Title: **Use of Sequential Extraction and Mercury Stable Isotope Analysis to Assess Remobilization of Sediment-Bound Legacy Mercury**

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Project Abstract:

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 this legacy Hg resides in relatively insoluble fractions, and has thus been considered to have little impact on dissolved Hg concentrations. However, recent studies suggest that dissolved Hg from hyporheic pore water contributes as much as a third of downstream dissolved Hg loads during base flow conditions. The goal of this project was to assess how anthropogenic legacy Hg is remobilized from streambed sediment to stream water. We used sequential extractions to quantify the different forms of Hg in the sediment, and Hg stable isotope analysis to track the cycling of Hg among those pools. Mercury isotope analysis of bulk streambed sediment revealed patterns that are consistent with equilibrium isotope effects between coexisting Hg(0) and Hg(II), which likely overprinted isotopic signatures imparted by kinetic Hg oxidation and reduction reactions, a phenomenon that had previously been demonstrated in laboratory experiments but not identified *in situ.* Mercury isotopic analysis of the five-step sequential extractions revealed that weakly-bound and recalcitrant Hg pools in the sediment were isotopically similar to one another, suggesting that the weakly-bound pools were derived from the recalcitrant pools by dissolution and rapid re-adsorption. This weakly-bound Hg can then be remobilized to the hyporheic pore water and surface water as dissolved Hg. Organically-bound Hg pools in the sediment were isotopically distinct at upstream sites, but converged with the isotopic composition of weakly-bound and recalcitrant sediment Hg pools along the flow path (shifting toward higher δ^{202}Hg and lower Δ^{199}Hg values). A similar trend in the mercury isotopic composition of suspended particulates and streambed biofilm has been previously observed. This suggests both physical mixing among these components and the transfer of weakly-bound sediment Hg into biofilm and suspended particulates which are then reincorporated into the organically-bound sediment Hg pool. Overall, these sediment sequential extractions and Hg isotope analyses provide evidence that sediment-bound legacy Hg within the streambed can be remobilized. Thus, large pools of recalcitrant legacy Hg have the potential to be a long-term source of dissolved Hg to stream water as well as a source of Hg to streambed biofilm, a basal resource of aquatic food webs.