



Changes in the sorption capacity of Coastal Plain sediments due to redox alteration of mineral surfaces

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Abstract

Chemical characteristics of grain coatings in a Coastal Plain sandy aquifer on the Eastern Shore of Virginia were investigated where sediments have been exposed to distinct groundwater redox conditions. Dissolved O₂ was 5.0 to 10.6 mg L⁻¹ in the regionally extensive aerobic groundwater, whereas in a narrow leachate plume it was only <0.001 to 0.9 mg L⁻¹. The amount of dissolved Fe in the aerobic groundwater was only 0.005 to 0.01 mg L⁻¹, but it was 12 to 47 mg L⁻¹ in the anaerobic zone. The amount of extractable Fe was an order of magnitude higher for the aerobic sediments than for the anaerobic sediments indicating that reductive dissolution removed the oxide coatings. The capacity for anion sorption on the sediment surfaces, as indicated by the sorption of ³⁵SO₄²⁻ was an order of magnitude higher in the aerobic vs. anaerobic sediments. The presence of anaerobic groundwater did not significantly alter the amount of extractable Al oxides on the surface of the sediments, and those coatings helped to maintain a high surface area. The removal of the Fe oxides from the grain surfaces under anaerobic conditions was solely responsible for the significant reduction of SO₄ sorption observed. This loss of capacity for anion sorption could lead to more extensive transport of negatively charged constituents such as some contaminant chemicals or bacteria that may be of concern in groundwater. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

1.1. Sorption to aquifer solids

Among the chemical properties affecting transport of reactive constituents in groundwater, the surface charge of aquifer solids is a dominant factor controlling retardation by sorption. In laboratory and field-scale experiments, the presence of metal-oxide coatings on quartz sand greatly affects the sorption and transport of reactive constituents including metals, anions, and bacteria (Scholl et al., 1990; Scholl and Harvey, 1992; Mills et al., 1994; Coston et al., 1995; Fuller et al., 1996). These metal-oxide coatings have high surface areas and retain

a more positive surface charge at the pH of most natural waters than many soil and aquifer minerals, especially quartz. For instance, Fe oxyhydroxide has a zero point of charge (zpc) of 8.5 and is positively charged at neutral pH. The underlying quartz surface has a zpc of 2.0 and, in the absence of a metal-oxide coating, would be negatively charged under similar conditions (Stumm and Morgan, 1996).

The mineralogy of the metal oxide affects the affinity its surface has for ion sorption. Amorphous oxides of both Al and Fe are generally believed to be more reactive on a per weight basis than crystalline oxides (Davis and Kent, 1990). Amorphous forms retain anions more readily than crystalline oxides, with the capacity for sorption decreasing with increasing age and crystallinity (McLaughlin et al., 1981; Simms and Ellis, 1983). Bowell (1994) observed that the association of As with sediments in a mining region was much greater for amorphous than for crystalline Fe-oxide phases.

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The presence of more than one oxide in a system may affect the sorption characteristics as well. Al oxides in soils sorb the PO_4^{3-} and SO_4^{2-} more readily than Fe oxides (Chao et al., 1964). The sorptive properties of binary-oxide suspensions have been demonstrated to be different from their component parts. Al oxides can mask the presence of other oxides and determine the overall surface characteristics (Anderson and Benjamin, 1990). Warren and Zimmerman (1994) suggested that in mixed-oxide systems, layering of the metal oxides reduces the exposed surface area of the individual minerals. This effect may cause an overestimation of sorption capacity based on summation of the contribution of the component minerals as determined by extraction techniques or by estimation from literature-based values for single-component sediments.

In addition to metal-oxide abundance, another estimator of total sediment sorption capacity commonly employs measurements of surface area by gas adsorption (Chiou and Rutherford, 1993; Warren and Zimmerman, 1994). The positive correlation found between surface area and sorption of radionuclides (Inch and Killey, 1987) and of trace metals (Horowitz and Elrick, 1987) suggests that variations in surface area may account for variable sorption to aquifer minerals. Previous studies have also observed a strong dependence of cation adsorption on surface area in materials in which oxide surface coatings contribute most of the surface area (Jackson and Inch, 1983). Furthermore, Borggaard (1983) suggested that differences observed between sorption onto amorphous and crystalline oxides is a function of the surface area (decreasing as the oxides age and crystallize) rather than a function of changes in their surface electrical properties. Horowitz and Elrick (1987) found that the trace-metal content of stream sediments was most strongly correlated with surface area, with a weaker dependence on amount of extractable oxides. Coston et al. (1995) and Fuller et al. (1996), on the other hand, found weak or no correlation with surface area for Pb^{2+} and Zn^{2+} sorption; however, variability in sorption was best described by the amount of extractable Al- and Fe-oxide coatings when normalized to specific surface area. The results indicate that adsorption may occur at specific, more reactive portions of aquifer solids, whereas surface area measurements employing chemically unreactive N_2 quantify the entire area of the sample. In these studies, the amounts of Al, Fe, or Mn were not correlated with surface area, suggesting that the extractions dissolved metals from multiple layers of oxide coatings that were not accessible to N_2 adsorption. Similarly, increasing the amount of Fe-oxide coatings on quartz sand (in the 0.075 to 0.21 mm size range) from 0.6 to 1.2 wt.% (corresponding to 104 and 225 $\mu\text{mol g}^{-1}$ extractable Fe, respectively) did not alter the amount of surface area (3.4 $\text{m}^2 \text{g}^{-1}$) measured by N_2 adsorption (Szecsody et al., 1994). This result

would again suggest a layering on the quartz surface of the Fe-oxide coatings. From the above discussion, it is evident that sorption to aquifer solids may be controlled by a number of factors including the surface charge of the solid, its mineralogy and crystallinity, and the surface area of the mineral exposed at the solid surface.

