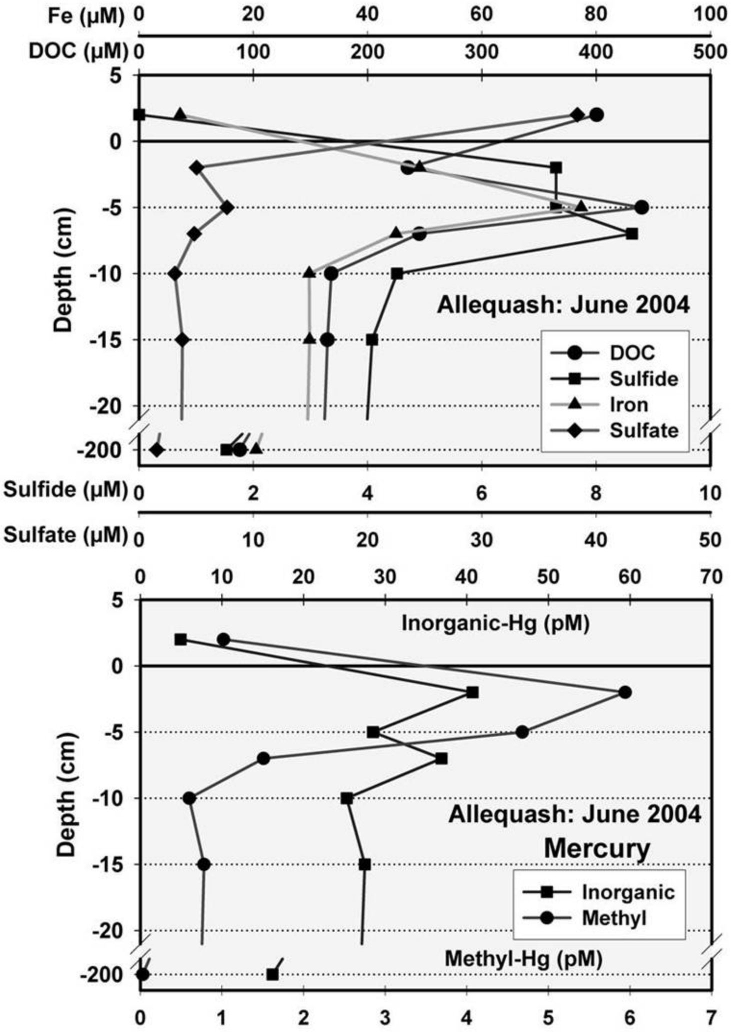

Figure 3. *Example profiles illustrating relation of total Hg and MeHg concentrations to biogeochemical processes in the hyporheic zone near Allequash Creek.*

Mercury in Ground Water and Hyporheic Zone Waters

Relatively high concentrations of MeHg were found in the hyporheic zones (Fig. 3, 4), indicating their importance for MeHg production. Concentrations varied considerably with site, depth, and time, likely reflecting differences in methylation – demethylation rates and partitioning between the aqueous and solid phases. MeHg concentrations peaked in the 0-5 cm zone of active sulfate reduction, as indicated by the declining sulfate and increasing sulfide concentration in this region (Fig. 3). Concentrations of MeHg in the hyporheic zones (0.2 to 1.2 ng/L) were higher than in either ground water (often < 0.03 ng/L, detection limit) or suface water (0.05 to 0.5 ng/L). This indicates that ground water discharge is not important as a direct source of MeHg to the hyporheic zone. Together, the data indicate that MeHg is largely produced within the hyporheic zone, and that the hyporheic zone is a source of MeHg to stream waters. In contrast, both ground waters and surface waters may be sources of Hg(II) to the hyporheic zone as shown by the overlapping concentrations observed in these waters. Concentration ranges observed were approximately 0.3 to 10, 0.5 to 6, and 1 to 10 ng/L for ground water, stream water, and hyporheic water, respectively.

