

Microbially mediated alteration of iron mineral phases in contaminated sedimentary aquifers

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ABSTRACT: We investigated the stability of iron mineral phases in contaminated aquifers. The focus of our interest is on the role of Fe(III)-bearing minerals and grain coatings as sorption substrates influencing the transport of reactive constituents such as metals, anions, and bacteria and as electron acceptors facilitating the further biodegradation of contaminant organics. The geochemistry of two sandy surficial aquifers has been characterized. Sediments were subjected to metal-oxide extractions and determination of iron and aluminum. The amount of total HCl-extractable Fe was an order of magnitude higher for the aerobic, uncontaminated sediments than for the anaerobic, organic-contaminated sediments indicating that reductive dissolution removed the iron coatings. Comparison of different extraction methods indicates that microbially mediated iron reduction is dissolving amorphous or poorly crystalline oxides rather than crystalline phases. The presence of anaerobic conditions did not significantly alter the amount of extractable aluminum oxides. The sorption capacity of the sediment surfaces was an order of magnitude higher in the aerobic vs. anaerobic sediments. The removal of iron oxides from the mineral surfaces under anaerobic conditions was solely responsible for the reduction of sediment sorption capacity. Improved understanding of the biogeochemistry of iron in contaminated sedimentary aquifers likely will lead to a better ability to anticipate the rate of transport of a variety of solutes and colloids.

1 INTRODUCTION

Two different investigations of shallow sandy aquifers inform our thinking about the role of reactive iron minerals in hydrogeological systems. Groundwater in a number of settings has been described as having elevated concentrations of dissolved iron in anoxic portions of contaminant plumes (e.g. Baedecker et al. 1993, Lyngkilde & Christensen 1992), and the coupling of microbial reduction of Fe(III) to the degradation of organic compounds links the study of the biogeochemistry of iron to our desire to understand processes influencing contaminated aquifers. Questions about the transport and fate of reactive constituents in groundwater are linked to the study of iron through recognition of the importance of sorption processes on sesquioxide mineral surfaces common in sedimentary aquifers limiting the migration of metals, anions, and bacteria. We have been grappling with questions related to the stability of iron mineral phases in contaminated aquifers

and the role of Fe(III)-bearing minerals and grain coatings as sorption substrates.

2 SORPTION OF REACTIVE SOLUTES AND BACTERIA

In our ongoing study of the transport of bacteria through an unconsolidated sandy aquifer in the Coastal Plain of Virginia, we address a number of questions related to the potential for bacterial attachment to mineral solids. In laboratory and field-scale experiments, the presence of these positively charged metal-oxide coatings on quartz sand has been shown to greatly affect the sorption and transport of reactive constituents. The mineralogy of the metal oxide affects the affinity its surface has for ion sorption. The presence of more than one oxide in a system may affect the sorption characteristics as well. In addition to metal-oxide abundance, surface area is commonly employed as an estimator of total sediment reactivity, and the result can be inconsistent

with an assessment of that portion of the surface that actually participates in reactions.

Our investigation was undertaken on the Eastern Shore near the village of Oyster where depositionally similar sediments have been exposed to chemically distinct groundwater conditions. In a narrow, organic-rich leachate plume derived from vegetable waste pits, dissolved oxygen was only 0 to 0.9 mg L⁻¹, whereas it was 5.0 to 11 mg L⁻¹ in the regionally extensive aerobic, uncontaminated groundwater. In addition, the amount of dissolved iron in the aerobic groundwater was 0.001 to 0.01 mg L, but it was 12 to 42 mg L in the anaerobic zone. Samples of sediments from cores were subjected to metal-oxide extractions and determination of operationally defined fractions of iron (ferrous and ferric) and aluminum. The amount of extractable iron was an order of magnitude higher for the aerobic sediments than for the anaerobic sediments indicating that reductive dissolution removed the oxide coatings. The total iron in the HCl extracts of the aerobic sediments ranged from 3.2 - 52 µmol/g whereas it was only 0.9 - 2.4 µmol/g in the anaerobic sediments (Table 1). There was very little ferrous iron (Fe(II)) extracted from either of the two zones, and the values from each zone only ranged from 0.01 - 0.5 µmol/g of Fe(II) extracted. It is likely that microbial oxidation of

organic contaminants is linked to the reduction of iron from the surfaces of sediments in the polluted portion of the aquifer. Although the majority of the iron had been removed from the surfaces of the anaerobic sediments, there was still an appreciable amount of surface area measured.