1.2. Anaerobic geochemistry

Water-table aquifers are often aerobic because, under non-contaminated conditions, the indigenous microorganisms are more C-limited than O_2 -limited. With the introduction of organic chemical contaminants, however, the situation often changes; C limitations disappear and O_2 is rapidly consumed (Chapelle, 1993). As anoxic conditions develop in a contaminant plume, anaerobic degradation reactions become more important (e.g., Barker et al., 1986; Baedecker et al., 1993). A redox-zone sequence of methanogenic, SO_4^{2-} -reducing, Fe(III)-reducing, Mn(IV)-reducing, NO_3^- -reducing, and aerobic conditions may be formed under conditions of highest to lowest organic contaminant concentrations, respectively (Christensen et al., 1994; Nielson et al., 1995). This sequence is based on the energetics of the reactions and the availability of the electron acceptors (Stumm and Morgan, 1996). As redox conditions in a contaminant plume change with the depletion of dissolved O_2 (DO) and NO_3^- , the oxidation of organic matter is coupled to Fe(III) which is consumed as an electron acceptor (Lovley et al., 1990). Due to the widespread availability of Fe(III) oxide in subsurface environments (vanBreeman, 1988; Heron et al., 1994), it is likely that microbial oxidation of organic contaminants is a significant contribution to the reduction of Fe from the surfaces of sediments in polluted aquifers. In the crude-oil contaminated aquifer at the USGS Toxic Substances Hydrology site near Bemidji, MN, accumulations of Fe(II) were observed in the groundwater over time (Cozzarelli et al., 1994), whereas no Fe(II) was found in the uncontaminated background water. The aerobic sediments had 4 times the amount of extractable Fe(III) as compared to the anaerobic sediments (Tuccillo et al., 1999). Heron et al. (1994) showed that both amorphous and crystalline Fe oxides were removed in the Fe-reducing zone of a contaminated aquifer.

Within anaerobic zones, Fe(III) reduction may alter the abundance and type of the metal oxide coating the aquifer sands. Overall, the changes in the sediment that can occur with changing redox status driven by microbiological activities and the concomitant effect on sorption are fundamental to understanding the transport properties of the aquifer. The objective of the present study was to quantify the changes in sorption characteristics in sediments exposed to anaerobic groundwater and to determine the relationship with sediment geochemical properties.

2. Site description

The study site is located at the Virginia Coastal Research Center on the seaward shoreline of the Eastern Shore of Virginia near the town of Cape Charles (Fig. 1), where the mainland is separated from the ocean by a broad lagoon-marsh-barrier island complex. Here the Atlantic Coastal Plain consists of unconsolidated shore-face deposits that formed on the tip of a spit that prograded across the mouth of the Chesapeake Bay during the upper Pleistocene and Holocene (Mixon, 1985). The sediments are primarily quartz sands (95%), have a mean grain diameter of 180–500 μm , and are coated with varying amounts of Fe and Al oxides (Dobson, 1997; Knapp, 1997). The study site slopes toward the marshes and is bisected by the Mappsburg Scarp, a slightly steeper slope that represents an ancient beach face. The elevation of the field above the scarp is about 7–8 m above mean sea level (MSL), and that of the area east of the scarp is about 2–5 m above MSL. The depth to groundwater is about 1.5–2 m in the lower elevations of the field (e.g., D1) to 6 m below ground surface in the higher elevations (e.g., B2). The unconfined aquifer extends to a depth of

approximately 15 m below ground surface and the direction of groundwater flow is generally eastward toward the Atlantic Ocean (Callaghan, 1999; Richardson, 1992).

Burial pits of decaying vegetable matter from a tomato cannery are located on the northern border of the site in Fig. 1, and they were active from approximately 1974 to 1983 (Sitler, 1997). The buried material provides a source of readily available organic matter that depletes the O_2 in the water because of microbial decay. A portion of the study site is underlain by anaerobic groundwater (Fig. 1). The proximity of two groundwater zones with distinct chemical differences within sediments from comparable depositional environments enabled an investigation of the impact of redox conditions on sediment geochemical properties.

3. Methods

3.1. Groundwater and sediment sampling

Groundwater sampling from each of the wells was done monthly over a period of two years (from June

