

Sources of Sulfate Supporting Anaerobic Metabolism in a Contaminated Aquifer

GLENN A. ULRICH,[†] GEORGE N. BREIT,[‡]
ISABELLE M. COZZARELLI,[§] AND
JOSEPH M. SUFLITA^{*,†}

University of Oklahoma, Norman, Oklahoma, 73019,
U.S. Geological Survey, Denver, Colorado 80225, and
U.S. Geological Survey, Reston, Virginia 20192

Field and laboratory techniques were used to identify the biogeochemical factors affecting sulfate reduction in a shallow, unconsolidated alluvial aquifer contaminated with landfill leachate. Depth profiles of ³⁵S-sulfate reduction rates in aquifer sediments were positively correlated with the concentration of dissolved sulfate. Manipulation of the sulfate concentration in samples revealed a Michaelis–Menten-like relationship with an apparent K_m and V_{max} of approximately 80 and 0.83 $\mu\text{M SO}_4^{2-}\cdot\text{day}^{-1}$, respectively. The concentration of sulfate in the core of the leachate plume was well below 20 μM and coincided with very low reduction rates. Thus, the concentration and availability of this anion could limit in situ sulfate-reducing activity. Three sulfate sources were identified, including iron sulfide oxidation, barite dissolution, and advective flux of sulfate. The relative importance of these sources varied with depth in the alluvium. The relatively high concentration of dissolved sulfate at the water table is attributed to the microbial oxidation of iron sulfides in response to fluctuations of the water table. At intermediate depths, barite dissolves in undersaturated pore water containing relatively high concentrations of dissolved barium ($\sim 100 \mu\text{M}$) and low concentrations of sulfate. Dissolution is consistent with the surface texture of detrital barite grains in contact with leachate. Laboratory incubations of unamended and barite-amended aquifer slurries supported the field observation of increasing concentrations of barium in solution when sulfate reached low levels. At a deeper highly permeable interval just above the confining bottom layer of the aquifer, sulfate reduction rates were markedly higher than rates at intermediate depths. Sulfate is supplied to this deeper zone by advection of uncontaminated groundwater beneath the landfill. The measured rates of sulfate reduction in the aquifer also correlated with the abundance of accumulated iron sulfide in this zone. This suggests that the current and past distributions of sulfate-reducing activity are similar and that the supply of sulfate has been sustained at these sites.

Introduction

Sulfate reduction, a major process linked to the degradation of naturally occurring and contaminant forms of organic

matter, has been detected in many anaerobic subsurface environments (1–4). The factors controlling this process in the subsurface can include the availability of utilizable organic matter as electron donors (2, 4–7), the water potential, the pH, the sediment pore throat diameter, and the availability of thermodynamically more favorable electron acceptors (8–15). In addition, the lithologic, climatic, hydrological, and biogeochemical processes that control the sulfate supply can moderate sulfate reduction in anoxic aquifers. For example, sulfate derived from the oxidation of pyrite in shallow oxidized subsurface areas, in conjunction with advective transport, serves as an important source of this electron acceptor to anaerobic regions of an unconsolidated aquifer in east central Texas (4, 16).

The aim of the study described herein was to identify the factors that regulate sulfate supply and reduction in a landfill-leachate-contaminated alluvium of the Canadian River near Norman, OK. Previous work indicated that sulfate reduction is an important process in a location containing elevated levels of sulfate whereas methanogenesis dominates in sulfate-depleted regions (17). This paper provides a more detailed analysis of the vertical distribution of sulfate reduction and identifies three important sources of sulfate that influence sulfate-reducing activity in the alluvial aquifer.

Materials and Methods

Field Site. The study site (Figure 1) is on recent alluvium of the Canadian River in Norman, OK, that underlies and extends down the hydrologic gradient from a now-closed municipal landfill. The aquifer is contaminated with leachate from the landfill. The alluvium consists primarily of medium-grained quartz sand with discontinuous mud layers that are typically only a few centimeters thick. The alluvium is 10–15 m thick and underlain by low-permeability siltstone of the Hennessey group (18). Alluvium immediately above the Hennessey rocks consists of coarse-grained sands, gravel, and some mud. Estimates of hydraulic conductivity based on slug tests range from 8.4×10^{-7} to $2.5 \times 10^{-4} \text{ m s}^{-1}$, with a median value of $6.6 \times 10^{-5} \text{ m s}^{-1}$ (19). The highest and lowest values were measured in the deep gravel layer and clay-rich interval, respectively.

Groundwater Sampling. Groundwater samples were collected from a network of small-diameter temporary wells and permanent multilevel samplers as described by Cozzarelli et al. (17) (Figure 1). The temporary wells were driven to the desired sampling depth, and water was pumped through 8.7-cm-long screens using Teflon tubing and a peristaltic pump. Samples were collected from three locations immediately downgradient from the landfill (wells 35, 38, and 40) and from a “background” location (MLSNPD) upgradient from the landfill. Samples were stored in glass bottles at 4 °C prior to analysis (17). Dissolved sulfide was determined in the field using the method of Cline (20).