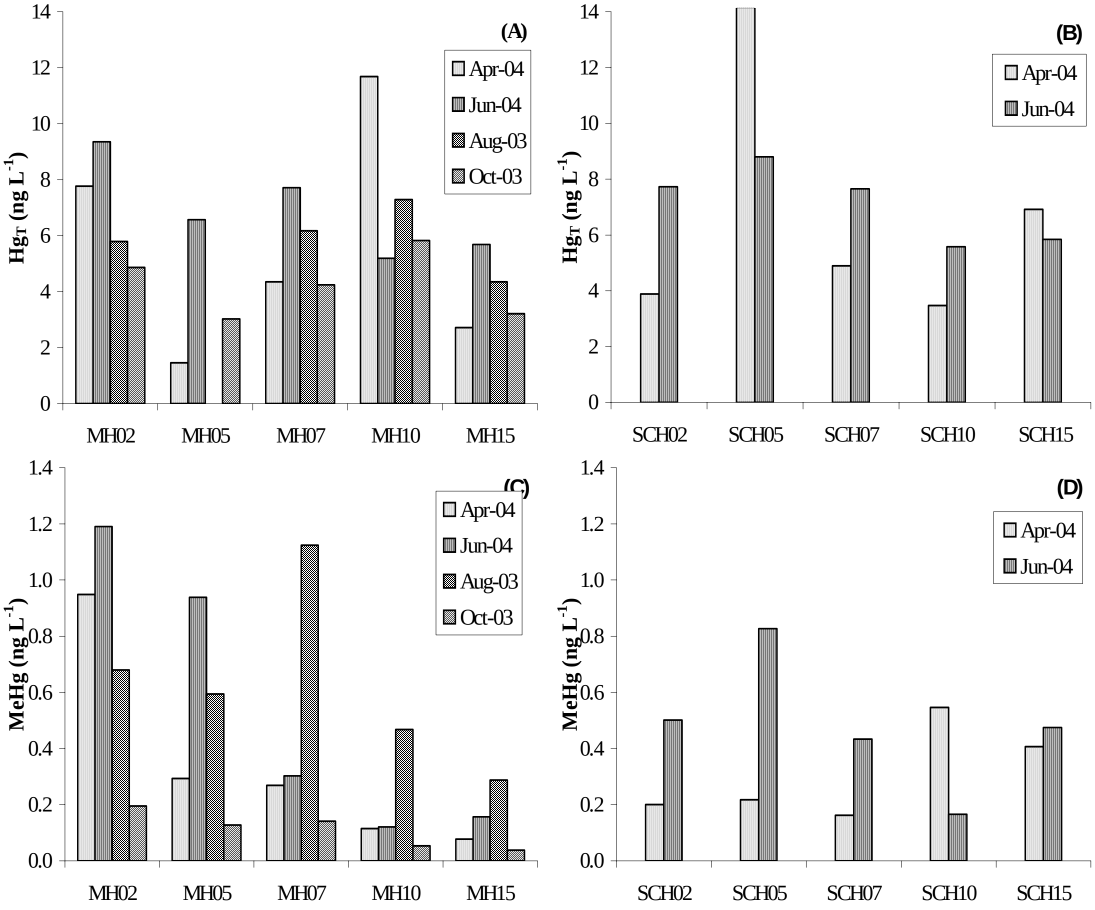

Figure 4: Concentrations of HgT and MeHg in hyporheic porewaters for Allequash Creek Middle Wetland (MH) and Stevenson Creek (SCH). The numbers on the x-axis are depth below the sediment surface (cm). (Meyer, 2005)

DOC likely plays a major role the transport of inorganic Hg(II) from ground water and surface water into the hyporheic zone where production of MeHg occurs. As observed in other systems, total Hg concentration was related to DOC (data not shown). Similarly, transport of MeHg from the hyporheic zone into surface waters is likely linked to transport of DOC. Evidence that the hyporheic zone is a source of MeHg to stream waters is observed in the relation of MeHg concentrations to Fe (Fig. 5). Concentrations of Fe are elevated in the anoxic hyporheic zone, apparently through reduction of solid-phase Fe(III) hydrous oxides. This leads to concurrent transport of Fe(II) and MeHg from the hyporheic zone into the stream.

