ABSTRACT: This project utilizes stable Hg isotopes to reveal locations of Hg methylation in the East Fork Poplar Creek (EFPC) watershed, TN and to place constraints on processes that lead to methylmercury (MeHg) production, transport and degradation. During the first 16 months of the project we: 1) completed three sampling campaigns (fall, spring, and summer) in which water, sediment, and periphyton from EFPC, Hinds Creek and adjacent wetlands were collected, 2) developed protocols and collected samples of dissolved gaseous mercury (DGM) from EFPC stream water, 3) obtained samples of fish tissues from the ORNL Ecological Assessment Group, 4) obtained samples of Clinch River and EFPC sediments from TN Dept. of Environ and Conservation, 5) completed Hg and MeHg concentration analyses and Hg isotopic analyses of sediments, suspended particulates, surface waters, pore waters, and periphyton from one entire field sampling campaign, as well as fish tissues, and 6) conducted photochemical and dark oxidation experiments with EFPC water and model ligands to investigate Hg isotope fractionation.

Sediments downstream of Y-12 in EFPC had elevated THg concentrations (3.2 to 60 ug/g) compared to background sediments, and average δ²⁰²Hg of 0.11 ± 0.11‰ and Δ¹⁹⁹Hg of -0.08 ± 0.03‰ (mean ± 1s.d.; n=6). The THg concentration of sediments downstream in Poplar Creek (PC) and the Clinch River remains elevated (0.24 to 3.9 ug/g) and δ²⁰²Hg has a range between -0.82‰ and 0.07‰. Sediments in the Clinch River and Hinds Creek upstream of the confluence with PC have THg concentrations between 0.01 and 0.05 ug/g and the Hg isotopic composition is distinct from downstream sites (δ²⁰²Hg of -1.40 ± 0.06‰ and Δ¹⁹⁹Hg of -0.25 ± 0.03‰). The results demonstrate that Y-12 impacted sediments have a unique Hg isotopic composition that persists in EFPC and can be traced downstream to PC and the Clinch River.

Mercury isotopic composition within the EFPC stream corridor changes with distance from the Y-12 complex to its confluence with PC. Stream water concentrations of dissolved total mercury (THg,ₐ) decreased from 66 ng/L at Station 8 within the Y-12 complex, to 17 ng/L near the confluence with PC, δ²⁰²Hg decreased from -0.11‰ to -0.19‰, and Δ¹⁹⁹Hg decreased from 0.06‰ to -0.06‰. Isotopic composition of suspended sediment also shifts from the Y-12 complex (δ²⁰²Hg = -0.60‰, Δ¹⁹⁹Hg = 0.02) to downstream reaches (δ²⁰²Hg = 0.07‰, Δ¹⁹⁹Hg = -0.12‰). The isotopic composition of DGM ranged from δ²⁰²Hg values of 0.97‰ to 1.10‰ and Δ¹⁹⁹Hg values of -1.52‰ to -0.29‰, differing significantly from that of stream water, suspended particulate matter, and sediments. Changes in mercury concentration and isotopic composition along the flow path within the EFPC can be interpreted within the context of isotopic data from laboratory Hg(0) photochemical and dark oxidation experiments.

We used fish mercury isotope composition and %MeHg to estimate the isotopic composition of the sources of inorganic Hg (IHg) and MeHg accumulating in fish. In the heavily IHg contaminated EFPC, we estimated