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Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations

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Abstract—Freshly collected sediments from Bangladesh were incubated for two months to study the release of arsenic to groundwater in a low-oxygen environment. The aquifer sands, diluted to concentrations of 3 to 22 g/L with anoxic well water, covered a range of redox conditions, as indicated by gray to orange color. Suspensions amended with either acetate or a respiratory inhibitor were incubated in parallel with unamended suspensions. Two batches of unamended gray sediment gradually released the equivalent of 0.5 to1.0 μg/g As to the dissolved phase in the presence of some dissolved oxygen (~1 mg/L) and without any detectable increase in dissolved Fe. The quantity of As released accounted for 30 to 80% of the initial As fraction that could be leached from the particles in hot acid. A suspension of gray sediment amended with fresh antibiotic did not release As. The addition of acetate to the gray sediment resulted in the release under anaerobic conditions of only 1 to 3% of the acid-leachable Fe fraction; the quantity of As released during these incubations was comparable to that released from the unamended suspensions. Amendment with acetate was required to release acid-leachable As from the suspensions containing some or mostly orange Fe(III) oxyhydroxides. These observations suggest that mobilizable As is distributed heterogeneously in the Fe phases that coat aquifer sands. Truly anoxic conditions may not be required for the release of As from reducing (gray) sediment in Bangladesh. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Growing concerns about the carcinogenicity of submicromolar levels of dissolved As in surface water and groundwater consumed by humans has stimulated in recent years a wide range of investigations of the multifaceted biogeochemistry of this metalloid. The health concerns are particularly pronounced in South Asia where tens and possibly hundreds of millions of people consume untreated groundwater containing levels of As that exceed the World Health Organization (WHO) guideline of 10 μg/L (0.13 μmol/kg), often by one to two orders of magnitude (Smith et al., 2000). The widespread microbial contamination of surface water, combined with easy access to subsurface aquifers in the unconsolidated river floodplain and delta deposits of the region (BGS and DPHE, 2001; Goodbred et al., 2003), have led to a massive shift of consumption to groundwater in recent decades. Although groundwater is the cause of numerous cases of arsenicosis documented since the problem was first recognized in West Bengal, India, in the mid-1980s (Chakraborty and Saha, 1987) and in Bangladesh about a decade later (Dhar et al., 1997), groundwater is probably also the solution. This is because the distribution of groundwater As is highly variable spatially (BGS and DPHE, 2001; van Geen et al., 2003a), and most households in Bangladesh with a high-As well could therefore shift their consumption to low-As wells that are, or hopefully will be, installed within walking distance (van Geen et al., 2002; van Geen et al., 2003b). It is worrisome, however, that the current understanding of the mechanism of As mobilization in Bangladesh groundwater is insufficient to determine whether As levels could rise if consumption is shifted to the subset of presently safe aquifers, particularly if irrigation water starts to be drawn from the same sources on a significant scale (Harvey et al., 2002; Aggarwal et al., 2003; van Geen et al., 2003c).

The conditions that lead to As mobilization in Bangladesh groundwater are understood only in a general sense. An important characteristic of the sandy floodplain and delta aquifers of the region is that they typically are anoxic. This is widely thought to be caused by oxygen consumption coupled to the mineralization of organic matter deposited over the past ~10000 yr, as sea level rose from the previous glacial low stand (Nickson et al., 1998; BGS and DPHE, 2001; Zheng et al., 2004). Variants of this scenario attribute particularly reducing conditions in Bangladesh aquifers to the reducing power of interspersed peat layers enriched in organic matter (McArthur et al., 2001) or the entrainment of dissolved organic matter with recharge from surface water bodies (Harvey et al., 2002). Once dissolved oxygen and nitrate supplied by recharge are consumed, further mineralization of organic matter results in the reduction and dissolution of Mn and Fe oxides. Since a significant amount of As is typically associated with reducible Fe oxyhydroxides (BGS and DPHE, 2001; Harvey et al., 2002), a simple mass balance calculation shows that reductive dissolution of these phases could significantly increase groundwater As concentrations.

Groundwater data from Bangladesh presented by Nickson et al. (1998, 2000) and a more extensive set gathered by BGS and DPHE (2001) broadly support the Fe-reduction and dissolution hypothesis, although there are inconsistencies pointed out by

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the same authors as well as Appelo et al. (2002). Of the 1710 samples containing less than 1 mg/L Fe in the extraordinary data set of BGS and DPHE (2001) of over 3500 samples distributed across the country, 6% contain over 50 μg/L As. This suggests that either Fe dissolution is not always required for significant As release or that Fe reprecipitates or readsorbs after dissolution. Of the 337 samples in the BGS and DPHE (2001) data set containing $>$10 mg/L Fe, 27% contain less than 10 μg/L As, which indicates in turn that Fe dissolution is not necessarily associated with a measurable increase in dissolved As. Nickson et al. (2000) and BGS and DPHE (2001) recognized that considerably less dissolved Fe was present in Bangladesh groundwater than could be expected from the mineralization of organic matter inferred from increasing HCO_3^- concentrations. Detailed profiles of dissolved As, NH_3, and Ca obtained from a single site in Bangladesh, on the other hand, allowed Harvey et al. (2002) to argue that the mineralization of organic matter was closely coupled to the generation of HCO_3^-, dissolution of $CaCO_3$, as well as the mobilization of As. There was no consistent relation between dissolved As and Fe at the same site, however (Swartz et al., in press). Whereas the relation between As mobilization and the reductive-dissolution of Fe oxyhydroxides may not be consistent with all the available data, no convincing evidence has been presented to date to support alternative explanations such as the oxidation of iron sulfide enriched in As, or the desorption of As caused by the use of fertilizer containing phosphate (BGS and DPHE, 2001; Ravenscroft et al., 2001).

The coupling of reductive dissolution of Fe phases to microbially mediated As mobilization, and in some cases the lack thereof, has been studied extensively with synthetic precipitates and amended sediments. Ahmann et al. (1997) demonstrated that reduction to As(III), rather than the reduction of Fe, was a key step leading to mobilization during anaerobic incubation of iron arsenate inoculated with a dissimilatory As reducer isolated from an As-contaminated watershed. Using an organism obtained from an As-contaminated agricultural soil, Jones et al. (2000) also documented the mobilization of As from a suspension of goethite without any detectable accumulation of Fe(II) in solution. Zobrist et al. (2000) showed that As reduction can lead to mobilization without the dissolution of the sorbent phase by anaerobically incubating As(V) coprecipitated with aluminum hydroxide in the presence *Sulforospirillum barnesii*. While dissolution of the sorbent phase may not be required for mobilization of As, it does appear to favor the process. The mobilization of As coprecipitated with ferrihydrite, a phase prone to reductive dissolution, is considerably faster than for As coprecipitated with goethite (Jones et al., 2000) or As coprecipitated with aluminum hydroxide (Zobrist et al., 2000).

Reduction of As favors mobilization under certain conditions, but it does not appear to be a requirement for mobilization. Cummings et al. (1999) showed that sediment enriched in Fe by mining activities and saturated in the laboratory with As(V) released As during anaerobic incubation with *Shewanella alga*, an organism that reduces Fe oxyhydroxides, but not As(V). Using an organism that reduces As but not Fe that was concentrated from the same As-contaminated soil as Jones et al. (2000), Langner and Inskeep (2000) demonstrated that desorption of As(V) was required before reduction to As(III) could to take place under the conditions of their anaerobic incubations of ferrihydrite sorbed with As. The demonstration that As(III) adsorbs more strongly to Fe oxyhydroxides than As(V) under certain conditions, contrary to widely held belief, has also led to a reconsideration of the necessity of As reduction for mobilization (Manning and Goldberg, 1997; Manning et al., 1998; Inskeep et al., 2002; Dixit and Hering, 2003).

