

Poster #21-24

Kinetics of Mercury Methylation Revisited

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BER Program: SBR

Project: ORNL Critical Interfaces Scientific Focus Area (CI-SFA)

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Anthropogenic activities have disrupted the natural mercury (Hg) cycle releasing large amounts of this naturally occurring toxic element. The neurotoxin methylmercury (MeHg) is rarely a direct pollutant rather it is formed in the environment by a microbially mediated process known as mercury methylation. MeHg can also be demethylated via biotic and abiotic processes. To build models that predict MeHg levels in natural systems, scientists measure methylation and demethylation rates in laboratory experiments. We previously demonstrated that periphyton biofilms can be important sources of MeHg in East Fork Poplar Creek in Oak Ridge, TN (Olsen et al. 2016). Examination of our results and other published data sets suggested a new model of methylation/demethylation kinetics was needed because the data are typically analyzed using simple first-order rate expressions even though these data often exhibit kinetics that are inconsistent with first-order kinetic models. We hypothesized that apparent non-first-order dynamics in methylation/demethylation experiments was the result of competing kinetic reactions that reversibly converted Hg and MeHg to unavailable states. Using time-resolved measurements of filter passing Hg and MeHg during methylation/demethylation assays, a multisite kinetic sorption model, and re-analyses of previous assays, we show that competing kinetic sorption reactions can lead to time-varying availability and apparent non-first-order kinetics in Hg methylation and MeHg demethylation. The new model employing a multi-site kinetic sorption model for Hg and MeHg can describe the range of behaviors for time-resolved methylation/demethylation data reported in the literature including those that exhibit non first-order kinetics. Additionally, we show that neglecting competing sorption processes can confound analyses of methylation/demethylation assays, resulting in rate constant estimates that are systematically biased low. Simulations of MeHg production and transport in a hypothetical periphyton biofilm bed illustrate the implications of our new model and demonstrate that methylmercury production may be significantly different than projected by single-rate first-order models (Olsen et al., in press). Future work will seek to expand this model for application to metabolically active transient storage zones within the creek sediments.

References:

Olsen et al, 2016. Environ. Sci. Technol. 50, 10843-10850. Olsen et al, 2018. Environ. Sci. Technol. *In press*.