

Isotopic composition of methane and ΣCO_2 from Arsenic affected area of West Bengal, India

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Ground water is a potential source of methane (CH_4) in Arsenic affected area of Bengal Basin. Harvey *et al.* (2002) observed high CH_4 concentration in the water with high As abundances at depth and predicted increase in CH_4 concentration during dry seasons. We present our study on tube well water samples collected during dry season (middle of February 2007) from two different localities in West Bengal, belonging to two different palaeodrainage systems i.e. Bhagirathi Ganges delta (BL) and Damodar river fan delta (BG) (tributary of river Bhagirathi) (Acharyya and Shah, 2007). Many of these wells were previously studied for As concentration (Acharyya and Shah, 2007).

CH_4 and ΣCO_2 present in the water samples were analyzed for carbon isotopic ratios to trace the sources of carbon to the ground water. Most of the samples analyzed for ΣCO_2 in this study have $\delta^{13}\text{C}$ in the range -10.8‰ to -13.5‰, suggesting that the CO_2 in these samples originate from silicate weathering with CO_2 from vegetation (C_3 type). Barring one sample, we saw two distinct clusters of $\delta^{13}\text{C}$ values in CH_4 : -74.9‰ to -87.5‰ for BL water compared to a range of -30.5 to -40.2‰ in BG water. Isotopic signatures suggest a predominance of the carbonate reduction pathway in BL sites and high activity of CH_4 oxidation or substrata depletion in BG sites. Our preliminary results suggest that the process of release of arsenic from hydrated iron oxide is triggered by the activities of anaerobic bacteria in a reducing environment with consequent production of CH_4 with distinctly depleted isotopic character.

We also observed an anomalous enrichment of $\delta^{13}\text{C}$ value (+55 per mil) in one of the samples with low CH_4 concentration from BL locality.

References

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Nanoscale size effects on reduction of hematite nanoparticles and surface reactions of Uranium(VI)

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The high surface area to mass ratios of hematite nanoparticles can increase the extents of surface reactions that affects the environmental biogeochemistry of pristine and contaminated environments. Surface reactions of interest include adsorption and surface-mediated reduction. Microbial iron reduction can produce Fe(II), which, when adsorbed to Fe(III) oxides, is an effective reductant of contaminants including uranium(VI). In order to understand nanoscale effects on the rate of microbial iron reduction and surface-mediated uranium(VI) reduction, hematite nanoparticles with diameters of 8, 50, and 200 nm were synthesized using gas phase methods that provide control of their composition and sizes.

The microbially-mediated rate of hematite reduction by the iron-reducing bacteria *Geobacter sulfurreducens* has been studied in anaerobic batch experiments. Abiotic reductive dissolution rates using ascorbic acid and the reduced form of the electron shuttle AQDS have also been studied. The dissolution rates increase with decreasing particle size; however, when normalized to surface area, the dissolution rates are similar for all but a few conditions.

Uranium(VI) adsorption to the three sizes of hematite particles was evaluated over the range of pH (3-11) and total uranium concentration (10^{-6} to 10^{-4} M) to elucidate the size dependence of U(VI) adsorption to hematite. All experiments were conducted in a CO_2 -suppressed glovebox to prevent the formation of dissolved U(VI)-carbonate complexes, which can affect U(VI) adsorption. Surface complexation modeling was used to provide a quantitative reaction-based framework for evaluating the effects of particle size on adsorption. A model was developed that can predict U(VI) adsorption over a range of pH values and total U(VI) loadings.

Rates of U(VI) reduction by adsorbed Fe(II) were investigated in batch experiments. Reduction is interpreted as a pseudo-first-order reaction with respect to the activity of the adsorbed U(VI) with an excess of Fe(II) relative to U(VI). At each sampling time, a portion of the suspension was filtered and analyzed for dissolved iron and uranium using ICP-MS. Additional portions of the suspension were chemically treated for the extraction of total U(VI) and Fe(II). Selective extraction of U(VI) uses 0.1 M NaHCO_3 while that of Fe(II) uses 0.5 M HCl. The concentration of Fe(II) was subsequently measured using the ferrozine method.