

Bacterial sulfate reduction limits natural arsenic contamination in groundwater

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ABSTRACT

Natural arsenic contamination of groundwater, increasingly recognized as a threat to human health worldwide, is characterized by arsenic concentrations that vary sharply over short distances. Variation in arsenic levels in the Mahomet aquifer system, a regional glacial aquifer in central Illinois, appears to arise from variable rates of bacterial sulfate reduction in the subsurface, not differences in arsenic supply. Where sulfate-reducing bacteria are active, the sulfide produced reacts to precipitate arsenic, or coprecipitate it with iron, leaving little in solution. In the absence of sulfate reduction, methanogenesis is the dominant type of microbial metabolism, and arsenic accumulates to high levels.

Keywords: arsenic, groundwater, aquifer, bacteria, sulfate reduction.

INTRODUCTION

Groundwater drawn from unconsolidated sediments is prone to natural arsenic contamination, a phenomenon that has been observed in a number of geologically young aquifers worldwide (Smedley and Kinniburgh, 2002), including the Ganges Delta of Bangladesh and West Bengal (Anawar et al., 2003; Dowling et al., 2002; Harvey et al., 2002; McArthur et al., 2001; Nickson et al., 2000; Stüben et al., 2003), the Huhhot Basin of Inner Mongolia (Smedley et al., 2003), the Red River alluvial tract of Vietnam (Berg et al., 2001), and the Stuarts Point groundwater system of New South Wales, Australia (Smith et al., 2003). Chronic exposure to arsenic has been linked to serious medical conditions, including a variety of cancers (National Research Council, 1999). U.S. drinking water quality standards were revised recently to decrease the acceptable level of arsenic from 50 $\mu\text{g}\cdot\text{L}^{-1}$ to 10 $\mu\text{g}\cdot\text{L}^{-1}$, increasing the immediacy of the need to better understand the origin of natural arsenic contamination.

Aquifers subject to natural arsenic contamination are characterized by arsenic concentrations that vary sharply, from below detection limits to hundreds of $\mu\text{g}\cdot\text{L}^{-1}$, over short lateral and vertical distances (Smedley and Kinniburgh, 2002). Explaining this variation is a key to understanding natural arsenic contamination. The explanation is complicated, however, by the difficulty in differentiating the ef-

fects of the heterogeneous distributions of arsenic within aquifer sediment from the controls on whether the element, once introduced to a groundwater, remains in solution. Considerable attention has been paid to explaining arsenic distribution in terms of how it is supplied to groundwater, whether by the dissolution of arsenic-bearing minerals (Peters et al., 1999), desorption from sediment surfaces caused by bacterial arsenate reduction (Ormland and Stolz, 2003), or the bacterial reduction of sorbent ferric iron minerals (Korte, 1991). Somewhat less attention has been paid to factors that may remove arsenic from solution, such as precipitation with sulfide, a reaction observed in the laboratory and in surface waters (McCreadie et al., 2000; Moore et al., 1988; Rittle et al., 1995).

We consider here the origin of natural arsenic contamination in the Mahomet aquifer system, a regional water supply for central Illinois, United States, where arsenic levels $>250 \mu\text{g}\cdot\text{L}^{-1}$ have been observed, and levels $>50 \mu\text{g}\cdot\text{L}^{-1}$ are common (Holm, 1995; Holm et al., 2004; Warner, 2001). The Pleistocene glacial aquifer system was deposited in an ancient river valley by continental glaciations during the past several hundred thousand years (Kempton et al., 1991). The water-bearing sediments are largely unconsolidated sands and gravels, whereas the confining layers are composed of glacial till.

