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

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This project utilizes stable Hg isotopes in the East Fork Poplar Creek (EFPC) watershed, TN to place new constraints on methylmercury (MeHg) production, transport and degradation. We seek to better understand mechanisms leading to decoupling of inorganic Hg and MeHg concentrations in the EFPC ecosystem. We are conducting ecosystem level studies of natural samples and experimental studies of Hg isotope fractionation. Natural samples have been collected from: wetland sediments and pore waters; stream sediments, surface waters and pore waters; stream bottom periphyton; and young-of-year stoneroller minnows and redbreast sunfish. We have: 1) completed three seasonal sampling campaigns and analyses of THg, MeHg, and isotopic composition of sediments, suspended particulates, surface waters, pore waters, and periphyton from EFPC, Hinds Creek and adjacent wetlands; 2) analyzed the isotopic composition of archived fish and invertebrate tissues obtained from the ORNL EA Group; 3) collected samples of dissolved gaseous mercury (DGM) from EFPC stream water, and 4) conducted photochemical and dark oxidation experiments with EFPC stream water to investigate Hg isotope fractionation.

Recently published results from this project show Y-12 impacted sediments have a distinct Hg isotopic composition that can be traced from EFPC to Poplar Creek and the Clinch River, and that the isotopic composition of Hg in sediments within the EFPC vary little along the flow path (Donovan, Blum, Demers, Gu, Brooks, Peryam, 2014, Environ. Sci. Technol. 48, 3666-3674). In contrast, additional analyses show that the Hg isotopic composition of total suspended solids and the dissolved phase within EFPC change with distance downstream. There are shifts in the average isotopic composition of Hg in suspended sediment (THgp) from Y-12 (Î´202Hg = -0.46‰, Δ199Hg = -0.03‰) to downstream reaches (Î´202Hg = 0.08‰, Δ199Hg = -0.08‰). Changes in isotopic composition of dissolved Hg (THgd) is less consistent across seasons and along the flow path. The isotopic composition of DGM ranged in Î´202Hg values from 0.97‰ to 1.10‰ and in ˆ†199Hg values from -1.52‰ to -0.29‰, differing significantly from that of stream water, suspended particulate matter, and sediments. Analyses of riparian wetland and hyporheic pore waters suggests that near-stream sources of Hg may be isotopically distinguishable from THgp and THgd within the stream channel. Analyses of biota suggest different isotopic compositions of MeHg and inorganic Hg in the stream ecosystem. Combining field measurements with experimental results we assess potential sources and processes driving changes in Hg concentrations and isotopic compositions along the EFPC flow path.