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Hydrological and Biogeochemical Controls on the Formation of a Fe-oxide Permeable Natural Reactive Barrier (PNRB) along the Meghna River, Bangladesh

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In Bangladesh, geogenic groundwater As contamination in shallow deltaic aquifers is an ongoing health crisis. Major rivers crosscutting the delta receive shallow groundwater discharge. The Meghna Riverbanks experience tidally driven flow reversals, creating bi-directional mixing zones between anoxic dissolved Fe and As rich groundwater and oxic river water. These riverbanks mixing zones contain high solid-phase As (>500 mg/Kg) associated with Fe-oxides, which may precipitate from groundwater mixes with oxic river water, acting as a permeable natural reactive barrier (PNRB). However, the individual processes controlling PNRB formation and breakdown are not fully discernable from a complex field scenario and computational models with limiting assumptions. Thus, an *ex-situ* experimental approach with constrained fluxes is valuable and offers advantages for evaluating flow and transport processes under simultaneously dynamic river stage and hydraulic gradients.

Our objective is to experimentally investigate the biogeochemical reactions that form and break down such reactive barriers under tidally driven mixing frequencies and gaining, neutral, and losing hydraulic gradients. It is hypothesized that: H1) PNRB formation and fate are influenced by periodic regular river stage driven mixing of As, Fe, DOC rich groundwater with oxic river water, and sediment POC; H2a) a gaining river hydraulic gradient (start of dry season) favors PNRB growth via Fe-oxide precipitation; H2b) neutral hydraulic gradient (end-of dry season) favors re-crystallization of less crystalline Fe-oxides; and H2c) losing hydraulic gradient (start of monsoon season) favors the reductive dissolution of Fe-oxides.

A set of reversing flow, 1-D column experiments will simulate the aforementioned conditions using sediment from the banks of the Meghna River. Column effluent will be measured for Fe, As, POC, and DOC using with the ferrozine method, a modified molybdenum blue method, deionized water extraction, and a total carbon analyzer, respectively. Solid-phase As associated with specific Fe-oxide minerals will be measured with sequential extractions on extruded column sediments. These measurements will be utilized to estimate an equilibrium As and Fe^{2+} sorption model, and precipitation and dissolution kinetics of Fe-oxides within a reactive flow and transport model. The findings will help predict PNRB formation and fate under different river-stage fluctuation regimes and seasonal hydraulic gradients.