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The effect of physical and chemical heterogeneities in a porous medium on the transport of bacteria
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George M. Hornberger, Aaron L. Mills, Janet S. Herman
Program of Interdisciplinary Research in Contaminant Hydrogeology
Department of Environmental Sciences
University of Virginia
Charlottesville, VA 22903
804.924.6762

This project has resulted in several new findings which are summarized below.

Effect of heterogeneous vs. homogenous distribution of metal oxide coatings on bacterial transport through unconsolidated porous media.

Among the demonstrated processes influencing the transport of bacteria through aquifers, the deposition of cells on mineral surfaces is one of the most important. For example, understanding the transport of introduced bacteria through aquifers is essential to designing some in situ bioremediation schemes. The impact of the presence and distribution of Fe(III)-oxyhydroxide-coated sand grains on bacterial transport through porous media was evaluated in column experiments in which bacteria (short rods; 1.2 µm length) were eluted through columns of quartz sand (0.5-0.6 mm in diameter) for several conditions of chemical heterogeneity of mineral substrate. Fe(III)-oxyhydroxide coated sand was present as 10% of the mass, and it was arranged in three treatments: (1) homogeneously distributed, and present as a discrete layer (2) at the top and (3) at the bottom of 14-cm-long sand columns. A pulse input of 10^8 cells ml^{-1} was introduced in an artificial groundwater solution flowing at 14 cm h^{-1} through the column, and eluted cells were counted. Peak breakthrough occurred at 1.0 pore volume. A large proportion of cells were retained; 14.7-15.8% of the cells were recovered after three pore volumes of solution had eluted through clean quartz sand, and only 2.1-4.0% were recovered from the Fe(III)-oxyhydroxide-coated sand mixtures. The three physical arrangements of the chemical heterogeneity resulted in essentially the same breakthrough of cells, indicating that the spatial distribution of iron coating does not affect the transport of bacteria. The results of the column transport experiments, which mimic hydrogeological conditions encountered in field problems, are consistent with our mechanistic understanding of bacterial sorption.

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Heterogenous distribution of sediment permeability and its effect on transport of bacteria through porous media

We examined two major questions: (1) can the effects of transverse mixing of bacteria in a system constructed to have a permeability discontinuity in the direction parallel to the flow be measured; and (2) if the effects are measurable, can they be calculated using a transverse dispersion coefficient estimated from experiments using a conservative tracer? Pulses of chloride and bacteria were transported downward through heterogeneous columns constructed with a tubule of coarse, quartz sand surrounding an annulus of fine, quartz sand. Pulses of each were also transported through homogeneous columns of the two sands. Doubly peaked breakthrough curves resulted from the columns containing two distinct sand sizes. Modeling of the breakthrough curves was performed taking into account advection, dispersion, deposition, entrainment, and pore-size exclusion. The results revealed that transverse mixing does occur during transport of bacteria through heterogeneous material and that this mixing can be estimated using a conservative tracer.

Effect of alteration of metal oxide coatings on aquifer solids on the potential retention of reactive substances advecting through unconsolidated porous media

An investigation of a Coastal Plain sandy aquifer on the Eastern Shore of Virginia was undertaken where depositionally similar sediments have been exposed to chemically distinct groundwater conditions. In a narrow leachate plume, dissolved O_2 was only 0 to 0.9 mg L^{-1}, whereas it was 5.0 to 10.6 mg L^{-1} in the regionally extensive aerobic groundwater. In addition, the amount of dissolved iron in the aerobic groundwater was 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 iron was an order of magnitude higher for the aerobic sediments than for the anaerobic sediments indicating that reductive dissolution removed the oxide coatings. In addition, the reactivity of the sediment surfaces, as indicated by the sorption of $^{35}SO_4^{2-}$, was an order of magnitude higher in the aerobic vs. anaerobic sediments. The presence of anaerobic groundwater 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 even in the presence anaerobic conditions. 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.

Retardation of a reactive tracer upon passage through aquifer sediments containing greater or lesser amounts of metal oxide due to differences in the system redox potential

Transport of SO_4^{2-} was retarded compared to Br^- in laboratory columns packed with sands from the aerobic portion of the aquifer with retardation coefficients (R_d) of 1.2 and 1.3. There was, however, no retardation of SO_4^{2-} observed in columns containing material from the anaerobic portion of the aquifer. Similarly, in field-scale tracer experiments, SO_4^{2-} was retarded in the aerobic (iron-coating rich) aquifer (R_d=1.1 to 1.6), but the SO_4^{2-}

was transported with the conservative tracer (Br⁻) in the anaerobic ground water (Rd=1.0). These results suggest that reductive dissolution of the iron caused a loss of the electropositive sorption sites, The differences observed between the surface reactivity of these two chemically heterogeneous sediments may lead to less sorption, therefore less retardation and greater transport, of reactive constituents, including other anions and negatively charged bacteria, through anaerobic groundwater zones in which mineral surfaces would otherwise be predominantly coated with metal oxides.

Publications resulting from this grant:
Copies of completed papers or submitted manuscripts are appended as part of this report. The remaining paper Knapp et al in preparation will be forwarded upon submission.

Knapp, E.P., J.S. Herman, G.M. Hornberger, and A.L. Mills. 1998. The effect of distribution of iron-oxyhydroxide grain coatings on the transport of bacterial cells in porous media. Environ. Geol. 33:243-248.

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Redox Alteration of Reactive Mineral Surfaces in Biologically Active Groundwater

Elizabeth P. Knapp*, Janet S. Herman, Aaron L. Mills, and George M. Hornberger

Department of Environmental Sciences

University of Virginia, Charlottesville, VA 22903

Corresponding author (JSH) address:

Department of Environmental Sciences

Clark Hall

University of Virginia

Charlottesville, VA 22903

Phone: 804.924.0553

Email: jherman@virginia.edu

*Current Address:

Department of Geology

Washington and Lee University

Lexington, VA 24450

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Abstract

An investigation of a Coastal Plain sandy aquifer on the Eastern Shore of Virginia was undertaken where depositionally similar sediments have been exposed to chemically distinct groundwater conditions. In a narrow leachate plume, dissolved O_2 was only 0 to 0.9 mg L^{-1}, whereas it was 5.0 to 10.6 mg L^{-1} in the regionally extensive aerobic groundwater. In addition, the amount of dissolved iron in the aerobic groundwater was 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 iron was an order of magnitude higher for the aerobic sediments than for the anaerobic sediments indicating that reductive dissolution removed the oxide coatings. In addition, the reactivity of the sediment surfaces, as indicated by the sorption of $^{35}SO_4^{2-}$, was an order of magnitude higher in the aerobic vs. anaerobic sediments. The presence of anaerobic groundwater 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 even in the presence anaerobic conditions. 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.

