Graham Lab
Summer 2016 Research Description

Overview
The Graham Research Laboratory investigates the biogeochemistry of minor and trace elements in aquatic systems. We are interested in understanding how biogeochemical cycling of C, S, and Fe impact trace element cycling, with a special focus on mercury (Hg). There are two projects planned for Summer 2016 related to this theme.

Project 1: Reconnaissance of Hg Biogeochemical Cycling in a Lower Cedar River Floodplain
Mercury contamination is a serious environmental problem due to methylmercury (MeHg) bioaccumulation in aquatic food webs and associated impacts to wildlife and human health (Driscoll et al., 2013). Inorganic forms of mercury (inorganic Hg(II) and Hg(0)) are released into the environment primarily by coal combustion and artisanal gold mining (Streets et al., 2011). Inorganic forms of mercury are converted to the more toxic and bioaccumulative organic form MeHg by a variety of microorganisms that inhabit anoxic environments such as lake bottom sediments, flooded soils, and wetlands (Compeau and Bartha, 1985; Gilmour et al., 1992; Fleming et al., 2006; Kerin et al., 2006; Gilmour et al., 2013). Understanding the biogeochemical cycling of Hg is essential to developing environmental management strategies designed to limit the deleterious effects of Hg pollution.

During Summer 2016, we will investigate Hg cycling in a savanna floodplain along the Cedar River in East-Central Iowa. Iowa is within a zone of relatively high wet deposition of Hg (MDN, 2015), but the fate of this Hg in Iowa’s terrestrial and aquatic ecosystems is largely unknown; our investigation will be among the first attempts to characterize MeHg and total Hg fluxes within Iowa’s ecosystems. Beginning this summer, we aim to measure MeHg and total Hg concentrations within shallow groundwaters and surface waters within and near the Swamp White Oak (SWO) Nature Preserve (see maps below).

Figure 1. Google Earth images of the Swamp White Oak Preserve field site.
In addition to measuring Hg/MeHg concentrations, we will monitor river discharge, water table elevations, and various geochemical parameters (dissolved oxygen, Fe and Mn, N species, and dissolved organic carbon). We hypothesize that significant MeHg production occurs in seasonally anoxic/suboxic alluvial groundwaters at the SWO preserve, and that these groundwaters are net sources of MeHg to the Cedar River. Furthermore, we expect that temporal and geomorphic variation in the quality and quantity of dissolved organic matter (DOM) will play an important role in spatiotemporal variations in MeHg production within the floodplain (Graham et al., 2012; 2013). The student working on this project will learn methods of trace-element field sampling of surface and groundwaters, methods for MeHg (isotope dilution gas-chromatography inductively coupled plasma mass spectrometry; ID-GC-ICP-MS), total Hg (SnCl₂ reduction with gold trap amalgamation and ICP-MS) analysis, and various other wet chemical techniques common to the geochemistry laboratory.

**Project 2: Kinetics of Methylmercury Degradation in Sulfidic Solutions**

Methylmercury produced in anoxic environments can be degraded and/or transformed by photochemical (Zhang and Hsu-Kim, 2010) and biological processes (Barkay et al., 2003). The impact of MeHg on ecosystems and human health ultimately depends on net MeHg accumulation – the balance between MeHg production and MeHg degradation. MeHg degradation by microorganisms possessing the *mer* operon has been thoroughly studied (see review by Barkay et al., 2003), but MeHg degradation by anaerobes lacking the *mer* operon (e.g. sulfate reducing bacteria (SRB)) has received minimal attention (Bridou et al., 2010; Marvin-DiPasquale et al., 2000; Oremland et al., 1991; Pak and Bartha, 1998). Complicating matters further, MeHg may undergo purely chemical transformation in sulfide-rich aqueous solutions (Rowland et al., 1977; Asaduzzaman and Schreckenbach, 2010), like those expected in wetland soils or bottom sediments with active SRB. The proposed research aims to study biological and chemical transformations of MeHg in sulfidic solutions. Findings of the proposed research will inform models for the global biogeochemical cycling of Hg and the development of strategies to protect human health and the natural environment.

This past summer, two MAP students (Emma Leverich and Xiaoxuan Yang) looked at the impact of MeHg speciation on MeHg degradation by a model SRB, *Desulfovibrio desulfuricans* DSM Strain 6949. We found that MeHg bound to thioacetic acid and glutathione was not degraded by *D. desulfuricans* but MeHg bound to cysteine or inorganic sulfide was rapidly degraded. These exciting findings suggested a previously unrecognized impact of MeHg speciation on biological MeHg degradation. More recent experiments have suggested that the observed MeHg loss may be purely chemical in nature, and may involve degradation of MeHg by sulfide via formation of a bis(methylmercury)sulfide complex and subsequent degradation to dimethylmercury and mercuric sulfide (HgS) (Asaduzzaman and Schreckenbach, 2010). This summer we plan to continue investigations of both biological and abiotic MeHg degradation to help clarify the mechanism(s) of the observed MeHg loss.

In a first track of experiments, we will determine the kinetics of abiotic MeHg transformation in the presence of inorganic sulfide. Briefly, we will vary the concentrations of MeHg, sulfide, solution pH, and other ligands (e.g., thiols and dissolved organic matter) and measure loss of MeHg over time. By determining the reaction rate as a function of these experimental conditions, we will gain insight into the reaction mechanism and develop a predictive rate law. All experiments will be carried out under strict O₂-free conditions in zero headspace bottles to prevent losses of volatile products. MeHg concentrations will be measured using a direct ethylation ID-GC-ICP-MS method (Bowman and Hammerschmidt, 2011). The GC-ICP-MS method also affords us the potential to determine one of the proposed products of the reaction, dimethylmercury. Total Hg will be determined using on-line SnCl₂ reduction with detection of Hg⁰ vapor ICP-MS to determine mass balance (Graham et al., 2012). In parallel experiments, we will measure MeHg losses in the presence of a model sulfate-reducing
bacterium, *Desulfovibrio desulfuricans* DSM strain 6949 conditions mirroring those of abiotic experiments. By comparing the results of the two sets of experiments, we will more clearly determine the role of direct vs. indirect biological MeHg transformation in previously observed losses of MeHg in active cultures (Leverich, 2015; Yang, 2015). In these experiments, MeHg will be quantified as total MeHg (monomethylmercury and dimethylmercury) using steam distillation and ID-GC-ICP-MS. As in abiotic experiments, total Hg will be quantified to close mass balance. The student working on this project will learn methods of culturing obligate anaerobic bacteria, methods of trace Hg and MeHg analysis, computer-based modeling of MeHg equilibrium speciation, and possibly mathematical modeling of kinetic data.

**References**


