



Distribution of arsenic and its mobility in shallow aquifer sediments from Ambikanagar, West Bengal, India

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ABSTRACT

Sediments from a core retrieved during installation of a shallow drinking water well in Ambikanagar (West Bengal, India) were analyzed for various physical and chemical parameters. The geochemical analyses included: (1) a 4-step sequential extraction scheme to determine the distribution of As between different fractions, (2) As speciation (As^{3+} vs. As^{5+}), and (3) C, N and S isotopes. The sediments have a low percentage of organic C and N (0.10–0.56% and 0.01–0.05%, respectively). Arsenic concentration is between 2 and 7 mg kg⁻¹, and it is mainly associated with the residual fraction, less susceptible to chemical weathering. The proportion of As^{3+} in these sediments is high and ranges from 24% to 74%. Arsenic in the second fraction (reducible) correlates well with Mn, and in the residual fraction As correlates well with several transition elements. The stable isotope results indicate microbial oxidation of organic matter involving SO_4 reduction. Oxidation of primary sulfide minerals and release of As from reduction of Fe-(oxy)hydroxides do not seem important mechanisms in As mobilization. Instead, the dominance of As^{3+} and presence of As^{5+} reducing microorganisms in this shallow aquifer imply As remobilization involving microbial processes that needs further investigations.

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1. Introduction

Arsenic is commonly found in an insoluble form associated with rocks and minerals. The metalloid occurs in four oxidation states: arsenite (As^{3+}) under reducing conditions, arsenate (As^{5+}) under oxidizing conditions, arsine (As^{3-}) as traces in gases emanating from anoxic environments, and elemental As (As^0) (Cullen and Reimer, 1989). In natural waters, the common species are the trivalent arsenite (H_3AsO_3 ; As^{3+}) with pK_a around 9.3, and the pentavalent arsenate (H_3AsO_4 ; As^{5+}) with pK_a values around 2.3, 6.8 and 11.3. The As^{3+} species are generally believed to be more mobile than As^{5+} due to the stronger affinity of the latter for Fe-, Mn- and Al-oxides (Korte and Fernando, 1991).

Arsenic has been known for its acute toxicity for hundreds of years (Ehrlich, 2002; Oremland and Stolz, 2003). However, this has become a global problem affecting the health of millions of people (Bhattacharya et al., 2002; Kapaj et al., 2006). The oxidized species As^{5+} substitutes readily for phosphate in living cells, and inhibits oxidative phosphorylation (Oremland and Stolz, 2003). In contrast, As^{3+} impairs the function of many proteins by binding with the sulfhydryl groups (Oremland and Stolz, 2003). For human beings, As^{3+} is reportedly more toxic than As^{5+} . The problem is most serious in the

fertile Bengal Delta Plain (BDP) aquifers of India and Bangladesh where millions of people drink As-rich groundwater (Bhattacharya et al., 2002; Ahmed et al., 2004; Hossain et al., 2005; Kapaj et al., 2006; Nath et al., 2008a,b). Aquifers in this region have As concentrations up to mg L⁻¹ levels (Bhattacharya et al., 2002; Ahmed et al., 2004; Kapaj et al., 2006), whereas the World Health Organization guideline for drinking water is 10 µg L⁻¹ (WHO, 2004). Chronic As poisoning from groundwater was first reported in West Bengal in 1982 (Saha, 1984), and since then, As-related health problems in the Indo-Gangetic plains have been reported by different research groups (Guha Majumdar et al., 1988; Mandal et al., 1998; Chakraborty et al., 2001; Kapaj et al., 2006).

In the BDP aquifers, the primary source for As is geogenic, and it is thought to have been carried in as adsorbed phases on suspended solids (Bhattacharya et al., 1997; McArthur et al., 2001; Nath et al., 2008a). Arsenic is subsequently mobilized from these alluvial sediments into groundwater; and several competing theories have been proposed to explain the reaction (McArthur et al., 2004). Of these theories, the most widely accepted one suggests that As is released to solution by reductive dissolution of Fe-(hydr)oxides (Bhattacharya et al., 1997; McArthur et al., 2004). The reduction is driven by microbial metabolism of buried peat deposits or other sources of organic matter (Mukherjee and Fryar, 2008). Recent studies have also proposed dissimilatory microbial processes such as SO_4 or As^{5+} reduction in As mobilization (Oremland and Stolz, 2003; Islam et al., 2004; Routh et al., 2005;

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Routh and Saraswathy, 2005). However, the actual efficiency of these microbial processes in natural systems is unknown.

Research in the BDP aquifers primarily focuses on groundwater geochemistry, and sediments have rarely been studied. Recently, the authors have investigated the sub-surface microbes involved in As cycling in a sediment core retrieved from a shallow aquifer in Ambikanagar, a small village in the North 24 Parganas district in West Bengal (Routh et al., 2005; Routh and Saraswathy, 2005). The purpose of the present study is to characterize in detail the physical and chemical properties of sediments in this core, and relate the *in situ* biogeochemical processes as a follow-up to ongoing studies on microbial processes associated with As remobilization. The study involved investigation of: (1) the distribution of different elements based on sequential extraction to assess the geochemical fraction(s) with which As is most closely associated, (2) As speciation in sediments to assess the role of microbial As^{5+} reduction, and (3) stable C, N and S isotope signatures in sediments. Understanding the biogeochemical processes involved in As mobilization in these aquifers could provide insight into the As crisis in the BDP, as well as in floodplains and deltas of other major rivers in South-east Asia, e.g., the Chao Phraya in Thailand, and the Red and Mekong River deltas in Vietnam and Cambodia (Berg et al., 2001, 2007; McArthur et al., 2004).

2. Methods

2.1. Study area and sampling

Ambikanagar is located in the Deganga block of North 24 Parganas district (Fig. 1). The district has 19 As-affected blocks. The

area is a flat alluvial plain with the River Hugli to the west. The flat deltaic floodplains consist of numerous streams, marshlands, oxbow lakes, and paddy fields. The floodplains were formed due to the erosion of sediments by three major rivers (Ganges, Brahmaputra, and Meghna) and their tributaries from the Himalayas and the adjoining region, during late Quaternary or the Holocene (Umitsu, 1993). The underlying thick Quaternary alluvium consists of complete or partly truncated fining-upward sequences dominated by coarse to fine sand, silt and clay. The soil type in this area varies from sandy to clayey loam. Aquifer sediments in deep wells are mostly coarse sand, whereas shallow wells tap fine to medium sand. The water table in the aquifer occurs at a depth of ~5 m below land surface. Rainfall during the summer monsoons is the principal source of surface and groundwater recharge. The annual rainfall in the area is ~1570 mm. The annual temperatures are 41 °C in summer and 10 °C in winter, and the relative humidity is >65% (Statistical Handbook, 2003).

Reconnaissance sampling of groundwater (in 2004) from tube wells (30–80 m deep) in Ambikanagar indicated high concentrations of As ($45\text{--}130\text{ }\mu\text{g L}^{-1}$), Fe ($2500\text{--}7100\text{ }\mu\text{g L}^{-1}$) and Mn ($270\text{--}400\text{ }\mu\text{g L}^{-1}$; Routh et al., 2004). Arsenic detected in these tube wells predominantly occurred as As^{3+} species. In 2005, sediments were retrieved from a shallow drinking water well that was being installed in Ambikanagar. The well was made by air-jet drilling, which was chosen to avoid cross contamination of samples from drilling fluids. The well was 18 m deep and samples were collected at 3, 6, 9, 12, 15, 16.5 and 18 m (Fig. 1). The samples were numbered from 1 to 7, with sample 1 being the sediment on top. The samples were stored in N_2 -filled Anerocult™ bags (Merck Euro AB, Sweden) in the field and shipped to Stockholm the same day. On arrival, the samples were split into two halves, for various microbial and geochemical analyses, inside a glove bag and then kept at $-20\text{ }^\circ\text{C}$ until the analyses began. All sediment samples were freeze-dried and disaggregated using a mortar and pestle before further analyses. All chemicals used during the analyses were of reagent grade.