We sought a means to characterize the aquifer solids for their potential for bacterial attachment, and we developed a single-point sorption determination for a reactive anion. In attempting to evaluate the reactivity of mineral surfaces in an aquifer setting, sorption of solutes directly probes that portion of the solid surface that participates in reactions involving other negatively charged reactive constituents, including bacteria. The reactivity of the sediment surfaces, as indicated by the sorption of ³⁵SO₄²⁻, was an order of magnitude higher in the aerobic vs. anaerobic sediments. The sulfate sorbed to the aerobic sediments (2.2 to 50 µmol/g) was an order of magnitude greater than for the anaerobic sediments (0.007 to 0.25 µmol/g). The presence of anaerobic conditions did not significantly alter the amount of extractable aluminum oxides on the surface of the sediments, and those coatings helped to maintain a high surface area for the anaerobic sediments. It appears that the removal of the iron oxides from the surfaces under anaerobic conditions was solely responsible for the significant reduction of sediment reactivity observed.

The iron-oxide content was the only one of the surface properties to be significantly altered by the anaerobic conditions with a concomitant alteration in the ability of the sediments to retain the anion sulfate (Knapp et al., in revision). It appeared, therefore, the presence or absence of iron oxides was the dominant factor controlling sulfate sorption. These results would indicate an alteration in the reactive surfaces of minerals when exposed to anaerobic groundwater and the potential for greater movement of reactive constituents, including bacteria, through these aquifer sediments.

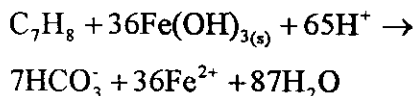
3 REDUCTIVE DISSOLUTION OF Fe(III) MINERALS

As redox conditions in a contaminant plume change with the depletion of oxygen and nitrate as electron acceptors, ferric iron is consumed as an electron acceptor coupled to the oxidation of organic matter (e.g. Lovley et al. 1989). The glacial-outwash, sandy aquifer at the USGS Toxic Substances Hydrology site near Bemidji, MN, became contaminated by

Table 1. Concentration of total HCl-extractable iron with depth (below water table) for samples from aerobic and anaerobic cores.

Aerobic Core		Anaerobic Core	
Depth (m)	Total Fe (µmol/g)	Depth (m)	Total Fe (µmol/g)
		-0.31	3.35
		-0.81	18.4
		-1.31	5.49
-1.36	2.10		
-1.44	1.54		
-1.53	1.88		
-1.61	2.16		
-1.69	2.12		
-1.77	2.32		
		-1.81	10.5
-1.88	2.45		
-2.32	2.40		
-2.80	1.27		
		-2.31	52.4
		-2.81	10.5
		-3.31	4.26
		-3.81	3.16
-3.88	1.97		
-4.26	1.34		
		-4.31	10.9

crude oil in 1979. Observations since nearly the time of the pipeline burst show accumulations of Fe(II) in the site groundwater over time, whereas no ferrous iron was found in the uncontaminated background water (e.g. Baedecker et al. 1993). Previous field and microcosm results (Baedecker et al. 1993, Lovley et al. 1989) indicate the degradation of toluene may proceed according to



In this study, we examined the distribution of Fe in the sediments of the aquifer in order to assess the magnitude of impact of Fe(III) reduction in the contaminant plume on the geochemistry of the sediments. Sampling and extraction of sediments revealed that the average HCl-extractable Fe(III) concentration in the most contaminated portion of the aquifer was 16.2 $\mu\text{mol/g}$, a 30% reduction from the value in background sediments of 23.8 $\mu\text{mol/g}$ (Tuccillo et al. 1999). Comparison between HCl extractions that should capture poorly crystalline Fe(III) solids and Ti-citrate-EDTA-bicarbonate extractions that should reductively dissolve amorphous and crystalline Fe(III) oxides indicates that the bulk of the microbially mediated iron reduction is dissolving amorphous or poorly crystalline oxides.

In contrast to the study in Virginia in which virtually no Fe(II) was extracted from aquifer solids, at Bemidji we found 19.2 $\mu\text{mol/g}$ Fe(II), as much as 4 times the background sediments with 4.6 $\mu\text{mol/g}$ Fe(II) (Figure 1). Scanning electron microscopy detected authigenic ferroan calcite in the anoxic sediments (Baedecker et al. 1992, Tuccillo et al. 1999). Likely the contrast can be attributed to the availability of minerals that buffer pH, giving the contaminated groundwater at Bemidji at pH near 6.9 whereas at the Oyster, VA, site it is closer to 6.3 in the anaerobic groundwater.