In this study, we attempt to relate the laboratory observations reviewed above to incubations of Bangladesh aquifer material under controlled conditions during which concentrations of both As and Fe were monitored. Groundwater injection experiments conducted in Bangladesh by Harvey et al. (2002) provide the most direct evidence to date of a connection between the supply of organic substrate and the mobilization of As and the removal of As upon addition of an oxidant. The response of dissolved Fe to these perturbations was not reported, however.

The first of the following sections provides a geological context for the sample material used in the incubations. Significant differences between the two sets of incubations that were conducted in June to August 2001 and February to April 2002 are described, including limitations on the quality of the measurements of some of the parameters that were monitored. The results section describes the mobilization of As and Fe, or lack thereof, for a total of 12 incubations conducted without amendment, with the addition of acetate, or with the addition of a respiratory inhibitor. Concentrations of dissolved Mn, P, and S were also monitored during these experiments. The amounts of As, Fe, Mn, and P released during the incubations, or removed in the case of S for the incubations amended with acetate, are compared with the composition of hot acid leaches of the same aquifer material. The discussion focuses on the observation that the microorganisms naturally present in Bangladesh aquifer material mobilized most of the leachable As over a 2-month period, but only a small fraction of the leachable Fe and P. These observations and the field data discussed in a companion paper by Horneman et al. (this volume) are used to demonstrate that As and Fe mobilization can be decoupled under certain conditions. The paper concludes by pointing out that the divergent behavior of As, Fe, and P observed during the incubations helps explain the considerable scatter in the relations between the concentrations of these constituents in Bangladesh groundwater.

2. MATERIAL AND METHODS

2.1. Geological Setting

Different regions of Bangladesh are not affected to the same extent by elevated As concentrations in groundwater. Broad patterns in the proportion of low- and high-As wells across distances of 10 to 100 km are related largely to the depth of older Pleistocene sediments. Groundwater As concentrations associated with these orange-brown sandy deposits, frequently referred to as the Dupi Tila formation, are typically below 10 μg/L (BGS and DPHE, 2001). In areas where this formation is located no more than ~30 m (100 ft) below the surface, the vast majority of existing tube wells are low in As. In regions where these deposits are overlain with a thick layer of more recent Holocene sediment, often gray in color, the groundwater pumped from existing tube wells less than 30 m (100 ft) deep is frequently elevated in As (BGS and DPHE, 2001). The samples collected for the incubations of the present study were collected from a transitional area where the depth of the upper portion of the Dupi Tila formation rapidly changes over a few kilometers (van Geen et al., 2003a). Figure 1 is a map of a portion of Araihazar upazila, where a long-term health, social, and

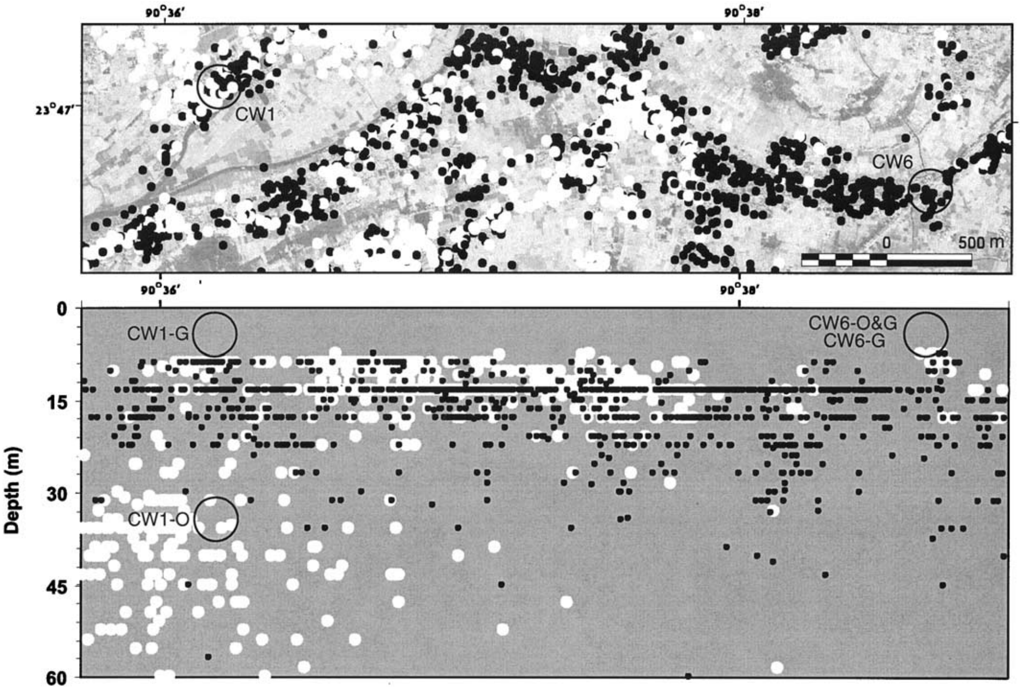


Fig. 1. Distribution of groundwater As in a 8 km^2 area of Araihazar upazilla, Bangladesh, based on sampling of 1600 tube wells (van Geen et al., 2003a). Wells that meet the national drinking water standard of 50 μg/L are shown as white circles; wells that exceed the standard are shown as black circles. The background of the upper panel is a high-resolution Ikonos satellite image that shows numerous rectangular-shaped irrigated fields in the regions that separate the clusters of wells, which correspond to the villages. The lower panel is a depth section of the same, showing a highly mixed distribution of high and low As in shallow aquifers. Below 30 m (100 ft) depth, groundwater As concentrations are consistently below 50 μg/L in the western portion of the area, and above 50 μg/L in the eastern portion.

earth science study of the origin and impact of elevated groundwater arsenic, coupled to a mitigation program, is underway (http://superfund.ciesin.columbia.edu). Also shown is a depth section of As concentrations based on the same set of wells that illustrates the two-layered structure of the subsurface in the area. The boundary between a mixed population of shallow wells that are either high or low in As and a deeper aquifer that is typically low in As dips downwards from ~30 m to 90 m (100 to 300 ft) in eastward direction (Fig. 1). The combination of the map and depth section also shows that over distances of 0.1 to 1 km, i.e., from one village to the other, and even within a village, there are considerable variations in groundwater As concentrations within shallow Holocene aquifers (van Geen et al., 2003a).

2.2. Collection of Sediment and Groundwater

Four samples of aquifer material used in the incubations were collected during drilling of community wells CW1 and CW6 in two villages of Araihazar upazila in June 2001 and January 2002, respectively (Fig. 1). A rhythmic drilling technique used throughout Bangladesh and called the "hand-flapper" or "sludger" method generates a stream of sediment-laden slurry originating from a depth known from the length of PVC pipe that extends into the drill hole. The sand and silt particles that rapidly settled from this slurry constituted the starting material for 3 of the 4 series of incubations. These samples may be biased towards the coarse fraction of the sediment, although the aquifers that groundwater can be extracted from are typically well sorted and contain >90% sand (BGS and DPHE, 2001; Zheng et al., in review). The grain size of one additional sediment sample is representative of the original sandy aquifer material since it was collected with an improvised PVC coring device equipped with a check valve at the top to prevent the loss of sediment. For all incubations, groundwater used to dilute the sediment was hand pumped from a well in the region (ID 4135) that taps into the Dupi Tila aquifer at ~40 m (135 ft) and contains little dissolved As and Fe compared to the range of groundwater concentrations in the study area (Table 1). Additional characteristics of groundwater from well 4135 determined by methods described in Zheng et al. (2004) include a barely detectable dissolved oxygen content of 0.02 mg/L (CHEMet detection limit ~0.01 mg/L); Eh = +25 mV; pH = 6.29; and Alk = 2.74 ±0.03 meq/L.