2.2. Sample preparation and analysis

The sediments were dry sieved through a $63\text{ }\mu\text{m}$ sieve. Samples of the fine fraction, 2.5–3.0 g, were shaken overnight with 80 mL of 0.5 g L^{-1} Na_3PO_4 solution (Calgon) for dispersion. The grain size distribution in the sediment suspension was determined with a Micrometrics Sedigraph 5100 for % sand, silt, and clay.

Sequential extraction was performed according to the standard BCR protocol of the Standards, Measurement and Testing Program (formerly the Community Bureau of Reference) of the European Commission (Quevallier et al., 1997; Rauret et al., 2000). The BCR method involved four consecutive extraction steps (Table 1); operational details of the method are indicated in the original references (Quevallier et al., 1997; Rauret et al., 2000). Unlike other sequential extraction methods (Tessier et al., 1979; Martin et al., 1987), the BCR method does not specify a particular phase that is extracted during the procedure. Instead, the authors referred to trace elements fractionating into weak acid, reducible, oxidizable, and residual fractions. However, the different extraction steps in the BCR method have been compared to other sequential procedures (e.g., Tessier et al., 1979; Martin et al., 1987), and the equivalent 'operationally defined' fractions involved in the release of trace metals were indicated by Hjorth (2003, 2004).

Because researchers are often restricted by the amount of available sediment (or standard) for different analyses, the authors have experimented with smaller sample masses than the amount suggested in the original BCR method (Rauret et al., 2000). The results indicate that using half the amount of sediment or standard specified in the original method for sequential extraction still provides

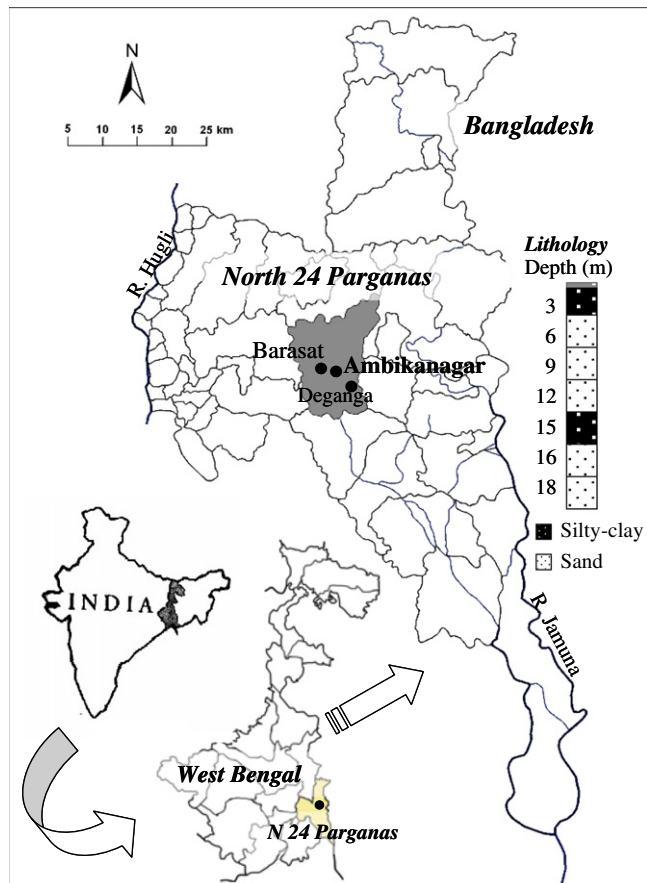


Fig. 1. Location map of study area and lithological characteristics of the core retrieved from Ambikanagar, North 24 Parganas in West Bengal (India).

Table 1
Sequential extraction of trace elements from sediments involving the BCR scheme.

Steps	Extraction conditions	Target phase ^a and comments
1	20 ml 0.11 HO Ac, 16 h shaking	Carbonates (pH sensitive), includes soluble and exchangeable elements involves sorption–desorption process due to change in ionic strength
2	20 ml 0.11 NH ₂ OH-HCl, pH 2, 16 h shaking	Fe–Mn oxides (sensitive to pH change)
3	5 ml 8.8 M H ₂ O ₂ , 1 h 5 ml 8.8 M H ₂ O ₂ , 85 °C, 1 h 25 ml 1 M NH ₄ OAC, pH 2, 16 h shaking	Organic matter and sulfides
4	10 ml 7 M HNO ₃ , 200 kPa, 120 °C, 30 min in autoclave ^b	Residual (silicate/crystalline structure)

^a From Quevallier et al. (1997) and Rauret et al. (2000).

^b SIS (1993).

reliable results (Hjorth, 2003, 2004; T. Hjorth, pers communication). Therefore, half the prescribed amount was used i.e., 0.5 g of sediment and reagents as suggested in the original method (Rauret et al., 2000). After each extraction step, the samples were centrifuged for 20 min at 3000g, and the supernatant was decanted. Every step was followed by a washing step with 10 mL of deionized distilled water. To test the extraction efficiency, a sample of the certified reference sediment CRM-601 was included during the sequential extractions. The mineral fractions associated with the different extraction steps are hereafter referred to as fractions 1–4. The extracts were analyzed on a Varian Vista AX Pro ICP-OES. Error for the certified values in standards for the ICP runs was within 2%. The detection limits were as follows: As 5.2 µg L⁻¹, S 15.2 µg L⁻¹, P 15.9 µg L⁻¹, Co 1.6 µg L⁻¹, Pb 2.3 µg L⁻¹, Ni 2.5 µg L⁻¹, Zn 1.1 µg L⁻¹ and <1 µg L⁻¹ for other elements. Two samples were replicated (starting from the BCR digestion step) to test the reproducibility and precision of the analyses.

Total dissolution of the sediments was performed according to the Swedish standard method (SIS, 1993) using the same amount of sample (0.5 g) as in the BCR method. The sediment was digested in 10 mL 7 M HNO₃ at 200 kPa and 120 °C for 30 min in an autoclave. After cooling, the solution was transferred to a centrifuge tube and centrifuged at 10,000 rpm (14000g) for 15 min. The supernatant was transferred into a 50 mL volumetric flask. In addition, the reference standard CRM-601 was also extracted with the samples.

Arsenic speciation in sediments was determined according to Chappell et al. (1995). Five grams of sediment was digested in 20 mL of 10 M HCl. The samples were shaken for 30 min and centrifuged at 2500g for 5 min, and the supernatant gravity-filtered through a filter paper. The process was repeated twice, and the extract volume was made up to 100 mL. Ten mL of this acid extract was added to 80 mL of 10 M HCl. This was followed by extraction of As³⁺ with CHCl₃ (4 × 10 mL aliquots); the strongly acidic aqueous fraction was discarded. Arsenic was thereafter back-extracted from the CHCl₃ fraction into deionized distilled water (2 × 20 mL aliquots), and the extract was diluted to 100 mL. To determine the total As concentration, another 10 mL of the acid extract was treated with 10 mL of 50% KI solution, and heated in a water bath at 60 °C for 30 min. The sample was again extracted with CHCl₃ and water as described above. Arsenic(V) was calculated as the difference between total and As³⁺ species.

The extracts were analyzed on a Varian Spectra AA 220 FS atomic absorption spectrometer at 193.7 nm. To control the accuracy of the analysis, Standard Reference Material SRM-1640 of the US National Institute of Standards and Technology (As content 26.7 µg L⁻¹; NIST, 2005) was analyzed together with the samples. The measured concentration in SRM-1640 was 23.9 µg L⁻¹ of As.

