Methylmercury Bioavailability and Dynamics in the Streams of Piasa Creek Watershed: New Methods of Sampling and Analysis

Basic Information

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Publication

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Research Problem:

Relatively little is known about Hg contamination in Illinois surface waters. In particular, very few measurements of dissolved methylmercury (MeHg) – the most potent neurotoxin of all the Hg species and the only form of Hg that biomagnifies in aquatic food webs – in rivers and streams draining agricultural watersheds have been reported. Thus, little basis exists for linking the impacts of atmospheric deposition of Hg to MeHg in aquatic food webs, particularly in the main class of aquatic ecosystems in Illinois: riverine or lotic ecosystems.

Methodology:

The field work and lab analysis phase of our study involved obtaining measurements of filterable (or dissolved) total Hg (FTHg) and MeHg (FMeHg) levels in a small, mixed land use watershed in southwestern Illinois. We are now in the data analysis/modeling phase of the project. The study was designed to serve the following purposes:

1) Expand our knowledge of the hydrogeochemical factors influencing FTHg and FMeHg levels in Illinois' rivers and streams by measuring dissolved Hg_T and MeHg monthly at 12 sites across the Piasa Creek watershed along with *p*H, dissolved organic carbon (DOC), UV absorbance, and a suite of anions (NO_3^-, Cl^-, and SO_4^{2-}).
2) Test a newly-developed approach for sampling bioavailable MeHg – DGT probes – that could help reduce the cost of monitoring MeHg levels in surface water systems.
3) Measure MeHg in biota: crayfish, stonefly nymphs, shiners, and darters were sampled at the same 12 sites as surface water samples in June 2007. Crayfish and stonefly nymphs are less mobile than the free-swimming darters and shiners and therefore should represent location-specific indicators of MeHg bioavailability in the Piasa Creek food web.

Principal Findings and Significance.

1) Filterable MeHg and THg in streamwater were measured every month (13 events) over the period from June 2007 through June 2008 at twelve sites in the Piasa Creek watershed (Fig. 1). A total of 153 samples were analyzed for FTHg and 162 for FMeHg.
2) There is significant variation in average MeHg across the watershed (Fig. 2) that we will seek to explain using spatial data analysis and modeling. MeHg is highest in headwaters catchments with low forested area.

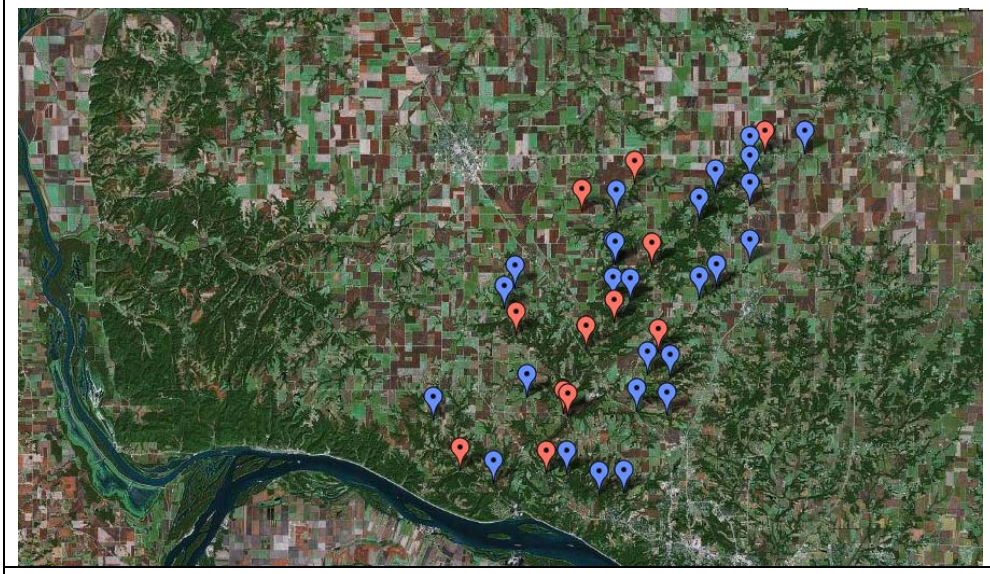

Figure 1. Sampling locations in Piasa Creek near Alton, IL. Orange symbols indicate monthly sampling locations. Blue symbols indicate locations for detailed survey of organic matter in streamwater. Image courtesy of Google Maps.