Sediment Sampling. Sediment cores were obtained within a few meters of the water sampling wells in March of 1996 using a Geoprobe Macro-Core Soil Sampler (Figure 1). Immediately after retrieval of the cores in polycarbonate liners, each end of the core tube was flushed with N_2 and capped with large butyl rubber stoppers, and the cores were stored at 4 °C under N_2 . Sediments used to evaluate the kinetics of sulfate reduction and the dissolution of barite were obtained from beneath the water table (21). Splits of the sediment were frozen on site and freeze-dried to prepare grain mounts that were examined using a JEOL JSM5600LV scanning electron microscope (SEM) equipped with an Oxford Isis energy-dispersive X-ray analyzer. Selected samples

* Corresponding author phone: (405)325-5761; fax: (405)325-7541; e-mail: jsuflita@ou.edu.

[†] University of Oklahoma.

[‡] U.S. Geological Survey, Denver, CO.

[§] U.S. Geological Survey, Reston, VA.

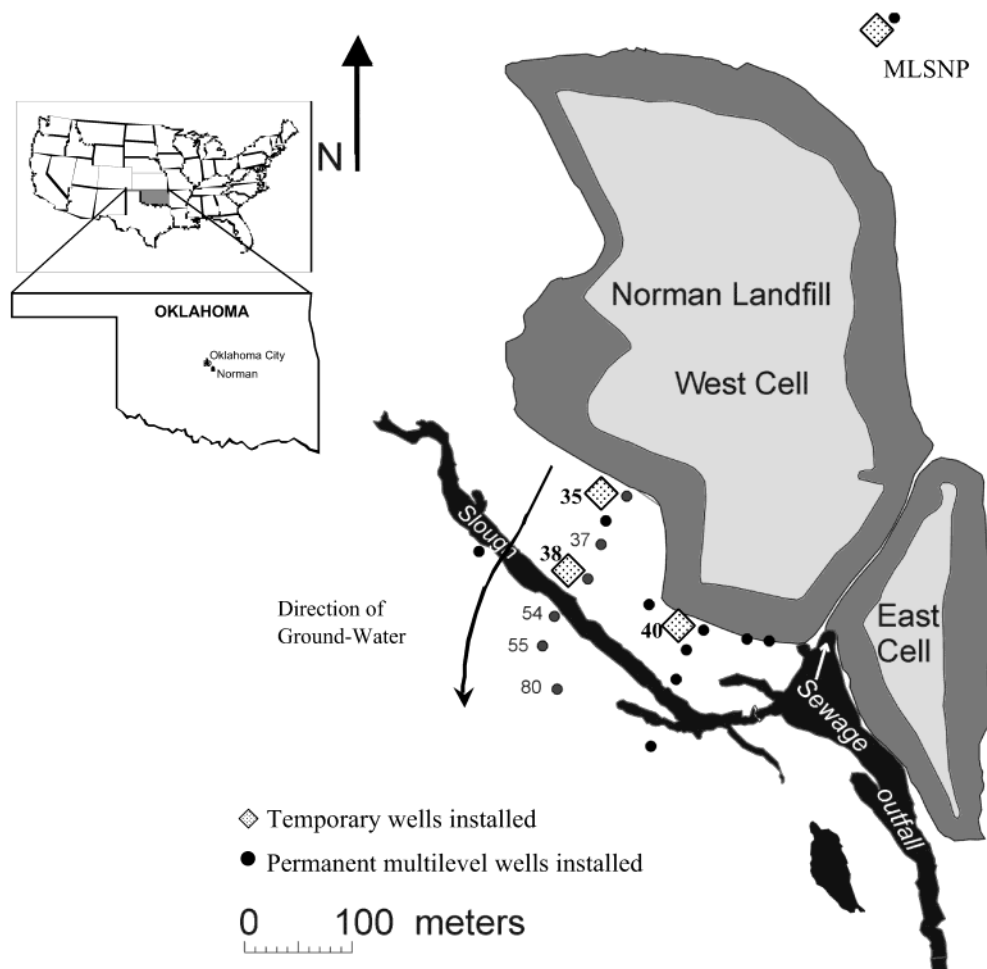


FIGURE 1. Map of the study area. Numbers refer to wells installed along the groundwater gradient. General site characteristics can be found at <http://csdskokl.cr.usgs.gov/norlan/>, and specific parameters are detailed in ref 17.

were chemically analyzed for major and trace elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES) following a standard four-acid digestion procedure (22).

Sulfate Reduction Activity, Iron Sulfide, and Anion Analyses. Measurements of sulfate reduction rates and geochemical analyses were performed within 2 days after the cores had been obtained. Sediments were handled inside an anaerobic glovebag filled with 100% N_2 . Iron monosulfides extractable with 6 N HCl were determined in sediment samples (1–2 g) using a passive extraction technique (23). Pore waters were centrifuged from 20-g aliquots of sediment collected from the cores and analyzed for dissolved SO_4^{2-} , NO_3^- , and Cl^- by ion chromatography (4). For determination of sulfate reduction rates, small samples of sediment were obtained by pushing 5-mL syringes (with distal ends cut and removed) into the cores. An anoxic solution of $^{35}SO_4^{2-}$ (100 μ L, 20 μ Ci mL^{-1} , carrier-free, ICN) was injected into the small core samples with a syringe and needle. The incubations, contained inside the syringes, were sealed with butyl rubber stoppers and stored under a N_2/CO_2 (80:20) headspace for 17 h at 18°C, the approximate in situ temperature of the aquifer at the time of sampling. Sulfate reduction rates and abundances of iron sulfides were determined (23) after the 17-h incubation period.

