

## Use of Stable Mercury Isotopes to Assess Mercury and Methylmercury Transformation and Transport across Critical Interfaces from the Molecular to the Watershed Scale

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Historical and ongoing releases of mercury (Hg) have resulted in a legacy of Hg contamination in streambed sediment, streambanks, and floodplain soils downstream of the Y-12 National Security Complex (Y12), along the flow path of East Fork Poplar Creek (EFPC) near Oak Ridge, Tennessee. Much of the Hg associated with streambed sediments, streambanks, and floodplain soils resides in relatively insoluble fractions, and has thus been considered to have little impact on dissolved total Hg (THg) concentrations. However, recent studies suggest that additional dissolved Hg from the hyporheic pore water or groundwater discharge may variably contribute as much as a third of downstream dissolved Hg loads during baseflow conditions. Thus, the over-arching goal of this project is to use natural Hg stable isotope signatures, imparted by molecular-scale reactions, to gain a more comprehensive quantitative and mechanistic understanding of the processes that supply dissolved Hg to surface water, drive observations of watershed-scale Hg fluxes, and result in bioaccumulation of methylmercury (MeHg).

To achieve this goal, we are combining a multi-seasonal field study with mechanistic laboratory experiments. First, we are coupling the Hg isotopic composition of dissolved Hg in stream water and in critical subsurface ecosystem compartments (i.e., hyporheic zone, riparian floodplains, and groundwater) with hydrologic fluxes in four reaches of EFPC to establish an isotope mass balance that assesses the relative importance of dissolved Hg contributed to the stream across these critical interfaces. Second, we are utilizing sequential extraction methods to characterize the isotopic composition of legacy Hg potentially re-mobilized from streambed sediment. This will provide insight into the sources and mechanisms that replenish the supply of dissolved Hg within critical subsurface zones. Third, we are assessing the isotopic composition of MeHg in biota of EFPC, as a step toward identifying the source(s) of bioaccumulative MeHg in the EFPC ecosystem.

Here, we present: (1) Hg concentration and isotopic composition of surface water, hyporheic pore water, and riparian groundwater; (2) isotopic mass balance assessments regarding legacy inputs of dissolved Hg to stream water of EFPC; and (3) Hg isotopic composition of sequentially extracted Hg from streambed sediment. We provide an overarching synthesis that shows: (i) recalcitrant fractions of legacy Hg in sediment is likely contributed to dissolved pore water and stream water; (ii) soluble sediment Hg fractions are likely derived from periphyton; and (iii) recalcitrant Hg released from legacy sediment may be incorporated into more soluble periphyton materials downstream along the flow path.