INTRODUCTION

Sorption to aquifer solids

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3   Of the chemical properties affecting transport of reactive constituents in groundwater, the

4   surface charge of aquifer solids is a dominant factor controlling retardation by sorption. In

5   laboratory and field-scale experiments, the presence of metal-oxide coatings on quartz sand

6   affected greatly the sorption and transport of reactive constituents including metals, anions, and

7   bacteria (Coston et al., 1995; Fuller et al., 1996; Mills et al., 1994; Scholl and Harvey, 1992;

8   Scholl et al., 1990). These minerals have high surface areas and retain a more positive surface

9   charge at higher pH's than many soil and aquifer minerals, especially quartz (Stumm and

10   Morgan, 1996).

11   The mineralogy of the metal oxide affects the affinity its surface has for ion sorption.

12   Amorphous oxides of both Al and Fe are generally believed to be more reactive on a per weight

13   basis than crystalline oxides (Davis and Kent, 1990); the amorphous forms retain anions more

14   readily than crystalline oxides, with the capacity for sorption decreasing with increasing age and

15   crystallinity (McLaughlin et al., 1981; Simms and Ellis, 1983). Bowell (1994) observed that the

16   association of arsenic with sediments in a mining region was much greater for amorphous than

17   for crystalline Fe-oxide phases.

18   The presence of more than one oxide in a system may affect the sorption characteristics

19   as well. Aluminum oxides in soils sorb the PO_4^{3-} and SO_4^{2-} more readily than Fe oxides (Chao et

20   al., 1964). The sorptive properties of binary-oxide suspensions have been demonstrated to be

21   different from their component parts. Aluminum oxides can mask the presence of other oxides

22   and determine the overall surface characteristics (Anderson and Benjamin, 1990). Warren and

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1   Zimmerman (1994) suggested that in mixed-oxide systems, a layering effect of the metal oxides

2   reduces the exposed surface area of the individual minerals. This effect may cause an

3   overestimation of sorption based on summation of the contribution of the component minerals as

4   determined by extraction techniques or by estimation from literature-based values for single-

5   component sediments.

6   In addition to metal-oxide abundance, another estimator of total sediment reactivity

7   commonly employs measurements of surface area by gas adsorption (Chiou and Rutherford,

8   1993; Warren and Zimmerman, 1994). The positive correlation found between surface area and

9   sorption of radionuclides (Inch and Killey, 1987) and of trace metals (Horowtiz and Elrick,

10   1987) suggest that surface area may account for variable sorption to aquifer minerals. Previous

11   studies have also observed a strong dependence of cation adsorption on surface area with oxide

12   surface coatings contributing most of the surface area (Jackson and Inch, 1983). Furthermore,

13   Borggaard (1983) suggested that the differences observed between sorption onto amorphous and

14   crystalline oxides is a function of the surface area (decreasing as the oxides age and crystallize)

15   rather than a function of changes in their surface electrical properties. Horowitz and Erlick

16   (1987) found that trace-metal content of stream sediments was most strongly correlated with

17   surface area, with a weaker dependence on amount of extractable oxides. Fuller et al. (1996) and

18   Coston et al. (1995), on the other hand, found weak or no correlation with surface area for Pb^{2+}

19   and Zn^{2+} sorption; however, variability in sorption was best described by the amount of

20   extractable Al- and Fe-oxide coatings when normalized to specific surface area. The results

21   indicate that adsorption may occur at specific, more reactive portions of aquifer solids, whereas

22   surface area measurements employing chemically unreactive N_2 quantify the entire area of the

23   sample. In these studies, the amounts of Al, Fe, or Mn were not correlated with surface area,

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1   suggesting that the extractions dissolved metals from multiple layers of oxide coatings that were

2   not accessible to N_2 adsorption. Similarly, increasing the percentage of Fe-oxide coatings on

3   quartz sand (in the 0.075 to 0.21 mm size range) from 0.6% to 1.2% (corresponding to 104 and

4   225 μmol g^{-1} extractable iron, respectively) did not alter the amount of surface area (3.4 m^2 g^{-1})

5   measured by N_2 adsorption (Szecsody et al., 1994). This result would again suggest a layering

6   on the quartz surface of the Fe oxides coatings.

7   From the above discussion, it is evident that sorption to aquifer solids may be controlled by a

8   number of factors including the surface charge of the solid, its mineralogy and crystallinity, and

9   the surface area of the mineral exposed at the solid surface.

10   *Anaerobic chemistry*

11   Water-table aquifers are often aerobic because, under non-contaminated conditions, the

12   indigenous microorganisms are more carbon-limited than oxygen-limited. With the introduction

13   of organic chemical contaminants, however, the situation often changes; carbon limitations

14   disappear and oxygen is rapidly consumed (Chapelle, 1993). As anoxic conditions develop in a

15   contaminant plume, anaerobic degradation reactions become more important (e.g., Baedecker et

16   al., 1993; Barker et al., 1986). A redox-zone sequence of methanogenic, SO_4^{2-}-reducing, Fe(III)-

17   reducing, Mn(IV)-reducing, NO3- -reducing, and aerobic conditions may be formed under

18   conditions of highest to lowest organic contaminant concentrations, respectively (Christensen et

19   al., 1994; Nielson et al., 1995). This sequence is based on the energetics of the reactions and the

20   availability of the electron acceptors (Stumm and Morgan, 1996). As redox conditions in a

21   contaminant plume change with the depletion of dissolved oxygen (DO) and NO_3^-, the oxidation

22   of organic matter is coupled to Fe(III) which is consumed as an electron acceptor (Lovley et al.,

3

1   1990). Due to the widespread availability of Fe(III) oxide in subsurface environments (Heron et

2   al., 1994; vanBreeman, 1988), it is likely that microbial oxidation of organic contaminants is a

3   significant contribution to the reduction of Fe from the surfaces of sediments in polluted

4   aquifers. In the crude-oil contaminated aquifer at the USGS Toxic Substances Hydrology site

5   near Bemidji, MN, accumulations of Fe(II) were observed in the groundwater over time

6   (Cozzarelli et al., 1994), whereas no Fe(II) was found in the uncontaminated background water.