Sulfate Reduction Kinetics. We evaluated the factors that limit sulfate reduction, including electron acceptor and donor availability, using sediment in contact with landfill leachate and groundwater obtained from the aquifer. Sediments for these experiments were rinsed with anoxic, low-sulfate (<5

μ M) groundwater that had comparable levels of dissolved organic carbon (DOC). Sediment (5 g) and groundwater (2 mL) were placed inside 25-mL serum bottles that were sealed with butyl rubber septa and flushed with N_2/CO_2 (80:20). Triplicate incubations were amended with dissolved sulfate ranging from 5 μ M to 1 mM. Other incubations received amendments of both 1 mM SO_4^{2-} and an electron donor, either acetate (1 mM), lactate (1 mM), or H_2 [as a H_2/CO_2 (80:20) headspace]. Radiolabeled sulfate was added (2.5 μ Ci per incubation) to measure sulfate reduction activity. The bottles were incubated at 25 °C for 26 h in the dark.

Barite Dissolution Experiments. Barite as a source of sulfate was investigated using duplicate sediment slurries (20 g/20 mL of anoxic groundwater) in 60-mL serum bottles. The barite was either barite rose rock from the Garber Sandstone (24), which occurs naturally in the sediments, or 20 mg of synthetic $BaSO_4$, which simulates barite that might precipitate within the alluvium from oversaturated pore water. All of the slurries were amended with sodium lactate (to 20 mM) in an effort to stimulate sulfate reduction. The barite was prepared by crushing barite-cemented sandstone by hand, sieving to a size range of 45 to 75 μ m, rinsing for 24 h in warm 2 N HCl, and then thoroughly rinsing with deionized water. Particle size and mineralogy were verified by SEM examination. The synthetic $BaSO_4$ was prepared by reacting H_2SO_4 with $BaCl_2$ (25). The $BaSO_4$ suspension was heated and stirred for 4 days to increase crystallinity and particle size and was thoroughly rinsed in deionized water. Examination of the synthetic barite with an SEM identified uniform rounded particles ranging from 0.1 to 0.5 μ m in

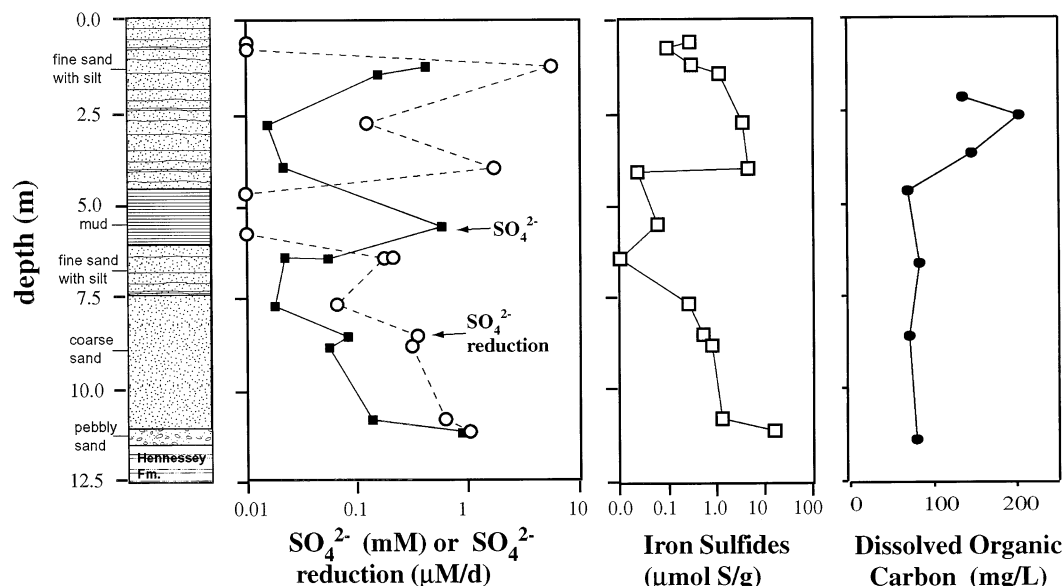


FIGURE 2. Depth profile (meters below land surface) of the stratigraphy, sulfate reduction rate, sulfate concentration, iron sulfide content of sediments, and dissolved organic carbon in groundwater obtained from an area adjacent to well 40.

diameter. Sodium molybdate (5 mM) was amended to inhibit sulfate reduction in selected experiments. Autoclaved incubations served as abiotic controls. The bottles were incubated at 25 °C in the dark. Liquid samples were withdrawn from the slurries over the course of the experiment, filtered (0.25 μm), and stored at 20 °C prior to analysis. Barium concentrations were determined using standard methods of atomic adsorption spectrophotometry. Sulfate concentration was analyzed by ion chromatography (4).