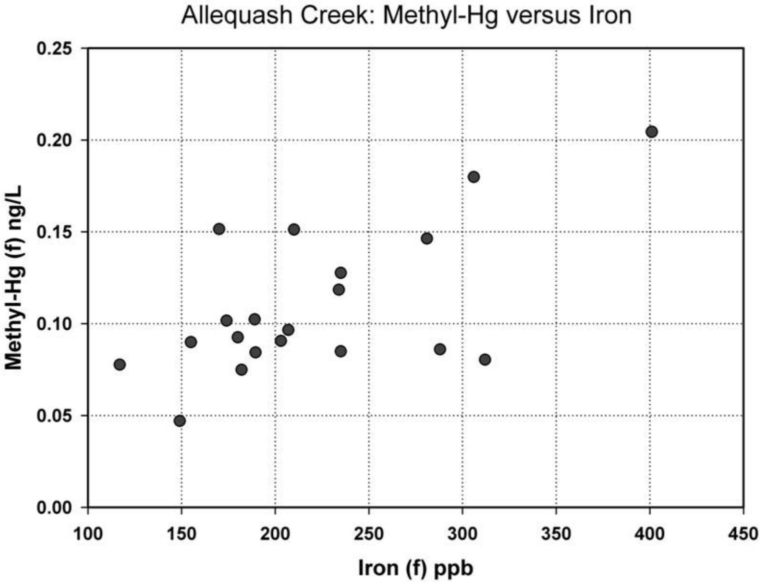

Figure 5. *Relation between MeHg and Fe indicates hyporheic zone is a source of MeHg to Allequash Creek (Shafer et al., 2005)*

Mercury Speciation

The production of MeHg is dependent in part on the bioavailability of Hg(II) to sulfate-reducing bacteria. The bioavailable species of Hg(II) is believed to be a neutral sulfide complex (Benoit et al., 1999). However, Hg(II) bound to DOC may not be bioavailable. Thus, bioavailability may be linked to concentrations of sulfide and DOC in the hyporheic zone. We investigated speciation through chemical modeling and experimental approaches. Modeling involved speciation calculations using reported binding constants and typical hyporheic zone conditions. These conditions included concentrations of sulfide, DOC, Fe(II), and pH as shown in Fig. 3. In addition, we used a anion exchange resin technique to experimentally probe the association of both Hg(II) and MeHg with sulfide and with DOM in anoxic waters comparable to those in hyporheic zones.

Speciation Modeling: Speciation calculations were performed using the chemical equilibrium modeling program MINEQL+ (Schecher and McAvoy, 1998). Modeling of the binding of Hg(II) by DOM was based on the best fit values for conditional equilibrium constants and a binding-site density of $5x10^{-9}$ sites per mg of DOC. Both the equilibrium constants and binding-site density were developed by Haitzer et al. (2003) in their investigation of seven DOM isolates. The equilibrium expressions obtained for deprotonation of the bidentate binding site and for association of Hg^{2+} with the fully deprotonated binding site are shown below. A log K for formation of the species HgS^0 was derived by Benoit et al. (1999).

$$H_2DOM \leftrightarrow HDOM^- + H^+ \quad \log K_1 = -6.3$$

$$HDOM^- \leftrightarrow DOM^{2-} + H^+ \quad \log K_2 = -10.3 \qquad Hg^{2+} + HS^- \leftrightarrow HgS^0 + H^+ \quad \log K = 26.5$$

$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$

Binding constants for the other Hg(II) sulfide species and for complexes with Cl^- and OH^- were used as reported in the MINEQL+ thermodynamic database. For equilibrium calculations, reactions with Hg^{2+} were converted to corresponding reactions with $Hg(OH)_2$, the Hg(II) "component" in MINEQL+ (see APPENDIX B for details).

MeHg complexation by sulfide was based on values from Stumm and Morgan (1996).

$$CH_3Hg^+ + S^{2=} \leftrightarrow CH_3HgS^- \quad \log K = 21.0$$

$$2CH_3Hg^+ + S^{2=} \leftrightarrow (CH_3Hg)_2S \quad \log K = 16.34$$

MeHg association with DOM was modeled based on the Amirbahman et al. (2002) investigation of binding of MeHg by humic acids. Values reported for the dominant DOM site, $RS(2)^-$, OH^-, and Cl^- are as follows:

$$MeHg^+ + H_2O \leftrightarrow MeHgOH + H^+ \quad \log K = -4.63$$

$$MeHg^+ + Cl^- \leftrightarrow MeHgCl \quad \log K = 5.22$$

$$H^+ + RS(2)^- \leftrightarrow RS(2)H \quad \log K = 7.0$$

$$MeHg^+ + RS(2)^- \leftrightarrow MeHg - RS(2) \quad \log K = 14.74$$

The corresponding equilibrium equations in MINEQL+ format using $MeHg^+$ as the component are shown in APPENDIX B:

Speciation Results: Modeling predicted dominance of Hg(II) sulfide complexes under "typical" hyporheic zone conditions (pH = 6.5, total S(-II) = 1 x10^{-6} M, Fe(II) = 1 x 10^{-4} M, Cl^- = 2 x 10^{-6} M, DOC = 6 mg/L; see Fig. 6). The dominant species was HgS^0 over pH range of 4 to 9 at this total sulfide concentration. Speciation is also influenced by the sulfide concentration. Dominance of the $HgHS_2^-$ negatively-charged species is important above total sulfide concentrations of 2 x 10^{-5} M, well above concentrations observed in hyporheic zone waters (see Appendix B, Fig. B-1). In the absence of sulfide, predicted speciation of Hg(II) is dominated by DOM, and the dominant species is HgDOM (Appendix B, Fig. B-2). The HgDOM species becomes dominant when the DOM site concentration exceeds 0.9 x 10^{-12} molar, i.e., when the DOM site concentration is about one-third of the total Hg(II) concentration. Thus, even though Hg(II) binds strongly to DOM, sulfide complexes will dominate even if concentrations of sulfide are low (i.e., when total sulfide concentration approaches the total Hg(II) concentration). Based on the formation equations used, modeling predicts that a DOM site concentration approximately 10^8 times higher than the HS^- concentration is required for equal concentrations of the HgDOM and HgS^0 species at pH = 6.5. When sulfide is absent, HgDOM complexes are predicted to dominate when the DOM site concentration approaches the total Hg(II) concentration (Fig. B-2).

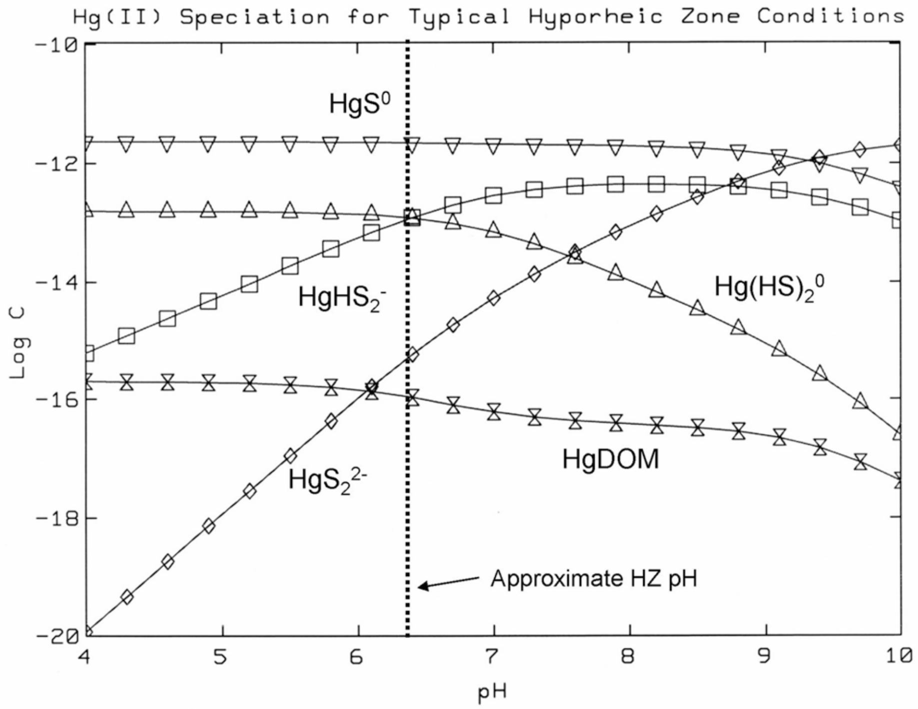

Figure 6. Modeled speciation of Hg(II) when S(-II) = 1E-6M and DOC = 6 mg/L, conditions typical of hyporheic zones.