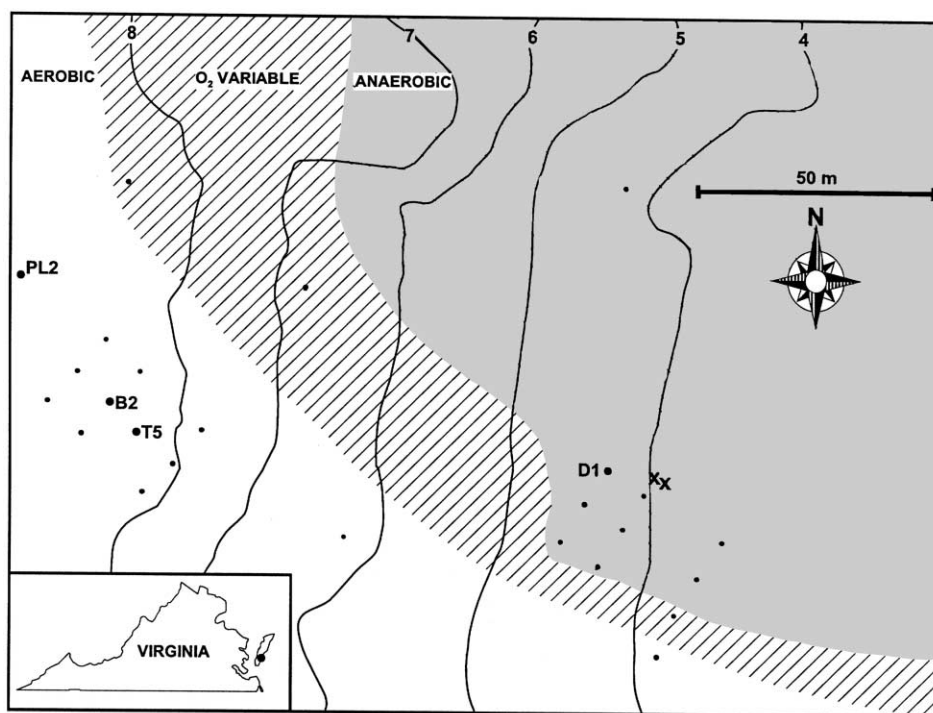


Fig. 1. Map of the study site at the Virginia Coastal Research Center. Unlabeled points indicate wells from which dissolved O_2 measurements were made to estimate the extent of the aerobic and anaerobic regions. Labeled points locate sources of sediment cores or wells used for chemical analysis in this study. Additional cores from the anaerobic region were collected at the locations marked by x. The O_2 status of the groundwater is indicated by the coloring: the white area has O_2 levels above 2 mg L^{-1} , the hatched area has O_2 levels that vary in time and space from 0.5 to 2 mg L^{-1} , and the gray areas are below 0.5 mg L^{-1} . Contour lines are surface elevations in meters above mean sea level. The Mappsburg Scarp is the area on the map between about 7 m and 5 m elevation. The southernmost edge of the vegetable burial pits is located just north of the two northern-most wells plotted in the map.

1994 to 1996) and quarterly thereafter. After purging for at least 3 well volumes with a peristaltic pump, samples were filtered in-line through a 0.45- μm filter, stored in polyethylene bottles, and chilled on ice for return to the laboratory. In the field, DO was determined using CHEMets (self-filling ampoules for colorimetric analysis), temperature was measured with a Hg thermometer, and pH was measured with an Orion meter and glass pH electrode calibrated to pH 4 and 7 buffers. Alkalinity was determined by potentiometric titration in the field. Major cations were determined by atomic absorption spectroscopy, major anions were determined by ion chromatography, and dissolved organic C (DOC) was measured on a Dohrmann C analyzer. The Fe, Mn, and Al concentrations were determined by inductively coupled plasma emission spectroscopy (ICP–AES).

Assessment of the thermodynamic saturation state of the two groundwater solutions with respect to various plausible mineral phases was accomplished using an equilibrium aqueous speciation code, WATEQ4F (Ball and Nordstrom, 1991). For all the anaerobic samples, the total dissolved Fe was assigned entirely to Fe(II), consistent with the results (Knapp, 1997) of occasional direct determination of dissolved Fe species in filtered, acidified samples analyzed by UV-vis spectrophotometry (Gibbs, 1979) and the absence of dissolved O_2 . For the aerobic samples, the total dissolved Fe was assigned entirely to Fe(III).

Aerobic sediment cores (3.5-inch diameter) were collected during installation of wells. The cores were collected in Lexan liners and capped immediately following recovery. The samples for this study were collected from below the water table in cores from B2 and T5 (Fig. 1). Samples were collected in 10 cm^3 , detipped syringes at 0.5-m intervals along the length of the core; the collection procedure is detailed in Knapp (1997).

For the acquisition of samples from the anaerobic zone, in situ conditions had to be maintained so that the sediments would not be exposed to O_2 . Two anaerobic sediment cores were collected adjacent to the lower field wells using a vibracore. The 3-inch diameter cores were collected in Al tubing and were sealed with expansion plugs immediately upon recovery and returned to the laboratory. The porewater was then removed under a N_2 atmosphere in an anaerobic chamber. The cores were then resealed and frozen (to preclude any further microbial action) until sub-sampling and analysis could be done. All further sample handling was done under a N_2 atmosphere in either a glove box or a glove bag.

3.2. Sediment analysis

The composition of the grain-surface coatings on the sediment samples collected from both the aerobic and anaerobic portions of the aquifer was characterized using metal-oxide extractions on individual 1-g (dry

weight) samples for Fe and Al phases to determine operationally defined types and amounts of coatings present in each zone. For sands from the aerobic zone, 3 separate extractions for metal oxides were done for determination of various phases and crystallinities of the metal oxides. The hydroxylamine hydrochloride (HA) treatment extracts amorphous oxides (Chao and Zhou, 1983); the ammonium oxalate (AO) extraction removes poorly crystalline oxides (Fey and Le Roux, 1977; Phillips and Lovely, 1987); and the dithionite citrate bicarbonate (DCB) extraction removes oxides including crystalline Fe oxides such as goethite (Mehra and Jackson, 1958). Sand from the anaerobic zone was also subjected to extraction by DCB. All these extraction procedures remove similar fractions of Al minerals with less distinction and more overlap of phases among the methods (Chao et al., 1964). All extraction solutions were separated by filtration through 0.45- μm filters. Extraction solutions were analyzed for total Fe, Al, and Mn by ICP–AES.

The redox speciation of the Fe phases in both the aerobic and anaerobic portions of the aquifer was determined for extractions performed with 0.5 M HCl (Heron et al., 1994). Extractions of the sediments from the anaerobic zone were performed under O_2 -free conditions in sealed 60-mL serum bottles with N_2 as the headspace gas. The method targets amorphous and poorly crystalline Fe(III) and reduced Fe(II) phases such as siderite. Following filtration through 0.45- μm filters, the extraction solutions were analyzed for total Fe and for Fe(II) using the ferrozine method, with Fe(III) determined by difference (Gibbs, 1979).

Solute sorption was employed as a probe of that portion of the solid surface that participates in sorption reactions. As a divalent anion of moderate ionic potential, SO_4^{2-} should sorb reversibly to positively charged Fe (III)- and Al-oxyhydroxide grain coatings which have been demonstrated to be the primary substrate for adsorption in this type of hydrogeological setting (Fuller et al., 1996). The use of SO_4^{2-} is advantageous because very small samples of aquifer material can be assessed in laboratory experiments for sorption potential by using easily detected $^{35}\text{SO}_4^{2-}$, because SO_4^{2-} can be introduced into the subsurface environment in field trials, and because, as an anion, SO_4^{2-} is likely to be an indicator of how other negatively charged reactive constituents, including bacteria, will interact with aquifer solids.