Iron Sulfide Oxidation Experiments. The oxidation of iron sulfide minerals, the dominant reduced sulfur species in the aquifer, was evaluated using sediment slurries (10 g/10 mL) (site 35, 6.4-m depth). Dissolved sulfide was less than 1 μM in the groundwater at this location. The potential oxidants included 1 mL of a poorly crystalline manganese oxide suspension (26), NO₃⁻ (5 mM), 1 mL of an iron oxyhydroxide suspension (27), and O₂. The O₂ incubations were closed with sterile cotton to allow for air exchange, whereas the other incubations were sealed with butyl rubber septa. Anoxic incubations that were not supplemented with potential oxidants served as background controls.

Results

Sulfate Reduction and Associated Sulfur Geochemistry. The experimentally determined sulfate reduction rates in a vertical profile of the alluvium ranged from 0.06 to 5.6 μM SO₄²⁻ day⁻¹ (Figure 2) at a location near the edge of the landfill (well 40, Figure 1). The highest activity occurred in sediment immediately beneath the water table. Sulfate reduction was not detected in the oxidized sediments above the water table or in the thick mud layer at ~4 m. Dissolved sulfate concentrations in the pore water from sediments ranged from 10 μM near the center of the alluvium to approximately 1 mM near the water table (Figure 2). Nitrate was below detection (~5 μM) in all of the samples except those collected at the water table (17). The concentration of iron sulfides in the sediment correlated with the sulfate reduction rate, suggesting that hydrogen sulfide precipitated rapidly, likely owing to the abundance of dissolved iron (Table 1). This correlation was most pronounced beneath the mud interval at 4–5 m in depth. The amount of iron sulfide in the sediments ranged from 0.01 to 16.8 μmol of S g⁻¹ (Figure 2). These minerals were most abundant at the water table, above and below the clay layer, and in the interval above the consolidated bedrock.

TABLE 1. Concentrations of Selected Chemical Parameters from a Well Upgradient from the Landfill (MLSNPD) and from a Well within an Anoxic Plume (MLS38)^a

constituent	well (screen elevation)	
	MLSNPD	MLS38
specific conductance (μS cm ⁻¹)	1570	5470
pH	7.01	6.78
alkalinity (mM HCO ₃ ⁻)	10.3	43.3
DOC (mg L ⁻¹)	2.9	159
chloride (mM)	5.1	29.0
sulfate (mM)	1.2	0.1
sulfide (μM)	<0.5	<0.5
calcium (mM)	4.2	12.9
magnesium (mM)	2.2	9.5
potassium (mM)	0.06	0.36
silica (mM)	8.7	16.8
barium (μM)	1.0	52
iron (μM)	2.3	330
ammonium (mM)	2.1	15
methane (mM)	0.03	13.6

^a Water samples were collected from depths of 9 and 7 m below the land surface or from an elevation of 323.7 m in both wells. Methane samples were collected in 1999. All other analyses were done on samples collected in May 1997.

Excluding the sample from the mud layer, sulfate reduction activity measurements parallel the concentration of dissolved sulfate in the sediment pore water (Figure 2). During periodic sampling of wells, higher concentrations of dissolved sulfate were present near the water table and at the base of the alluvium, where the highest rates of sulfate reduction were detected. The correlation of sulfate reduction rates and sulfate concentrations suggests that sulfate is an important factor controlling sulfate-reducing activity. In consistent fashion, sulfate reduction activity in aquifer sediment slurries amended with various concentrations of SO₄²⁻ exhibited Michaelis–Menten-like kinetics (Figure 3A). These experiments yield an apparent *K_m* and *V_{max}* of 84 μM and 0.13 nmol of SO₄²⁻ g⁻¹ day⁻¹ (0.83 μM SO₄²⁻ day⁻¹), respectively. Pore water sulfate concentrations at most depth intervals of the aquifer (Figure 2) were well below the apparent *K_m*. Sediment slurries that were amended with saturating levels of SO₄²⁻ (1000 μM) and hydrogen as an electron donor reduced sulfate at an increased rate (~3 times) relative to incubations that received only SO₄²⁻ (1000 μM). The addition of acetate and

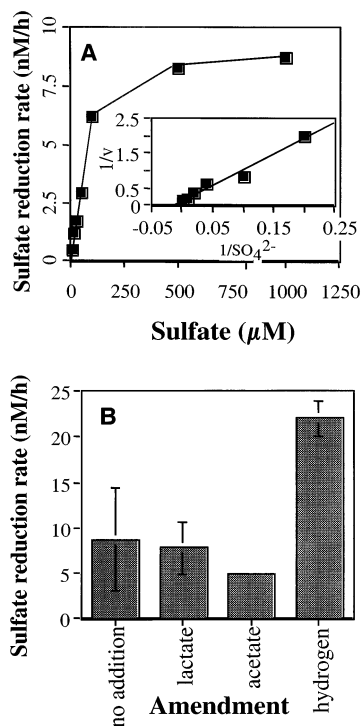


FIGURE 3. (A) Initial rates of sulfate reduction in sediment slurries at various sulfate concentrations. The inset shows the corresponding Lineweaver–Burk plot. (B) Sulfate reduction rates at a saturating level of sulfate (1 mM) with the addition of potential electron donors. The values represent the means of triplicate determinations, with the standard errors (error bars) illustrated.

lactate did not stimulate sulfate reduction during the 26-h incubation period (Figure 3B).