Catalano (1999) studied sediment cores from five wells in the Mahomet aquifer system, each from a different county, that produce water high in arsenic. Arsenic content in the bulk sediment varied little, ranging only from 7.2 to 8.3 $\mu\text{g}\cdot\text{g}^{-1}$ in glacial till and from

3 to 5 $\mu\text{g}\cdot\text{g}^{-1}$ in sand and gravel. In a single control well producing low-arsenic water, the sediment arsenic concentrations were 16 $\mu\text{g}\cdot\text{g}^{-1}$ in till and 6.6 $\mu\text{g}\cdot\text{g}^{-1}$ in sand and gravel. Therefore, arsenic in the sediments, freshly exposed and homogenized during deposition, is distributed uniformly. The study area, furthermore, is located in a recharge zone, so groundwater migrates downward from the surface (Panno et al., 1994). The relative homogeneity of sediments in the study area, as well as the water's singular origin as recharge, allows study of the effect of arsenic mobility on natural arsenic contamination, separate from the effect of variation in the distribution of the arsenic source.

METHODS

To better assess the local controls on the distribution of arsenic in the aquifer, we sampled 21 domestic wells completed at various depths in the system. The wells had recently been sampled and analyzed for their major ion compositions (Holm et al., 2004). We sampled and analyzed them for dissolved methane, sulfide, and dihydrogen (Table DR1 and Appendix DR1¹). We also filtered the groundwater to extract microbial biomass from two wells with high arsenic levels and two wells with low arsenic levels; we then analyzed the trapped biomass for community structure by using terminal restriction fragment length polymorphism (T-RFLP) analysis (Appendix DR1; see footnote 1).

RESULTS

Each of the groundwater samples is anaerobic. Nitrate concentrations are below detection limits (Table DR1; see footnote 1), except for three samples from shallow, unconfined parts of the aquifer that contain small amounts of nitrate (wells 126, 128, and 132; Table DR1

¹GSA Data Repository item 2004156, Table DR1, well depths and groundwater compositions, Figure DR1, archeal terminal restriction fragment length polymorphism (T-RFLP) profiles, and Appendix DR1, detailed methods, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

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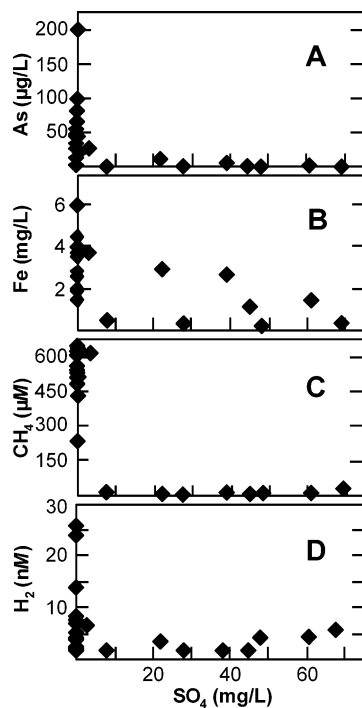


Figure 1. Variation with sulfate content of (A) arsenic, (B) iron, (C) methane, and (D) dihydrogen concentration in groundwater samples from Mahomet aquifer system (data from Table DR1; see footnote 1).

[see footnote 1]). Sulfate concentration is variable, ranging from below the detection limit ($0.25 \text{ mg}\cdot\text{L}^{-1}$) to $69 \text{ mg}\cdot\text{L}^{-1}$. Dissolved arsenic is found predominantly as arsenite [As(III)] rather than arsenate [As(V)] (Holm et al., 2004; Warner, 2001).

Arsenic levels are elevated only where sulfate content is low (Fig. 1A), as previously noted (Holm, 1995; Holm et al., 2004; Warner, 2001). Samples containing $<10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ arsenic show variable concentrations of sulfate, ranging up to $\sim 69 \text{ mg}\cdot\text{L}^{-1}$. In samples containing more than this level of arsenic, however, sulfate concentrations fall near or below the detection limit of $0.25 \text{ mg}\cdot\text{L}^{-1}$. Ferrous iron concentrations show a similar, if less distinct, pattern with sulfate content (Fig. 1B). Iron content is relatively high where sulfate is absent, ranging from ~ 1.4 to $5.9 \text{ mg}\cdot\text{L}^{-1}$. Less iron is observed where sulfate is present; iron concentrations in these samples range from below the detection limit ($0.1 \text{ mg}\cdot\text{L}^{-1}$) to $2.9 \text{ mg}\cdot\text{L}^{-1}$. Methane concentration is also elevated only in the absence of sulfate (Fig. 1C). Methane levels are low in almost all samples containing sulfate, but high, ranging up to $\sim 650 \text{ }\mu\text{M}$, where sulfate is depleted. The relationship between hydrogen and sulfate follows a similar pattern (Fig. 1D): hydrogen content ranges from 0.7 nM to 5.3 nM in sam-