7   The aerobic sediments had four times the amount of extractable Fe(III) as compared to the

8   anaerobic sediments (Tuccillo et al., 1999). Heron et al. (1994) showed that both amorphous and

9   crystalline Fe oxides were removed in the Fe-reducing zone of a contaminated aquifer. Because

10   of the importance of oxide coatings in controlling reactivity of aquifer solids, the reductive

11   removal of the specific Fe phases from the solid surface may also have important implications

12   for the reactivity of aquifer sediments. Within anaerobic zones, Fe reduction may alter the

13   nature of the metal-oxide coated surfaces of the aquifer sands. Iron oxyhydroxide has a zero

14   point of charge (zpc) of 8.5 and is positively charged at neutral pH. The underlying quartz

15   surface, potentially exposed as the iron is removed, has a zpc of 2.0 and is negatively charged at

16   the pH's of most natural waters (Stumm and Morgan, 1996). The removal of Fe-oxide coatings

17   from quartz grains in an aquifer may alter the nature and extent of reaction between sorbing

18   solutes and the mineral surfaces.

19   Overall, the changes in the sediment that can occur with changing redox status driven by

20   microbiological activities and the concomitant effect on sorption are fundamental to

21   understanding the transport properties of the aquifer under evolving chemical conditions. The

22   objective of the present study was to quantify the nature and extent of changes that occur in

23   sediments exposed to anaerobic groundwater conditions and to determine the relationship

1 between sediment geochemical properties and the sorption of reactive constituents in

2 groundwater.

SITE DESCRIPTION

4   The field site is located at the Virginia Coastal Research Center on the seaward shoreline of

5 the Eastern Shore of Virginia near the town of Cape Charles (Fig. 1), where the mainland is

6 separated from the ocean by a broad lagoon-marsh-barrier island complex. Here the Atlantic

7 Coastal Plain consists of unconsolidated shoreface deposits that formed on the tip of a spit that

8 prograded across the mouth of the Chesapeake Bay during the upper Pleistocene and Holocene

9 (Mixon, 1985). The sediments are primarily quartz sands (95%), have a mean grain diameter

10 from 180-500 μm, and are coated with varying amounts of Fe and Al oxides (Dobson, 1997;

11 Knapp, 1997). The field slopes toward the marshes and is bisected by the Mappsburg Scarp, a

12 slightly steeper slope that represents an ancient beach face. The elevation of the field above the

13 scarp is about 7-8 m above mean sea level (MSL), and that of the area eastward of the scarp is

14 about 2 m above MSL. The depth to groundwater is about 1.5-2 m in the lower elevations of the

15 field (e.g. D1) to 6 m below ground surface in the higher elevations (e.g. B2). The unconfined

16 aquifer extends to a depth of approximately 15 m below ground surface and the direction of

17 groundwater flow is generally eastward toward the Atlantic Ocean (Callaghan, 1999;

18 Richardson, 1992).

19   Burial pits of decaying vegetable matter from a tomato cannery are located on the far north

20 side of the field, and they were active from approximately 1974 to 1983 (Sitler, 1997). The

21 buried material provides a source of readily available organic matter that depletes the oxygen in

22 the water because of microbial decay. A portion of the field plot exhibits anaerobic conditions

1   (Fig. 1). The proximity of these two groundwater zones with distinct chemical differences

2   within sediments from similar depositional environments enabled an investigation of the impact

3   of redox conditions on sediment geochemical properties.

4   **METHODS**

5   *Groundwater and sediment sampling*

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

7   (from June 1994 to 1996) and quarterly thereafter.   After purging for at least 3 well volumes

8   with a peristaltic pump, samples were filtered in-line through a 0.45-μm filter, stored in

9   polyethylene bottles, and chilled on ice for return to the laboratory. In the field, DO was

10   determined using CHEMets (self-filling ampoules for colorimetric analysis), temperature was

11   measured with a mercury thermometer, and pH was measured with an Orion meter and glass pH

12   electrode calibrated to pH 4 and 7 buffers. Alkalinity was determined by potentiometric titration

13   in the field. Major cations were determined by atomic absorption spectroscopy, major anions

14   were determined by ion chromatography, and dissolved organic carbon (DOC) was measured on

15   a Dohrmann carbon analyzer. The metals Fe, Mn, and Al were determined by inductively

16   coupled plasma emission spectroscopy (ICP-AES).

17   Assessment of the thermodynamic saturation state of the two groundwater solutions with

18   respect to various plausible mineral phases was accomplished using an equilibrium aqueous

19   speciation code, WATEQ4F (Ball and Nordstrom, 1991). For all the anaerobic samples. The

20   total dissolved iron was assigned entirely to Fe(II), consistent with the results of occasional

21   direct determination of dissolved iron species in filtered, acidified samples analyzed by UV-Vis

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1 spectrophotometry (Knapp, 1997) and the absence of dissolved oxygen. For the aerobic samples,

2 the total dissolved iron was assigned entirely to Fe(III).

3 Aerobic sediment cores (3.5-inch diameter) were collected during installation of wells in the

4 upper field. The cores were collected in Lexan liners and capped immediately following

5 recovery. The cores used for this study were sub-sampled from below the water table in cores

6 from B2 and T5 (Fig. 1). Samples were collected in 10 cm^3, detipped syringes at 0.5-m intervals

7 along the length of the core; the collection procedure is detailed in Knapp (1997).

8 For the acquisition of samples from the lower field, *in situ* conditions had to be

9 maintained so that the sediments would not be exposed to oxygen. Two anaerobic sediment

10 cores were collected adjacent to the lower field wells using a vibracore. The 3-inch diameter

11 cores were collected in aluminum tubing and were sealed immediately upon recovery with

12 expansion plugs and returned to the laboratory. The porewater was then removed under a N$_2$

13 atmosphere in an anaerobic chamber. The cores were then resealed and frozen (to preclude any

14 further microbial action) until sub-sampling and analysis could be done. All further sample

15 handling was done under a N$_2$ atmosphere in either a glove box or a glove bag.