On separate splits of the core samples, the amount of surface available for sorption of reactive solutes was determined by a $^{35}\text{SO}_4^{2-}$ -sorption assay. Non-radioactive SO_4 was combined with $^{35}\text{SO}_4^{2-}$ to yield a 3.3 mM SO_4^{2-} solution with radioactivity in the range of 10,000–30,000 dpm L^{-1} . Three mL of the solution were added to 3 g of sediment. After shaking the vials for 24 h, the samples were removed and the liquid was filtered through a 0.45- μm filter. A 100- μL portion of the filtered

solution was removed and the $^{35}\text{SO}_4^{2-}$ determined by liquid scintillation counting. The amount of SO_4^{2-} in solution was then subtracted from the amount added to determine the amount of SO_4^{2-} sorbed in $\mu\text{mol g}^{-1}$.

Specific surface area measurements were made by N_2 gas adsorption with a Gemini 2360 (Micromeritics, Norcross, GA) surface area analyzer. The single-point method was employed on 1-g samples from each zone both before and after metal-oxide extractions.

4. RESULTS

4.1. Groundwater chemistry

Differences in groundwater chemistry are evident across the study site (Table 1). In a narrow leachate plume, the groundwater (as measured in well D1) was depleted in DO. In contrast, the groundwater under much of the site (as measured in well PL2) had not been affected by the organic matter from the waste burial pits and had DO levels consistent with the background groundwater. There were different concentrations of dissolved Fe in the groundwater of the two zones, with high concentration of dissolved Fe in the anaerobic zone and several orders of magnitude less dissolved Fe in the aerobic zone. Variations in the concentrations of other redox species, like NO_3^- and NH_4^+ , were consistent with strongly contrasting redox conditions in the groundwater. The alkalinity

of the anaerobic groundwater was greater than the aerobic groundwater.

Other chemical characteristics of the aerobic and anaerobic groundwater were similar. The pH was in the same general range, although a bit higher for the anaerobic zone as compared to the aerobic zone. The amount of DOC was comparable although again slightly higher in the anaerobic groundwater. The highest SO_4^{2-} concentrations were observed in the aerobic groundwater.

The results of the WATEQ4F calculations on two representative groundwater compositions showed the aerobic-zone groundwater to be supersaturated with respect to a number of Fe(III) minerals, including goethite and ferrihydrite. In contrast, the water from the anaerobic zone collected at Well D1, with orders of magnitude more dissolved Fe all present as Fe(II), was undersaturated with respect to all Fe(III) minerals. Instead, the solution was slightly supersaturated with respect to the Fe(II) mineral siderite.

4.2. Relationships among surface properties of aerobic sediments

The greatest amount of Fe was removed from the aerobic sediments using the DCB extraction (Table 2). Significant concentrations of Al were measured, with less specificity by extraction method. Manganese concentrations in all extracts were negligible. Herein total metal extracted is defined as Fe plus Al.

Table 1

Range of concentrations of groundwater constituents in the aerobic and anaerobic zones of the aquifer. Values shown represent the range of observations for groundwater collected at two wells for 16 sampling times from June 1994 to November 1996. All concentrations are reported as mg L^{-1}

	Aerobic zone (Well PL2)	Anaerobic zone (Well D1)
pH	5.3–6.5	5.9–6.6
Alkalinity (as HCO_3^-)	18.3–39.7	153–384
DOC	1.72–4.47	1.87–5.89
DO	5.0–10.6	< 0.001–0.9
Dissolved Fe	0.005–0.01	12–47
SO_4^{2-}	11.0–74.0	12.0–44.2
NO_3^-	15–50	< 0.22–4.8
NH_4^+	< 0.06	0.558–3.12

Table 2

Amounts of Fe and Al removed from 27 aerobic and 14 anaerobic sediment samples by various extraction methods. Values are the medians with the range in parentheses. All concentrations are reported as $\mu\text{mol g}^{-1}$

Extraction method	Aquifer sediments	Total Fe	Al
DCB	Aerobic	7.63 (1.83–154)	5.45 (1.49–75.8)
DCB	Anaerobic	1.82 (0.519–4.17)	17.3 (11.8–29.5)
AO ^a	Aerobic	4.46 (0.417–41.6)	5.82 (2.51–41.7)
HA	Aerobic	2.99 (0.216–23.2)	5.44 (2.67–44.6)

^a AO extractions were analyzed for only 25 aerobic sediment samples.

The relationship of the sorption of SO_4^{2-} to various sediment surface properties was determined in order to gain insight to the factors controlling SO_4^{2-} sorption on the 27 aerobic sediment samples. The SO_4^{2-} sorbed was related to both the amount of DCB-extractable metal oxides and the magnitude of surface area (Fig. 2). Strong correlations were observed among the properties of surface area and DCB-extractable metal oxides for the aerobic sediments (Fig. 3). The Al and Fe contents were highly correlated ($r=0.997$; Table 3 and Fig. 3A). In addition, the surface area was highly correlated with the DCB-extractable Fe ($r=0.92$; Fig. 3B and Knapp, 1997) and the total extractable metals ($r=0.91$; Knapp, 1997).

For comparison to the results for “total metal” (amorphous and crystalline phases) in Fig. 2, the relationships between SO_4^{2-} sorption and the HA-extractable “amorphous” phases and the AO-extractable “amorphous and poorly crystalline” phases were also computed for the aerobic cores. Lower values of r for SO_4^{2-} sorption and

HA-extractable phases were obtained (Table 3). The r values for sorption and the AO phases (Table 3) were intermediate to those for DCB (total) and for HA. In addition, for each of the types of extraction, the correlation between Al and Fe content was high (Table 3).