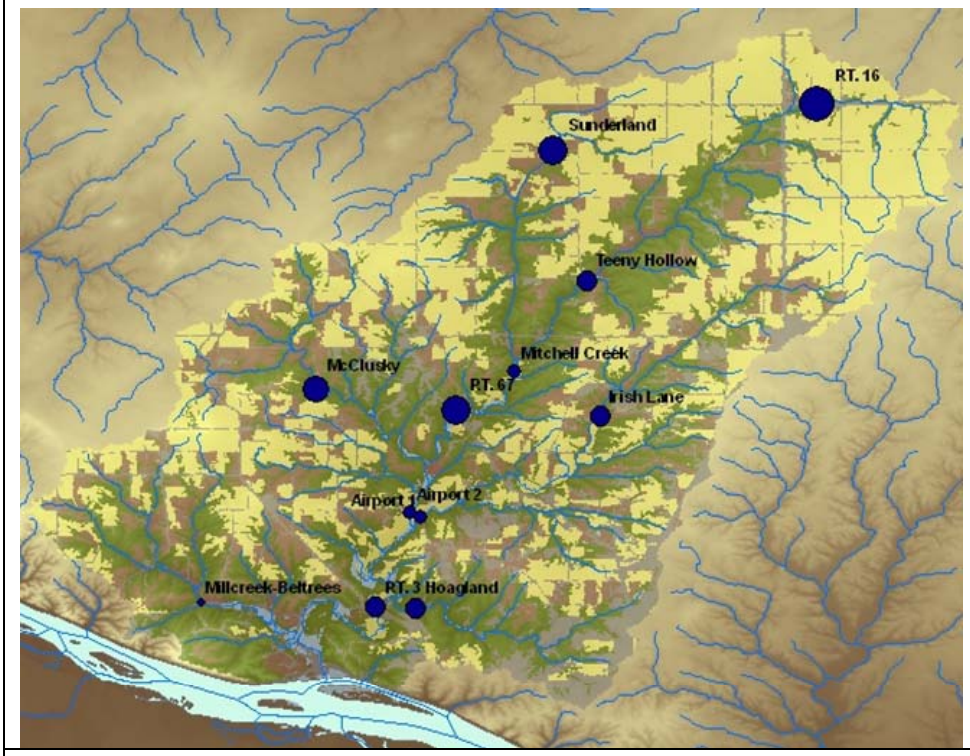

Figure 2. Spatial variability in mean MeHg in Piasa Creek. Land use is indicated by color of shading: Agriculture = Yellow, Forest = Green. Image by Chris Ivanovich.

3) As is frequently observed elsewhere, we found that total Hg and MeHg are best correlated with dissolved organic matter, measured as DOC in Piasa Creek (Fig. 3A,B). Interestingly, MeHg is correlated even more strongly with UV absorbance, a measure of hydrophobic organic matter, than with DOC (Fig. 3C).