16 *Sediment analysis*

17 The surface mineralogy of the sediment samples collected from both the oxic and anoxic

18 portions of the aquifer was characterized using metal-oxide extractions on 1-g sample splits for

19 Fe (Fe(II) and Fe(III)) and Al phases to determine operationally defined types and amounts of

20 coatings present in each zone. For sands from the aerobic zone, three separate extractions for

21 metal oxides were done for determination of various phases and crystallinities of the metal

22 oxides. The hydroxylamine hydrochloride (HA) treatment extracts amorphous oxides (Chao and

1   Zhou, 1983); the ammonium oxalate (AO) extraction removes poorly crystalline oxides (Fey and

2   Le Roux, 1977; Phillips and Lovely, 1987); and the dithionite citrate bicarbonate (DCB)

3   extraction removes oxides including crystalline Fe oxides such as goethite (Mehra and Jackson,

4   1958). These extraction procedures remove similar fractions of Al minerals with less distinction

5   and more overlap of phases among the methods (Chao et al., 1964). The samples were analyzed

6   for Fe, Al, and Mn by ICP-AES.

7   Characterizing the sediment from the anaerobic portion of the aquifer required an

8   additional extraction for speciating reduced Fe phases. All of the extractions were performed

9   under anaerobic conditions and run in sealed 60-mL serum bottles with N_2 as the headspace gas.

10   The Fe phases were extracted using 0.5 M HCl (Heron et al., 1994); the method targets

11   amorphous and poorly crystalline Fe(III) and reduced Fe phases. The Fe (II) was determined by

12   the ferrozine method (Gibbs, 1979). For total iron and aluminum determination, the extraction

13   solutions were analyzed by ICP-AES.

14   The physical properties of the mineral-water interface constrain the nature of sorption reactions,

15   and charge interactions commonly drive adsorption reactions (Hochella and White, 1990). In

16   attempting to evaluate the reactivity of mineral surfaces in an aquifer, sorption of solutes directly

17   probes that portion of the solid surface that participates in reactions. Sulfate is developed here as

18   a tool to measure the extent of reactive mineral surfaces in an unconsolidated sandy aquifer in

19   which the oxide surfaces in contact with groundwater are primarily quartz and the sesquioxide

20   coatings on the quartz. As a divalent anion of moderate ionic potential, SO_4^{2} should sorb

21   reversibly to positively charged Fe (III)- and Al-oxyhydroxide grain coatings which have been

22   demonstrated to be the primary substrate for adsorption in this type of hydrogeological setting

1 (Fuller et al., 1996). The use of SO_4^{2-} is advantageous because very small samples of aquifer

2 material can be assessed in laboratory experiments for sorption potential by using easily detected

3 $^{35}SO_4^{2-}$, because SO_4^{2-} can be introduced into the subsurface environment in field trials, and

4 because, as an anion, SO_4^{2-} is likely to be an indicator of how other negatively charged reactive

5 constituents, including bacteria, will interact with aquifer solids.

6 On separate splits of the core samples, the amount of surface available for sorption of

7 reactive solutes was determined by a $^{35}SO_4^{2-}$-sorption assay. Non-radioactive sulfate was

8 combined with $^{35}SO_4^{2-}$ to yield a 3.3 mM SO_4^{2-} solution with radioactivity in the range of 10,000

9 - 30,000 dpm. Three mL of the solution were added to 3 g of sediment. After shaking the vials

10 for 24 hours, the samples were removed and the liquid was filtered through a 0.45-μm filter. A

11 100-μL portion of the filtered solution was removed and the $^{35}SO_4^{2-}$ determined by liquid

12 scintillation counting. The measured amount of SO_4^{2-} left in solution was then subtracted from

13 the amount added to determine the amount of SO_4^{2-} sorbed in $\mu mol\ g^{-1}$.

14 The relationship of sorption to the extent of extractable metal-oxide coverage was

15 explored by performing specific surface area measurements by N_2 gas adsorption with a Gemini

16 2360 (Micromeritics, Norcross, GA) surface area analyzer. The single-point method was

17 employed on 1-g samples from each zone both before and after metal-oxide extractions.

18 **RESULTS**

19 *Relationships among surface properties*

20 The relationship of the sorption of SO_4^{2-} to various sediment surface properties was

21 calculated in order to gain insight to the factors controlling SO_4^{2-} sorption on the 27 aerobic

1   sediment samples. The total amount of metal extracted in the DCB method that removes both

2   amorphous and crystalline phases was quantified. Manganese concentrations in extracts from

3   the site sediments were negligible; therefore, total metal extracted is herein defined as Fe plus

4   Al. The SO_4^{2-} sorbed was related to both the amount of extractable metal oxides and the

5   magnitude of surface area (Fig. 2).

6   Strong correlations were observed among the properties of surface area and extractable

7   metal oxides (Fig. 3). The Al and Fe contents were highly correlated (r= 0.997, presented with 3

8   significant figures to show that the correlations were extremely high but less than 1.0). In

9   addition, the surface area was highly correlated with the total extractable metals (r = 0.91).

10   *Relationship to crystallinity of oxide phases*
11   For comparison to the results for "total metal" (amorphous and crystalline phases) in

12   Figure 2, the relationships between SO_4^{2-} sorption and the HA-extractable "amorphous" phases

13   and the AO-extractable "amorphous and poorly crystalline" phases were also computed for the

14   aerobic cores. Lower values of r for SO_4^2 sorption and HA-extractable phases were obtained

15   (Table 1). The r values for sorption and the AO phases (Table 1) were intermediate to those for

16   DCB (total) and for HA. In addition, for each of the types of extraction, the correlation between

17   Al and Fe content was high (Table 1 for HA and AO, Fig. 3 for DCB).

18   *Comparison of groundwater chemistry*
19   Differences in groundwater chemistry are evident across the experimental plot. The groundwater

20   in the lower field (as measured in well D1) was depleted in DO with concentrations ranging from

21   0 - 0.9 mg L^{-1} (Table 2). The upper flow cell has not been affected by the organic matter from

22   the waste burial pits and has DO concentrations (as measured in well PL2) consistent with the

1   background regional groundwater of 5.0 to 10.6 mg L^{-1}. There were different concentrations of

2   dissolved Fe in the groundwater of the two zones as well. The concentrations in the lower flow

3   field ranged from 12 - 47 mg L^{-1}, whereas they were only 0.005 - 0.01 mg L^{-1} in the upper field,

4   again consistent with regional groundwater composition (Table 2). The concentrations of other

5   redox species also varied. The NO_3^- concentrations in the anaerobic well were 0 – 4.8 mg L^{-1},

6   but were between 15 and 50 mg L^{-1} in the aerobic well; the NH_4^+ in the anaerobic well was 0.56

7   – 3.12 mg L^{-1}, but was not detectable in the aerobic well. The alkalinity of the anaerobic zone

8   was elevated relative to the aerobic groundwater, most likely because of the microbial activity

9   and the presence of organic acids in the contaminated groundwater. The alkalinity values in the

10   anaerobic zone ranged from 153 to 384 mg L^{-1} HCO_3^- and from 18.3 to 39.7 mg L^{-1} HCO_3^- in the

11   aerobic groundwater.