4.3. Comparison of aerobic and anaerobic sediments

Fe has been removed from the surfaces of the sediments in the anaerobic zone. The amount of Fe that could be extracted with a 0.5 M HCl solution from the anaerobic sediments was less than 10% of that in the aerobic sediments (Table 4). The values from the two zones were compared using Student's t -test and were significantly different with $P=0.0086$. The 0.5 M HCl extraction was used to speciate the Fe(II) and Fe(III) removed from the sediment surfaces. There was very little Fe(II) extracted from either of the two zones (Table 4), the vast majority of the total extracted Fe being Fe(III).

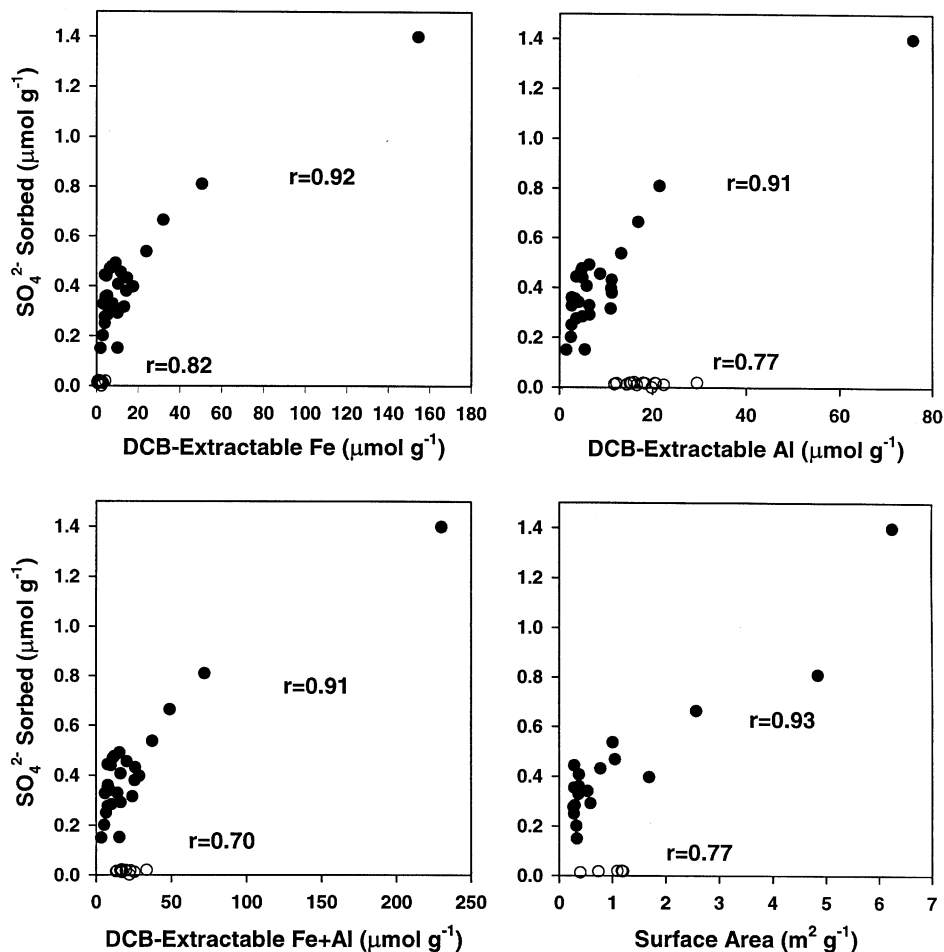


Fig. 2. Relationship of SO_4 sorption to mineral surface properties. DCB-extractable metals are reported for 27 sediment samples from the aerobic zone (●) and from 14 sediment samples from the anaerobic zone (○). Only 19 and 6 surface area measurements were obtained for the aerobic and anaerobic samples, respectively. Correlation coefficients (r) are listed for each relationship.

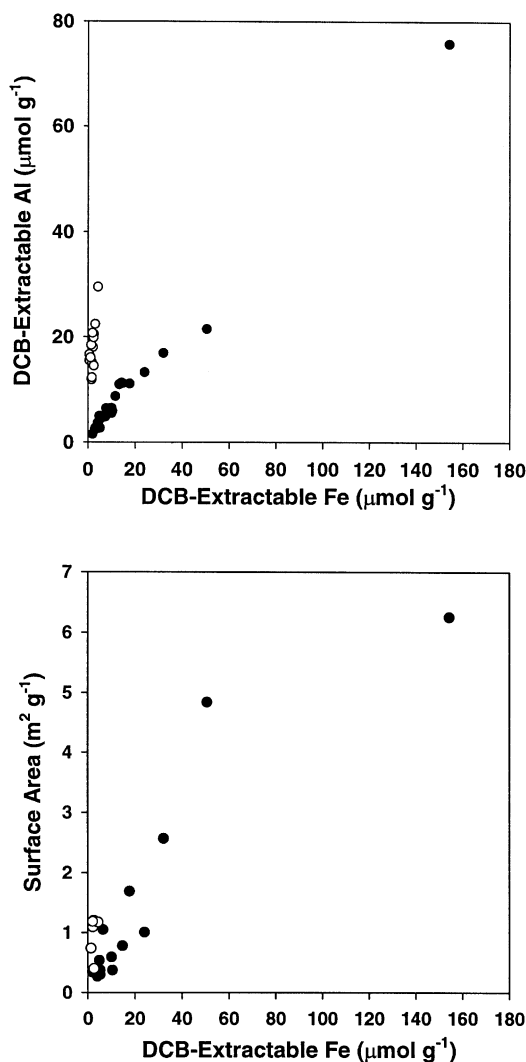


Fig. 3. Relationships among surface properties of aquifer sediments. DCB-extractable metals are reported for 27 sediment samples from the aerobic zone (●) and from 14 sediment samples from the anaerobic zone (○). Only 19 and 6 surface area measurements were obtained for the aerobic and anaerobic samples, respectively. The amount of surface area on all samples after extraction of total metals was 0.10 to 0.13 m² g⁻¹.