The first sediment sample collected from a slurry at ~4.5 m (15 ft) depth at CW6, in the eastern portion of the study area (Fig. 1), was a mixture of gray and orange-coated sands containing Fe(II) and Fe(III) oxyhydroxides, as indicated by ferrozine analysis of the acid leachate of similar material (Horneman et al., this volume). This relatively oxic aquifer material is referred to hereon as CW6-G&O and is considered representative of the early stage of sediment transformation towards a more reduced state. Another slurry sample from a slightly greater depth was uniformly gray (CW6-G), indicating a predominance of Fe(II) in the solid phase, and was evidently further along the path towards reducing conditions (Horneman et al., this volume). The third sample of shallow aquifer material, from the western portion of the study area (Fig. 1), was collected at ~4.5 m (15 ft) with the coring device and was also uniformly gray (CW1-G). The last slurry sample collected from

Table 1. Composition of groundwater used to dilute the sediment for the incubations, and range in dissolved concentration of As, P, and Fe at the beginning of the incubations.

	As μg/L	P μmol/L	Fe μmol/L
Well 4135	0.9	4.6	17
Local groundwater	<0.1–800	<0.01–80	<0.01–300
CW6 G&O	1.1–1.9	2.5	0.4–1.0
CW6 G	2.5–4.0	2.1–3.2	0.3–6.0
CW1 G	1.7–2.1	2.4–2.9	0.5–1.7
CW1 O	1.1–1.2	3.4–3.8	0.0

CW1 at a depth of 34 m (115 ft) was uniformly orange/brown (CW1-O), indicating a particularly high proportion of Fe(III) oxyhydroxides in the sand coatings (Horneman et al., this volume). Radiocarbon dating of sediment in the region indicates that the three shallow samples of aquifer material sediment used in the incubations were deposited within the past several thousand years (Zheng et al., in review). In contrast, the deeper sands of CW1-O were deposited at least 40000 yr ago and probably were exposed to extensive weathering under oxic conditions during a previous sealevel low-stand (Zheng et al., in review).

2.3. Preparation of the Incubations

Slurry samples CW6-G&O and CW6-G were diluted on the day of collection and placed inside a nitrogen-filled glove bag with anoxic groundwater in a series of six 1-L Nalgene high-density polyethylene bottles. Sodium acetate (1 g/L) and an antibiotic (40 mL of Guillard reagent/L), respectively, were also immediately added to suspensions of the two aquifer samples from CW6. The Guillard reagent had been prepared by adding 16250 U of penicillin G, 2 mg of chloramphenicol, and 5 mg of streptomycin to 100 mL of MQ water. During the first week of the incubation, the suspensions were kept in a nitrogen-filled glove bag in Bangladesh. They were then shipped by air to France without special precautions. After each sampling, the headspace of each bottle was flushed with nitrogen before closing. The bottles themselves stood in ambient air throughout this first set of experiments, however.

Samples CW1-G and CW1-O, a core sample, and a slurry sample, respectively, were collected in plastic bottles that were then filled with groundwater from well 4135 until no headspace was left. The samples, in addition with more water from well 4135, were then sent by air to France. The second set of incubations sediment was started by diluting aquifer material sampled from the center of a 2 kg mass of sediment with groundwater in 1-L Nalgene bottles under a 98% N_2/2% H_2 atmosphere 14 d after collection in Bangladesh. The suspensions were again amended in the same manner with sodium acetate and Guillard reagent, but the latter was unfortunately prepared with expired reagents. These suspensions remained in the glove chamber for the continuation of the experiment. The glove chamber was flushed several times with 98% N_2/2% H_2 after each sampling. The laboratory temperature varied between 20 to 25°C during the incubations, slightly below the range of groundwater temperatures in Araihazar (25–27°C).

2.4. Sampling and Analyses

Although the suspensions were not agitated continuously during the incubations, they were vigorously shaken and then allowed to settle for ~30 min each time before sampling. Over a period of two months, aliquots of the supernatant were taken from the incubations with a syringe at intervals that increased in duration from hours in Bangladesh to weeks in France. In ambient air, the aliquots were filtered immediately out of the same syringe though 0.45 um Nuclepore syringe filters. Typically, 3 filters had to be used to filter an entire 5 mL sample. For the second batch of experiments, an aliquot of filtered sample was also immediately passed through a small disposable ion exchange column that retains As(V) but not As(III) marketed by Metalsoft Center, Highland Park, New Jersey (Meng et al., 1998). After filtration or passage through the ion exchange column, all samples were acidified to 1% by volume with Optima HCl. In ambient air in the case of the first set of incubations and inside the glove chamber for the second set, pH, Eh, and oxygen saturation were measured in the suspensions using a Bioblock Scientific glass electrode and Consort P107 pH meter, a Schott platinum electrode, and a YSI Model 55 oxygen sensor. These electrodes were calibrated with appropriate solutions before each use.

The filtered and acidified samples were analyzed for dissolved As, Fe, Mn, P, and S at LDEO by High-Resolution Inductively-Coupled Plasma Mass Spectrometry (HR ICP-MS) on a VG Axiom instrument. The samples were diluted 1:5 in a 2% Optima HNO_3 solution containing 10 μg/L Ge added to monitor any drift in the sensitivity of the instrument. The instrument was calibrated with mixed As, Fe, Mn, P, and S standards added to a 2% HNO_3/Ge solution. Standard additions performed on a limited number of samples showed no detectable dependence of instrument response on the nature of the matrix. The method predates but is very similar to the multielement method described by Cheng et al. (in press). Detection limits were calculated from the variability of blank counts for repeated analysis of HNO_3/Ge solutions: ~0.1 μg/L for As and below 0.5 μmol/L for Fe, Mn, P, and S. Replicate analyses and the inclusion of a consistency standard with each run indicate an overall reproducibility of the method on the order of ±5% for all analytes.

The quantity of As, Fe, Mn, P, and S that is moderately bound to the surface of the sediment used in the incubations was estimated with a hot HCl leach. The extractions were performed by adding ~50 mg of freeze-dried sediment in 1.5 mL centrifuge tubes, adding 1 mL of 1.2 N HCl, and heating in hot water bath at ~80°C for 30 min (Horneman et al., this volume). After leaching, the suspensions were centrifuged at 10000 rpm and the supernatant transferred to a new set of acid-leached centrifuge tubes. The acid leachates were diluted in a 2% HNO_3/Ge solution and also analyzed by HR ICP-MS. This leaching procedure is likely to have released As, Fe, and P adsorbed on the sediment and the fraction of the same elements associated with poorly crystallized Fe oxhydroxides (Frederickson et al., 1998; Roden and Urrutia, 2002; Zachara et al., 2002). A remarkable correspondence between the reflectance spectrum of Bangladesh sediment and the Fe(II)/(III) ratio of the hot-leachable fraction documented in the companion paper by Horneman et al. (this volume) suggest that, probably because of the heating step, the leaching procedure used in this study dissolved some crystalline phases such as goethite or hematite.

