

Role of sedimentary organic matter on arsenic mobilization in a potential natural reactive barrier (NRB) along the fluctuating Meghna River, Bangladesh

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Arsenic (As) contamination in the shallow aquifers of Bangladesh threatens the health of millions of people who rely on this groundwater for drinking and agriculture. The presence of As-bearing iron (Fe) (oxy)hydroxide-rich sediments, metal-reducing microbes, natural organic matter (OM), and reducing conditions, together regulate the mobility of As in these groundwaters. Along the tidally and seasonally fluctuating Meghna River in Bangladesh, interactions between the river and groundwater within the hyporheic zone cause fluctuating redox conditions which are presumed to be responsible for the formation of a Fe-rich natural reactive barrier (NRB). To understand the NRB's impact on As mobility, the geochemistry of riverbank sediment (< 3 m depth) and the underlying aquifer sediment (up to 37 m depth) were analyzed. A sediment-water extraction experiment was conducted to simulate the behavior of the sediments when submerged in oxic river water, and the inorganic and organic chemical parameters of the extracts were determined. The riverbank and aquifer sediments contained similar bulk elemental concentrations, with 40±12 g/kg of Fe and 7±2 mg/kg of As. However, riverbank extracts contained only 0.2±0.4 mg/kg of Fe and 0.7±0.6 µg/kg of As, compared to 4±2.6 mg/kg of Fe and 14±10 µg/kg of As in the aquifer extracts. Although the sedimentary organic matter (SOM) content was similar in the riverbank and aquifer sands (2±0.6 %), their water-extractable fractions were 2±2 % and 34±7 %, respectively. Further analyses with fluorescence spectroscopy and molecular weight distribution showed that the riverbank SOM was protein-like, fresh, low molecular weight, and relatively labile. In contrast, SOM in aquifer sands was humic-like, older, high molecular weight, and relatively recalcitrant. During the dry season, oxic conditions and labile OM supports aerobic and nitrate-reducing metabolisms, limiting As mobility within the NRB. However, in the wet season when conditions are reducing, labile OM may facilitate heterotrophic metabolisms driving the

reductive dissolution of Fe-oxides in the NRB, potentially liberating large amounts of the sequestered As. The processes at the river-groundwater interface play a significant role in the regional cycling of As and this study improves our understanding of the biogeochemical controls regulating As mobility at the river-groundwater interface.