Evidence for Barite Dissolution in the Canadian River Alluvium. We evaluated whether the dissolution of barite (BaSO_4) could be an important source of sulfate because barite is a known constituent of rocks in the Canadian River drainage basin (24, 28, 29). SEM examination of the alluvium confirmed the presence of detrital grains of barite (Figure 4). Barite grains in sediment affected by the leachate plume are etched and considered too fragile to have survived sediment transport compared to grains in sediment in contact with background levels of dissolved sulfate. The pervasive occurrence of detrital barite is supported by its detection in 12 samples and the anomalously high content of barium in the sediment.

The median barium concentration of the alluvium is 540 ppm, which is higher than the $280 \mu\text{g g}^{-1}$ expected for typical quartz-rich sediment (30). The barium enrichment was verified by comparing its abundance to potassium. Among the detrital phases, both potassium and barium tend to concentrate in feldspars and clay minerals. The weight ratio of barium to potassium in the alluvium ranges from 0.030 to 0.044, whereas typical ratios for the continental crust range from 0.02 to 0.025 (30). The barium/potassium ratio and absolute barium enrichment relative to other quartzose sediments are consistent with approximately $1.8 \mu\text{mol g}^{-1}$ of barite in the Canadian River alluvium.

Vertical concentration profiles adjacent to the downgradient side of the landfill (Figure 1) illustrate that the Ba^{2+} and SO_4^{2-} concentrations are inversely related (Figure 5). Dissolved Ba^{2+} is highest near the center of the aquifer, where the SO_4^{2-} concentrations are lowest. A sharp decrease in Ba^{2+} occurs just beneath the water table (well 35, Figure 1), where the SO_4^{2-} concentrations are highest. Barium concentrations are typically between 50 and $100 \mu\text{M}$ in leachate-impacted areas and between 0.5 and $3 \mu\text{M}$ in groundwater that is not

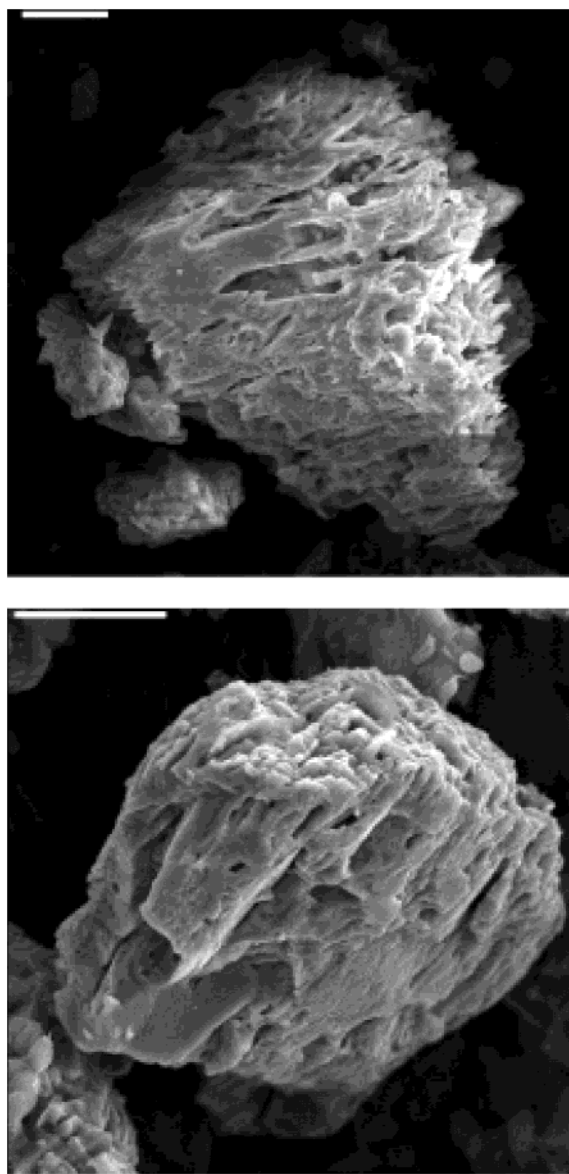


FIGURE 4. Micrographs (SEM) contrasting the texture of detrital barite grains. Grain on the top with dissolution textures was collected from sediment exposed to leachate; nearby pore water contains $<10 \text{ mg/L}$ sulfate. Grain on the bottom was collected from sediment not exposed to leachate and containing 100 mg/L sulfate. Bar scale is $10 \mu\text{m}$.

impacted by leachate. Barite saturation indices calculated using the program PHREEQC v. 2.5 (31) indicate oversaturation in the shallow sediment where sulfate can form by sulfide oxidation related to water table fluctuations and slight undersaturation within the core of the plume. Precipitation of BaSO_4 from oversaturated pore water is consistent with fine-grained authigenic barite ($\sim 0.5 \mu\text{m}$) detected within one sediment sample during SEM examination. The undersaturation likely results in barite dissolution, as is evident in Figure 4. The data in Table 1 indicate that Ba^{2+} and Fe^{2+} are the most enriched elements in the plume compared to their concentrations in upgradient groundwater (MLSNPD, Figure 1). The high enrichment factors for Ba (60) and Fe (145) in leachate-contaminated relative to background groundwater are much greater than those of other metals likely present in the landfill waste. Ba and Fe are therefore likely derived by dissolution of constituents of the alluvium.

