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Attenuation of As transport by iron oxides at the groundwater surface water interface and possible microbial contribution

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The Groundwater Surface Water Interface (GSI) is a transition zone with bio/geo/chemical properties determined by both the adjacent groundwater and surface water bodies. Because reduced iron is frequently abundant in polluted groundwaters, we postulated that iron oxide formation in the GSI might be a significant mechanism for pollutant attenuation. Further, we hypothesized that iron oxidizing bacteria (IOB) might be, in part, responsible for iron oxide formation.

Freeze core samples were obtained from the near-shore sediments at a GSI impacted by a reduced groundwater due to a nearby leaky landfill, with arsenic as the dominant pollutant of concern. The cores were subsectioned with 0.8 cm resolution and subject to sequential extraction to identify various pools of arsenic and iron. The proposed sequential extraction method of Keon *et al*. (2001) was simplified to 4 steps because preliminary analysis had shown arseno-sulfide solids to be minor contributors to the total arsenic inventory. Most of the iron in the sediments was incorporated into amorphous iron oxyhydroxides, as defined by the chemical extraction procedure. Between 10 and 20% of the iron was present as crystalline oxide solids. Up to 20% of the total iron was sorbed to the solids in the +II (ferrous) oxidation state. Almost all of the arsenic in the sediments was strongly sorbed on particle surfaces with only small amounts co-precipitated in the iron oxides. The molar ratio of arsenic-to-iron was rel-

atively constant at 0.013 mol/mol over all cores with iron accounting for 20 to 30% by weight of the sediments. This value is much greater than the dissolved arsenic-to-iron ratio in the upgradient groundwater suggesting that may be preferential arsenic accumulation in sediments.

IOB enrichments and quantifications were obtained with an opposing iron/oxygen gradient tube cultivation method from similarly retrieved freeze core samples. The IOB density was highest in the few centimeters of the surface sediment and decreased sharply with depth below 7cm. The drop in IOB density by several orders was congruent with a decrease in iron oxide concentration. A small-subunit rRNA clone library was developed from these enrichments. Phylogenetic analyses indicated that the IOB clones clustered with known sequences from clones of other IOB enrichments or known or suspected IOB. 12 of all clone sequences belong to the gamma proteobacterial group, while 2 of them fell within the beta proteobacteria and were related to the known auto- and mixotrophic IOB *Gallionella ferruginea* and the mixotrophic IOB *TW2*. Two low GC-gram-positive sequences were also retrieved. Fluorescence in situ hybridization was preformed on the IOB enrichment with labeled group-specific probes developed from the available clone library to confirm the presence of the retrieved species in IOB enrichments. These initial surveys provide us with information to start a detailed assessment of IOB activity at GSI, and identify and characterize the significance of microbial iron oxidization in retention of pollutants at the GSI.