There was a strong correlation ($r=0.92$) between the amount of extractable Fe on the sediments and the surface area for the samples from the aerobic zone (Fig. 3B). Although in the anaerobic samples the majority of the Fe had been removed from the surfaces of these sediments, there was still an appreciable amount of surface area measured. The surface areas for the anaerobic sediments were from 0.39–1.2 m² g⁻¹ and were within the range of the aerobic samples (values from 0.27–6.3 m² g⁻¹). The surface area values for the anaerobic- and the aerobic-zone samples were compared using Student's *t*-test and

Table 3

Correlation coefficients (r) among surface properties for the aerobic sediments. Hydroxylamine hydrochloride (HA) extraction operationally defines amorphous oxide phases. Ammonium oxalate (AO) extraction operationally defines amorphous and poorly crystalline phases. Dithionite citrate bicarbonate (DCB) extraction operationally defines amorphous and crystalline phases. Graphical presentations of the correlations for DCB-extracted metals are shown on Figs. 2A–C and Fig. 3A

	HA	AO	DCB
SO ₄ ²⁻ Sorbed vs. Extractable Fe	0.68	0.87	0.92
SO ₄ ²⁻ Sorbed vs. Extractable Al	0.76	0.89	0.91
SO ₄ ²⁻ Sorbed vs. Extractable Fe + Al	0.73	0.88	0.91
Extractable Fe vs. Extractable Al	0.97	0.98	0.99 ^a

^a Computed value of r was 0.997.

Table 4

Amounts of Fe extracted by 0.5 M HCl from 15 anaerobic samples and 9 aerobic samples. Values are the medians with the range in parentheses. All concentrations are reported as μmol g⁻¹

	Fe(III)	Fe(II)	Total Fe
Anaerobic	1.96 (0.902–2.45)	0.123 (0.061–0.299)	2.06 (1.01–2.57)
Aerobic	9.97 (3.08–50.5)	0.320 (0.011–0.495)	10.3 (3.31–51.0)

were not significantly different. When both Fe and Al were removed from the samples by DCB extraction in the laboratory, however, the resulting surface area was only 0.10–0.13 m² g⁻¹ for each of the zones. This was a significant reduction in the surface area as compared to that observed during removal of Fe under anaerobic conditions in the aquifer. Further, it is important to note that this loss of surface area upon DCB extraction of the metal oxides was greater than would be expected by geometric (spherical) calculation based on the grain size of the sand (Knapp, 1997). This result suggests that metal-oxide coatings remain on the surface of the anaerobic samples that contribute substantially to the surface area.

The nature of the oxide coatings on the anaerobic sediments is further elucidated by comparing the amounts of total Al vs. Fe for each of the two zones (Fig. 3A). A strong correlation ($r=0.997$) was observed between the two metals for the aerobic sediments. For the anaerobic sediments, the amount of Al extracted from the sediments was comparable to the amount in the aerobic sediments (Table 2). The ratios of DCB-extractable Fe to Al in the aerobic (range 1.23–2.03) and the anaerobic (range 0.0440–0.141) sediments were evaluated with Student's *t*-test and were significantly different with $P < 0.001$, because of the removal of the Fe and the persistence of Al on the surfaces.

Changes in the metal-oxide composition of the sediment coatings may affect the reactivity of the surfaces. It was clearly observed that the removal of oxides on the surfaces had a profound effect on the sorption of SO_4^{2-} to these sediments (Fig. 2). The SO_4^{2-} sorbed to the aerobic sediments ($0.150\text{--}1.40 \mu\text{mol g}^{-1}$) was an order of magnitude greater than for the anaerobic sediments ($0.00722\text{--}0.0251 \mu\text{mol g}^{-1}$). The SO_4^{2-} sorption was, in fact, significantly different for these two zones ($P < 0.001$).

5. Discussion

5.1. Redox chemistry

A number of other changes in groundwater chemistry occur concomitantly with the consumption of DO in the anaerobic zone. It is likely that what is observed now as the anaerobic groundwater is a remnant of O_2 consumption and alkalinity generation during DOC biodegradation as the plume moved downgradient to its present position. Additional groundwater samples obtained from wells further to the north and closer to the source have DOC concentrations as high as 32 mg L^{-1} (unpublished data). The fact that the DOC concentration is about the same in the anaerobic groundwater as in the aerobic groundwater at this time is coincidental.

At the site, the groundwater in the anaerobic zone is dominated by Fe reduction. Comparison of the chemistry of the groundwater from each zone of the aquifer suggests that Fe has been reductively dissolved from the anaerobic sediments. This reduction is evident in the results of the chemical analysis (Table 1) where, in addition to changes in the redox status of the two zones as shown by the consumption of O_2 in the anaerobic zone, there were much higher dissolved Fe concentrations compared to the aerobic groundwater.

The results of the sediment extractions also support the reduction of Fe (Table 4). Given the results of the WATEQ4F calculations, it is plausible that the anaerobic groundwater (e.g., Well D1), in disequilibrium with respect to Fe(III) minerals, has acted to dissolve those Fe(III)-bearing grain coatings whereas the Fe(III) phases are stable in aerobic groundwater (i.e., Well PL2). Compared to the high Fe(II) in the anaerobic groundwater, the results of the 0.5 M HCl extraction for solid Fe(II) phases indicated that there was no appreciable amount in either the aerobic or anaerobic sediments (Table 4). These results would indicate that reduction of the Fe in the anaerobic zone was not resulting in appreciable formation of Fe(II) mineral phases such as siderite and that reduced Fe was remaining dissolved in groundwater.