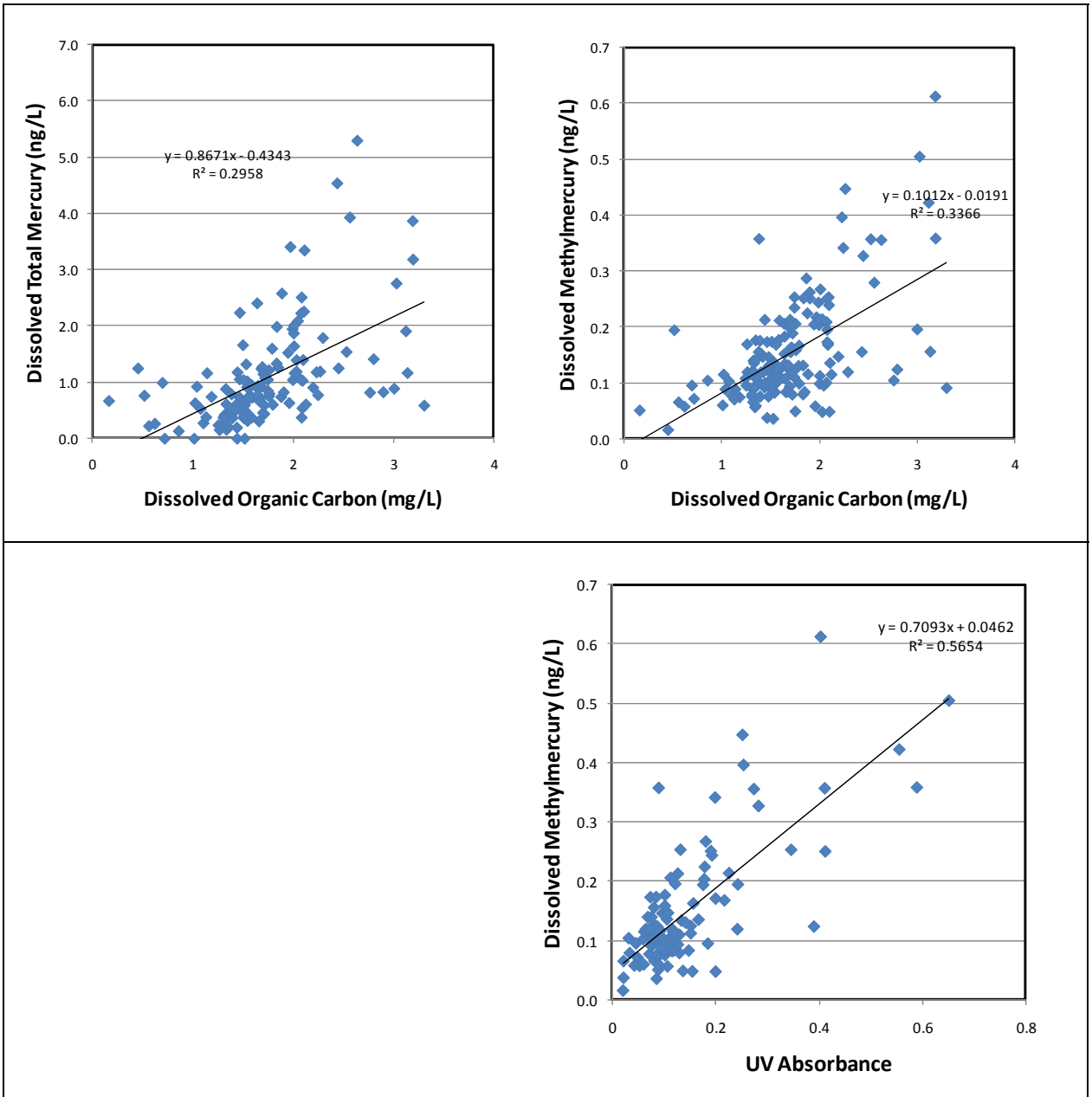

Figure 3. Bivariate plots of filtered Total Hg and MeHg in Piasa Creek samples from 2007-08 with dissolved organic matter and UV absorbance at 254 nm. A: Top right; B: Top right; C Bottom right.