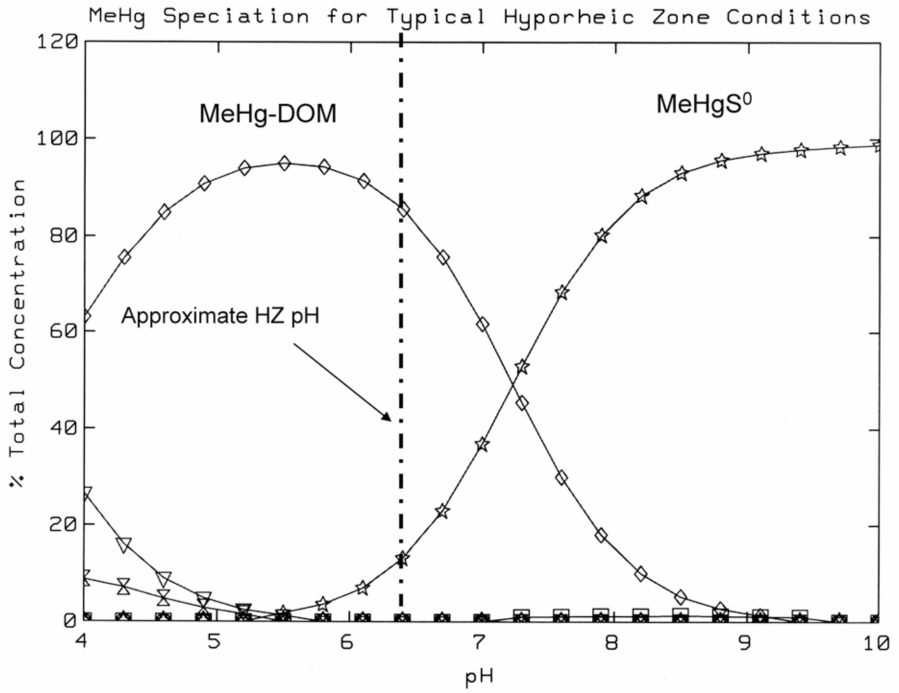

Figure 7. Modeled speciation of MeHg when total S(-II) = 1E-6 M and DOC = 6 mg/L

In contrast to Hg(II), DOM complexes of MeHg are predicted to be important in the presence of sulfide (Fig. 7.) For typical hyporheic zone conditions, the dominant species is a MeHg-DOM complex (designated MeHgRSb), but MeHgS still represents about 20% of the total aqueous MeHg. Species dominance is influenced by total S(-II) concentration. At pH = 6.5, sulfide and DOM complexes of MeHg are equally important at approximately 5 x 10^{-6} molar S(-II). At higher sulfide concentrations, MeHgS is the predicted dominant species (Appendix B, Fig. B-3).

While modeling indicated that neutral sulfide species of Hg(II) should be dominant in sulfidic pore waters, experimental measurements indicated DOM complexes of Hg(II) may be important in both oxic and anoxic waters (Table 1). We used a DEAE resin techniques to probe Hg speciation (Chadwick, 2006). The resin is expected to retain anionic species, including Hg(II) and MeHg complexed by DOM, while allowing neutral species to elute. The expected behavior of the resin was verified using synthetic solutions; anionic species were retained, and neutral species passed through the resin columns (Table 1). In oxic surface waters, the Hg was largely retained by the resin, consistent with binding of Hg to DOM. In anoxic waters the Hg was also retained by the resin, indicating Hg-DOM complexes remain dominant, even though modeling predicted dominance of neutral sulfide complexes of Hg(II). The smaller amounts of Hg that passed through the column could be either Hg(II) or MeHg bound in neutral sulfide complexes. The reasons for the apparent differences between modeled and measured speciation are uncertain, but modeled speciation is strongly influenced by the assumption of equilibrium and the accuracy of stability constants for Hg binding to sulfide.

Table 1. *Fractionation of Hg(II) and MeHg complexes based on net charge using a DEAE resin technique. Negative complexes are retained by the resin column; neutral complexes are eluted (from Chadwick, 2006). Equilibrium calculations indicate Hg(II) speciation should be dominated by neutral sulfide complexes in anoxic waters while experimental results indicate Hg(II) is dominated by negative (DOM) complexes in both oxic and anoxic waters. DL is the analytical detection limit.*

Description	Retained	Eluted
Synthetic Waters		
Neutral chloride complexes		
Hg(II)	< DL	> 95 %
MeHg	< DL	> 98 %
Neutral sulfide complexes of Hg(II)	< DL	> 94%
Anionic chloride complexes of Hg(II)	102 %	< DL
Natural Waters (Lake 658, West Basin; 8-18-03)		
Anoxic water; S(-II) = 8.3 nM	83 %	17 %
Anoxic water; S(-II) = 8.5 nM	80 %	20 %
Oxic water, 2 m	82 %	18 %
Oxic water, 5 m	85 %	15 %

CONCLUSIONS AND RECOMMENDATIONS

Hyporheic zones are important sites for MeHg production and transport to surface waters. High DOC concentrations combined with sulfate (introduced mainly from surface water) promote the activity of sulfate-reducing bacteria (SRB). Derived partly from groundwater, inorganic Hg(II) is converted to MeHg and transported into surface waters. Speciation modeling indicates that HgS^0 is dominant in these sulfidic waters, and that should facilitate methylation because neutral species of Hg(II) are presumed to be more available for uptake by SRB. However, experimental data indicates Hg(II) is bound mainly by dissolved organic matter (DOM), indicating bioavailability of Hg(II) to SRB may be impeded by binding to DOM. Further investigations should explore the factors and conditions controlling methylation rates in hyporheic zones so that practices that might limit MeHg production can be incorporated into wetland management.