3. RESULTS

The concentration of acid-leachable As in the sediment used for the incubations ranged from 0.6 μg/g for CW1-O to 1.8 μg/g for CW6-G&O (Table 2). The leachable Fe fraction varied over a wider dynamic range: from 2000 μg/g (0.2%) in CW1-O to 17000 μg/g (1.7%) in CW6-G. Sample CW1-O also contained the lowest concentration of leachable P (100 μg/g); the highest concentration of P was measured in CW1-G (630 μg/g). Collection of all particles with the coring device in the case of CW1-G, as opposed to settling particles for the slurry samples, does not appear to have drastically affected the acid-leachable As, P, or Fe content of the starting material used for the incubations.

Eh and oxygen levels in the suspensions generally declined over the duration of the experiments, but the pattern was more consistent for the second batch of incubations conducted in the glove box (Fig. 2). Eh and oxygen levels measured in the suspensions amended with acetate were generally lower than in the unamended suspensions. Suspensions amended with acetate were probably truly anoxic during the second month of the incubations; a low but measurable level of oxygen (<10% saturation, i.e., below ~1 mg/L) remained in the unamended suspensions of CW1-G and CW1-O. Oxygen sensor data for suspensions in the glove box amended with the antibiotic were intermediate between values recorded for the unamended suspensions and the suspensions amended with acetate.

Table 2. Composition of the sediment used in the incubations. The concentration of As, P, and Fe leachable in hot acid is listed in μg/g dry weight; the proportion of the leachable As, P, and Fe released by the incubations amended with acetate is indicated in (%).

	As μg/g (%)	P μg/g (%)	Fe μg/g (%)
CW6 G&O	1.8 (80)	420 (4)	15000 (0.5)
CW6 G	1.4 (70)	610 (9)	17000 (2.0)
CW1 G	1.6 (80)	630 (20)	12000 (1.4)
CW1 O	0.6 (70)	100 (2)	2000 (1.0)

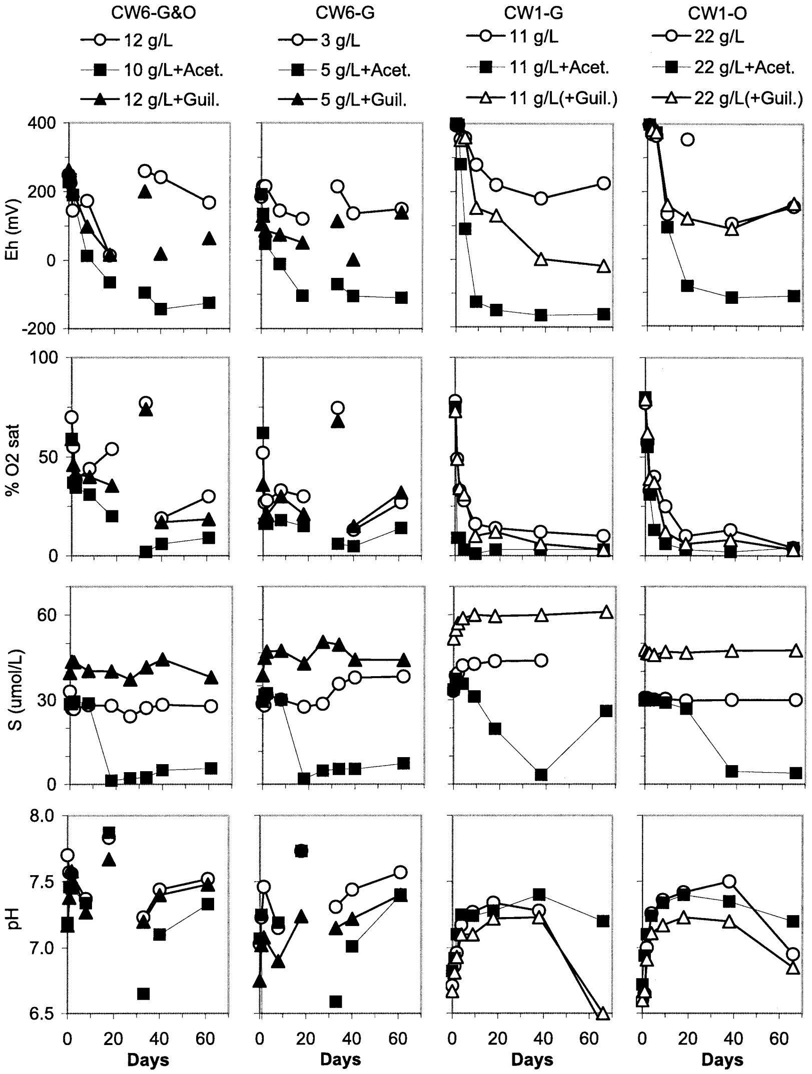
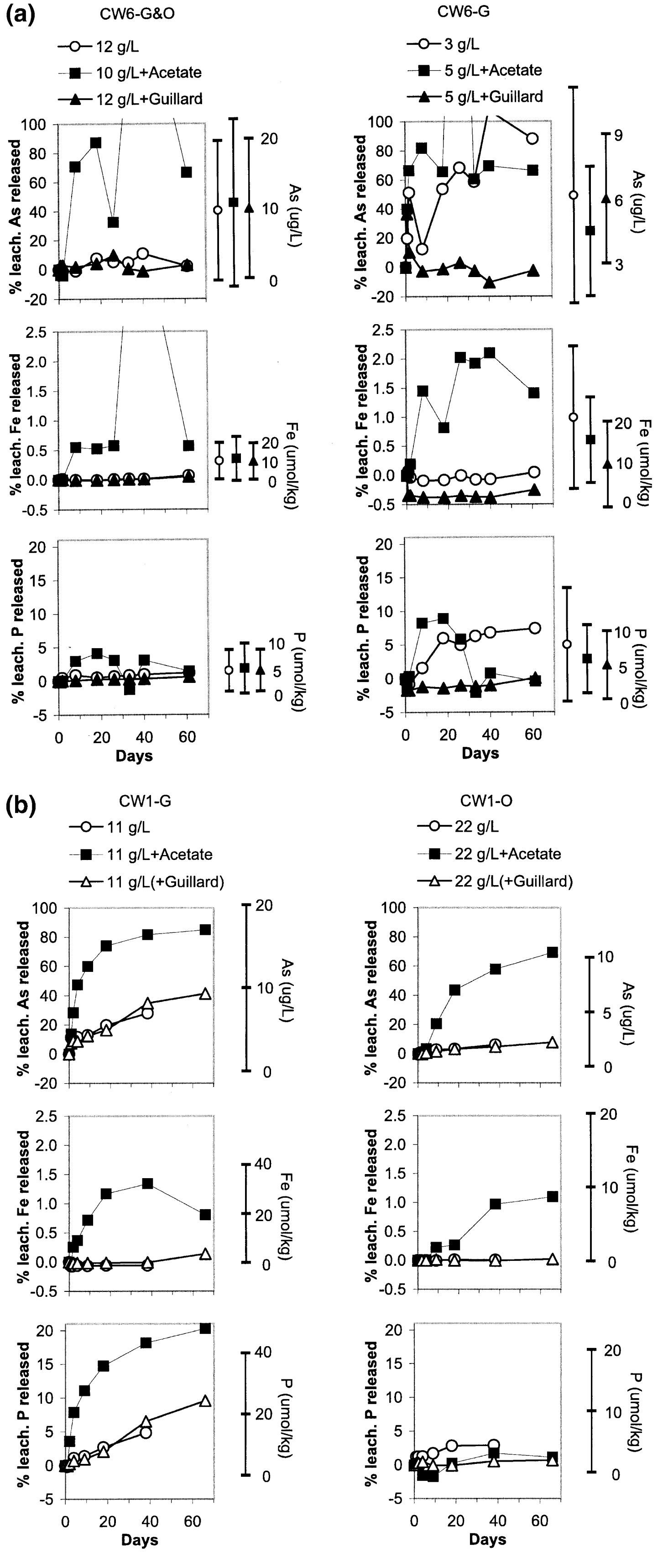