12   Other groundwater characteristics were similar between the two zones. The pH was in

13   the same range, although a bit higher for the anaerobic zone (5.9 - 6.6) as compared to the

14   aerobic zone (5.3 - 6.5). The amount of DOC in each zone was comparable although again

15   slightly higher in the anoxic groundwater (1.87-5.89 mg L^{-1}) compared with the aerobic

16   groundwater (1.72 - 4.47 mg L^{-1}). The SO_4^{2-} concentration was between 11.0-74.0 mg L^{-1} for the

17   aerobic zone and 12.0 - 44.2 mg L^{-1} in the anoxic zone. The H_2S was measured on only one

18   sampling date and the concentrations were 0.13 and 0.16 mg L^{-1} for the aerobic and anaerobic

19   zones, respectively.

20   The results of the WATEQ4F calculations on two representative groundwater compositions

21   (Table 3) showed the aerobic-zone groundwater to be supersaturated with respect to a number of

22   Fe(III) minerals, including goethite and ferrihydrite. In contrast, the water from the anaerobic

1   zone collected at Well D1, with orders of magnitude more dissolved iron all present as Fe(II),

2   was out of equilibrium with respect to all Fe(III) minerals.

3   *Comparison of sediment chemical properties*

4   Iron has been removed from the surfaces of the sediments in the anaerobic zone. In fact,

5   the amount of Fe that could be extracted with a 0.5 M HCl solution from the aerobic sediments

6   was over an order of magnitude higher than that in the anaerobic sediments (Fig. 4). The Fe in

7   the extracts of the aerobic sediments ranged from 3.2 - 52 μmol g^{-1} while it was only 0.9 - 2.4

8   μmol g^{-1} in the anaerobic sediments. The values from the two zones are significantly different

9   with P = 0.0086. These values are for total Fe extracted. The 0.5 M HCl extraction was also

10   used to speciate the Fe(II) and Fe(III) removed from the sediment surfaces. There was very little

11   Fe(II) extracted from either of the two zones, and the values from each zone only ranged from

12   0.01 - 0.5 μmol Fe(II) extracted g^{-1}. The vast majority of the total extracted Fe was Fe(III).

13   There was a strong correlation (r = 0.92) between the amount of extractable Fe on the

14   sediments and the surface area for the samples from the aerobic zone (Fig. 5). The anaerobic

15   zone, however, showed an interesting relationship. Although the majority of the Fe had been

16   removed from the surfaces of these sediments, there was still an appreciable amount of surface

17   area measured. The values were from 0.39 - 1.2 m^2 g^{-1} and were in the range of the aerobic

18   samples (values from 0.27 - 6.3 m^2 g^{-1}) that had one to two orders of magnitude more Fe on the

19   surfaces. The surface area values for the anaerobic- and the aerobic-zone samples were not

20   determined to be significantly different with P = 0.75. When both Fe and Al were removed from

21   the samples by extraction, however, the surface area was only 0.10 to 0.13 m^2 g^{-1} for each of the

22   zones. This was a significant reduction in the surface area as compared to that observed during

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1   removal of Fe under anaerobic conditions. This result suggests that metal oxide coatings

2   remained on the surface of the anaerobic samples that are contributing the surface area.

3   The nature of the oxide coatings on the anaerobic sediments is further elucidated by comparing

4   the amounts of total Al vs. Fe for each of the two zones (Fig. 6). A strong correlation (r = 0.99)

5   was observed between the two metals for the aerobic sediments. For the anaerobic sediments,

6   the amount of Al extracted from the sediments was comparable to the amount in the aerobic

7   sediments. The range for the aerobic sediments was 2.6 - 75.8 $\mu mol\ g^{-1}$ and for the anaerobic

8   sediments was 11.8 - 29.5 $\mu mol\ g^{-1}$. Because of the removal of the Fe and the persistence of Al

9   on the surfaces, the ratios of the Fe and Al in the aerobic (0.42 to 1.03) and the anaerobic

10   sediments (7.06 to 32.0) were significantly different with $P = 3.8 \times 10^{-9}$.

11   Changes in the metal oxide composition of the sediment coatings may affect the

12   reactivity of the surfaces. It was clearly observed that the alteration of the surfaces had a

13   profound effect on the sorption of SO_4^{2-} to these sediments (Fig. 3). The SO_4^{2-} sorbed to the

14   aerobic sediments (2.2 to 50 $\mu mol\ g^{-1}$) was an order of magnitude greater than for the anaerobic

15   sediments (0.007 to 0.25 $\mu mol\ g^{-1}$). The SO_4^{2-} sorption was, in fact, significantly different for

16   these two zones ($P = 9.9 \times 10^{-8}$).

17   **DISCUSSION**

18   *Relationship of surface properties to sorption*

19   The results from analysis of the uncontaminated sediments indicated that each of the

20   sediment properties, extractable metals and surface area, was able to explain a high percentage of

21   the variance in sediment reactivity (Fig. 2). Because the extraction methods removed both the Fe

1   and Al oxides, distinction between the phases was not possible by extraction. The correlation

2   results indicated a slightly stronger relationship of sorption to total (DCB extractable) Fe than

3   total (DCB extractable) Al (0.92 vs. 0.91). Complicating the separation of effects of Fe and Al

4   on sorption was the fact that these metals were highly correlated with each other (r = 0.997).

5   Previous work by Dobson (1997) demonstrated a similar strong correlation (r = 0.985) between

6   total Al and Fe on sands from this site and suggested from regression analysis of SO_4^{2-} sorption

7   to total metals that the relative reactivity of Fe oxides may be greater than the Al phases.