4) MeHg and inorganic Hg were measured in 110 organisms collected during the summer of 2007. As these organisms are relatively low trophic level organisms, none exceeded EPA's Hg criterion of 0.3 ppm. However, when the biota MeHg data generated here are combined with the USGS National Descriptive Model of Mercury in Fish, it predicts that other resident

species (white bass and black crappie) of the Piasa Creek watershed will contain levels of MeHg that exceed the 0.3 ppm human consumption guideline designated by the USEPA at relatively small lengths of 6-8 inches. Such a prediction needs to be substantiated by measuring the MeHg content of these other resident fish species, because they are popular among human that consume fish for sustenance.

5) The DGT-type passive sampling devices were deployed during June 2007 at the twelve regular sampling locations. However, data were obtained from only 10 sites as humans disturbed the probes deployed at two sites. Some probes appeared to have not functioned properly, apparently because the high water velocities in the stream caused leakage of water past the diffusive gel layer. Modifications to the design of the physical properties of the probes are needed before re-testing. Nevertheless, a weak relationship of DGT-MeHg to MeHg in biota was observed (Fig. 4B).

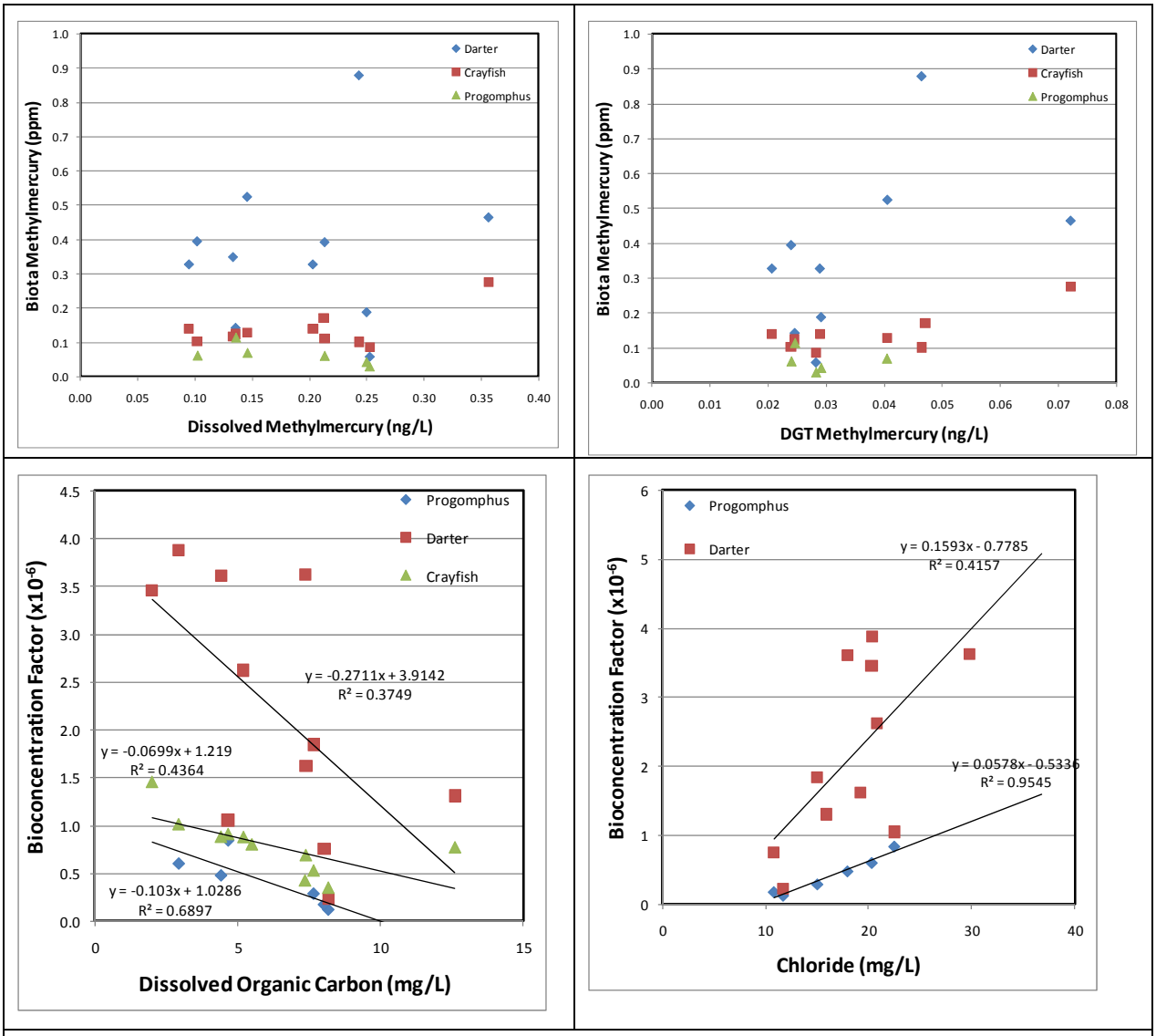

Figure 4. Relationships between MeHg in biota and FMeHg (A: upper left), DGT-MeHg (B: upper right).

6) The relationship of MeHg in biota to FMeHg is weak (Fig. 4A). We hypothesize that this is due to the dependence of MeHg bioavailability on other parameters, such as DOC, Cl, and pH. One approach to investigating this issue is to search for relationships between these parameters and the MeHg bioconcentration factor, which is calculated as the ratio of MeHg in biota to that in FMeHg for the same site. We found that the MeHg bioconcentration factors depend negatively on DOC and positively on Cl (for two species). This is consistent with the standard model for MeHg bioavailability in freshwater, which suggests that MeHg uptake into food webs may be controlled by a set of reactions that can be approximated by:

$$MeHg - DOM + Cl^{-} \longleftrightarrow MeHgCl^{0} + DOM$$

$$MeHgCl^{0} \longrightarrow MeHg_{BIOTA}$$

