Biogeochemical transformations at critical interfaces in a mercury perturbed watershed scientific focus area

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Project Abstract: Freshwater resources supplied by headwater streams and their surrounding watersheds are being threatened by severe pollution from anthropogenic releases of nutrients and trace metals (e.g., mercury [Hg]). Preserving these services for future use requires developing a deeper understanding of watershed structure and function. Research findings during Phase I of the Critical Interfaces Scientific Focus Area (SFA) project have led to the realization that transient storage zones (TSZs), and more specifically metabolically active transient storage zones (MATSZs), are hot spots for biogeochemical transformations that can exert a controlling influence on downstream water quality. TSZs are surface and subsurface locations (e.g., hyporheic zone) that delay the downstream flow of water in comparison to the main channel. In Phase II, the project aims ***to determine the fundamental mechanisms and environmental controls on Hg biogeochemical transformations in MATSZs in low-order streams***. A key component of this effort is to parameterize our biogeochemical modeling framework for predicting Hg transformations in East Fork Poplar Creek (EFPC).

In FY20, the SFA team has (1) added new capabilities to Advanced Terrestrial Simulator modeling software that integrates multiple components of EFPC watershed hydrology, (2) refined our transient availability model by including the impact sediment type has on net methylmercury (MeHg) production, (3) explored the transcriptional regulation of *hgcA* under different growth parameters, (4) examined complex biogeochemical controls on Hg methylation, and (5) performed assays of the HgcAB complex in a *E. coli* expression host and have taken significant steps to evaluate potential cellular metabolites essential for methylation activity. We have also explored the mechanisms of abiotic dimethylmercury formation using density functional theory (DFT) calculations and determined that Hg isotope exchange reactions can alter native mercury isotope compositions, complicating the interpretation of Hg methylation and demethylation assays. We developed a new approach that definitively determined the functional group assignments, electronic structure, and coordination geometry and binding interactions that characterize methanobactin-metal complexes and used this information to help explain the differences in Hg methylation potential caused by different types of methanobactin. Collectively, the aforementioned activities are providing a deeper understanding of Hg transformations in EFPC and allowing us to gain the process knowledge needed to improve predictions of Hg transformations at the scale of individual stream reaches and small watershed catchments.