8   A difficulty in the use of the DCB extraction for these comparisons of total oxides arises

9   from controversy about the mineral sources of Al extracted by DCB (Arnseth and Turner, 1988;

10   McKeague and Day, 1966). However, when similar comparisons were done using the AO-

11   extraction results (commonly considered a total for Al oxides) similar results occurred. The

12   correlation between Al and Fe was still high (r = 0.98) for the AO extraction and the relative

13   relationships with SO_4^{2-} sorption were similar to the DCB extractions where the r values were

14   0.92 and 0.91 for Fe and Al, respectively, for the DCB extraction, and 0.89 and 0.88 for the AO

15   extraction.

16   Because of the well known affinity for sorption to amorphous Fe oxyhydroxides, many studies

17   have modeled metal adsorption to oxides by fixing the total sorption site density from estimates

18   derived from studies with pure amorphous Fe oxyhydroxides (Dzombak and Morel, 1990).

19   Determining the appropriate surface density of adsorption sites, however, can cause difficulties

20   in applying sorption models to the mixed mineral surfaces in heterogeneous natural systems

21   (Davis and Kent, 1990). Adsorption by aquifer material has been successfully modeled by

22   Stollenwerk (1994) using a total site density defined by amorphous extractable phases; however,

1   Coston et al. (1995) showed that the site density of an aquifer sand is underestimated when only

2   the amorphous extractable phases are considered and that sorption to sands decreases only after

3   both the amorphous and crystalline phases have been removed.

4   The dependence of sorption on metal-oxide coatings has been suggested to be a function

5   of the amount of amorphous phases that have greater surface area than the more crystalline

6   oxides (Davis and Kent, 1990). When using operationally defined extractions, it was apparent

7   from the data that the amorphous phases were not the only ones contributing to the reactive

8   surface. The relationships between sorption of SO_4^{2-} and the metals extracted by the method

9   considered to extract only the amorphous phases (HA) were the weakest ($r = 0.68$ for Fe, and

10 0.76 for Al). The relationship of sorption to the metals removed by the method operationally

11 defining amorphous and poorly crystalline phases (AO) was improved ($r = 0.92$ for Fe, and 0.91

12 for Al). However, the extraction method considered to remove the total metals (DCB), including

13 the crystalline phases, explained the greatest variance in the sorption data set ($r = 0.92$ for Fe and

14 0.91 for Al). These results were consistent with the findings of Fuller et al. (1996) where a

15 stronger relationship between Pb^{2+} sorption and extractable metals was found from methods that

16 remove the more crystalline phases. These results would indicate that the crystalline oxide

17 minerals are important substrates for the sorption of reactive solutes.

18   The relationship of sorption to surface area, as determined by gas adsorption, was also

19 significant ($r = 0.96$) for the aerobic sediments. The surface area was highly correlated with

20 total amount of extractable metals ($r = 0.91$). These results were consistent with Inch and Killey

21 (1987) and Jackson and Inch (1983) who observed a strong dependence of cation adsorption on

22 surface area and a high correlation of oxide surface coatings contributing most of the surface

15

1   area. Similarly, Horowitz and Erlick (1987) found that trace-metal content of stream sediments

2   was most strongly correlated with surface area, with a weaker dependence on amount of

3   extractable oxides.

4   The surface area results are in contrast to those of Fuller et al. (1996) and Coston et al.

5   (1995) on studies of Pb^{2+} and Zn^{2+} sorption to Cape Cod sediments. They found weak or no

6   correlation of sorption with surface area; however, the variability in sorption was best described

7   by the amount of extractable Al- and Fe-oxide coatings when normalized to specific surface area.

8   The authors indicated that adsorption may have occurred at specific regions of the sand surface

9   that were more reactive, whereas surface area is a measurement by unreactive N_2 covering the

10   entire, geometric area of the sample. These studies did not find Al, Fe, or Mn to be correlated

11   with surface area, suggesting that the extractions dissolved metals from multiple layers of oxide

12   coatings that were not accessible to N_2 adsorption.

13   A slightly weaker dependence of sorption on the oxide content as observed in these

14   sediments may be a function of the presence of layering of the oxide coatings on the quartz

15   surface. Szecsody et al. (1994) found that increasing the percentage of synthetically prepared

16   Fe-oxide coatings on quartz sand (in the 0.075 to 0.21 mm size range) from 0.6% to 1.2%

17   (corresponding to extractable Fe of 104 and 225 μmol g^{-1}, respectively) did not alter the amount

18   of surface area (3.4 m^2 g^{-1} for both sands) measured by N_2 adsorption. This layering could lead to

19   a slight overestimation in the amount of sorption expected by extraction methods. In this same

20   study, however, a similarly sized sand, coated with 50 μmol g^{-1} Fe-oxide, had a surface area of

21   only 0.4 m^2 g^{-1}. Only one sample from our study site had an extracted Fe value (154 μmol g^{-1})

22   that was within the range of amounts extracted by Szecsody et al. (1994), and only one other

16

1   sample was greater than 50 µmol g^{-1}; thus, a similar layering of the oxides is not expected to be

2   confounding the surface area measurements.

3   *Redox Chemistry*

4   With the consumption of DO in the anaerobic zone comes a number of other changes in

5   groundwater chemistry. At the site, the groundwater near the lower flow cell appeared to be

6   dominated by Fe reduction. Comparing the chemistry of the groundwater from each flow cell, it

7   is evident that Fe has been reductively dissolved from the anaerobic sediments. This reduction

8   was demonstrated by the results of the chemical analysis (Table 2) where, in addition to changes

9   in the redox status of the two zones as shown by the consumption of oxygen in the lower field,

10   there were much higher Fe concentrations (12 - 47 mg L^{-1}) as compared to the regional

11   groundwater (0.005 - 0.01 mg L^{-1}).

12   The reduction of Fe was evidenced by the results of the sediment extractions as well. The

13   extractable Fe in the background, aerobic sediments was from 3.2 to 52 µmol g^{-1} whereas it was

14   only 0.9 to 2.4 µmol g^{-1} in the contaminated anaerobic sediments (Fig. 4). Given the results of

15   the WATEQ4F calculations, it is plausible that the anaerobic-zone groundwater (*e.g.*, Well D1),

16   in disequilibrium with respect to Fe(III) minerals, has acted to dissolve those Fe(III)-bearing

17   grain coatings whereas the aerobic-zone groundwater (*i.e.*, Well PL2) has no capacity to remove

18   Fe(III) from the solid phase through dissolution (Table 3). Compared to the high Fe(II) in the

19   anaerobic groundwater, the results of the 0.5 M HCl extraction for solid Fe(II) phases indicated

20   that there was no appreciable amount (Fe(II) from 0.01 - 0.5 µmol g^{-1}) of it in either the aerobic

21   or anaerobic sediments. These results would indicate that reduction of the Fe in the anaerobic

1   zone was not resulting in appreciable formation of Fe(II) mineral phases as coatings on the

2   sediment surfaces and that Fe was reductively dissolved from the solid phase.