The relative standard deviation was 8.75%, and the detection limit was 1.8 µg L⁻¹ of As.

For organic C isotope analysis, approximately 10 mg of sediment was weighed into a Ag capsule, treated with dilute HCl to remove carbonates, and dried overnight (40 °C) before analysis. For N isotope analysis, approximately 10 mg of sediment was directly weighed into a Sn capsule. Sulfur was extracted from sediments using a two-step procedure. To extract the oxidized S, 5 g of sediment was digested in 20 mL of 6 M HCl at room temperature overnight. The acid was diluted with 20 mL deionized distilled water. The sediments were centrifuged at 2500g for 5 min and the supernatant decanted into a beaker. The sediments were washed with 2 × 30 mL deionized distilled water and centrifuged, and the supernatant was decanted into the beaker. The sediments were dried and put aside for extraction of reduced S. The extracts were heated and 20 mL 0.25 M BaCl₂-solution was added. The extracts were concentrated by heating at 90 °C overnight. The BaSO₄ precipitate was filtered on a Millipore Isopore 0.4 µm HTTP membrane filter, which was dried at 60 °C and subsequently combusted, leaving behind the pure BaSO₄ residue. To extract the reduced S, 20 mL concentrated HNO₃ and 2–3 mL Br₂ (aqueous) were added to the sediments. The sediments were left under cover to react at 90 °C for 24 h and dried. After drying, the sediments were extracted with HCl as above. Approximately 0.5 mg of the BaSO₄ precipitate was weighed into a Sn capsule with 0.5 mg V₂O₅ for S isotope analysis.

C, N and S isotopes were determined on a Finnigan MAT Delta Plus mass spectrometer coupled to a Fisons elemental analyzer. Carbon and N isotopes were determined in the same run, whereas S was determined separately. Data are reported in the conventional delta (δ) notation, which is the ‰ deviation from the Vienna Pee Dee Belemnite standard (V-PDB) for C, atmospheric N₂ for N, and the Vienna Canyon Diablo Troilite standard (V-CDT) for S. The precision for C, N and S isotope analyses was ±0.18‰, ±0.06‰ and ±0.2‰, respectively.

Heavy minerals in samples containing the highest As concentrations (samples 1, 5, 7) were separated by the standard gravity method using lithium sodium heteropolytungstate (LST; 80% sodium heteropolytungstate dissolved in water), which helped in separating minerals with specific gravity >2.9 g cm⁻³. Warm LST (68 °C) was added to the sediments and centrifuged at 4000 rpm. The centrifuge tubes were held in liquid N₂, which allows the heavy minerals to settle. The lighter fraction was removed, whereas the heavy mineral fraction once it thawed out was transferred to filter paper, and dried in an oven. The fraction consisting of dark colored minerals (>2.9 g cm⁻³) was mounted (wet) and analyzed on a scanning electron microscope (Philips XL-30 ESEM FEG SEM).

3. Results

The aquifer sediments were reddish brown to gray in color; the deeper sediments were darker (more gray). The sediments predominantly consisted of sand (up to 90%), except for samples 1 and 5, which were mainly silty (up to 70%). Total organic C in sediment ranged between 0.10 and 0.56 wt.%, and the highest concentration occurred in fine-grained sediments, i.e., samples 1 and 5. Total N (organic) in sediments varied between 0.01 and 0.05 wt.%.

In order to assess the reliability of the sequential extraction procedure, the reference standard CRM-601 was extracted and analyzed in the same manner as the sediment samples. The CRM-601 standard was analyzed for 6 trace elements extracted during the different extraction steps, and for the pseudo-total elemental content (Rauret et al., 2000). For extracting trace elements in the residual fraction and from pseudo-total extraction, the BCR method used aqua regia, while in this study 7 M HNO₃ was used.

The results for these steps were, therefore, not comparable in the strictest sense.

In Table 2 the trace element concentrations in fractions 1–3 of CRM-601 are reported, together with the half width of the 95% con-

fidence interval (similar to Rauret et al., 2000). The table shows the trace element concentrations measured in this study, and whether these concentrations are within the confidence limit. The measured concentrations for Cu, Ni and Zn in fraction 1 are not within

Table 2
Trace element results in the CRM-601 standard. Concentrations cited by Rauret et al. (2000) and those obtained in this study.

Element	Step 1: Trace metal concentration (mg kg ⁻¹)				Step 2: Trace metal concentration (mg kg ⁻¹)				Step 3: Trace metal concentration (mg kg ⁻¹)			
	BCR (2000)	95% Confidence	Present study	Within confidence	95% Confidence	Present study	Within confidence	95% Confidence	Present study	Within confidence	95% Confidence	Present study
Cd	4.45	1.31	3.70	Yes	3.95	1.04	3.17	Yes	1.91	2.80	1.62	Yes
Cr	0.35	0.16	0.34	Yes	10.6	1.76	9.43	Yes	14.4	5.10	17.2	Yes
Cu	10.5	1.57	15.3	No	72.8	9.60	67.7	Yes	78.6	17.4	66.8	Yes
Ni	7.82	1.65	6.04	No	10.6	2.35	9.30	Yes	6.04	2.49	7.36	Yes
Pb	2.28	0.86	2.13	Yes	205	21.6	187	Yes	19.7	11.4	24.2	Yes
Zn	261	25.5	232	No	266	33.3	234	Yes	106	21.6	127	Yes

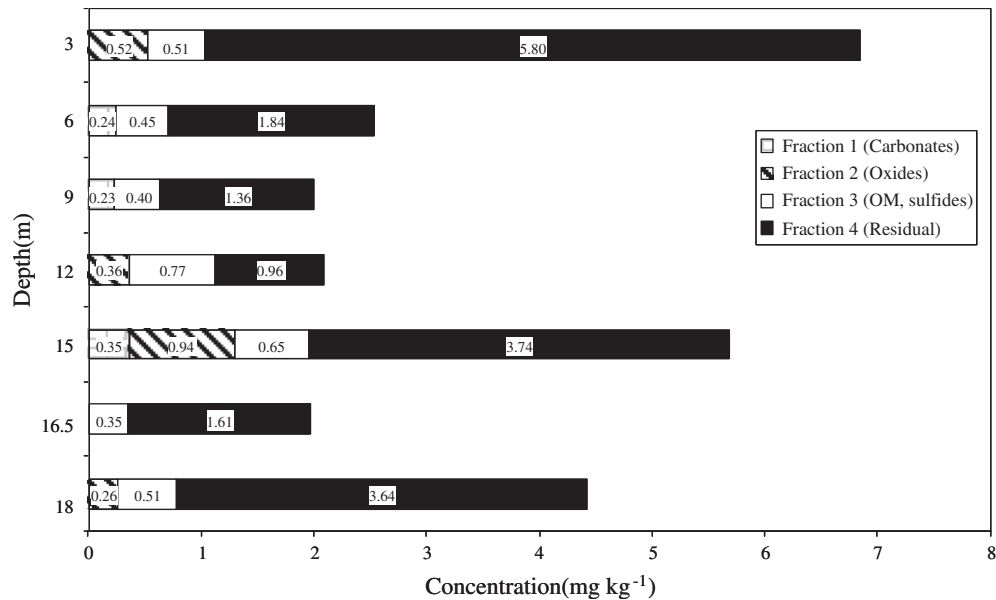


Fig. 2. Distribution of As in different geochemical fractions in Ambikanagar sediments.