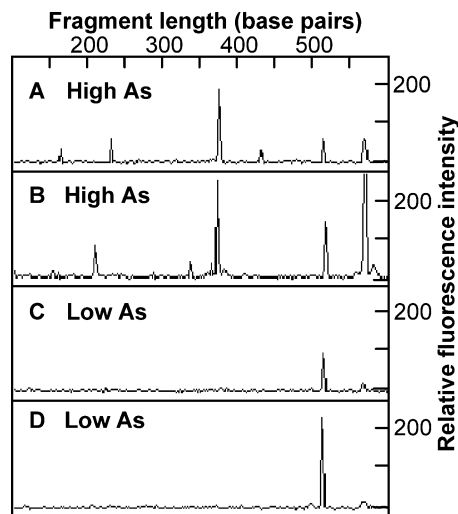


Figure 2. Electropherograms showing 5' terminal fragment lengths of 16S rDNA PCR products amplified from biomass filtered from groundwater. A and B: Profiles of *HhaI* digests of eubacterial populations in samples collected from high-arsenic waters (wells 92 and 90; $50 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ and $21 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ As, respectively). C and D: Profiles of *HhaI* digests of eubacterial populations in samples collected from low-arsenic waters (wells 88 and 89; $4.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ and $5.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ As, respectively). Results from duplicate DNA extractions with independent amplifications and digestions with *HhaI*, *MspI*, and *RsaI* were consistent with results shown. Well depths and groundwater composition for these samples are given in Table DR1 (see text footnote 1).

ples containing sulfate, and from 1.3 nM to 24.9 nM where sulfate is absent.

We were able to amplify bacterial DNA from the biomass filtered from all four wells. T-RFLP profiles of the bacterial DNA from the samples collected from high-arsenic waters (Figs. 2A, 2B) are similar and have more peaks than the profiles from samples collected from low-arsenic waters (Figs. 2C, 2D). We were able to amplify archeal DNA from all of the biomass samples collected from high-arsenic water but from only one of the samples collected from low-arsenic water (Fig. DR1; see footnote 1).

DISCUSSION AND CONCLUSIONS

We interpret these results as reflecting the distribution of microbial populations in the aquifer system. Fermentation of organic matter deposited within the glacial sediments, especially the paleosols and tills that compose the confining layers, contributes dihydrogen, carbon dioxide, and simple organic species such as acetate and formate to the groundwater. As has been demonstrated in other aquifer systems (McMahon and Chapelle, 1991), these species diffuse into the aquifer sediments, where they serve as substrates for microbial respiration and, in the case of acetate,

dismutation into CO_2 and CH_4 . Respiring microbes couple oxidation of these substrates to the reduction of terminal electron accepting species in the aquifer. Little oxygen or nitrate, together constituting the most energetically favorable electron acceptors, is available to the population of respiring microbes. The most significant electron acceptors remaining in the aquifer are ferric iron, sulfate, and bicarbonate. These electron acceptors are utilized by iron-reducing bacteria, sulfate-reducing bacteria, and reductive methanogens, respectively, which produce ferrous iron, sulfide, and methane. Methane may also be produced by acetotrophic methanogens, which dismutate acetate.

Microorganisms may become segregated into zones according to electron acceptor, owing to competitive exclusion (Lovley and Goodwin, 1988). In the presence of abundant reactive ferric minerals, for example, iron-reducing bacteria can outcompete sulfate-reducing bacteria, dominating the ecological niche by holding electron donor concentrations too low for sulfate reduction to proceed. A mixed metabolic zone may develop where the availability of ferric minerals is limited, slowing the rate of iron reduction (Lovley and Goodwin, 1988). In this case, electron donors may accumulate to levels that allow iron and sulfate reduction to proceed simultaneously.