3   The presence of organic matter in the groundwater may have an impact on the reactivity

4   of sediments in contaminated aquifers. Many studies have investigated the sorption of organic

5   compounds in aquifers (e.g., Barber, 1994; Swartzenbach and Westall, 1981). In addition,

6   organic sorption has been shown to compete with anions for reactive sorption sites (Stollenwerk,

7   1995). Because of the similarity of the DOC in the two areas sampled, it is unlikely that

8   sorption of organic matter in the anaerobic plume can explain the decrease in the ability of the

9   sediments to retain SO_4^{2-}. Specific extractions targeting surface-associated organic matter were

10 not performed, but total organic matter (TOC) was determined to be similar in sediments from

11 the aerobic (0.01% -0.05%) and anaerobic (0.01 - 0.08%) zones.

12 *Sediment properties*

13   The high degree of correlation among the variables makes difficult the attribution of

14 observed differences in SO_4^{2-} sorption between aerobic and anaerobic samples to a specific

15 variable or subset of variables. An attempt to examine the relative importance of the variables

16 was made by subjecting the data for surface area, extractable Fe, extractable Al, and Fe+Al to a

17 principal components analysis. Only one component was extracted; it explained 92% of the

18 variance and consisted of all four variables, each having a loading of 0.9 or greater. Thus, a

19 quantitative separation of the relationship of the variables to SO_4^{2-} sorption could not be

20 achieved.

21   There is a strong correlation (r = 0.92) between surface area and Fe oxides in the aerobic

22 portion of the field. In the anaerobic zone, however, the relationship between surface area and Fe

1   content was not simple (Fig. 5). Although the majority of Fe was removed from the surfaces of

2   these sediments, leaving them with an order of magnitude less Fe than on the aerobic-zone

3   sediments (Fig. 4), there was still an appreciable amount of specific surface area measured (0.3 -

4   1.3 $m^2 g^{-1}$). The measured surface areas for the anaerobic samples were within the range of the

5   aerobic samples that had one to two orders of magnitude more Fe on the surfaces.   Once the

6   total extractable metal oxides (both the Fe and Al) had been removed from both the aerobic- and

7   anaerobic-zone sediments, however, the measured surface area was only 0.10 - 0.13 $m^2 g^{-1}$ for

8   both zones. This significant decrease in surface area from that observed in either type of

9   sediment prior to extraction additionally indicated that the oxides were responsible for the high

10   surface area.

11   The results of surface area analysis further suggested that although the Fe has been

12   removed, there were oxide coatings remaining on the surface of the anaerobic sediments

13   contributing to surface area. The existence of remaining oxides was clearly observed when

14   comparing the amounts of Al vs. Fe extracted in each zone (Fig. 6). In the anaerobic samples

15   there was a removal of the Fe oxides; however, there was a significant amount of Al extracted

16   that was comparable to the amount of Al extracted in the aerobic sediments. Aluminum oxides

17   are not redox sensitive and should not be removed from the surfaces in the anaerobic sediments

18   if they exist as discrete phases on the surface and are not present as substitutions in the Fe-oxide

19   minerals.

20   From the results of the sorption studies with the anaerobic sediments, it was clear that

21   they were less reactive than the non-contaminated sediments (Fig. 3). Because there was

22   persistence of the Al oxides and a significant surface area remaining on the anaerobic sediments,

1 it was evident that the removal of the Fe oxides controlled this change. Although the Al was

2 persistent in the anaerobic flow cell, it did not appear to have contributed significant reactive

3 surface to the sediments. In fact, at the pH of interest in this system (5.3-6.6), the zpc of Al

4 hydroxide ($Al(OH)_3$ = 5.0) has been exceeded and these oxide surfaces would not be expected to

5 carry a positive charge. It is then clear that the presence or absence of Fe oxides controls the

6 majority of the affinity of these surfaces for negatively charged groundwater constituents.

7

8   **SUMMARY**

9   Analysis of the geochemistry of the groundwater and sediments from the anaerobic

10 groundwater zone the lower field at the Virginia Coastal Research Center site has shown that the

11 Fe-oxyhydroxide minerals have been reductively dissolved from the sediment surfaces. This

12 conclusion was evidenced by the presence of elevated concentrations of Fe(II) in the

13 groundwater and the extremely lower amount of extractable Fe on the sediment surfaces as

14 compared to the sediments of the upper flow cell. The presence of anaerobic condition does not

15 appear to have altered the presence of Al oxides on the surface of the sediments. Naturally, Al is

16 not a redox sensitive metal and the Al-oxide minerals are not expected to be very soluble at pH's

17 above 6.

18   It was evident that the removal of the Fe from the anaerobic sediments has not

19 significantly changed the surface area of these sediments. The continued presence of the Al

20 oxides has contributed to a specific surface area that persisted despite the onset anaerobic

21 conditions. It is important to note that the significant surface area (greater than would be

1   expected by geometric calculation based on grain size) was removed when all of the oxides were

2   extracted from the sediment surfaces.

3   The Fe-oxide content was the only one of the surface properties to be significantly altered

4   by the anaerobic condition with a concomitant alteration in the ability for the sediments to retain

5   SO_4^{2-}. It appeared, therefore, the presence or absence of Fe oxides was the dominant factor

6   controlling SO_4^{2-} sorption. These results would indicate an alteration in the reactive surfaces of

7   minerals when exposed to anaerobic groundwater and the potential for greater movement of

8   reactive constituents through aquifer sediments under evolving chemical conditions.

