Isotopic Characterization of Biogeochemical Pools of Mercury and Determination of Reaction Pathways for Mercury Methylation

University-Led Research

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The project objective is to use stable Hg isotope measurements to reveal locations of Hg methylation in the Poplar Creek (PC) watershed, TN and place new constraints on the processes that lead to methyl mercury (MeHg) production, transport and degradation. We seek to better understand the decoupling of inorganic Hg and MeHg concentrations in the East Fork PC (EFPC) ecosystem. We are using a two-pronged approach that involves 1) an ecosystem level study of natural samples, and 2) experimental studies of Hg isotope fractionation. Natural samples are being collected from wetland sediments, stream sediments and waters, stream bottom periphyton and, as a monitor of the MeHg in the ecosystem, young-of-year herbivore/ detritivore stoneroller minnows and omnivore/piscivores redbreast sunfish. During the first 6 months of this new project we: 1) completed a sampling campaign for water, sediment and periphyton from EFPC, Hinds Creek and adjacent wetlands, 2) obtained archived samples of fish tissues from the ORNL Ecol. Assess. Group, 3) obtained splits of samples of Clinch River, PC, and EFPC sediments from TN Dept. of Envir. and Conser., 4) completed Hg isotopic analyses of sediments, suspended particulates and periphyton, and 5) conducted preliminary experiments on Hg(0) oxidation by natural organic matter (NOM) to investigate Hg isotope fractionation.

Sediment samples from the Clinch River upstream of the confluence with PC (and from Hinds Creek) establish very low background Hg concentrations [Hg] of 11-23 ng/g. The background mass dependent isotopic composition displays a narrow range ($\delta^{202}Hg_{NIST\text{-}3133}$ = -1.43 to -1.46‰) and there is a deficit of the odd mass isotopes ($\Delta^{199}Hg$ = -0.24 to -0.29‰). Two samples from the Clinch River downstream of PC have elevated [Hg] of 242 and 763 ng/g, with Hg isotopic compositions ($\delta^{202}Hg$ = -0.26 and -0.31‰; $\Delta^{199}Hg$ = -0.07 and -0.08‰) that are highly contrasting from background values. Sediments from PC below EFPC have even more highly elevated [Hg] (2150 to 3870 ng/g) and isotopic compositions close to the downstream Clinch River samples ($\delta^{202}Hg$ = -0.13 to 0.07‰; $\Delta^{199}Hg$ = -0.02 to -0.13‰). Suspended sediment in EFPC collected near the Y-12 outflow pipe has $\delta^{202}Hg$ = -0.63‰ and $\Delta^{199}Hg$ = 0.03‰. Isotopic values of suspended sediment and periphyton change systematically with distance downstream reaching values of $\delta^{202}Hg$ = 0.07‰ and $\Delta^{199}Hg$ = -0.12‰ after 19 km. Patterns in Hg isotopic variation in stream sediments around the PC watershed can be summarized as follows. 1) Background sediment [Hg] is very low with a narrow range of Hg isotopic composition. 2) Sediments in EFPC near Oak Ridge have much higher [Hg] and have $\delta^{202}Hg$ and $\Delta^{199}Hg$ that are highly contrasting from background values. 3) $\delta^{202}Hg$ and $\Delta^{199}Hg$ in EFPC sediments vary with distance downstream likely due to fractionation associated with chemical transformations of Hg. 4) When PC mixes into the Clinch River the [Hg] and Hg isotopic compositions of sediments shifts dramatically; consistent with the addition of ~10% sediment from PC.

Preliminary experiments were conducted to investigate Hg isotope fractionation during dark and photochemical oxidation of Hg(0) by NOM. Results from dark oxidation of Hg(0) by reduced soil humic acid suggest that both mass dependent and mass independent isotope fractionation occur, and that the oxidation enriches heavy isotopes in the product Hg(II), which is opposite to the Hg(II) reduction processes. Results of photo-oxidation experiments indicate that the presence of NOM can substantially enhance the oxidation rate of Hg(0) particularly in EFPC water.