Our analyses suggest that the aquifer is divided into zones of mixed microbial activity, some dominated by sulfate-reducing bacteria, others by methanogens; iron-reducing bacteria appear to be active in both types of zones. Sulfate-reducing zones are characterized by the presence of sulfate in solution (Fig. 1). Dissolved iron in these zones is less abundant than in methanogenic zones, because the sulfide generated there reacts with the ferrous iron species, causing them to precipitate as iron sulfide. Depending on the balance between ferrous iron and sulfide production, some or all of the ferrous iron produced may be lost from solution (Fig. 1B). Sulfide levels are near or below the detection limit in all samples (Table DR1; see footnote 1), suggesting that in the areas we sampled, ferrous iron production typically exceeds sulfide production. Consumption of electron donors by both sulfate and iron reduction in these zones holds down the concentration of organic species in the groundwater. In this way, the bacteria exclude methanogens, so little methane accumulates in solution (Ward and Winfrey, 1985). Notably, all samples in sulfate-reducing zones contain $<2 \text{ mg}\cdot\text{L}^{-1}$ total organic carbon (Fig. 3).

Methanogenic zones are characterized by a lack of sulfate and the accumulation of dissolved methane. The threshold sulfate concentration required for acetotrophic sulfate reduc-

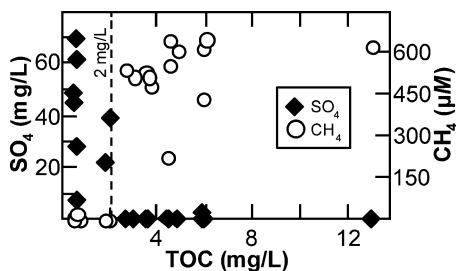


Figure 3. Variation with total organic carbon (TOC) of sulfate (SO_4) and methane (CH_4) concentration in groundwater samples.

tion to proceed is $\sim 2.9 \text{ mg}\cdot\text{L}^{-1}$ (Lovley and Klug, 1986). Sulfate concentrations in the methanogenic zones fall below this level (Fig. 1C), preventing sulfate reduction. As a result, organic species accumulate to levels that permit methanogenesis, which in turn causes methane to accumulate in the groundwater. As shown in Figure 3, all samples containing organic matter in concentrations of $>2 \text{ mg}\cdot\text{L}^{-1}$ contain little sulfate but considerable methane. In the absence of sulfide produced by sulfate-reducing bacteria, the ferrous iron generated by iron reducers, lacking a precipitation pathway, also accumulates in solution.

Arsenic concentration in areas interpreted to host sulfate reduction is invariably low, $<10 \mu\text{g}\cdot\text{L}^{-1}$ (Fig. 1A). Arsenic dissolving into groundwater in these zones either precipitates directly by reaction with sulfide species or coprecipitates with other sulfide minerals (Rittle et al., 1995). The methanogenic zone, conversely, lacks a source of sulfide, so there is no precipitation pathway for the arsenic. In this zone, arsenic accumulates to high levels in solution, producing natural arsenic contamination (Fig. 1A). Arsenic levels in this zone are $>10 \mu\text{g}\cdot\text{L}^{-1}$ in all but one sample.

Two lines of direct evidence, the distribution of dihydrogen, a marker for microbial metabolism, and T-RFLP analyses of subsurface biomass, serve to confirm the role of microbial communities in controlling arsenic mobility. Populations of sulfate-reducing bacteria, reductive methanogens, and iron-reducing bacteria each have different affinities for the dihydrogen produced during fermentation of organic matter (Chapelle et al., 1995; Lovley and Goodwin, 1988). For this reason, the steady-state concentration of dihydrogen that develops can be indicative of the dominant type of microbial respiration in an aquifer: dihydrogen concentrations of 0.2 nM to 0.8 nM have been cited as indicating iron reduction, 1 nM to 4 nM concentrations imply sulfate reduction, and concentrations $>5 \text{ nM}$ suggest reductive methanogenesis (Chapelle et al., 1995).