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Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005b. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

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APPENDIX A: Awards, Publications, Reports, Patents, and Presentations

Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract – Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.

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APPENDIX B: Supplemental Information

Speciation Calculations.

Speciation calculations were performed using the chemical equilibrium model MINEQL+ (Schecher and McAvoy, 1998). Modeling of the binding of Hg(II) by DOM was based on the best fit values for conditional equilibrium constants and binding site density ($5\text{x}10^{-9}$ sites per mg of DOC) developed by Haitzer et al. (2003) in their investigation of seven DOM isolates. The equilibrium expressions obtained for deprotonation of the bidentate binding site and for association of Hg^{2+} with the fully deprotonated binding site are as follows:

$$H_2DOM \leftrightarrow HDOM^- + H^+ \quad \log K_1 = -6.3$$
$$HDOM^- \leftrightarrow DOM^{2-} + H^+ \quad \log K_2 = -10.3$$
$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$

For equilibrium calculations, reactions with Hg^{2+} were converted to corresponding reactions with $Hg(OH)_2$, the Hg(II) "component" in MINEQL+, e.g.,

$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$
$$Hg(OH)_2 \leftrightarrow Hg^{2+} + 2OH^- \quad \log K = -21.2$$
$$2OH^- + 2H^+ \leftrightarrow 2H_2O \quad \log K = 28.0$$
$$\therefore Hg(OH)_2 + DOM^{2-} + 2H^+ \leftrightarrow HgDOM + 2H_2O \quad \log K = 35.5$$

A log K for formation of the species HgS^0 was derived by Benoit et al. (1999).

$$Hg^{2+} + HS^- \leftrightarrow HgS^0 + H^+ \quad \log K = 26.5$$

Binding constants for the other Hg(II) sulfide species and for complexes with Cl^- and OH^- were used as reported in the MINEQL+ thermodynamic data base. In MINEQL+ format, the following reactions were used for calculation of Hg(II) binding to DOM and S(-II):

$$[HDOM^-] = [H^+][DOM^{2-}] \cdot 10^{10.3}$$
$$[H_2DOM] = [H^+]^2[DOM] \cdot 10^{16.6}$$
$$[HgDOM] = [Hg(OH)_2][H_2O]^{-2}[H^+]^2[DOM^{2-}]$$
$$[H_2S_{(aq)}] = [H^+][HS^-] \cdot 10^{7.02}$$
$$[S^{2-}] = [H^+]^{-1}[HS^-] \cdot 10^{-17.3}$$
$$[Hg(HS)_2^0] = [H_2O]^{-2}[H^+]^2[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{44.51}$$
$$[HgHS_2^-] = [H_2O]^{-2}[H^+]^1[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{38.12}$$
$$[HgHS_2^{2-}] = [H_2O]^{-2}[H^+]^0[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{29.41}$$
$$[HgS^0] = [H_2O]^{-2}[H^+]^1[Hg(OH)_2]^1[HS^-]^1 \cdot 10^{32.69}$$

Reactions of for complexation of MeHg with sulfide are reported by Stumm and Morgan (1996):

$$CH_3Hg^+ + S^{2=} \leftrightarrow CH_3HgS^- \quad \log K = 21.0$$
$$2CH_3Hg^+ + S^{2=} \leftrightarrow (CH_3Hg)_2S \quad \log K = 16.34$$

Amirbahman et al. (2002) investigated the binding of MeHg by humic acids. Through modeling of experimental data, they obtained three binding sites, designated RS(1)$^-$, RS(2)$^-$, and RS(3)$^-$. Reactions for formation of OH$^-$ and Cl$^-$ complexes for deprotonation of the DOM binding sites were modeled as:

$$MeHg^+ + H_2O \leftrightarrow MeHgOH + H^+ \quad \log K = -4.63$$
$$MeHg^+ + Cl^- \leftrightarrow MeHgCl \quad \log K = 5.22$$
$$H^+ + RS(1)^- \leftrightarrow RS(1)H \quad \log K = 4.0$$
$$H^+ + RS(2)^- \leftrightarrow RS(2)H \quad \log K = 7.0$$
$$H^+ + RS(3)^- \leftrightarrow RS(3)H \quad \log K = 10.0$$