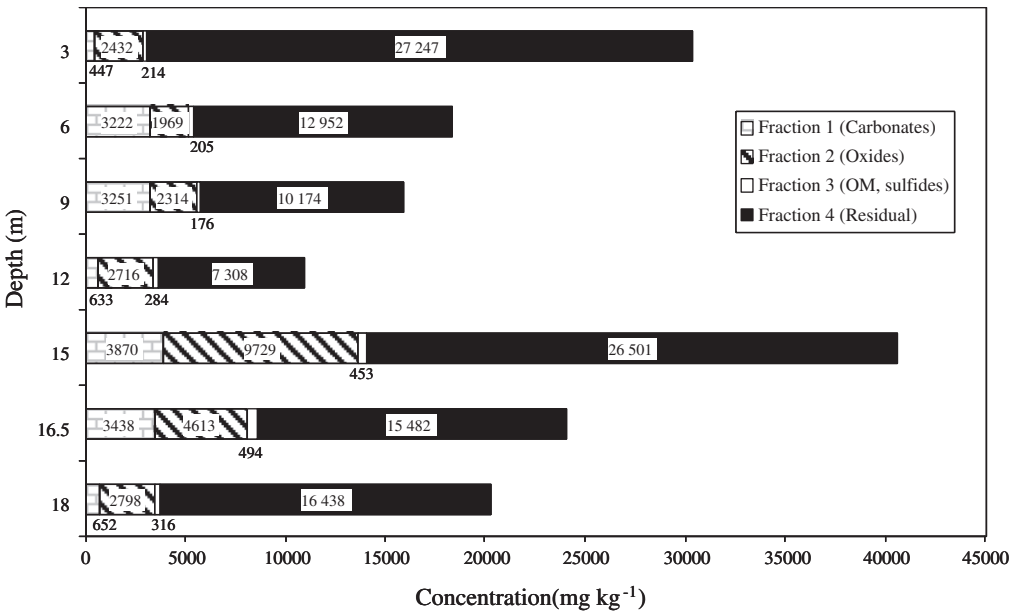


Fig. 3. Distribution of Fe in different geochemical fractions in Ambikanagar sediments.

the confidence limit. In fractions 2 and 3, trace metal concentrations for all elements are within the confidence limit. From these results, it is concluded that steps 2 and 3 in the BCR extraction scheme are reliable, whereas trace element concentrations in step 1 are probably questionable.

Samples 1 and 5 had the highest concentrations for most elements. Total As concentration in these sediments varied between 2.0 and 7.0 mg kg⁻¹ (Fig. 2). The highest As concentration occurred in samples 1, 5 and 7. Arsenic was primarily associated with the residual fraction. Concentrations of more readily available As (e.g., As complexes with organic matter and Fe–Mn (oxy)hydroxides) present in fractions 1–3 ranged between 0.3 and 2.0 mg kg⁻¹. Arsenic associated with the reducible fraction 2 occurred in samples 1, 4, 5 and 7, and ranged from 0.3 to 0.9 mg kg⁻¹ (Fig. 2).

The total Fe concentration in sediments varied between 11,000 and 40,000 mg kg⁻¹ (Fig. 3); the highest concentration occurred in

fraction four followed by fractions 1 and 2. The total Mn concentration varied between 140 and 480 mg kg⁻¹. Manganese was mainly found in fractions 1, 2 and 4 (Fig. 4). The total P content varied between 320 and 480 mg kg⁻¹ (Fig. 5). Phosphorus mostly occurred in fractions 2 and 4. The concentration for S was close to the detection limit after blank correction.

Correlation between As and other trace elements in the different fractions were considered (Table 3). In general, fraction 4 showed the best correlations, but some elements in fraction 2 and those in the pseudo-total fraction also correlated well with As. There was an absence of significant correlation in fractions 1 and 3 between As and other trace elements (data not shown). As³⁺ species ranged from 24% in sample 1 to 76% in sample 5 (Fig. 6).

The isotope ratio for organic C varied between –20‰ and –24‰ (Fig. 7). The isotope ratio for N varied between –1.2‰ and +4.4‰.

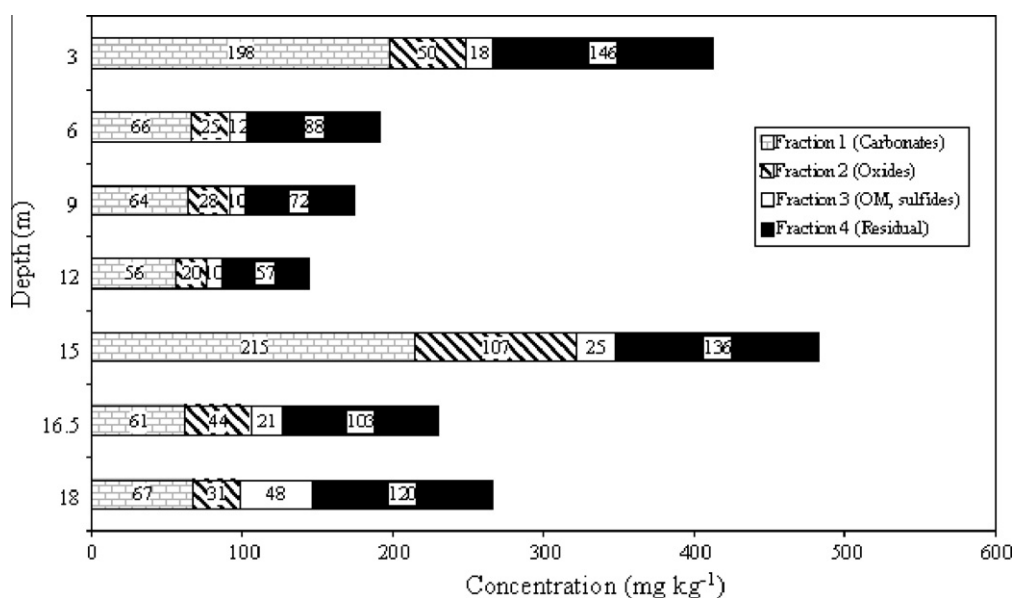


Fig. 4. Distribution of Mn in different geochemical fractions in Ambikanagar sediments.

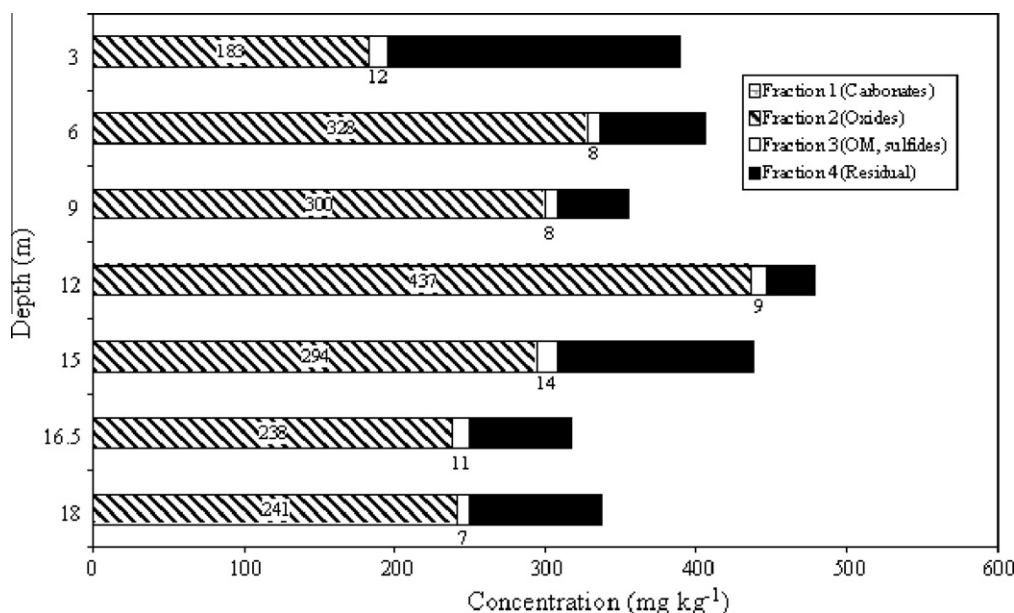


Fig. 5. Distribution of P in different geochemical fractions in Ambikanagar sediments.