Fig. 2. Time series of indicators of experimental conditions during the incubations. Open circles and black squares correspond to incubations without amendment and incubations amended with acetate, respectively. The black triangles correspond to the successful addition of the inhibitor during the first set of incubations; the open triangle corresponds to the addition of the expired antibiotic during the second set.

Sulfur concentrations remained very constant in the unamended suspensions containing some or mostly orange sands (CW6-G&O and CW1-O). In all the acetate-amended suspensions, concentrations of S (presumably sulfate) systematically declined within the first week from ~30 μmol/L to less than 5 μmol/L (Fig. 2). Sulfur concentrations in all suspensions amended with the antibiotic were systematically higher by ~15 μmol/L than in the unamended incubations. The offset closely matches the calculated contributions from penicillin ($C_{16}H_{17}N_2O_4SNa$) and the sulfate salt of streptomycin ($2\ C_{21}H_{39}N_7O_{12}.\ (H_2SO_4)_3$). The two unamended suspensions of uniformly gray sediment show an additional increase in S concentrations of ~10 μmol/L. In the case of CW6-G, the rise occurs over the two weeks that follow day 30 of the experiment; a similar rise takes place at the beginning of the experiment in CW1-G (Fig. 2). Certainly in the case of CW1-G, and perhaps also CW6-G, a similar pattern is observed, albeit with an offset, in the suspensions amended with the antibiotic.

Measurements of pH during the first batch of incubations were erratic but ranged mostly between 7.0 and 7.5 (Fig. 2). During the second batch of incubations, the pH of the suspensions rose from ~6.6 to 7.4 within a week and then remained steady until day 40. The various amendments did not significantly affect the pH of the incubations. The groundwater from well 4135 used to dilute the sediment was initially highly supersaturated in CO_2: the 5.6 mM DIC concentration calculated from the measured pH and alkalinity is equivalent to ~9% P_{CO2}. Under the simplifying assumption of constant alkalinity, a 10-fold drop in PCO_2 due to degassing should be accompanied by an increase in pH to ~7.3. At that stage, saturation with respect to calcite (Ksp = $10^{-8.3}$; Morel and Hering, 1993) is predicted based on the 0.2 mM Ca concentra-


(a)
CW6-G&O
12 g/L
10 g/L+Acetate
12 g/L+Guillard
CW6-G
3 g/L
5 g/L+Acetate
5 g/L+Guillard
% leach. As released
As (ug/L)
% leach. Fe released
Fe (umol/kg)
% leach. P released
P (umol/kg)
Days
(b)
CW1-G
11 g/L
11 g/L+Acetate
11 g/L(+Guillard)
CW1-O
22 g/L
22 g/L+Acetate
22 g/L(+Guillard)
% leach. As released
As (ug/L)
% leach. Fe released
Fe (umol/kg)
% leach. P released
P (umol/kg)
Days

tion measured in groundwater from a nearby monitoring well tapping the same aquifer (Zheng et al., in review). We speculate that the drop in alkalinity resulting from calcite precipitation may have prevented the pH of the incubations from rising further.

Dissolved As concentrations measured in the suspensions at the beginning of the incubations (1–4 μg/L), a few hours after dilution with low-As groundwater, were generally within a factor of ~2 of the As content of the well water used to dilute the sediment (Table 1). P concentrations (2–4 μmol/L), on the other hand, started from levels about half the initial concentration in well water. Fe concentrations (0–6 μmol/L) at the beginning of the incubations typically were an order of magnitude below concentrations measured in the freshly collected well water. To facilitate comparison between the different incubations, variations in dissolved As, Fe, and P concentrations were normalized to the initial concentration of these elements in the acid-leachable component of the sediment (Fig. 3).

Dissolved As concentrations gradually increased from 2 to 3 μg/L to ~10 μg/L in both unamended suspensions of uniformly gray aquifer material (CW6-G and CW1-G). Although these As concentrations may seem relatively low, they are significant because the concentration of solids used in the incubations was about two orders of magnitude lower than for an actual aquifer. When normalized to concentrations in the uniformly gray sediment, the amount of As released corresponds to 30 to 80% of the acid-leachable As initially present on the solid phase (Fig. 3). In contrast to the behavior of uniformly gray sediment, neither samples of aquifer material containing some or mostly orange Fe(III) oxyhydroxides released comparable amounts of As (Fig. 3). The limited release that was measured for these two unamended incubations is equivalent to only 6 to 11% of the initial acid-leachable As concentration in the solid phase.

Addition of the antibiotic to CW6-G prevented any detectable release of As; it did not in the case CW1-G. Instead, the incubation of CW1-G amended with the antibiotic progressed very much like the unamended incubation. These contradictory results and the fact that the reagents used to make the Guillard reagent in February 2002 were over 10 yr old suggests that the inhibition probably did not replicate because the antibiotic was degraded. On this basis, we infer that the microorganisms whose activities were inhibited by the antibiotic during the incubation of CW6-G play a significant role in mobilizing As.

Acetate additions stimulated the relatively fast release of As from all suspensions, including those containing some or mostly orange sands such as CW6-G&O and CW1-O (Fig. 3). In the case of CW6-G amended with acetate, As concentrations reached after about one month are comparable to those reached by the corresponding unamended suspension. For CW1-G, the acetate addition led to a release of As roughly twice as high as observed for the unamended suspension. For all incubations amended with acetate, the quantities of As mobilized consistently correspond to 70 to 80% of the acid-leachable fraction initially present on the sediments (Table 2).

Column separations of As species performed during the second batch of experiments show that the oxidation state of arsenic in solution was sensitive to the amendments. Starting at 60 to 80%, the proportion of dissolved As(III) in suspensions of CW1-G that were unamended and spiked with acetate rapidly diverged to steady levels of ~15 and 85%, respectively (Fig. 4). The proportion of As (III) in CW1-O started from a lower level of 35%, then increased to 90%. Although the initial oxidation state of As on the sand particles is not known, it appears that the addition of acetate prevented a gradual oxidation of As(III) to As(V) in solution and/or may have led to the reduction of As(V).

The behavior of other groundwater constituents provides a broader perspective of the evolution of the incubations. None of the unamended incubations or the incubations amended with the antibiotic released a significant amount of Fe to solution (Fig. 3). In contrast, the incubations amended with acetate all released a quantity of Fe corresponding to 0.5 to 2.0% of the acid-leachable Fe content of the sediment. This is considerably less than the proportion of acid-leachable As released from the unamended incubations and the incubations amended with acetate (Table 2).

