

## Dynamics of Mercury Release in Flooded Soils from Oak Ridge, Tennessee

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Mercury transport from contaminated East Fork Poplar Creek (EFPC) floodplain soils in Oak Ridge, TN contributes to downstream mercury pools available for methylation, but the environmental controls of soil-to-stream mercury release are not well understood. Factors such as soil mercury speciation, fluctuations in soil redox status, soil geochemistry, and dissolved organic matter may control the mobilization and subsequent transport of mercury from contaminated soils to nearby streams. Our objectives were to identify the dominant source(s) and molecular controls on mercury release from contaminated soils, and characterize the hydrologic conditions (i.e., rising and falling water table) that may enhance or mitigate contaminant transport. In this study, mercury release was assessed from two EFPC soils, obtained from a stream bank site and a floodplain site, under saturation conditions. Characterization of the soils, from 0-65 cm depth at 10 cm intervals, included total mercury concentration, mercury physiochemical speciation via selective sequential extraction, organic matter content, elemental composition, cation exchange capacity, and soil mineralogy. Undisturbed, intact soil cores were collected at the sample sites from the O through A (0-30 cm depth) horizons which encompass the depth of historical contamination. Soil cores were artificially flooded with deionized water, and O- and A-horizon porewaters were sampled at 8-72 h intervals. To simulate the effects of a fluctuating water table, cores were drained at the end of the initial flooding event, allowed to dry for 7 d, and subjected to a second flooding event. Porewater analyses included pH, total dissolved mercury (0.45  $\mu\text{m}$  filtered), total dissolved metals (Fe, Mn, Al), anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ), dissolved inorganic carbon, and dissolved organic carbon. Additionally, porewater dissolved organic matter was characterized via UV/vis and fluorescence spectroscopy, and fluorescence excitation-emission matrix (EEM) spectra were modeled using parallel factor analysis (PARAFAC).

Results from streambank soil cores show that during initial flooding events, a rapid release ( $t = 3$  d) of dissolved mercury was observed in O-horizon porewaters following inundation, suggesting that the release mechanism is independent of redox-sensitive processes. Conversely, slow mercury release kinetics ( $t = 14$  d) were observed in A-horizon soils, inferring a release mechanism coupled to redox-sensitive processes. This hypothesis was supported by a robust positive relationship between porewater Mn(II) concentrations, which is an indicator for reductive dissolution processes, and dissolved mercury. Mercury release from the O-horizon during the second flooding events was much slower, suggesting that the labile mercury pool was exhausted during the first saturation period. A-horizon soils exhibited similar mercury release trends during second flooding events, signifying that these soils have a mercury pool that is accessible for a longer time under strongly reducing conditions. Mercury release trends were not explained by changes in dissolved organic matter concentration or composition. The effects of saturation events on soil cation exchange capacity were evaluated to identify potential modifications of mineral and/or mineral coating structures. Future objectives are to expand our experimental investigation to soils from the floodplain site, and complement intact core experiments with mercury release batch experiments.