Binding constants varied somewhat among the different humic acids investigated. For Suwanee River humic acids, the binding to the DOM sites was modeled as:

$$MeHg^+ + RS(1)^- \leftrightarrow MeHg - RS(1) \quad \log K = 10.39$$
$$MeHg^+ + RS(2)^- \leftrightarrow MeHg - RS(2) \quad \log K = 14.74$$
$$MeHg^+ + RS(3)^- \leftrightarrow MeHg - RS(3) \quad \log K = 14.84$$

Site densities (nmol/mg DOC) for this humic acid were estimated as 0.15, 0.24, and 1.44 for RS(1)$^-$. RS(2)$^-$, and RS(3)$^-$, respectively.

The corresponding equilibrium equations in MINEQL+ format using MeHg$^+$ as the component are:

$$[MeHgOH] = [MeHg^+][H_2O]^1[H^+]^{-1} \cdot 10^{-4.63}$$
$$[MeHgCl] = [MeHg^+][Cl^-] \cdot 10^{5.22}$$
$$[RSaH] = [H^+][RSa^-] \cdot 10^{4.0}$$
$$[RSbH] = [H^+][RSb^-] \cdot 10^{7.0}$$
$$[RScH] = [H^+][RSc^-] \cdot 10^{10.0}$$
$$[MeHg - RSa] = [MeHg^+][RSa^-] \cdot 10^{10.39}$$
$$[MeHg - RSb] = [MeHg^+][RSb^-] \cdot 10^{14.74}$$
$$[MeHg - RSc] = [MeHg^+][RSc^-] \cdot 10^{14.84}$$

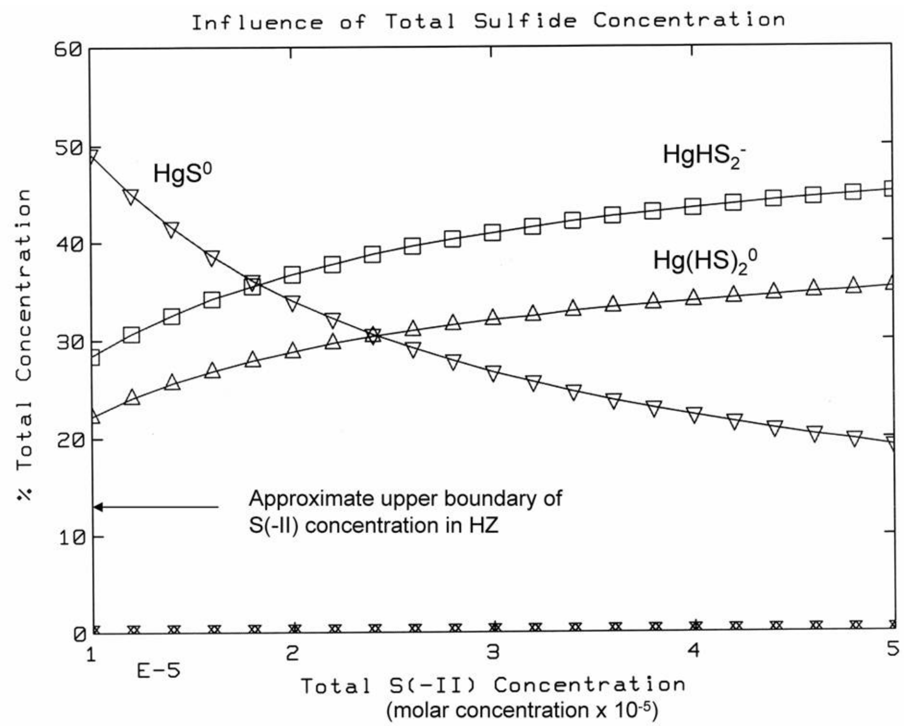


Figure B-1. Modeled influence of sulfide concentration on speciation of Hg(II); pH = 6.5 and DOC = 6 mg/L