The behavior of P was similar to that of As in the sense that comparable amounts were released from sediments CW6-G (at least initially) and CW1-G, and that the antibiotic inhibited the release of P in the first of these two experiments. The fraction of acid-leachable P (5–7%) released from the two unamended suspensions of gray sediment was significantly lower than for As, however. A parallel between the behavior of P and As is that less P was released (<3% of leachable fraction) from the unamended incubations of CW6-G&O and CW1-O containing some or mostly orange-brown Fe(III) oxyhydroxides than from the uniformly gray sediment. The additions of acetate produced a more complex set of responses in the case of P. By far the highest concentrations of dissolved P (~50 μmol/L) were measured at the end of the incubation of the acetate-amended suspension of CW1-G. This release corresponds to 20% of the acid-leachable P fraction, almost three times the fraction released from the same unamended suspension. Additions of acetate to CW6-G initially released a comparable fraction of acid-leachable P (9%) as for the unamended suspension, but P concentrations then rapidly declined during the second month of the incubation. Suspensions of CW6-O&G and CW1-O amended with acetate released only 4 and 2% of the leachable P fraction from the sediment, respectively.

Fig. 3. a, b Time series of dissolved As, Fe, and P concentrations normalized to the acid-leachable fraction of these elements initially in the solid phase. Proportions of acid-leachable As, Fe, and P released during the incubations were calculated by subtracting dissolved concentrations in the suspensions at the beginning of each of the incubations from the respective concentrations measured over time (Table 2). These differences in concentrations were then divided by the initial concentration of acid-leachable As, Fe, and P multiplied by the suspended loads. The scales in Figure 3 show both the percentage of leachable As, Fe, and P released on the left and, for reference, the corresponding changes in dissolved concentrations on the right. Symbols used are the same as in Figure 2.

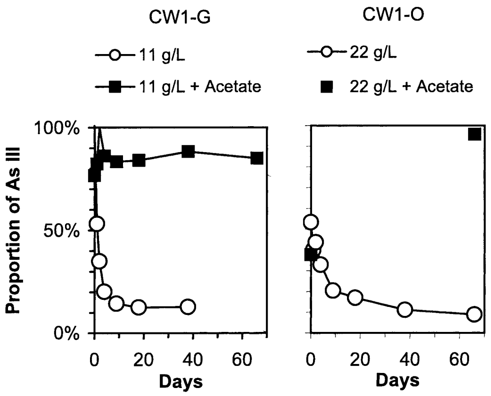


Fig. 4. Evolution of the redox state of As during the incubations of CW1-G and CW1-O, unamended and amended with acetate. Symbols are the same as in Figure 2.

4. DISCUSSION

4.1. Evolution of the Experimental Conditions

To what extent were the incubations representative of conditions in Bangladesh groundwater? Groundwater is typically anoxic in Bangladesh, but water pumped from the shallowest aquifers occasionally contains detectable levels of oxygen (BGS and DPHE, 2001; Zheng et al., 2004). The starting materials for these incubations were undoubtedly exposed to some atmospheric oxygen despite the precautions that were taken, even for the first batch of incubations that were initiated in Bangladesh. Brief exposure to oxygen of the sediment cuttings was unavoidable because the cuttings were collected by settling and decanting; oxygen is also likely to have diffused through the plastic wall of the jug used for storage of sediment and groundwater for several hours. For the second batch of incubations, oxygen had ample time to diffuse into the containers of well water and sediment from the time of collection to the moment when slurries were diluted and amended in the glove box in France. However, no obvious change in color was detected from the time of collection of the sediment to the onset of the incubations even though the redox state of Fe oxyhydroxides (and sediment color) is sensitive to exposure to atmospheric oxygen (Horneman et al., this volume). The release of As from gray sediments to groundwater does not appear to be very sensitive to the presence of oxygen since most of the release occurred during the first month of the incubations (Fig. 3), when oxygen was still clearly present (Fig. 2). These considerations, and the comparable outcomes for incubations of gray sediment with a different preparation history, suggest that the experimental conditions were representative of Bangladesh aquifers to the extent that it matters for the final stage of As mobilization, even if truly anoxic conditions were not necessarily maintained.

Eh and oxygen occasionally fluctuated considerably from one sampling of CW6-G&O and CW6-G to the next (Fig. 2). Since Fe and P rapidly adsorb or co-precipitate under even slightly oxic conditions (Zheng et al., 2004), the variable concentrations of these reactive species suggest that some ambient air may occasionally have entered the suspensions when the bottles were opened for sampling. This may have been compounded by some difficulties during filtration. It is worth noting, however, that the interval which included the flight from Bangladesh to France between days 2 and 9 of the experiment does not appear to have led to a systematic reduction in Fe and P concentrations. The starting material of the second set of six incubations, sediment and water, probably was more perturbed than the first batch when the slurries were prepared immediately in Bangladesh. But the second set of incubations remained essentially free of any obvious sampling artifacts over their entire duration.

The incubations suggest that S plays a limited role in the partitioning of As between the dissolved and particulate phase. Acetate additions appear to have triggered the reduction and precipitation of $\sim$30 10^{-6} mol/L S, presumably with Fe. A solution containing this level of sulfide and 30 10^{-6} mol/L Fe^{+2} would be supersaturated by about nine orders of magnitude relative to FeS(s) ($K_{sp} = 10^{-18.1}$; Morel and Hering, 1993). No detectable loss of As from the dissolved phase accompanied the formation of this Fe-sulfide phase. The origin of the rise in dissolved S concentrations midway trough the incubation of CW6-G and at the beginning of CW1-G is unclear. The timing does not correspond to that of the release of any of the other constituents that were monitored.

4.2. Decoupling Between the Release of As and Other Constituents

The outcome of the incubations sheds new light on the poorly understood process of As, Fe, and P mobilization in reducing groundwater. We discuss the behavior of Fe first, since Fe oxyhydroxides are likely to be an important carrying phase for As and P. The discussion of As and P behavior is limited in this section to the incubations of homogeneously gray sediment (CW6-G and CW1-G).

The rate of dissolution of Fe oxyhydroxides in the suspensions amended with acetate is probably considerably higher than in the natural environment. It is worth noting, however, that dissolved Fe concentrations seem to reach a plateau at the end of the incubations. By analogy to selective leaching procedures devised to distinguish phases of a complex sedimentary matrix, the extent of solubilization of Fe in the acetate-amended suspensions could therefore be interpreted, like the ascorbate-extractable Fe fraction (BGS and DPHE, 2001), as a measure of the fraction that can be mobilized fairly rapidly under reducing conditions.

Why does the fraction of Fe mobilized by the suspensions amended with acetate correspond to only 0.5 to 2% of the total amount of Fe released from the same sediment by the hot acid leach? We offer two possible explanations. The field data of Horneman et al. (this volume) indicate that, given enough time (100–1000 yr), the hot acid-leachable Fe fraction of the sediment can be converted entirely to Fe(II). Although this was not quantified, the suspensions amended with acetate darkened perceptibly over the course of the incubations. The small fraction of Fe released may therefore indicate that the short-term incubations with acetate led to the reduction of poorly crystallized phases, such as ferrihydrite, and not the reduction of goethite or hematite (Roden and Urrutia, 2002; Zachara et al., 2002). Another possibility is that a larger fraction of the acid-leachable Fe was reduced following the addition of acetate, but that most of the Fe(II) that was generated readsorbed on the sediment or reprecipitated. Adsorption is a distinct possibility given the documented strong affinity of Fe(II) for Fe oxyhydroxide surfaces (Frederickson et al., 1998; Ligier et al., 1999; Appelo et al., 2002). At a dissolved Fe^{+2} concentration of $\sim 30.10^{-6}$ mol/kg, the suspensions are also supersatured by nearly an order of magnitude with respect to siderite at pH~7.3 ($[CO_3^-] \sim 3\ 10^{-6}$ mol/L for $P_{CO2} = 0.9\%$; K_{sp} $FeCO_3 = 10^{-10.7}$; Morel and Hering, 1993). Suspensions containing over 1.10^{-6} mol/kg P are also highly supersaturated with respect to vivianite (K_{sp} $Fe_3(PO_4)_2 = 10^{-36}$; Morel and Hering, 1993). The complete transfer of a 30 μmol/L Fe(II) addition to CW1-G as part of an additional experiment at the end of the incubations could therefore have been the result of a number of processes. The processes that affected Fe during the incubations are therefore likely to be complex and to a large extent beyond the scope of this study.