One of the most striking features of the distribution of iron content of the aquifer sediments was the extreme concentration at the anoxic/oxic transition zone. HCl-extractable Fe(III) reached values as great as 49.8 $\mu\text{mol/g}$ at this boundary (Figure 1). This 70% increase in total extractable Fe at the interface indicates the reoxidation and precipitation of Fe mobilized from aquifer sediments located upgradient in the anoxic, contaminated groundwater plume as that water flows downgradient into an oxic background groundwater. Scanning electron microscopy

confirmed the abundant Fe(III) oxyhydroxides at the anoxic/oxic boundary (Tuccillo et al. 1999).

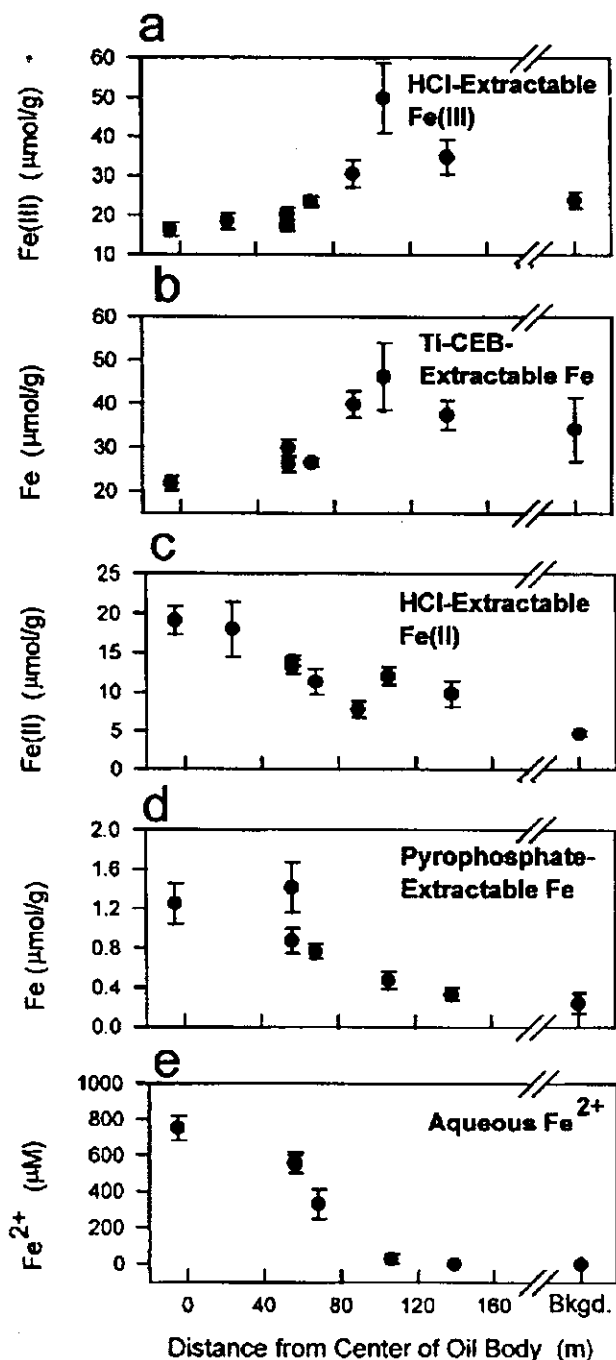


Figure 1. Graphs of various fractions of iron extracted from the sediments and of aqueous Fe²⁺ in pore waters vs. distance from the center of the oil body. Circles represent the mean of samples from all depths for each core. Error bars represent standard errors (s.d./n^{0.5}) which give an indication of within-core variability.

4 IMPLICATIONS FOR TRANSPORT

The alteration of sediment chemistry has implications for the availability of electron acceptors and the biodegradation of contaminant organics. As availability of Fe(III) decreases, alternate hydrocarbon degradation processes linked to methanogenesis will be less efficient and intermediate metabolic products of biodegradation will persist and be transported in the groundwater. The Fe(II) that is mobilized out of the sediments in the most contaminated portion of the aquifer will be reoxidized at some location downgradient and precipitate as an "iron curtain" that can alter not only the reactivity of the solid phase but can also change the permeability as mineral grains are cemented together and the interstitial spaces filled with Fe(III) precipitates. The high Fe(III) content of that anoxic/oxic boundary gives rise to a sorptive capacity of the transition-zone sediments that is enhanced above both background and anoxic sediments. The presence of the Fe(III) oxyhydroxides has implications for the reactivity of aquifer sediments, altering the nature and extent of reaction between sorbing species and mineral surfaces. The contaminants that may be retarded in their transport are not just those of the original crude oil spill but potentially include bacteria, anions, and metals. Improved understanding of the biogeochemistry of iron in contaminated sedimentary aquifers likely will lead to a better ability to anticipate the rate of transport of a variety of solutes and colloids.

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