Table 3

Correlation of arsenic with other elements in different fractions.

Fraction 2			Fraction 4			Pseudo-total		
Element	r	p	Element	r	p	Element	r	p
Na	0.901	0.006	P	0.964	0.001	Al	0.084	0.023
Sr	0.878	0.009	Co	0.929	0.002	V	0.820	0.024
Pb	0.869	0.011	Mn	0.920	0.003	Cr	0.816	0.025
K	0.848	0.026	Fe	0.898	0.006	Ba	0.808	0.028
Mn	0.811	0.027	Zn	0.885	0.008	Mn	0.804	0.029
Fe	0.727	0.064	Ni	0.880	0.009	Ni	0.801	0.031
			V	0.870	0.011	Cu	0.799	0.031
			Cr	0.823	0.023			

The highest $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values occurred in fine-grained sediments. The isotope ratio for reduced S varied between 1‰ and 8.4‰ (Fig. 7). Because it was not possible to extract enough oxidized S from these sediments, the isotope ratio of the SO_4 fraction was not determined.

4. Discussion

4.1. Sediment composition

The fining-upward layered sequences of fine sand to silt in the study area are typical of riverine depositional environments (Umitsu, 1993). The coarse sediments were probably deposited in channels and the fining-upward sequences occurred during channel migration; the finer silt bands probably represent bank deposits (Umitsu, 1993; Goodbred and Kuehl, 2000; McArthur et al., 2004). Notably, the predominantly gray color of the Ambikanagar sediments, their fine texture, and presence of abundant micas are similar to sediments found elsewhere in the BDP of known Holocene age (Umitsu, 1993; Goodbred and Kuehl, 2000; Rowland et al., 2006).

Various studies have suggested that lignite/peat layers are abundant in the Indo-Gangetic sediments, although they mostly occur as dispersed lenses, and that they play an important role in various microbial processes (Goodbred and Kuehl, 2000; Ravenscroft et al., 2001; McArthur et al., 2004; Rowland et al., 2006). The peats were deposited in waterlogged back-channel deposits

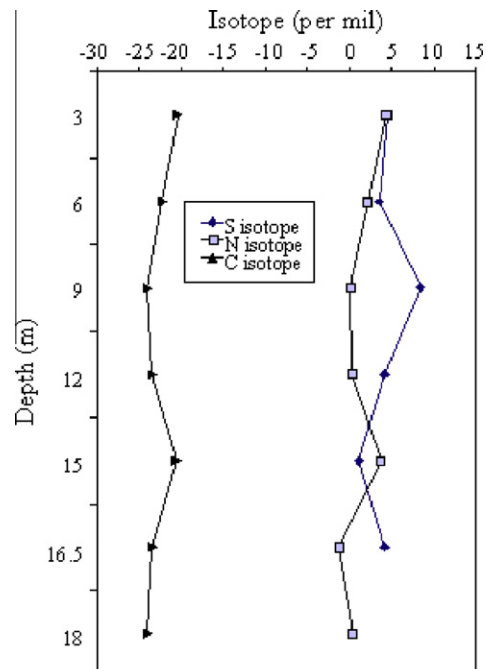


Fig. 7. $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ stable isotope values with depth in Ambikanagar sediments.

during the later stages of Quaternary sea-level changes (Umitsu, 1993; McArthur et al., 2004). Because the peat layers are widely dispersed, there is substantial heterogeneity in the distribution of organic matter in alluvial sediments (Ravenscroft et al., 2001; McArthur et al., 2004). The lack of black organic-rich layers in this shallow core from Ambikanagar suggests that the depositional environment was primarily riverine and not a swamp or marshland. The low % C (0.10–0.56%) and % N (0.01–0.05%) in the Ambikanagar sediments is not surprising because: (1) the distribution of organic matter in the BDP aquifer sediments is very heterogeneous, and high concentrations are primarily restricted to peat lenses (Ravenscroft et al., 2001; McArthur et al., 2004) and (2) alluvial

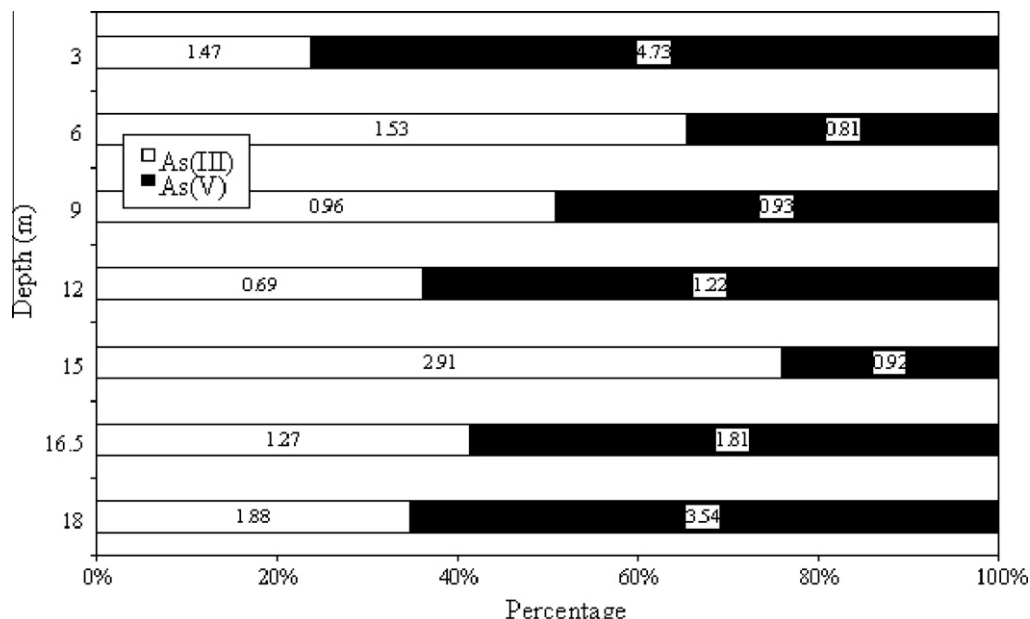


Fig. 6. Distribution of As^{3+} species in Ambikanagar sediments.

sediments typically contain degraded and reworked organic matter (Rowland et al., 2006).

Predominant terrestrial sources of organic matter in the BDP aquifer sediments (Ravenscroft et al., 2001; McArthur et al., 2004) imply that the C/N ratios should be high (>20; Meyers, 2003). Although there is hardly any input of algal or marine-derived organic matter; the C/N (atomic) ratios are decidedly low (8–15) in the Ambikanagar sediments. In the absence of different sources, it is most likely that microbial degradation of organic matter results in the low C/N ratio in sediments as a result of early diagenetic changes (e.g., Gälman et al. (2008) and references therein). Likewise, McArthur et al. (2004) suggest that organic matter in the BDP sediment influences sub-surface microbial processes, which drive the aquifers to anoxia and result in the subsequent release of As from sediments. Other studies have also invoked the role of microbial processes in organic matter and As cycling in the BDP sediments (Islam et al., 2004; Routh et al., 2005).