It is no great surprise that significant amounts of arsenic were released upon the additions of acetate that stimulated the microbial-reduction of Fe oxyhydroxides. Acid leaches and abiotic reductive dissolutions of Bangladesh aquifer material have previously been shown to release As in quantities ranging from 1 to 20 μg/g (Nickson et al., 2000; BGS and DPHE, 2001). Biotic reductive dissolution of Fe coupled to As release has been demonstrated previously with laboratory incubations of synthetic oxyhydroxides as well as natural sediment enriched in As but, to our knowledge, not for natural Bangladesh aquifer material (Ahmann et al., 1997; Cummings et al., 1999; Jones et al., 2000; Zobrist et al., 2000). An interesting observation is that similar quantities of As were released from incubations of gray sediment (CW6-G and CW1-G) amended with acetate and from the unamended incubations. The very different response compared to Fe must somehow be reconciled with the fact that, unlike Fe, the quantity of As released by these incubations accounts for much of the acid-leachable As (Table 2). The most likely explanation appears to be that the large fraction of As that was released is heterogeneously distributed on the sediment particles and concentrated in a labile phase. Another possibility is that Fe(II) was oxidized and readsorbed in the unamended experiments in the presence of oxygen. Spike recovery experiments with unamended incubations of gray sediment suggest that As is indeed no longer bound to this phase at the end of the experiments. Separate 50 μg/L spikes of As(III) or As(V) added to aliquots of unamended suspensions of CW1-G at the end of the incubations were entirely recovered in the dissolved phase (data not shown).

Phosphate bound to gray Bangladesh sediment combines aspects of the behavior of both As and Fe. At the end of the first month of incubation, the fraction of acid-leachable P released from suspensions of gray sediment amended with acetate (~10–20%) was intermediate relative to the proportions of leachable As and Fe that were released (Table 2). Unlike Fe, readsorption of P does not seem to have been a major factor since a 50 μmol/L P spike added to the unamended suspension CW1-G at the end of the experiment remained entirely in solution (data not shown). This response is consistent with the behavior of its chemical analog As(V). Unlike As, however, the addition of acetate led to a considerable enhancement of P release compared to the unamended incubation of CW1-G. The combined set of observations suggest that P is also concentrated in a labile Fe phase but probably less so than As. We have no explanation for the rapid decline in dissolved P during the second month of incubation of CW6-G (Fig. 3). Although the suspension is close to saturation with respect to vivianite, the solubility product is actually larger for the acetate-amended suspension of CW1-G where no such loss was observed.

4.3. Role of Microorganisms in As Mobilization

There is little doubt that Fe-reducing bacteria play some role in the mobilization of As in Bangladesh groundwater. Without what could be interpreted as the catalytic role of these organisms, abiotic dissolution of Fe oxyhydroxides, and therefore the release of As, would proceed more slowly and As concentrations would probably not build to the same extent in Bangladesh groundwater. Less clear is which stage of the microbially driven conversion of Fe(III) oxyhydroxides to more reduced Fe phases or the reduction of As may be important for the mobilization of As.

The inhibition of As release during the first incubation of gray sediment (CW6-G) amended with the antibiotic is a strong indication that microorganisms play an important role in As mobilization. If such a response had not been observed, it would have been difficult to rule out the possibility that the observed release of As simply reflected an abiotic reequilibration between solid and dissolved phase in response to the dilution of aquifer material from one location with water from a different aquifer. It is not clear, however, exactly what respiratory process was affected by the antibiotic. We speculate that the reduction of a surface coating of ferrihydrite enriched in As by dissimilatory Fe-reducing bacteria was perhaps inhibited. The significant stimulation of Fe release upon the additions of acetate indicates that Fe-reducing bacteria were present in the original Bangladesh aquifer material.

The reduction of As(V) to As(III) observed during the incubations of CW1-G and CW1-O amended with acetate suggests a process of dissimilatory microbial reduction stimulated by the addition of substrate rather than a detoxification activity, possibly by the same class of organisms responsible for S reduction (Inskeep et al., 2002; Oremland et al., 2002). But the release of As was not severely inhibited by the mildly oxic conditions in the unamended suspension of CW1-G indicated by the oxygen sensor data and the presence of As(V) (Figs. 3b and 4). In this incubation, as well as the unamended suspension of CW1-O, the gradual oxidation of As(III) could have been caused by low but detectable levels of oxygen, possibly catalyzed by Fe(II), or by Mn oxides (Scott and Morgan, 1995; Inskeep et al., 2002; Manning et al., 2002; Tournassat et al., 2002; Hug and Leupin, 2003). These observations suggest that microbial reduction of As may not be required for mobilization once the sediment itself has been altered under reducing conditions (Cummings et al., 1999; Langner and Inskeep, 2000). Whereas dissolved As is predominantly in the As(III) form in Araihazar groundwater, there are indeed reports of dissolved As(V) in groundwater from other parts of Bangladesh (BGS and DPHE, 2001; Zheng et al., 2004; Zheng et al., in review).

Comparison of the behavior of P(V), which does not change redox state even in reducing aquifers, with that of As suggests that reduction to As(III) may instead play a role in mobilization at an early stage of reduction of Fe oxyhydroxides. Horneman et al. (this volume) report that the As content of magnetic minerals separated from aquifer material in the same area is no different from that of the leachable Fe fraction, i.e., on the order of 1 to 2 μg/g. The Fe content of this same fraction averages 50% by weight, which is much higher than the 0.5 to 2% leached from the bulk sediment (Table 2). Although the bulk of these magnetic minerals appears to be of detrital rather than authigenic origin (Lovley, 1990; Lovley 1997; Benner et al., 2002; Nevin and Lovley, 2002), the exclusion of As during the formation of magnetite indicated by the two orders of magnitude lower As/Fe ratio compared to the acid-leachable fraction, may be relevant structurally. We speculate that the reason for the divergent behavior of As and P at the early stages of reduction of Fe oxyhydroxides may be the conversion to As(III) which, based on structural considerations, may not fit as well as P(V) in the lattice of magnetite or that of other mixed valence Fe structures. Indeed, the first coordination sphere of As(III) is composed of 3 oxygen atoms forming a pyramid. Since As is one of the four corners of this pyramid, the molecule is highly asymmetric as, for example, in $NaAsO_2$, stenhugarite $CaFeSbAs_2O_7$, and ludlokite $PbFe_4As_{10}O_{22}$ (Menary, 1958; Coda et al., 1977; Cooper and Hawthorne, 1996). In the case of phosphate, the first coordination sphere is composed of 4 oxygen atoms forming a pyramid (Mori and Ito, 1950). The P atom is at the center of the pyramid and the PO_4 molecule can be linked to, or incorporated in, minerals in a tetrahedral crystallographic site. The AsO_3 pyramid precludes this type of structure. The reduction to As(III) could therefore conceivably lead to exclusion from the Fe(III/II) structure and concentration in an external and therefore more easily mobilized phase. Comparison of the acid-leachable fraction of P with the considerably lower fraction released by the incubations with acetate (Table 2) suggests the partial reduction of Fe(III) oxyhydroxides may indeed not exclude P as effectively.

