Understanding Geochemical Effects on Mercury Speciation, Stability and Potential Remedial Strategies

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Background/Objectives. Significant mercury impacts to groundwater are relatively infrequent due to low solubility and the formation of stable sulfides. This presentation outlines the geochemical conditions at two New England sites where saturated zone mercury transport was a concern and compares the fate and transport mechanisms which govern under the very different conditions at each site.
Each site is located proximate to a river. At the first site, the source material exists in the mercuric form, at concentrations in the thousands of milligrams per kilogram. Based on the historic data, the mercury in soil is currently stable, but due to the presence of other site contaminants, capping was the preferred remedial strategy. This, however, raised the concern that capping would change the vadose zone geochemistry thereby altering the form of the mercury and increasing its potential to migrate. At the second site, elemental mercury is the source material and separate phase mercury has surfaced within the outcrops at the adjacent river. Prior work at this site included several transport hypotheses designed to explain the presence of separate phase (i.e., liquid) mercury in the river and concluded that current impacts would not pose a future downgradient risk; however, the limited geochemical evaluations performed at the site did not actually support the conclusion that mercury plume was well-defined or stable.

Approach/Activities. At the first site, a comprehensive sampling program was performed to assess the presence and form of mercury within the soil, groundwater, and soil vapor while simultaneously evaluating the in situ vadose zone geochemistry by collecting soil samples anoxically under a nitrogen blanket. The data generated were utilized in evaluating the potential for mercury transformation and mobilization under different remedial scenarios. At the second site, available speciated mercury data was limited; therefore, we reviewed the redox potential of the groundwater, compared aqueous mercury concentrations to the solubility limits of the different species, and evaluated the positioning and physical characteristics of bedrock fractures compared to known occurrences of separate phase mercury. The results of this evaluation were used to evaluate the potential for multiple transport pathways from the upland into the river.

Results/Lessons Learned. The results of the anoxic sampling at the first site indicated that subsurface conditions are generally reducing, likely due to high levels of organic carbon in soil, while the overall sulfate concentrations in groundwater may not currently be sufficient for methylmercury creation via biological processes. Based on these conclusions, the cap design was modified to maintain the current geochemical balance. At the second site, the oxidation state of the groundwater was highly variable and the dissolved phase concentrations were elevated (e.g., compared to the solubility of elemental mercury) which, along with reviews of Site geologic characteristics, indicate the potential for separate phase transport within the fractures, as well as for aqueous phase transport/mercury precipitation in the river bed. At both sites, an understanding of the geochemistry coupled with knowledge of the released species was crucial to understanding the transport mechanisms. Remedial measures at such sites need to be designed properly to maintain the geochemical balance so that mercury impacts are not exacerbated.