Estimating the reactivity of sedimentary organic matter based on detailed chemical and structural characterization, such as dividing organic matter into different compound classes such as proteins, lipids and carbohydrates (e.g., Rowland et al., 2006), could be helpful. However, chemical reactivity (and, therefore, As mobilization by microorganisms) has less to do with the presence or absence of these particular compounds than with *in situ* microbial communities and their enzymes. For example, lignin a dominant component in wood is commonly referred to as a recalcitrant material that is not susceptible to degradation (Kögel-Knabner, 2002). However, recent studies confirm that lignin is widely degraded on both short- and long-term scales (Dignac et al., 2005). Hence, it is not the compounds *per se*, but the presence of suitable enzymes in the relevant microbial community, which decide the fate of organic matter during early diagenesis.

4.2. Color and redox state of sediments

Some researchers have used the color of sediments as a proxy for redox state, where reddish sediments indicate oxidized and weathered conditions, as indicated by the presence of Fe-(hydr) oxide coatings on quartz, feldspar, and other mineral grains (Goodbred and Kuehl, 2000; McArthur et al., 2004; von Brömsson et al., 2007, 2008). The sediments investigated at this site vary in color

from reddish brown (at the surface) to various shades of gray (below 5 m). It is likely that the deeper samples have higher concentrations of reduced, amorphous Fe and Mn-oxides, which result in the dark color. Thus, fraction 2, which indicates the presence of Fe-oxides and is sensitive to redox conditions (Hjorth, 2004), is substantially different (ca. 3 times the concentration in the deeper sample at 15 m; Fig. 3) than fraction 4, in which Fe concentration is more or less the same at 3 m and 15 m. In this context, the results concur with previous studies, e.g., von Brömsson et al. (2008), which indicated that oxalate-extractable Fe and Mn contents are higher in the reduced (darker) unit than in the oxidized (reddish-brown) unit, where Fe and Mn are present in more crystalline phases. However, it must be cautioned that color-based prediction of redox status or characterization of chemical properties, e.g., high- or low-As aquifers, as suggested by Goodbred and Kuehl (2000) and von Brömsson et al. (2007, 2008), is purely qualitative.

Another property used as a proxy for estimating the redox status in sediments is the ratio between Fe and S (Bhattacharya et al., 2006). The Fe/S ratio (w/w) for these sediments calculated from the total (HNO₃) dissolution is shown in Fig. 8. The ratio is around 1000 in the two uppermost samples (which are above the water table); thereafter, the ratio decreases downwards to a minimum value at 12 m, and then it again increases. This trend is interpreted as downward decreasing redox potential until a minimum is reached at nearly 15 m; possible oxidizing conditions occur between 16.5 m and 18 m. A possible explanation could be that at 15 m the sediments are fine-grained material (consisting of 74% silt and 22% clay), which acts as a confining layer for the underlying aquifer. The aquifer below this depth is possibly recharged from a distant source, resulting in oxic conditions (McArthur et al., 2004). A similar explanation has been suggested in other groundwater systems to explain the redox status, *in situ* biogeochemical processes, and microbial survival in the deep sub-surface (McMahon and Chapelle, 1991; Routh et al., 2001).

4.3. Trace element distribution

Different physical and chemical factors in aquifer sediments, which play an important role in affecting the distribution of trace elements in Ambikanagar are: (1) grain size, (2) concentration of major oxides (Fe and Mn) and (3) sorption capacity. Sediment

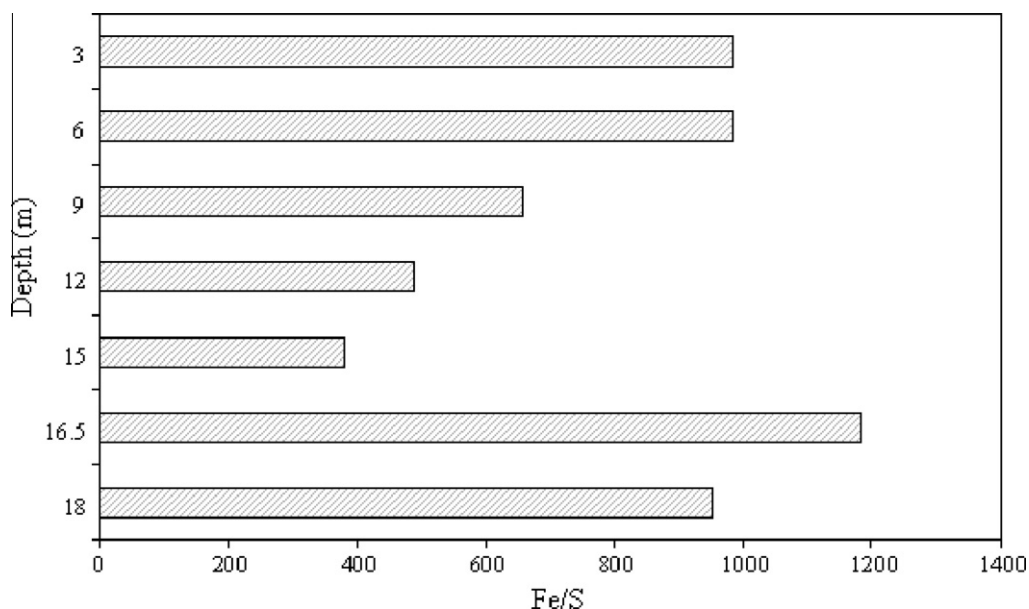


Fig. 8. Fe/S ratio in Ambikanagar sediments.

samples 1 and 5 (occurring at 3 m and 15 m, respectively) are fine-grained and, therefore, it is not surprising that they have the highest concentrations of different trace elements. A strong correlation between grain size and distribution of different trace and major elements in the BDP aquifer sediments has also been indicated in other studies (BGS and DPHE, 2001; Ravenscroft et al., 2001; Nath et al., 2008a,b).

The sediments in this study contain 2–7 mg kg⁻¹ of total As (Fig. 2), which is similar to the world average values for unconsolidated sediments (Smedley and Kinniburgh, 2002). This implies that the high concentration of As in Ambikanagar groundwater is not solely a consequence of aquifer sediment chemistry or anthropogenic input. Instead, this is a result of ongoing biogeochemical reactions in the sub-surface, which result in high As concentrations (see below). This is consistent with the conclusion of many other studies from the BDP aquifers (Nickson et al., 2000; Ravenscroft et al., 2001; BGS and DPHE, 2001; Smedley and Kinniburgh, 2002; Nath et al., 2008a).

The sediments have abundant carbonate content, which is evident from the high concentrations of Ca (15,000–34,000 mg kg⁻¹) and Mg (2700–3900 mg kg⁻¹) in fraction 1 of the sequential extraction procedure. This is also consistent with the high HCO₃⁻ (310–490 mg L⁻¹) and DOC (9–20 mg L⁻¹) concentrations in groundwater samples from nearby wells that were measured during reconnaissance sampling (Routh et al., 2004). Likewise, ESEM imaging of these samples indicates the occurrence of major elements in the proportion Ca > Si > Fe (Fig. 9).

Fraction 2 extracts are primarily (hydr)oxides, and consistent with this, high concentrations of Fe (2000–9700 mg kg⁻¹) and Mn (20–107 mg kg⁻¹) occur in these samples (Fig. 3). The correlation ($r = 0.81$) between As and Mn in fraction 2 suggests that As is adsorbed to Mn oxides. The correlation between As and Fe in fraction 2, however, fails to meet the 95% significance level. In contrast, As and Fe correlate well ($r = 0.89$, Table 3) in fraction 4. This may be due to the fact that very little As is extracted in fraction 2, and perhaps complexation of As with Mn oxides is preferred over Fe-oxides. Poor correlation between As and Fe in the BDP aquifers has been reported in other studies (Nickson et al., 2000; BGS and DPHE, 2001; McArthur et al., 2004), whereas others have indicated the opposite (von Brömsson et al., 2007; Nath et al., 2008a). The lack of covariance is suggested to be due to variable redox potential, which is controlled by sub-surface heterogeneity in lithology, *in situ* microbial communities, and presence of organic matter amongst many other factors, which result in vertical and

horizontal redox zoning in these aquifers (e.g., Wagner et al., 2005). Moreover, Fe-(hydr)oxides are more readily inclined to weathering and oxidation than Mn-(hydr)oxides in sedimentary environments and are therefore mobilized easily (von Brömsson et al., 2007).