To experimentally evaluate the importance of barite dissolution as a sulfate supply mechanism, we monitored

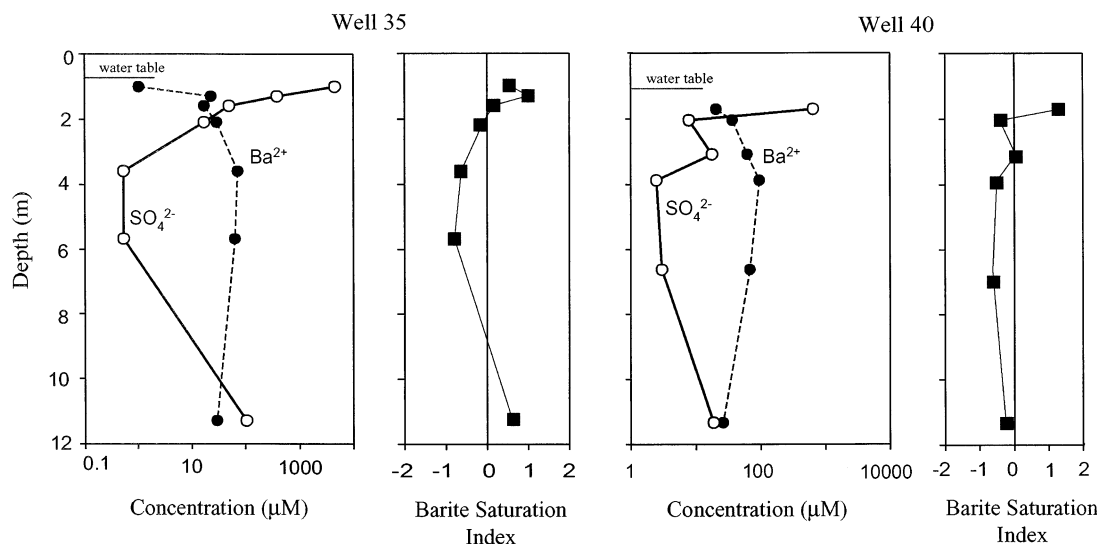


FIGURE 5. Concentrations of barium and sulfate and barite saturation index for wells at sites 35 and 40 as a function of depth. PHREEQC (37) was used to calculate saturation indices [$\log(\text{ion activity product}/K_{sp})$] on the basis of water composition.

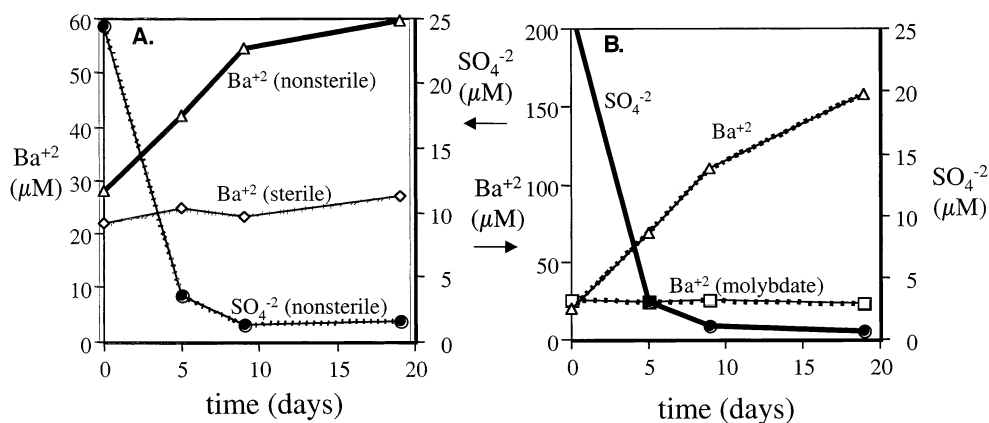


FIGURE 6. Barium accumulation and sulfate depletion in (A) sediment slurries and (B) sediment slurries amended with BaSO_4 . Molybdate refers to the treatment where sulfate reduction was inhibited.

dissolved barium production in aquifer slurries amended to stimulate sulfate reduction. Dissolved barium concentrations increased in sediment incubations amended with lactate. In these experiments, sulfate was consumed to concentrations of approximately $1 \mu\text{M}$ (Figure 6A). Similarly, barium accumulated at a faster rate and to higher concentrations when synthetic BaSO_4 was added to the lactate-amended incubations (Figure 6B). Sulfate decreased at essentially the same rate as the incubations unamended with BaSO_4 and approached an apparent steady-state value of $1 \mu\text{M}$. Consistent with this suggestion, the dissolved barium concentrations continued to increase in nonsterile incubations even after the sulfate concentrations reached this low level. Dissolved barium concentrations did not increase in autoclaved or molybdate-treated negative controls (Figure 6A,B). Comparable results were obtained with sulfate-reducing enrichment cultures amended with synthetic BaSO_4 as the sole source of sulfate and barium (data not shown).