2: Hg(HS)2 (△ 2: HgHS2-1 □ 2: HgS2-2 ◇ 2: DOMHg ⧖ 2: HgS(aq) ▽

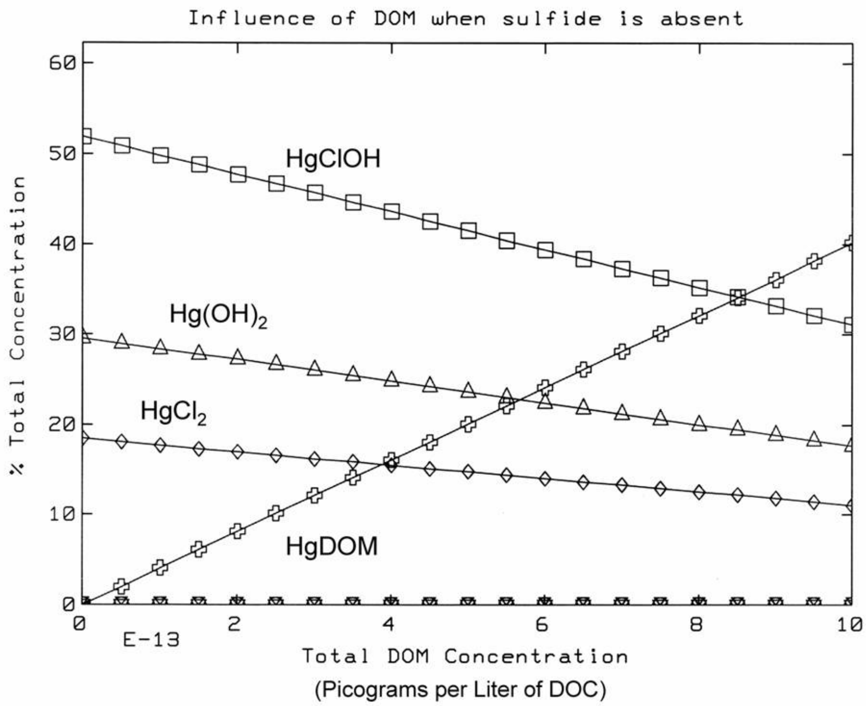
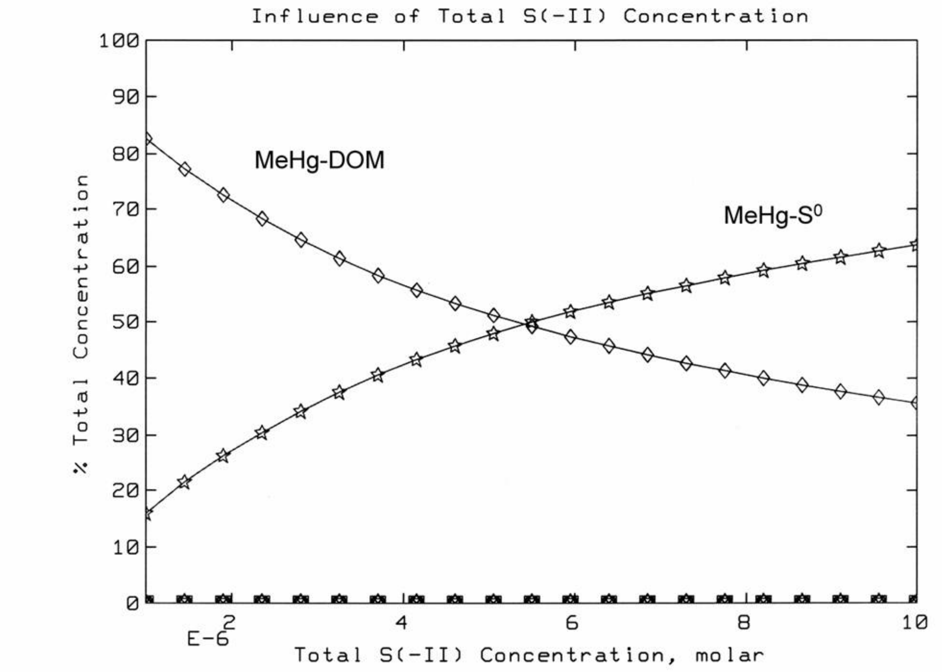


Figure B-2. Influence of DOM concentration on Hg(II) speciation when sulfide is absent and pH = 6.5

1: Hg(OH)2 △ 2: HgClOH (a □ 2: HgCl2 (aq ◇ 2: HgHCO3+ ⧖ 2: HgCO3 (aq ▽
2: HgOH+ ○ 2: DOMHg ✣



(molar concentration times 10^{-6})

Figure B-3. Influence of sulfide concentration on MeHg speciation at pH = 6.5

1: MeHg △ 2: MeHgRSc □ 2: MeHgRSb ◇ 2: MeHgRSa ⧖ 2: MeHgCl ▽
2: MeHgOH ○ 2: (MeHg)2S ✣ 2: MeHgS ☆