Fraction 3 has low concentrations of all trace elements. This is consistent with the low concentrations of organic C and total S in these sediments. Finally, in fraction 4, As correlates well with many transition metals (Table 3). This implies most trace elements are associated within the crystalline silicate lattice, and are therefore less prone to weathering (Tessier et al., 1979; Martin et al., 1987; Hjorth, 2004).

4.4. Arsenic speciation

Because As speciation studies are rarely done in sediments, the results from this study cannot be compared to results from other studies in the Bengal Delta Plain. It seems As³⁺ concentrations coincide with the general redox state qualitatively inferred from proxy measurements (e.g., sediment color, Fe/S ratio). The presence of 24–74% As³⁺ species in these sediments seems unexpectedly high for shallow aquifer sediments (water table at ~5 m depth). It is hard to infer if the present trend is purely chemical, i.e., redox based, or a manifestation of ongoing biological processes, e.g., As⁵⁺ reduction (Ahmann et al., 1997; Oremland and Stolz, 2003). Application of rigorous statistical analyses on the geochemical data is unfortunately limited ($n = 7$ analyses in one core) to prove a redox mechanism as the key driver influencing the distribution of As ions in this aquifer. However, As⁵⁺ reducing microorganisms have been isolated from these aquifer sediments, which perhaps contribute to the presence of high As³⁺ concentrations in these sediments (Routh et al., 2005; Routh and Saraswathy, 2005). A similar conclusion has been drawn at other sites, whereby sub-surface microbial communities play a crucial role in As remobilization (Ahmann et al., 1997; Islam et al., 2004; Routh et al., 2007a,b).

Total As concentrations in the speciation study (with 10 M HCl) are similar, but slightly higher than, the concentrations of total As extracted with HNO₃ (Table 4). The results should have been opposite because HNO₃ digestion is a more rigorous method, which supposedly breaks down the crystalline structure to release trace elements. In essence, despite the fact that HCl extraction is a pseudo-total dissolution scheme, this method perhaps dissolves the residual fraction (crystalline structure) in sediments. Therefore, this method is probably unsuitable for investigating microbial remobilization (Routh et al., 2005; Routh and Saraswathy, 2005) because it may be too harsh. It is unlikely that microorganisms are breaking down the silicate structure to release As. Moreover, such acidic conditions are probably not very common in aquifer sediments under natural (pristine) conditions. For future speciation studies, a milder extractant, e.g., oxalate or phosphate (e.g., von Brömsson et al., 2007), followed by a chromatographic method for separating As³⁺ and As⁵⁺ species, would probably be more appropriate.

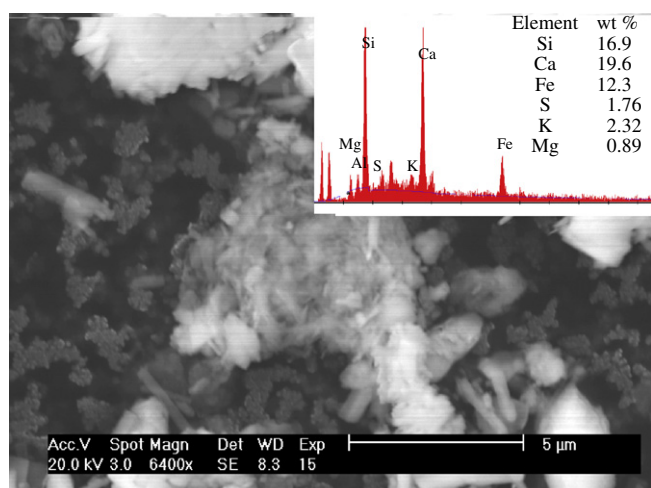


Fig. 9. ESEM imaging in wet mode illustrating the distribution of different elements based on EDAX X-emission spectrum in sediment sample 5.

Table 4

Arsenic concentration in samples during speciation (with HCl) and total (with HNO₃) extraction.

Depth (m)	As conc. (mg kg ⁻¹)	
	HCl	HNO ₃
3	6.20	5.45
6	2.32	2.36
9	1.89	1.62
12	1.92	1.39
15	3.83	4.44
16.5	3.08	1.90
18	5.42	3.93

4.5. Stable isotopes

The stable isotope measurements in this study serve as a proxy for organic matter source(s). In addition, they provide a better understanding of ongoing or extant biogeochemical reactions associated with microbial processes, and organic matter degradation in the sub-surface. Traditional microbial culturing techniques do not isolate >10% of the microbial communities (Chapelle, 2003) and are therefore restrictive in terms of the general insight they can provide about different ongoing biogeochemical processes. However, a combination of stable isotope measurements with advanced microbial culturing and genetic analyses can provide greater understanding of such complex processes in sedimentary environments.

The $\delta^{13}\text{C}$ value of sedimentary organic matter in these sediments is typical of a depositional environment consisting of terrestrial organic matter dominated by higher plants (Meyers, 2003). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values show a similar trend, and they indicate a maximum difference of $\sim 4\text{‰}$ between the fine and coarse-grained sediments. The high $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in samples 1 and 5 imply greater microbial activity in these intervals typical of early diagenetic changes in sedimentary environments. However, it is not necessary that a cause-and-effect relationship should always be evident in natural sediments, e.g. high Fe^{3+} reduction supported by the presence of higher $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. This is because of the simple fact that isotopic measurements are just a proxy for biogeochemical processes. Notably, both samples 1 and 5 are fine-grained, and they have organic matter content between 0.30% and 0.56% C, which is higher than other samples (0.10–0.14% C). It is possible that fermentation occurs in these sediments, resulting in higher $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. It has been demonstrated that fermentation in fine-grained sediments results in organic acid flux, which sustains microbial processes in aquifer sediments, e.g., Fe(III) and SO_4 reduction (McMahon and Chapelle, 1991; Routh et al., 2001; Chapelle, 2003). These microbial processes play an important role in As remobilization in sediments (Islam et al., 2004; McArthur et al., 2004).

Although these sediments have low S contents, enough reduced S was extracted to determine its $\delta^{34}\text{S}$ value, which ranges from 1‰ to 8.4‰ (Fig. 7). To the best of the authors' knowledge, this is the first study of S isotopes in BDP sediments. The results imply that SO_4 reducing conditions are prevalent in the shallow aquifer (Grossman and Desrocher, 2001; Choudhary et al., 2009). Sulfate reduction in the BDP aquifers has also been suggested in other studies (Zheng et al., 2004; Mukherjee and Fryar, 2008) based on different lines of geochemical and microbial evidence. The lack of SO_4 in these sediments suggests that it is rapidly consumed by ongoing microbial processes in the sub-surface, leaving behind the reduced sulfide fraction in sediments (Ulrich et al., 1998; Grossman and Desrocher, 2001). Nonetheless, investigation of the $\delta^{34}\text{S}$ of groundwater SO_4 is needed to decide whether the reduced S fraction in these sediments is biologically precipitated sulfide. Because microbial SO_4 reduction results in isotope fractionation of -19‰ to -45‰ , a $\delta^{34}\text{S}$ -value of about $+20\text{‰}$ or more in SO_4 can be interpreted as a sign that sulfides occurring in these sediments have precipitated biologically (Grossman and Desrocher, 2001). Because it was not possible to extract SO_4 from these samples such data are currently unavailable for this site. However, S isotope data from a nearby shallow well in Ambikanagar (3 sediment samples) indicate that $\delta^{34}\text{S}$ values for the oxidized and reduced S fractions in sediments are equal, i.e., within a few ‰ difference (Table 5; J. Routh and A. Bhattacharya, unpublished data). Lack of $\delta^{34}\text{S}$ fractionation implies that SO_4 that enters the system is quickly reduced (Grossman and Desrocher, 2001; Choudhary et al., 2009). Because most of the SO_4 is consumed, there is little isotopic fractionation. While precautions were taken

Table 5

Sulfur isotopes in sediments from a nearby well in Ambikanagar.

