THE INFLUENCE OF OXIDATION-REDUCTION AND ADSORPTION REACTIONS ON ARSENIC TRANSPORT IN THE OXIC, SUBOXIC, AND ANOXIC ZONES OF A MILDLY ACIDIC SAND AND GRAVEL AQUIFER

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Introduction
A set of natural gradient tracer tests was conducted to improve understanding of the effect of chemical and biological processes on the mobility of arsenic (As) in ground water. Experiments were conducted at the USGS Toxic-Substances Hydrology Research Site on Cape Cod, Massachusetts, USA.

The inorganic species arsenite (As(III)) and arsenate (As(V)), which are typically the dominant forms of As in ground water (Kondo and others, 1999), have different reactivity. Both species adsorb onto hydrous iron (Fe) and aluminum (Al) oxides with extent of adsorption decreasing with increasing pH (Davis and Kent, 1990; Dzombak and Morel, 1990). Arsenic(V) is generally considered to adsorb more strongly than As(III) and, therefore, be less mobile.

Oxidation-reduction (redox) reactions can effect changes in As speciation in ground water (Cherry and others, 1979). Recent studies have shown that manganese (Mn) oxides can oxidize As(III) to As(V) on time-scales of minutes to hours (Scott and Morgan, 1995; Chiu and Hering, 2000). Anaerobic microorganisms capable of reducing dissolved and adsorbed As(V) to As(III) have been found (Ahmann and others 1994; Oremland and others, 2000; Zobrist and others, 2000). Arsenic(V) can also be reduced to As(III) by organic compounds and dissolved sulfide (Rochette and others, 2000).

Natural gradient tracer tests were conducted in a well-characterized, sand and gravel aquifer in each of 3 distinct biogeochemical environments. Two tracer tests were conducted to examine oxidation of As(III) in either oxic or mildly reducing ground water, respectively, and a third test was conducted to examine reduction of As(V) in anoxic ground water.

Site Description
The test site, located on Cape Cod, Massachusetts, USA, has been described in detail elsewhere (LeBlanc and others, 1991; Davis and others, 2000). The shallow, unconfined aquifer consists of permeable, stratified glacial sand and gravel deposits. Ground-water flow velocities are approximately 0.4 m/day. Mineralogy is dominated by quartz with minor accessory minerals; surfaces of sediment grains are heavily coated with hydroxypolymer coatings containing Fe, Al and Mn (Coston and others, 1995; Fuller and others, 1996).

The biogeochemical zones in which the experiments were conducted are associated with a plume of sewage-contaminated ground water. The oxic zone has high dissolved oxygen

concentrations (200-300 μM, micromoles per liter), pH values 5.5-5.7, and low concentrations of dissolved salts (Kent and others, 1994; Davis and others, 2000). The suboxic zone has low concentrations of dissolved oxygen (1-6 μM), no detectable dissolved Fe(II) (<0.2 μM), pH values 5.8-6.2, concentrations of sewage-derived dissolved phosphate of 20-50 μM. The Fe(II)-zone in the vicinity of the As(V) tracer test was anoxic with Fe(II) concentrations of 500 μM, pH values 6.5-6.8, dissolved phosphate concentrations of 30-50 μM, and no detectable dissolved sulfide (<0.2 μM).

Experimental
Pulse injections of As(III) into the oxic and suboxic zones involved withdrawal of 900 liters of ambient ground water, adding As(III) to a concentration of 100 μM, which equals 7.6 milligrams As per liter, and bromide ion (Br⁻) to a concentration of 2.5 mM (millimoles per liter), and pumping the mixed injectate solution back into the aquifer over a period of about 4 hours. Pulse injections have been used previously to examine the transport of other redox-sensitive solutes (Kent and others, 1994, 1995; Davis and others, 2000).

The As(V) tracer test was conducted by continuously extracting ground water from the suboxic zone, adding As(V) to a concentrations of 6.7 μM, which equals 0.5 milligrams As per liter, and Br⁻ (to 1.6 mM), and re-injecting over a period of 4 weeks. Ground water from the suboxic zone was used rather than the ambient Fe(II)-containing anoxic ground water to avoid the possibility of oxidation of Fe(II) and precipitation of hydrous ferric oxide in the injection apparatus. This experimental design was preferred over a pulse injection to allow more time for microbial populations to respond to the presence of newly introduced solutes (Smith and others, in press).

Results and Discussion
Breakthrough of Br⁻, As(III), and As(V) observed 2.2 meters downgradient from the injection in the oxic zone showed that concentrations of As were attenuated by a factor of 10 compared to those of Br⁻ and the breakthrough curve for total dissolved As was retarded compared to that for Br⁻. Areas under the As(III) and As(V) breakthrough curves were approximately equal, indicating that about 50 percent of the As that broke through had been oxidized to As(V).

Much higher concentrations of total dissolved As were observed during breakthrough 2.2 meters downgradient from the injection in the suboxic zone. Significant oxidation of As(III) to As(V) occurred over the 2.2-meter transport distance. Both As(III) and As(V) appeared to be more mobile in the suboxic zone than in the oxic zone. This is consistent with the higher pH and higher concentrations of competing adsorbing anions like phosphate observed in the suboxic zone as compared to the oxic zone (Kent and others, 1994, 1995).

The mobility of As(V) observed during the 4-week injection in the Fe(II) zone was considerably lower than that observed in either of the As(III) tracer tests, where As(V) was generated by oxidation of As(III). Breakthrough of Br⁻ 1 meter downgradient was observed within 3 days of beginning the injection; breakthrough of As(V) was not observed until 22 days later. Arsenic(V) constituted all of the dissolved As detected 1 meter downgradient until 45 days after the beginning of the injection, after which time As(III) accounted for one fourth

to one half of the total As that broke through. Both As(V) and As(III) were observed until the end of the experiment, 4 months after beginning the injection.

Anoxic conditions in the Fe(II)-zone were slightly perturbed by the injection. Small concentrations of dissolved oxygen (less than 30 μM) were observed in sampling ports 0.2 meters above and below the injection port during the injection period. Concentrations of dissolved oxygen decreased with increasing distance downgradient of the injection. Anoxic conditions were restored shortly after ending the injection. This indicates that dissolved Fe(II) reacted with the injected oxygen to precipitate hydrous ferric oxide. Sufficient oxygen was injected to produce a mass of hydrous ferric oxide that was approximately equimolar to the mass of As(V) injected.

Results illustrate that ground-water chemistry can greatly influence the mobility of As in ground water. Oxidation of As(III) to As(V) was observed in oxic and mildly reducing ground water; reduction of As(V) to As(III) was observed in anoxic ground water with high concentrations of Fe(II). Observation of less extensive retardation of As(III) and As(V) in the suboxic zone than oxic zone is consistent with the expected lower extent of adsorption in the suboxic zone, owing to higher pH values and concentrations of phosphate, which competes for adsorption sites. Much greater retardation in the Fe(II)-zone likely resulted from extensive adsorption of As(V) owing to its low concentration and the presence of freshly precipitated hydrous ferric oxide.

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