

Residence times of the upper low-arsenic aquifers in Bangladesh at the onset of increased abstraction

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Elevated levels of dissolved arsenic in shallow aquifers in the Bengal basin will result in increased use of deeper, currently low-arsenic aquifers. Compared to the shallow aquifers, relatively little is known about the flow dynamics of the deeper systems (>100 m depth).

Radiocarbon, ³H, stable isotope, and noble gas data were obtained from both aquifer systems in our field area in Arai-hazar, 25 km east of Dhaka, Bangladesh. Noble gas temperatures of shallow groundwater generally reflect current water temperature at the water table despite elevated CO₂ (up to 12%) and depleted O₂ concentrations in the unsaturated zone. ³H and ³H/³He data are consistent with recharge during the past 50 years. Most of the deeper groundwater (>100m depth) underlying the high-arsenic zone is ³H free; and radiocarbon, stable isotope, and noble gas data indicate that recharge likely occurred at the transition between the late glacial period and the Holocene, a time of major changes in sea level, vegetation, and climate.

The relatively high residence time of water in the aquifer suggests a low recharge rate (cm's/year) until large-scale groundwater pumping for municipal supplies began in Dhaka in the 1960s.

Increased usage of this resource will result in higher recharge rates and might cause leakage from shallow high-arsenic aquifers and needs to be considered in management of water resources in Bangladesh.

Modulation of the product of U(VI) reduction by phosphate and calcium

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One bioremediation strategy for uranium-contaminated aquifers involves the enzymatic reduction of soluble U(VI) to less mobile U(IV) species. The mineral uraninite, UO_{2(s)}, is considered to be the most desirable product of bioremediation due to its relative stability under reducing conditions. However, it has been shown repeatedly that uraninite is not the sole product of U(VI) reduction. Among these other U(IV) products are monomeric U(IV) species, believed to coordinate to bacterial biomass via phosphate and/or carboxylate groups and likely to be less stable than uraninite. For bioreduction to be a viable remediation strategy, it is crucial to pinpoint the factors promoting the formation of uraninite versus monomeric U(IV). Investigations to date have suggested that certain solutes, including PO₄³⁻ and Ca²⁺, lead to preferential formation of monomeric U(IV). However, the mechanism of this process remains unknown.

In this study, we examine (1) the influence of PO₄³⁻ and Ca²⁺ on the product of U(VI) bioreduction and (2) the fate and behavior of those solutes during U(VI) reduction. Uranium L_{III} edge X-ray absorption spectroscopy and a wet chemical extraction technique were used to quantify the relative contribution of these two U(IV) species in systems in which the solute concentrations were systematically varied. We initially hypothesized that Ca²⁺ shields PO₄³⁻ from negatively charged groups and thus allows the binding of phosphate to the cell wall and the complexation of U(IV) by phosphate, leading to preferential monomeric U(IV) formation. To test this hypothesis, we measured the concentration of the two solutes during U(VI) reduction.

The results confirm that the U(IV) product of bioreduction is a mixture of uraninite and monomeric U(IV). The presence of calcium enhances the fraction of monomeric U(IV) produced. Moreover, even a low concentration of phosphate (1.9 mg/l) promotes greater formation of monomeric U(IV). However, the contribution of monomeric U(IV) does not change with increasing concentrations of this solute. The combination of calcium and phosphate results in a close to pure monomeric U(IV) product. Surprisingly, the aqueous concentrations of PO₄³⁻ or Ca²⁺ during U(VI) bioreduction are constant, suggesting little binding of these solutes to biomass. Hence, the direct association of these solutes with biomass cannot account for the observed effect. This suggests an indirect influence of phosphate and calcium on biological controls over the product of U(VI) reduction. For example, the production of bacterial extracellular polymeric substances could be limited by these solutes, restricting the number of nucleation sites for uraninite precipitation and promoting the formation of monomeric U(IV).

Our work provides a first glimpse into the complexity of the influence of geochemical factors on the biological controls of U(IV) product formation.