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Biogeochemical Processes Governing Arsenic Release in Shallow Mixed-Oxic State Groundwater

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Arsenic (As) concentration in groundwater is governed by complex site-specific biogeochemistry. Mechanisms of As mobilization in shallow and mixed-oxic state aquifers, such as in the middle Indo-Gangetic plain, are not clearly understood. This study aims to elucidate these processes by detailed investigation of both abiotic and biotic components of such polluted aquifers. Depth-wise porewater samples and associated aquifer sediments were collected from As-unpolluted [B1; total dissolved As ($As_{T,diss}$<10 µg/L)] and As-polluted [B2; $As_{T,diss}$>10 µg/L] locations from a previously identified site in Kanpur, India. To determine the dominant forms of arsenic, dissolved and solid-phase characterizations were performed. To identify the presence of different indigenous bacterial populations which could potentially play a role in As mobilization, metagenomics on soil samples was performed. Results from shallow depths of 7–15 m suggested higher $As_{T,diss}$ (Figure 1a) and Fe(II) (Figure 1b) concentrations in porewaters of B2 as compared to porewaters of B1. However, at deeper depths (15-34 m), $As_{T,diss}$ and Fe(II) were mostly not detected in both the locations. Dissolved total organic carbon (TOC) were relatively higher in the shallow aquifer (~54 mg/L) as compared to the deeper aquifer (~2 mg/L) in both the locations. Prevalence of lower pH was observed at shallow depths of B2 as compared to the porewaters at similar depth of B1. Elevated dissolved inorganic carbon (Figure 1c) and total calcium (Figure 1d) concentrations in shallow porewater samples of B2 could be indicative of potential calcite solubility controls which need further confirmation. X-ray diffraction on sediments confirmed the presence of solid solutions containing $Ca(Mg, Fe, Mn)(CO_3)_2$ in only shallow depths of B2. Sequential extraction of shallow sediment samples of B2 suggested that of the total As (12-20 mg/kg) an estimated 30-36% was present as PO_4/CO_3–exchangeable and 16-29% was likely associated with crystalline iron oxides. Metagenomics of sediments indicated 60% higher population of As-metabolizing bacteria belonging to the family of *Enterobacteriaceae*, *Moraxellaceae*, and *Aeromonadaceaes* in B2 as compared to B1 at 10 m below surface. Results from dissolved phase, solid phase and microbial characterization and associated geochemical analyses will be presented to elucidate the possible mechanisms controlling arsenic speciation in such groundwaters.

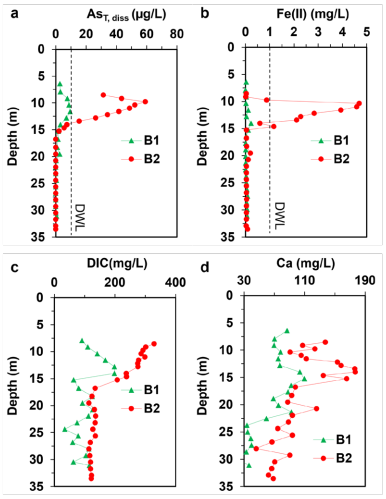

Figure 1. Depth-wise variation of total dissolved As ($As_{T,diss}$), Fe(II), dissolved inorganic carbon (DIC), and total dissolved calcium (Ca) in porewaters of borewells. B1 and B2 represent As-unpolluted and As-polluted locations at the study site in the middle Indo-Gangetic plain. Dotted lines indicate drinking water limits (DWL). Due to the non-availability of DWL of Fe(II), DWL of total iron is shown in Fig. 1b.