

Speciation and surface complexation of As on hydrous ferric oxide in soils modified by *in situ* chemical fixation

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Soils contaminated with arsenic-bearing herbicides in the 1940s and 1950s may leach arsenic into surface and ground water supplies and thus pose a potential environmental hazard. A soil sample containing 900 ppm arsenic was selected for study and characterized using XRD, SEM/EDX, EMPA and synchrotron techniques (micro-XRD and XANES). The arsenic was found to be As(V) and primarily disseminated on the surfaces of fine-grained soil particles in close association with aluminum. Although no crystalline arsenic phases were identified by XRD or SEM/EDX analyses, a few arsenic-rich particles were observed by EMPA and determined to be phaunouxite ($\text{Ca}_3\text{AsO}_4 \cdot 11\text{H}_2\text{O}$) using micro-XRD and XANES.

The arsenic-contaminated soil sample was treated with a solution of ferrous sulfate, which immobilized or “fixed” the arsenic within the soil. The treated soil sample was examined using synchrotron radiation techniques to deduce the mechanism of the *in situ* chemical fixation technique. Micro-XRF mapping performed on treated and untreated soil samples showed arsenic and iron were highly correlated after treatment. However, XANES analysis of the treated soil gave no indication of crystalline arsenic and iron phases being formed by the treatment process. Sequential chemical extractions performed on treated and untreated soil samples showed that arsenic becomes associated with amorphous ferric hydroxide produced by the treatment. EXAFS analysis of the treated soil sample shows similarities with the EXAFS spectrum of synthetic ferrihydrite precipitated from an arsenic-bearing solution. Interpretation of the treated soil’s EXAFS spectrum indicates that soil arsenic is fixed as inner-sphere bidentate surface complexes on the precipitated ferric hydroxide. EXAFS analysis of a treated soil sample aged more than a year showed no significant variation in the arsenic chemical bonding environment compared to the newly treated samples, which indicates that soil arsenic held as arsenate surface complexes on ferric hydroxide is stable in an aerobic environment.

Transformation of arsenic species in solids and porewaters from Yellowknife Bay, NWT, Canada

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Introduction

Sub-aqueous sediments are particularly suited for studying arsenic cycling owing to local and seasonal variations in redox conditions that influence speciation and hence As mobility. Historical mining activity adjacent to Yellowknife Bay has resulted in sediments and porewaters with As concentrations as high as 10000 ppm and 7450 ppb respectively. Our sampling strategy centred around two distinct biogeochemical environments: i) shallow, oxic, organic-poor, arsenic-rich (1150 ppm), submerged gold mine tailings with patchy microbial populations and ii) deep, suboxic, organic-rich, mining-impacted (910 ppm As) lacustrine sediments abundant in microbes.

Results and Discussion

Synchrotron-based analyses (micro-XRF, micro-XANES and micro-XRD) of silt-size roaster-derived iron oxides with 10 micron spatial resolution, allow for detailed characterisation of these potentially unstable As-bearing phases. Micro-XRD identifies the roaster oxides as nanocrystalline assemblages of maghemite and hematite, while micro-XANES indicates they carry mixtures of AsIII and AsV in oxic conditions. Under more reducing conditions the oxides persist, but AsIII dominates species ratios. This suggests the AsIII associated with these roaster-oxides remains stable in an oxic setting but the AsV has either undergone reduction to AsIII or been liberated to porewaters.

Sediment porewaters, sampled at the millimetre scale with dialysis arrays (peepers) and speciated for As with anion exchange techniques, show seasonal differences. Late summer porewaters contain equal proportions of AsIII and AsV (16-415 ppb), but late winter porewaters are dominated by AsIII (284-947 ppb). The oxic veneer at the sediment-water interface contracts to <1 cm during the open-water season releasing As to the benthic environment, likely due to the reductive capacity of labile organic matter from increased primary productivity. After lake freeze-up and decreased organic inputs, the oxic veneer expands attenuating upwardly diffusing As onto authigenic Fe phase(s).