

Geochemical controls on arsenic mobilization in a potential permeable natural reactive barrier (PNRB)

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Elevated concentrations of arsenic (As) in groundwater pose serious health concerns. Riverbank sediments along the Meghna river, Bangladesh enriched with iron (Fe)-oxy(hydroxides) have been shown to release adsorbed As under reducing conditions. Recent studies hypothesize that the mixing of oxic river water with Fe and As-rich reduced groundwater within shallow riverbank sediments cause Fe-oxide minerals to precipitate and accumulate As on their surfaces, acting as a permeable natural reactive barrier (PNRB).

Here we discuss data from riverbank sediment cores collected along a transect orthogonal to a generally gaining reach of the Meghna River (0-83m from the river, 0-3m depth) to test for a possible PNRB. Sediment samples were analyzed to identify zones of enriched As, Fe, Mn and association of other key elements using X-Ray Fluorescence (XRF). Fe(II) concentrations were determined by spectrophotometric analysis following HCl extraction. Sediment samples were incubated with deionized water under oxic conditions to simulate the geochemical interaction between the river water and sediments. The resulting extracts were analyzed for the major ion and trace element concentrations.

Results show that the riverbank sediment samples are primarily composed of fine sands with unevenly distributed As_T (5-10mg/kg). solid-phase Fe_T varied between 29-53g/kg and Fe(II) concentrations varied between 2-25mg/kg. Solid-phase Fe_T and Mn_T (475-860mg/kg) were positively correlated, decreasing from the river edge to 20m inland. The decreasing Fe_T and Mn_T along this distance demonstrate the weakening influence of infiltrating river water, highlighting the presumed extent of a potential PNRB. The abundance of water-extractable cations was Na⁺ > Ca²⁺ > K⁺ > Mg²⁺, while that of the anions was Cl⁻ > PO₄²⁻ > SO₄²⁻. The low concentration of total dissolved solids (TDS) in the riverbank extracts (5.4mg/L) relative to that of aquifer extracts at 2-37m depth (90.2mg/L) indicates the flushing of riverbank sediments with oxic river water. This flushing, while removing exchangeable ions from mineral surfaces, may promote the oxidation of Fe-oxides and removal of dissolved As from discharging groundwater. The results of this study, along with pore-water chemistry, and observed hydraulic