All the samples except one with arsenic levels below $10 \mu\text{g}\cdot\text{L}^{-1}$ have dihydrogen concentrations ranging from $\sim 1 \text{ nM}$ to 5 nM (group A

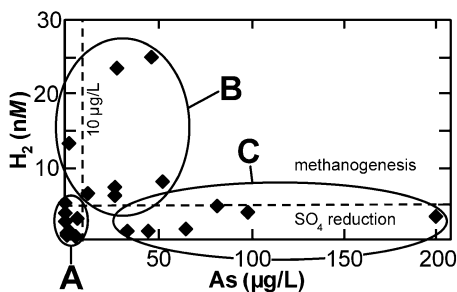


Figure 4. Concentrations of dihydrogen (H_2) and arsenic in Mahomet aquifer samples. Samples in group A have little methane, high concentrations of sulfate, and iron levels ranging from detection limit to $2.9 \text{ mg}\cdot\text{L}^{-1}$. In samples from groups B and C, sulfate concentration is near or below detection limit ($0.25 \text{ mg}\cdot\text{L}^{-1}$), methane is abundant, and iron concentration ranges from $1.4 \text{ mg}\cdot\text{L}^{-1}$ to $5.9 \text{ mg}\cdot\text{L}^{-1}$.

in Fig. 4), consistent with sulfate reduction. All the samples from this group, but none of the other samples, contain significant sulfate ($>3 \text{ mg}\cdot\text{L}^{-1}$), supporting the interpretation that sulfate reduction proceeds wherever sulfate is present. Samples with arsenic concentrations $>10 \mu\text{g}\cdot\text{L}^{-1}$ have dihydrogen concentrations ranging from 1.3 nM to 24.9 nM (Fig. 4). Dihydrogen concentrations here fall into two groups: one consistent with reductive methanogenesis (group B in Fig. 4) and one with dihydrogen levels associated with sulfate reduction (group C in Fig. 4). The dihydrogen concentrations in group B samples are consistent with our other geochemical findings. The organic carbon concentration in these samples is $>2 \text{ mg}\cdot\text{L}^{-1}$, sulfate content is low, and methane, iron, and arsenic levels are high.

The dihydrogen concentrations observed in group C samples, however, are unlikely to result from sulfate reduction, because these samples are devoid of sulfate. The samples, rich in iron and methane, probably come from areas in which iron reduction and methanogenesis proceed at significant rates simultaneously. The resulting dihydrogen concentration—above that associated with iron reduction, but less than that expected in the presence of methanogenesis—reflects the balance between the two processes; such a situation has been observed in microcosm experiments (Lovley and Goodwin, 1988). An unknown fraction of the methane in this zone, furthermore, is likely produced through dismutation by acetotrophic methanogens. This process, unaffected by the dihydrogen concentration, is not associated with a signature dihydrogen concentration.

T-RFLP analysis of biomass filtered from the groundwater confirms the presence of two types of microbial zones in the aquifer (Fig. 2). Nearly identical profiles obtained from water with high arsenic content demonstrate that the microbial communities in these areas are

similar. Likewise, communities in areas with low arsenic content are also similar; they differ significantly from those analyzed in water with high arsenic content. The limited amplification of archeal DNA from samples taken from low-arsenic water suggests that methanogens, as *Archea*, are less abundant there than in samples from water with high arsenic content.

On the basis of these findings, the ultimate control on arsenic concentration in the Mahomet aquifer system, and likely the cause of its characteristic spatial variability, appears to be the balance between the cumulative amount of substrates, organic and inorganic, and the amount of sulfate that has been supplied to the groundwater. Where the net flux of substrates has been small relative to the supply of sulfate to the water, the water's sulfate content has not been depleted, and sulfate-reducing bacteria hold arsenic levels low. Sulfate in waters that have received relatively greater amounts of substrates, however, has been depleted, preventing sulfide production and creating an environment that allows arsenic as well as iron and methane to accumulate.