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20

1   TABLES

2

3   Table 1. Correlation coefficients (r) among surface properties for the aerobic sediments.

4   Hydroxylamine hydrochloride (HA) extraction operationally defines amorphous oxide phases.

5   Ammonium oxalate (AO) extraction operationally defines amorphous and poorly crystalline

6   phases. For comparison, the correlations for DCB-extracted metals are shown on Fig. 2A-C and

7   Fig. 3A.

	HA	AO
SO_4^{2-} sorption vs. Extractable Fe	0.68	0.87
SO_4^{2-} sorption vs. Extractable Al	0.76	0.89
SO_4^{2-} sorption vs. Total extractable metals	0.74	0.88
Extractable Fe vs. extractable Al	0.97	0.98

8

1   Table 2. Typical concentrations of ground water constituents in the aerobic and anaerobic

2   sections of the aquifer. Values shown represent the range of observations collected at 16

3   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	0-0.9
Dissolved Iron	0.005 - 0.01	12-47
Sulfate)	11.0-74.0	12-44.2
Sulfide	0.13	0.16
Nitrate	15-50	4.8
NH_4^+	0	0.558-3.12

4

1   Table 3. Chemical composition of two groundwater samples representative of the aerobic and

2   anaerobic zones. Samples were collected on 06/27/1995. Concentrations are reported as mg L^{-1}. The

3   thermodynamic saturation state of the groundwater with respect to various mineral phases is reported

4   in terms of saturation indices, where S.I. = log (ion activity product/equilibrium solubility constant).

5   Positive values of S.I. indicate the groundwater is supersaturated with respect to the mineral, and

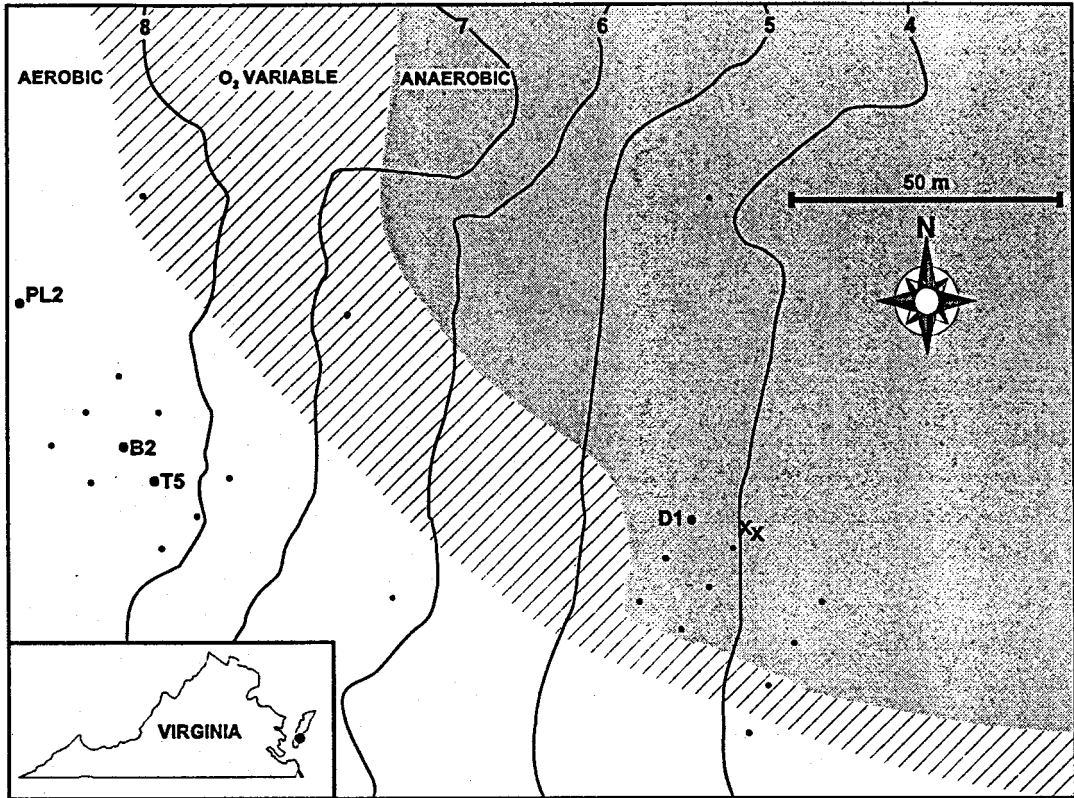6   negative values of S.I. indicate undersaturation.

	Aerobic zone (Well PL2)	Anaerobic Zone (Well D1)
T (°C)	17.8	17.8
pH	6.39	6.34
Alkalinity (as HCO_3^-)	24.4	384
DOC	1.62	4.8
DO	8.0	0
Cl^-	31.6	34.7
NO_3^-	27.8	1.24
SO_4^{2-}	65.1	25.9
PO_4^{3-}	0.99	0.086
Ca^{2+}	27.1	26.2
Mg^{2+}	7.39	11.2
Na^+	13.4	23.0
K^+	1.01	35.7
Fe (total)	0.0112	46.9
Mn (total)	<0.001	4.70
S.I. goethite	6.56	n.a.
S.I. ferrihydrite	0.67	n.a.

7   [a] n.a. indicates that the calculation is not applicable. No saturation state result can be calculated for

8   Fe(III) minerals in te anaerobic water where total Fe was taken to be Fe(II).

FIGURE CAPTIONS

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 oxygen status of the ground water is indicated by the coloring; the white area has oxygen levels above 2 mg L^{-1}, the hatched area has oxygen 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.

FIG. 2. Relationship of sulfate sorption to mineral surface properties. Data are from the 27 subsamples from the aerobic cores (●) and from the 14 anaerobic samples (○). Only 19 and 6 surface area measurements were obtained for the aerobic and anaerobic samples, respectively.

FIG. 3. Relationship between DCB extractable Fe and Al, and between surface area and total DCB extractable metals (Fe+Al).

Fig. 4. Concentration of total extractable iron with depth (below the water table) for samples from aerobic and anaerobic cores.

Fig. 5. Relationship between surface area and DCB extractable iron for the aerobic and anaerobic sediments. The amount of surface area on all samples after extraction of total metals was 0.10 to 0.13 $m^2 g^{-1}$.

Fig. 6. Comparison of DCB extractable Fe and Al for the aerobic and anaerobic sediments.

AEROBIC O₂ VARIABLE ANAEROBIC

8 7 6 5 4

50 m

N

PL2

B2

T5

D1 Xx

VIRGINIA

Knapp et al., Fig. 1

Knapp et al., Fig 2.

Knapp et al., Fig. 3

Knapp et al., Fig. 4

Knapp et al., Fig 5

Knapp et al., Fig. 6