

Site Biogeochemical Processes and Microcosm Studies (Hg SFA at ORNL)

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Site investigation and geochemical modeling provide key information on major chemical species and microbial communities involved in mercury (Hg) biogeochemical transformations in water and sediment along a longitudinal transect of East Fork Poplar Creek (EFPC).

Site investigations and source characterization. Total Hg concentrations decrease while MeHg concentrations increase with increasing downstream distance. Greater than 90% of the Hg in streambanks, streambed sediments, gravel, and biofilms is extracted only with relatively aggressive chemical extractants (12 M HNO₃, aqua regia). The majority of the MeHg is associated with biofilm or suspended solids, becoming more pronounced with increasing distance downstream. In the upper reaches of the creek, Hg concentration increases with sediment depth; dissolved Hg(0) approaches saturation with metallic Hg. Surface water rapidly exchanges water with the hyporheic zone to depths ≥ 70 cm delivering a significant load of Hg to the surface water of the creek (see below). Other geochemical parameters are indicative of microbial activity – NO₃⁻ and SO₄²⁻ decrease, Mn increases, with increasing depth. Total sulfide concentration ranged up to 100 μ g/L while dissolved sulfide was less than 3 μ g/L. These results are consistent with an active sulfate-reducing community; sulfate reducers are dominant microbes responsible for Hg methylation. To the extent that dissolved sulfide plays an important role in Hg methylation, the low dissolved sulfide concentrations may be one factor to explain why MeHg concentrations at this site remain low in the presence of the highest total and dissolved Hg concentrations in the creek.

To better understand the role of buried metallic Hg as a contaminant source, studies were conducted to measure Hg dissolution. Water containing traces of residual chlorine contacting metallic mercury, as could occur with the discharge of chlorinated cooling water or potable water leaks, greatly accelerates dissolution. The measured oxidative dissolution rate at the surface of an Hg bead in water without residual chlorine was 0.5 ng/cm²/h, but increased to 17,000 ng/cm²/h in the presence of residual chlorine concentration typical of potable water.

Methylation bioassay using pure cultures of methylating bacteria. Cultures of *Desulfovibrio desulfuricans* ND132 grown on a pyruvate/ fumarate media without sulfate were inoculated into bottles containing inorganic Hg or Hg plus Suwanee River NOM (SRNOM). Sacrificial samples were collected at various times during the growth curve for quantification of MeHg, filter-passing (0.2 μ m) and total Hg, Hg sorbed to bottle walls, organic acids, and cell enumeration. ND132 incompletely oxidized pyruvate to acetate and reduced fumarate with stoichiometric production of succinate. Methyl mercury production was not influenced by the presence of SRNOM at any sampling time. MeHg increased from 0.058 picograms MeHg per 10⁶ cells (pg/Mcell) at mid-log phase to 0.09 pg/Mcell at late stationary phase. When Hg or Hg-SRNOM was added at late stationary phase, MeHg production increased $\sim 4\times$ (0.35 pg/Mcell). No MeHg was produced from cell-free spent media harvested at this stage, suggesting that ND132 in this stressed condition is a more active methylator.

Future efforts will include *Desulfobulbus propionicus* (identified in our previous survey of multiple local creeks and sites; see microbial study of the SFA) or related isolates from EFPC in experiments, and targeted experiments to identify the role of sulfate reducers in MeHg production in EFPC.