Although such effects of DOM are not unusual, the enhancement of bioavailability by Cl is rarely reported despite it being a core prediction of the standard model for MeHg uptake into food webs. Therefore, we are excited about the prospect that further careful analysis of these data will shed new light on the bioavailability of MeHg in freshwater ecosystems.

Notable achievements:

1) Using novel analytical techniques developed in our lab at the University of Illinois Urbana-Champaign, we have measured:
   i) The MeHg content of four aquatic organisms (110 individuals) sampled in June 2007 from 12 locations in the Piasa Creek watershed,
   ii) The dissolved MeHg and THg content of 152-163 surface waters samples collected between June 2007 and June 2008 from 12 locations within the Piasa Creek watershed,
   iii) The amount of accumulated MeHg in 30 DGT probes deployed in June 2007 from 10 locations in the Piasa Creek watershed. However, as mentioned above due to a design flaw in the probes these data appear to be compromised.
2) The total Hg and MeHg data are most strongly correlated with measures of dissolved organic matter in the streamwater. The degree of correlation is greatest between FMeHg and UV absorbance, which measures hydrophobic dissolved organic matter.
3) Bioconcentration factors calculated by site for crayfish, stonefly nymphs, and shiners were inversely correlated with DOC and positively correlated with Cl, which is consistent with chemical models for biota-MeHg interactions with DOC.
4) Bioconcentration factors calculated by site for darters were not correlated with DOC, suggesting that darters either possess a unique MeHg uptake pathway, compared to the other organisms analyzed in this study, or are more mobile.

Students Supported:

Brian Vermillion, Department of Natural Resources and Environmental Sciences, University of Illinois, Ph.D. student, degree expected (8/2009).

Chris Ivanovitch was a National Great Rivers Research and Education Center intern in the summer of 2008. His internship was indirectly supported by this project since he worked these data.

Publications and Presentations:

Results were presented at the Illinois State Academy of Science meeting in April 2008 and at the Illinois Water conference in October 2008.