Several studies have reported that the concentration of arsenic in groundwater flow regimes is related to the distribution of sulfate, iron, organic carbon, and (where analyzed) methane. These studies include the Bengal Delta (Anawar et al., 2003; Dowling et al., 2002; Harvey et al., 2002; McArthur et al., 2001; Nickson et al., 2000; Stüben et al., 2003) and the Huhhot Basin of Inner Mongolia (Smedley et al., 2003). In interpreting these relationships, these studies have emphasized the release of arsenic due to the bacterial breakdown of iron oxyhydroxide, as controlled by the availability of organic species in solution, recognizing that sulfate reduction may lead to arsenic precipitation or coprecipitation. Our interpretation differs somewhat from those in previous studies in that, rather than emphasizing the role that bacteria play in supplying arsenic to the groundwater, we call on bacterial processes as controls on whether arsenic accumulates in solution. This perspective is in agreement with our finding that, whereas iron reduction occurs in both low-arsenic and high-arsenic areas of the aquifer system, sulfate reduction occurs only where arsenic concentration is low and methanogenesis wherever arsenic levels are high.

Our data, furthermore, do not support the hypothesis that arsenate-reducing bacteria control the distribution of natural arsenic contamination in our study area. According to this hypothesis (Oremland and Stolz, 2003), reduction of arsenate sorbed on aquifer sediments releases the element to solution as arsenite, which sorbs poorly under acidic conditions, where pH is $<\sim 7$. In this way, the

process enhances arsenic mobility. The bulk of arsenic in our water samples is present in reduced form, and some fraction of this arsenite may indeed have originated as arsenate. Where pH is >7, however, arsenite sorbs onto clays and ferric hydroxides more readily than arsenate (Dixit and Hering, 2003). Arsenate reduction in near-neutral and alkaline waters, therefore, works to decrease arsenic mobility.

Arsenic release is a necessary step in the development of natural arsenic contamination. For a high-arsenic groundwater to develop, however, the arsenic must accumulate in solution. In the Mahomet aquifer system, accumulation, rather than source, appears to control the distribution of arsenic. If the opposite were true, we would not observe the clear relationship between sulfate concentration and arsenic levels. In other words, if a varying source rate controlled the arsenic distribution, the metalloid would be found at differing concentrations, regardless of the amount of sulfate in solution. The same microbial controls on arsenic mobility we have observed in the Mahomet aquifer system may operate in other locales where high-arsenic groundwater is found in geologically young sediments, given that the studies cited here also noted a reciprocal relationship between sulfate and arsenic concentrations.

These findings suggest that high-arsenic groundwater might be identified and even remediated in ways that are simple and inexpensive, critical concerns in less-developed countries. If the presence of sulfate provides a reliable indication of the absence of natural arsenic contamination, as suggested, safe drinking water can be identified immediately. Unlike arsenic, which occurs in minute quantities and generally requires laboratory analysis, sulfate is a major ion component of groundwater whose concentration can be determined in the field by using a simple turbidimetric method (Eaton et al., 1995). This study also suggests that naturally contaminated groundwater might be remediated at little cost by stimulating sulfate-reducing bacteria in the subsurface, perhaps by injecting sulfate. Such remediation might require little advanced technology, be applicable on the scale of individual wells, and cost little, because sulfate salts are inexpensive and readily soluble.

ACKNOWLEDGMENTS

We thank George Roadcap, Walt Kelly, and Steve Wilson of the Illinois State Water Survey for providing data and assisting us in our work. This work was supported by U.S. Department of Energy Grant DE FG02-02ER15317 and the Morris M. and Ada B. Leighton Graduate Study Award.

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Manuscript received 18 May 2004
 Revised manuscript received 30 July 2004
 Manuscript accepted 30 July 2004

Printed in USA