The presence of organic matter in the groundwater has an impact on the sorption behavior of sediments in contaminated aquifers. Many studies have investigated the sorption of organic compounds in aquifers (e.g.,

Swartzenbach and Westall, 1981; Barber, 1994). In addition, organic sorption has been shown to compete with anions for reactive sorption sites (Stollenwerk, 1995). Because of the similar concentration of the DOC in the two areas sampled, it is unlikely that sorption of organic matter in the anaerobic plume can explain the decrease in the ability of the sediments to retain SO_4^{2-} . Specific extractions targeting surface-associated organic matter were not performed, but total organic matter (TOC) was determined to be similar in sediments from the aerobic (0.01–0.05%) and anaerobic (0.01–0.08%) zones.

5.2. Relationship of surface properties to sorption

The results from analysis of the aerobic sediments indicated that each of the sediment properties, extractable metals and surface area, was able to explain a high percentage of the variance in SO_4 sorption capacity (Fig. 2). Because the extraction methods removed both the Fe and Al oxides, distinction between the phases was not possible. The correlation results indicated comparable relationships of sorption to total (DCB-extractable) Fe and total (DCB-extractable) Al (0.92 vs. 0.91; Table 3 and Fig. 2A and B). Complicating the separation of the effects of Fe and Al on sorption was the fact that these metals were highly correlated with each other ($r=0.997$; Table 3 and Fig. 3A). Previous work by Dobson (1997) demonstrated a similar strong correlation ($r=0.985$) between total Al and Fe on sands from the study site, and regression analysis of SO_4^{2-} sorption to total metals suggested that the relative reactivity of Fe oxides may be greater than that of the Al phases.

The interpretation of the DCB-extractable total oxides is difficult due to controversy in the literature about the mineral sources of Al extracted by DCB (McKeague and Day, 1966; Arnseth and Turner, 1988). The amount of Al that was obtained in AO extraction in this study, however, was similar to that obtained by DCB extraction, suggesting that AO extraction for Al oxides for this aquifer sediment is complete. The correlation between Al and Fe was still high ($r=0.98$) for the AO extraction, and the relative relationships with SO_4^{2-} sorption were similar to the DCB extractions where the r values were 0.92 and 0.91 for Fe and Al, respectively, and 0.87 and 0.89 for the AO extraction (Table 3).

Because of the well known affinity for sorption to amorphous Fe oxyhydroxides, many studies have modeled metal adsorption to oxides by fixing the total sorption site density from estimates derived from studies with pure amorphous Fe oxyhydroxides (Dzombak and Morel, 1990). Determining the appropriate surface density of adsorption sites, however, can cause difficulties in applying sorption models to the mixed mineral surfaces in heterogeneous natural systems that include phases covering the spectrum from amorphous to crystalline materials (Davis and Kent, 1990). Adsorption by aquifer

material has been successfully modeled by Stollenwerk (1994) using a total site density defined by amorphous extractable phases; however, Coston et al. (1995) showed that the site density of an aquifer sand is underestimated when only the amorphous extractable phases are considered and that sorption to sands decreases only after both the amorphous and crystalline phases have been removed. The strong dependence of sorption on amorphous metal-oxide coatings has been suggested to arise from the fact that amorphous phases have greater surface area than the more crystalline oxides (Davis and Kent, 1990). When using operationally defined extractions, it was apparent from the present data that the amorphous phases were not the only ones contributing to the reactive surface. The relationships (Table 3) between sorption of SO_4^{2-} and the metals extracted by the method considered to extract only the amorphous phases (HA) were the weakest ($r=0.68$ for Fe, and 0.76 for Al). The relationship of sorption to the metals removed by the method operationally defining amorphous and poorly crystalline phases (AO) was improved ($r=0.87$ for Fe, and 0.89 for Al). However, the extraction method considered to remove the total metals (DCB), including the crystalline phases, explained the greatest variance in the sorption data set ($r=0.92$ for Fe, and 0.91 for Al). These results were consistent with the findings of Fuller et al. (1996) where a stronger relationship between Pb^{2+} sorption and extractable metals was found from methods that remove the more crystalline phases. These results would indicate that the crystalline oxide minerals are important substrates for SO_4^{2-} sorption.

The relationship of SO_4^{2-} sorption to surface area, as determined by gas adsorption, was also significant ($r=0.93$; Fig. 2D) for the aerobic sediments. The surface area was highly correlated with total amount of DCB-extractable metals ($r=0.91$; Knapp, 1997). These results were consistent with Inch and Killely (1987) and Jackson and Inch (1983) who observed a strong dependence of cation adsorption on surface area and a high correlation of oxide surface coatings contributing most of the surface area. Similarly, Horowitz and Erlick (1987) found that the trace-metal content of stream sediments was most strongly correlated with surface area, with a weaker dependence on amount of extractable oxides.

The surface area results are in contrast to those of Fuller et al. (1996) and Coston et al. (1995) on studies of Pb^{2+} and Zn^{2+} sorption to Cape Cod sediments. They found only weak or no correlation of sorption with surface area; however, the variability in sorption was best described by the amount of extractable Al- and Fe-oxide coatings when normalized to specific surface area. The authors indicated that adsorption may have occurred at specific regions of the sand surface that were more reactive, whereas surface area is a measurement by N_2 covering the entire, geometric area of the sample. These

studies did not find Al, Fe, or Mn to be correlated with surface area, suggesting that the extractions dissolved metals from multiple layers of oxide coatings that were not accessible to N_2 adsorption.

