**Measurement and Modeling of Methylmercury Production in Periphyton Biofilms**

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Biogeochemical gradients established across the water – periphyton – stream bed sediment interfaces create zones that can exert controlling influence on material transformations. In this task, we address the role of the water-biofilm interface on mercury (Hg) transformations as a use case. Previous SFA research demonstrates that actively photosynthesizing periphyton biofilms are net sources of the potent neurotoxin monomethyl mercury (MMHg) in East Fork Poplar Creek (EFPC) in Tennessee. Net MMHg production in environmental settings occurs in a broad and complex biogeochemical framework requiring bioavailable Hg, anaerobic conditions, active methylating microorganisms, and methylation rates that exceed those of competing reactions (e.g., demethylation, reactions that sequester Hg). Ancillary chemical analyses of the EFPC biofilms demonstrate active anaerobic communities are present. Microelectrode techniques demonstrate steep gradients in biogeochemical parameters and dynamic Fe and S redox cycling across a few millimeters of the water-biofilm interface. Bulk measurements of periphyton show low molecular thiol compounds that can enhance Hg bioavailability are present in the extracellular matrix.

Periphyton grown on surfaces at upstream (closer to the historic point source of contamination) and downstream locations (~17 km apart) were collected for use in laboratory time-course assays of inorganic Hg methylation and MMHg demethylation. Tin(II) reducible Hg was measured over time as a proxy measure of Hg available for methylation. Additionally, the influence of season and light exposure during biofilm growth were investigated.

The data were divided into a model training data set and validation data set. Methylation \( (k_m) \) and demethylation \( (k_d) \) rate constants were determined by fitting a series of increasingly complex kinetic models to the training data. Model formulations followed the progression: Model 1: methylation and demethylation were assumed to be irreversible over the incubation time course and each methylation and demethylation data set was modeled in isolation; Model 2: Hg was assumed to cycle between Hg and MMHg during experiments and paired methylation-demethylation rate data were modeled simultaneously; Model 3: same as Model 2 with the added assumption of a time-dependent accumulation of Hg in a pool that is unavailable for methylation.

Both Hg methylation and MMHg demethylation occur within the periphyton biofilms. Upstream versus downstream temperature-dependent differences in net methylation were driven by differences in \( k_d \) (lower downstream). Within-site temperature-dependent differences in net methylation were driven by changes in \( k_m \) (increased with temperature). Compared to samples grown and incubated in the light, samples grown and incubated in the dark had similar \( k_m \) values but \( k_d \) values that were 10× greater. Models 1 and 2 provided comparable fits to the data and could not capture the observed early time change in methylation rate. Model 3 outperformed Models 1 and 2, and reproduced the early change in the methylation rate. Using parameter estimates from fitting Model 3 to the training data, the validation data set was predicted. Overall, Model 3 approximated the validation data set reasonably well. Assessment of model-prediction uncertainty is ongoing.