4.4. Binding of As to Fe(III) Oxyhydroxides

The small fractions of leachable As and P released from the unamended incubations of CW6-G&O and CW1-O (Fig. 3) could indicate that the reduction of Fe(III) oxyhydroxides had not reached the stage where As and, to a lesser extent, P were concentrated in a labile phase, or that As and P were readsorbed on the remaining Fe(III) oxyhydroxides. The response of the same aquifer material to acetate additions could be consistent with either of these two scenarios. The dissolution of a relatively small fraction of the Fe oxyhydroxides stimulated by acetate led to the release of most of the acid-leachable As, but a considerably smaller portion of the acid-leachable P relative to the parallel incubations of gray sediment (Fig. 3). This could also indicate that the reduction of Fe oxydroxides more readily results in the concentration of As in a labile phase. Qualitatively, the color of the original suspension of CW1-O darkened significantly and indicates that a significant fraction of the Fe(III) oxyhydroxides may have been reduced. However, the redistribution of As and P between the solid and dissolved phase was not determined at the end of the incubations of either CW6 G&O or CW1-O. We therefore cannot exclude the possibility that P(V), and therefore perhaps As(V), was readsorbed on even a small fraction of remaining Fe(III) oxyhydroxides.

It is worth noting that during the 12 separate incubations described in this paper, significant As mobilization was accompanied by at least an initial release of P. Since dissolved P concentrations are about an order of magnitude higher than As concentrations in Bangladesh groundwater, the mobilization of As could be enhanced by desorption due to the release of P from the sediment (BGS and DPHE, 2001). Competition between P and As for adsorption sites on Fe oxyhydroxides is well established (e.g., Dixit and Hering, 2003, and references therein.) Displacement of As from Bangladesh sediment by P has also been documented with selective-leaching experiments (Harvey et al., 2002). Zheng et al. (in review) more recently showed that gray sediment recovered from a drill site in the same region that contained $<0.5 \mu$g/g of As extractable with a neutral solution high in P was associated with low-As groundwater. In contrast, groundwater As concentrations were high for depth intervals where gray sediment contained over 2 μg/g of P-extractable As. Although concentrations of P used in such extractions are much higher than in Bangladesh groundwater, this does suggest a relatively labile As phase can be displaced by P. phosphate may, therefore, play an indirect role in As mobilization, even if it is not linked to the application of fertilizer.

4.5. Implications for the Distribution of As in Bangladesh Groundwater

The incubations conducted under this study make a clear distinction between the properties of uniformly gray aquifer particles and particles that contain some or mostly orange Fe(III) oxyhydroxides. This is consistent with field observations documented in the companion paper by Horneman et al. (this volume). These observations show that the Fe oxyhydroxides coatings of very shallow aquifers material ($<$6 m, or $<$20 ft) that are not covered by an impermeable clay layer generally contain a major fraction of Fe(III). Low groundwater As concentrations in such shallow aquifers are consistent with the retention of As during the incubations of sediment containing some or mostly Fe(III) oxyhydroxides. The release of much of the acid-leachable As from the same type of sediment fraction upon addition of an organic substrate helps explain why groundwater As concentrations are typically high in shallow aquifers that are covered by a clay layer (Horneman et al., this volume). The profiles of water and sediment properties described by Horneman et al. (this volume) suggest that such an impermeable layer reduces local recharge, and the associated supply of oxidants such as oxygen and nitrate, to the point where shallow aquifer particles turn gray, Fe(II) or mixed Fe(II)/Fe oxyhydroxides dominate, and, according to the incubations, As is readily released to groundwater. These observations, combined with the highly variable nature of fluvio-deltaic deposits, may help explain the extreme spatial variability of As concentrations in shallow aquifers (Fig. 1).

Since groundwater has been flushing Holocene Bangladesh aquifers for thousands of years, it may seem puzzling that groundwater As concentrations are frequently elevated if the release of much of the acid-leachable As fraction from gray sediment took only two months. Results from a separate unamended incubation of CW1-G at a particle concentration that was 20 times higher than for the incubation of CW1-G described in this paper indicate this may be because dilution favors As mobilization. After two months of incubation of the more concentrated suspension, As concentrations had increased to 23 μg/L but had not yet reached a plateau (data not shown). This is consistent with the fact that only ~6% of the acid-leachable As had been mobilized by that time. The process of As mobilization stimulated by microorganisms may therefore be less pronounced at the even higher particle concentrations of an actual aquifer.

The release of As observed from the deeper Dupi Tila sands (CW1-O) amended with acetate confirms that the deeper aquifers of Bangladesh are low in dissolved As, not because solid phase As concentrations are particularly low, but because As is strongly adsorbed on or incorporated in the predominantly Fe(III) oxyhydroxides (Zheng et al., in review). The implication is that groundwater As concentrations could increase if the penetration of labile dissolved organic carbon into these deeper aquifers, naturally or because of irrigation pumping, were to reduce a significant proportion of the Fe(III) hydroxides (Harvey et al., 2002). Since tapping into the deeper aquifers of the Dupi Tila and similar Pleistocene formations for the provision of safe water is currently the most promising mitigation option for the 86000 villages of Bangladesh, it will be particularly important to preserve the integrity of these aquifers by ensuring proper installation of community wells and preventing the large water withdrawals for irrigation from these same deeper aquifers.

5. CONCLUSION

Our observations, considered jointly with the field data of Horneman et al. (this volume), indicate that As is mobilized from Bangladesh sediment only after orange Fe (III) oxyhydroxides have been reduced to gray or black solid phases of Fe(II) or Fe(II/III). Comparison of the incubations and leaching results suggest that As is concentrated in a relatively labile phase as the sediment progresses towards reduction. Microorganisms naturally present in Bangladesh aquifers evidently can mobilize much of this As fraction from sufficiently reduced (gray) sediment, and this perhaps without the need for extensive Fe dissolution. Phosphate in the sediment does not appear to be concentrated in a labile phase to the same extent, but may still play a role in promoting the release of As to groundwater. Whereas anoxia is likely to be required for Fe phases to become sufficiently reduced in the sediment, anoxia may not be required for mobilized As to remain in solution. These observations combined with the complex geology, and therefore hydrology, of river floodplain and deltaic aquifers, help explain the extreme degree of spatial variability of groundwater As concentrations in Bangladesh, as well as the very scattered relations between As, P, and Fe in Bangladesh groundwater (BGS and DPHE, 2001; van Geen et al., 2003a), (Bostick and Fendorf, 2003, Cooper and Hawthorne, 1996, Cornell and Schwertmann, 1996, Dowdle et al., 1996, Fredrickson et al., 1998, Kneebone et al., 2002, Meng and Wang, 1998, Meng and Wang, 1998, Parfitt et al., 1975, Randall et al., 2001, Royer et al., 2002, Saltikov et al., 2003, Zachara et al., 2001).

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