A slightly weaker dependence of sorption on the oxide content as observed in the sediments in the present study may be a function of the presence of layering of the oxide coatings on the quartz surface. If Fe-oxide coatings build up as layers or as overgrowths on previously formed Fe oxide, a lack of increase in measured surface area regardless of doubling the amount of synthetically prepared Fe-oxide coatings on quartz sand (Szecsody et al., 1994) would be anticipated. Such layering could lead to a slight overestimation in the amount of sorption expected by extraction methods used to determine the amount of Fe. In Szecsody et al.'s study, however, sand similar in size to that at the present study site and coated with $50 \mu\text{mol g}^{-1}$ Fe oxide, had a surface area of only $0.4 \text{ m}^2 \text{ g}^{-1}$. Only one sample from the present study site had a DCB-extractable Fe value ($154 \mu\text{mol g}^{-1}$) that was within the range of amounts extracted by Szecsody et al. (1994), and only one other sample was greater than $50 \mu\text{mol g}^{-1}$, and their surface areas were 6.3 and $4.8 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. 3B). The lower content of Fe oxide in the sediments in the present study may minimize the extent to which layering causes a departure in the measured surface area reflecting the amount of Fe oxide available as sorption substrate.

5.3. Sediment properties

The high degree of correlation among the variables makes difficult the attribution of observed differences in SO_4^{2-} sorption between aerobic and anaerobic samples to a specific variable or subset of variables. An attempt to examine the relative importance of the variables was made by subjecting the data for surface area and DCB-extractable Fe, Al, and Fe+Al to a principal components analysis. Only one component was extracted; it explained 92% of the variance and consisted of all 4 variables, each having a loading of 0.9 or greater. Thus, a quantitative separation of the relationship of the variables to SO_4^{2-} sorption could not be achieved. This analysis would seem to verify that surface area and SO_4^{2-} sorption are dependent variables of oxide abundance in these sediments.

There is a strong correlation ($r=0.92$) between surface area and Fe oxides in the aerobic portion of the field. In the anaerobic zone, however, the relationship between surface area and Fe content was not simple (Fig. 3B). Although the majority of Fe was removed from the surfaces of these sediments, leaving them with an order of magnitude less Fe than on the aerobic-zone sediments, there was still an appreciable amount of specific surface area measured (0.3 – $1.3 \text{ m}^2 \text{ g}^{-1}$). The measured surface areas for the anaerobic samples were within the range of

the aerobic samples that had one to two orders of magnitude more Fe on the surfaces. Indeed, when DCB-extractable Fe was less than $20 \mu\text{mol g}^{-1}$, the removal of Fe by anaerobic groundwater had no significant effect on surface area (Fig. 3B). Once the total DCB-extractable metal oxides (both the Fe and Al) had been removed from both the aerobic- and anaerobic-zone sediments in the laboratory, however, the measured surface area was only $0.10\text{--}0.13 \text{ m}^2 \text{ g}^{-1}$ for both sediments. This significant decrease in surface area from that observed in either type of sediment prior to extraction additionally indicated that both the oxides were responsible for the high surface area. Further, the similar value of surface area for extracted aerobic and anaerobic sediments is consistent with particle-size data from another portion of the study site that show the sediments to be nearly all sand with always less than 5% and usually less than 2% clay content (Dobson, 1997).

The results of surface area analysis further suggested that although the Fe has been removed by anaerobic processes, oxide coatings remain on the surface of the anaerobic sediments that contribute to surface area. The existence of residual oxides is apparent when comparing the amounts of Al vs. Fe extracted in each zone (Fig. 3A). In the anaerobic samples there was a removal of the Fe oxides; however, there was a significant amount of Al extracted that was comparable to the amount of Al extracted in the aerobic sediments. Al oxides are not redox sensitive and should not be removed by the reductive dissolution that removed Fe oxides from the surfaces in the anaerobic sediments if they exist as discrete phases on the surface and are not present as substitutions in the Fe-oxide minerals.

The results of the sorption studies with the anaerobic sediments indicate less capacity for SO_4 adsorption than for the aerobic sediments (Fig. 2). Because Al oxides are persistent and a significant surface area remains on the anaerobic sediments, it was evident that the removal of the Fe oxides resulted in the loss of anion sorption sites. Although the Al was persistent in the anaerobic portion of the aquifer, it did not appear to contribute significant reactive surface to the sediments. In fact, at the pH of interest in this system (5.3–6.6), the zpc of Al hydroxide ($\text{Al}(\text{OH})_3 = 5.0$; Stumm and Morgan, 1996) has been exceeded and these oxide surfaces would not be expected to carry a positive charge. In contrast, with a zpc of 8.5, $\text{Fe}(\text{OH})_3$ should have a positive surface charge. It is then clear that the abundance of Fe oxides controls the majority of the affinity of these sediment surfaces for negatively charged groundwater constituents.

6. Summary

Analysis of the geochemistry of the groundwater and sediments from the anaerobic zone at the Virginia

Coastal Research Center site has shown that Fe-oxide hydroxide minerals have been reductively dissolved from the sediment surfaces. This conclusion is based on the presence of elevated concentrations of Fe(II) in the groundwater and the lower amount of extractable Fe on the sediment surfaces as compared to the sediments of the aerobic zone of the aquifer. The presence of anaerobic conditions does not appear to have altered the presence of Al oxides on the surface of the sediments. The removal of the Fe from the sediments when extractable Fe was less than $20 \mu\text{mol g}^{-1}$ has not significantly changed the surface area of these sediments. Only rigorous chemical extraction of both Fe and Al oxides in the laboratory resulted in an order-of-magnitude decrease in measured surface area. The continued presence of the Al oxides contributes to the specific surface area that persists despite the onset of anaerobic conditions in the field.

The Fe-oxide content was the only one of the surface properties to be significantly altered by the anaerobic condition with a concomitant alteration in the ability of the sediments to retain SO_4^{2-} . It appeared, therefore, the presence or absence of Fe oxides was the dominant factor controlling SO_4^{2-} sorption. These results would indicate an alteration to the surfaces of minerals when exposed to anaerobic groundwater that directly increases the potential for transport of reactive constituents such as anions and bacteria through the unconsolidated sedimentary aquifer under evolving geochemical conditions.

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