The addition of barite from rose rock did not result in increased concentrations of dissolved barium above the levels measured for alluvial sediments without barite addition. Examination of these barite grains by SEM after treatment in a lactate-amended sediment identified textures that are consistent with incipient dissolution on grain edges. However, the coarse particle size and crystallinity very likely limited the rate of dissolution. The slow reactivity is also likely responsible for the undersaturation of barite within the core of the plume. Leachate depleted in sulfate moves through

the alluvium more quickly than the detrital barite can dissolve to maintain saturation.

Oxidation of Iron Sulfide Containing Minerals in Sediment. We evaluated whether the oxidation of iron sulfides also might contribute to the dissolved sulfate content of the aquifer. In situ evidence for this process was found at the water table where, despite relatively high sulfate reduction activity, the concentration of iron sulfides was low and dissolved sulfate was high (Figure 2). Laboratory studies indicated that sulfate was produced in aerobic sediment slurries at relatively high rates ($750 \mu\text{M}$ over 20 days) compared to anaerobic incubations (Figure 7). Anaerobic slurries containing manganese oxides produced sulfate but at much lower rates ($250 \mu\text{M}$ over 140 days). Less than $75 \mu\text{M}$ sulfate was produced above the unamended controls in anaerobic incubations amended with nitrate and ferric iron (Figure 7). Sulfate was not produced in the inhibited control experiments (data not shown).

Discussion

Soluble and solid-phase geochemical profiles coupled with laboratory rate experiments were used to evaluate the factors governing the in situ metabolic activities in a landfill-leachate-contaminated aquifer. In previous investigations at the Norman Landfill (17, 32), oxygen and nitrate were reported to be below detection levels, and evidence of iron reduction was observed in only a few samples. Methanogenesis was

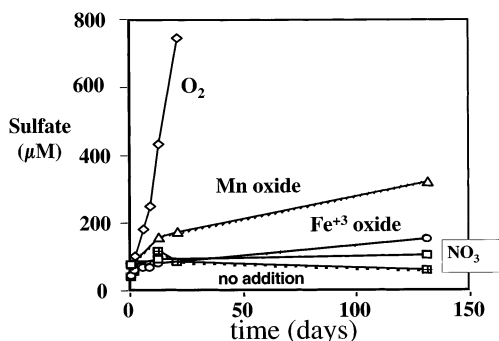


FIGURE 7. Production of sulfate in sediment slurries in response to the addition of potential iron sulfide oxidants.

important where dissolved sulfate concentrations were lowest near the center of the alluvium. In the current study, evidence of sulfate reduction was detected in most of the sediment samples.

The general correlation of sulfate reduction rates with concentrations of dissolved sulfate in sandy layers suggested that the availability of this anion is an important factor governing this metabolic process. In most regions of the aquifer, the ambient concentration of sulfate is below the estimated apparent K_m of $\sim 80 \mu\text{M}$. The K_m value is consistent with the range exhibited by pure cultures of sulfate-reducing bacteria ($4.8\text{--}244 \mu\text{M SO}_4^{2-}$) (33). This finding supports the contention that sulfate reduction could indeed be limited by the availability of this anion, and therefore, attention was focused on sulfate resupply mechanisms. We suggest that at least three sources of sulfate support sulfate-reducing activity in the leachate-impacted aquifer. Each of these sources supplies sulfate to a different depth interval: (a) sulfide oxidation near the water table, (b) barite dissolution at intermediate depths within the leachate plume, and (c) transport of sulfate in groundwater in transmissive sediments at the base of the alluvium.

The oxidation of iron sulfides to sulfate is important in shallow zones near the water table. Experiments conducted with sediment collected from the study site have shown that hydrogen sulfide precipitates rapidly in the sediments as immobile iron sulfide minerals (data not shown). Such minerals were found to be rather stable and not easily oxidized to sulfate under anaerobic conditions in the presence of a variety of potential electron acceptors (Figure 7). When aerobic conditions prevail, however, as is expected to occur seasonally at the water table, the iron sulfides readily oxidize, and the sulfate concentration increases in pore waters. These sulfate concentrations are greatest near the water table and decrease rapidly with depth (Figures 2 and 6). The amount of sulfate that interacts with the leachate as a result of oxidation at the water table could not be readily quantified, given the complexity of cycling driven by variable and seasonal water table fluctuations. The observation that iron sulfide oxidation near the water table contributes to the supply of SO_4^{2-} is analogous to findings from an uncontaminated aquifer in the Yegua formation of east central Texas (4). The oxidation of iron sulfide to sulfate has also been observed in deeper groundwater systems (34), including near recharge zones (35).