Depth (m)	$\delta^{34}\text{S}$	
	Oxidized S	Reduced S
1	8.01	8.25
20	3.64	−0.18
29	5.11	3.46

to preserve the original condition in sediments by preserving them in Anerocult™ bags and processing them as soon as possible (current study), the same precautions were not applied during reconnaissance sampling (samples listed in Table 5). These reconnaissance samples were air-dried in the open on a laboratory bench and stored at room temperature. In the process, some of the sulfide minerals may have oxidized, and consequently, enough SO_4 could be extracted from these sediments for S isotope analyses in both the sulfate and sulfide fractions. It is most likely that the sulfate fraction in these sediments retrieved during reconnaissance sampling is, in part or completely, a sample-handling artifact. It is, however, necessary to point the fact that although sulfide oxidation may have occurred in these sediments, this process exerts a minor effect on the $\delta^{34}\text{S}$ composition of sulfide minerals (Fry et al., 1995; Choudhary et al., 2009).

4.6. Arsenic (re)mobilization

The British Geological Survey (BGS and DPHE, 2001) pointed out that the high solid-solution ratio of As in aquifers makes the groundwater chemistry sensitive to small changes in sediment chemistry. In this context, it remains to be discussed if As can be actively (re)mobilized from these sediments by different biogeochemical interactions, e.g., oxidation of primary As-bearing minerals (Chakraborty et al., 2001), $\text{Fe}(\text{hydr})\text{oxide}$ reduction (Bhattacharya et al., 1997; Nickson et al., 2000), competition for adsorption sites (Smedley and Kinniburgh, 2002; Appelo et al., 2002), and/or other microbially mediated processes such as As^{5+} reduction (Ahmann et al., 1997; Islam et al., 2004; Routh and Saraswathy, 2005; Routh et al., 2005, 2007a,b).

The presence of As-bearing pyrite in aquifer sediments led various authors to invoke oxidation of pyrite as an important mechanism for release of As to groundwater (Das et al., 1996; Chakraborty et al., 2001). The present work does not support this interpretation because the groundwater in this area is generally reducing in nature. Likewise, the aquifer sediments are reducing (based on Fe/S ratio and color), and suggest the occurrence of SO_4 reduction (see above). Moreover, ESEM imaging of heavy minerals separated from the Ambikanagar sediments indicates the absence of pyrite/arsenopyrite (Fig. 9), consistent with other studies, which question the idea of pyrite oxidation in As remobilization from sediments (Nickson et al., 2000; McArthur et al., 2001; Nath et al., 2008b).

In Ambikanagar, As primarily occurs in the residual fraction of aquifer sediments. This fraction is less susceptible to weathering-related changes and, therefore, is less likely to contribute to the As pool in groundwater. A small fraction of total As is, however, associated with the oxide fraction in samples from 3, 12, 15 and 18 m depth intervals in this core (Fig. 2). In the remaining samples, As is absent (or below the instrumental detection limit) in the oxide fraction. The 18 m sediment interval may be oxidized from distal recharge of aerated groundwater (see above), and the samples at 3 m and 15 m occur in fine-grained sediments. The latter may serve as confining layers from which diffusion is likely to be very slow to transport As into groundwater. Hence, it seems unlikely that reduction of Fe- or $\text{Mn-}(\text{hydr})\text{oxides}$ contributes

significantly towards As release into groundwater at this site, unlike the conclusions of other studies (e.g., Bhattacharya et al., 1997; Nickson et al., 2000; McArthur et al., 2001; von Brömsson et al., 2007).

High concentrations (180–440 mg kg⁻¹) of P in fraction 2 of the sequential extraction suggest that competition for adsorption sites between PO₄³⁻ and As⁵⁺ could play a role in As mobilization. Likewise, HCO₃⁻ and Si(OH)₄ could compete with As for adsorption sites (Appelo et al., 2002; Smedley and Kinniburgh, 2002), and both solutes are abundant in Ambikanagar groundwater. Finally, DOC has been found to mobilize As in sorption experiments with hematite (Redman et al., 2002), and DOC concentrations are substantially high in Ambikanagar groundwater samples (9–20 mg L⁻¹; Routh et al., 2004). At present, the data are too limited in this study to infer the importance of these processes, and more analyses are needed.

Microbial processes involved in As cycling in the sub-surface include oxidation, reduction, and methylation reactions (Oremland and Stolz, 2003). Microbial processes are many times faster than abiotic reactions (Sohrin et al., 1997; Jones et al., 2000), and play an important role in transforming and mobilizing As (Ahmann et al., 1997; Macur et al., 2001; Islam et al., 2004). Microbial As⁵⁺ reduction is facilitated under anoxic conditions due to dissimilatory reduction, whereby As⁵⁺ is used as the terminal electron acceptor by anaerobic microorganisms (Ahmann et al., 1997; Newman et al., 1998; Oremland and Stolz, 2003). These microorganisms gain energy by coupling As⁵⁺ reduction with organic matter oxidation. Likewise, diverse microorganisms are capable of metabolizing As⁵⁺ for detoxification purposes under both aerobic and anaerobic conditions (Macur et al., 2001; Oremland and Stolz, 2003).

The presence of As⁵⁺ reducing microorganisms was confirmed in laboratory studies in this core from Ambikanagar (Routh et al., 2005; Routh and Saraswathy, 2005). These microbes were involved in As⁵⁺ reduction in laboratory incubations, which sharply ramped up within 1 week. High As³⁺ concentration correlated positively with bacterial growth in the cultures. Notably, the microbes tolerate high levels of As, and As⁵⁺ reduction occurs in sediments for detoxification and/ respiratory purposes (Routh et al., 2005). Therefore, it is likely that high As³⁺ concentration in Ambikanagar sediments and groundwater is a positive indication of microbial (re)mobilization of As in these aquifers. However, it is unknown to what extent these microorganisms are active in natural systems, and further investigations are needed. It is imperative to estimate the activity of *in situ* microbial communities through field-based measurements, and to understand the physico-chemical and biological conditions that favor these microbial processes. This could also provide a more credible alternative hypothesis towards geochemical remobilization of As in the BDP sediments. Finally, this and other studies (Ahmann et al., 1997; Macur et al., 2001; Routh et al., 2005, 2007b; Routh and Saraswathy, 2005) indicate that microbial As⁵⁺ reduction, if it is common, negates the value of the prediction of As species based simply on redox potential and equilibrium thermodynamics.

5. Conclusions

Grain size and redox conditions play an important role in the distribution of As and other elements in Ambikanagar sediments. Fine-grained sediments have high concentrations of most elements. Total As concentration in aquifer sediments ranges from 2 to 7 mg kg⁻¹; a considerable part of this occurs as As³⁺ species. It has been shown that As mostly occurs in the residual fraction on the basis of stepwise sequential extraction from different geochemical fractions. The residual fraction is less susceptible to

geochemical weathering and release of As in groundwater. The stable isotope records indicate microbial oxidation of organic matter, e.g., by SO₄ reduction. Biogeochemical i.e., bacterially mediated, processes are likely to play a role in regulating As (re)mobilization at this site.

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