The source of sulfate important at intermediate aquifer depths is dissolution of barite (BaSO_4) (Figures 4 and 5). Under conditions of low dissolved sulfate ($<10 \mu\text{M}$), as is the case in the center of the anoxic leachate plume, the groundwater is undersaturated with respect to barite, and barite dissolves, releasing both barium and sulfate into solution. The observation that dissolved barium increased at a higher rate and to a greater extent in sediment slurries amended with synthetic BaSO_4 (Figure 6) suggests that either the abundance

or the reactivity of the barite in the alluvium limits dissolution in situ. The particle size of authigenic barite detected in one natural sample was slightly coarser than that of the synthetic BaSO_4 , which could account for the difference in reactivity. Further, addition of coarser-grained natural barite did not significantly change the experimental results, suggesting that the increase in crystallinity and particle size of this barite decreases its susceptibility to dissolution.

The barium enrichment of the aquifer sediment is consistent with approximately 50% of the barium in the form of barite. This would equate to $1.8 \mu\text{mol g}^{-1}$ of sulfate in the typical sediment. If all of the barite dissolved instantly, the resulting aqueous sulfate concentration would approximate 6.5 mM, assuming typical sediment characteristics of 40% porosity and a solid-phase density of 2.4 g cm^{-3} . Rapid dissolution of barite is unlikely given its low solubility; nonetheless, the amount of barite inferred to be present is sufficient to affect the sulfate budget of the aquifer. For example, leachate moving through a 1-m^2 cross section at groundwater velocities typical in the sandy alluvium would receive $600 \text{ mmol year}^{-1}$ of sulfate from barite dissolution, assuming that barite in the sediment dissolves over 50 years [a reasonable assumption using the rates of dissolution observed in the sediment slurries (Figure 6)]. Although the amount of sulfate supplied by barite dissolution is likely to be substantially less than the advective flux at the base of the alluvium (described below), it is important to note that, in the center of the anoxic plume, barite is likely to be the only source of sulfate.

The final source of sulfate considered is the advective flux occurring just above the confining layer at the bottom of the aquifer. Hydraulic conductivity is relatively high (19) in this depth interval, where coarse-grained sands and gravel are the predominate sediment type. The lower chloride concentration and lower specific conductance (19) of groundwater in deeper portions of the aquifer relative to the leachate plume are consistent with mixing of leachate and uncontaminated groundwater. Dissolved sulfate in this interval approaches background concentrations and is important in maintaining the rates of sulfate reduction in the deep aquifer. The quantity of sulfate supplied to deeper portions of the aquifer by this flux, c , is estimated using the concentration of sulfate measured in the upgradient water (MLSNPD-6, Table 1) and hydraulic properties of the alluvium. Using the MODFLOW code (36), the estimated advective fluxes of sulfate to the lower portion of the plume at site 35 range from 4600 to $46\,000 \text{ mmol year}^{-1}$ across each 1-m^2 cross section. Studies of the plume biogeochemistry (17) indicate that the influx of electron acceptors by mixing with recharge or upgradient groundwater is limited to the boundaries of the plume.

The three spatially distributed sources of sulfate identified here might also support a complex cycling of barium as the leachate moves through the alluvium. The calculated barite saturation indices (Figure 5) suggest that barium might be cycled between the groundwater and the sediment in the vicinity of the leachate plume. Mixing of barium-rich leachate with the high-sulfate water found at the water table and near the bottom of the aquifer is expected to precipitate BaSO_4 . Advance of leachate into a zone of mixing beneath the plume would favor reductive dissolution of the newly formed barite as sulfate is consumed and, eventually, the less-reactive detrital barite grains. Near the water table, the relation is more complex because the seasonal rise and fall of the water table affects both the redox condition in the sediment and the hydrologic drive of the leachate plume. Clarification of the dynamics of the seasonal change of the redox conditions, iron sulfide formation and oxidation, and probable precipitation and dissolution of BaSO_4 will require further investigation.

Dissolved sulfide was not detected, and very little sulfate was measured in many zones of the aquifer, despite the measurement of substantial rates of sulfate reduction. Thus, methods for evaluating the predominant electron-accepting conditions in sedimentary ecosystems that are based solely on the concentration of dissolved electron acceptors and reduced end products can be erroneous.

The distribution of iron sulfides in contaminated sediments vs background zones was useful in determining the localization of in situ sulfate reduction. In deeper portions of the aquifer, the distribution of solid-phase inorganic sulfides tracked the sulfate reduction rate measurements and sulfate concentration. This correlation has been observed at other locations in the aquifer (17). Iron sulfide content would not, however, be a useful indication of sulfate reduction in regions where substantial sulfide oxidation occurs, in aquifers that do not contain sufficient reactive iron to precipitate all of the hydrogen sulfide (37), or in sediments that contain high background levels of iron sulfides. Clearly, the combined multidisciplinary approach used herein is an essential part of evaluating the supply and reactivity of important electron acceptors.

Acknowledgments

This project was conducted with the support of the U.S. Geological Survey Toxic Substances Hydrology Program. We thank Michele Tuttle and Laura Sacks and three anonymous reviewers for their helpful comments. We also thank Scott Christenson, Steve Harris, and Lonnie Kennedy for help with sampling and Jeanne Jaeschke for analytical support. The use of brand, trade, firm, or company names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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Received for review September 18, 2001. Revised manuscript received December 12, 2002. Accepted December 19, 2002.

ES011288A