ORIGINAL ARTICLE

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Distribution of arsenic and other trace elements in the Holocene sediments of the Meghna River Delta, Bangladesh

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Abstract Geochemical study of the Holocene sediments of the Meghna River Delta, Chandpur, Bangladesh was conducted to investigate the distribution of arsenic and related trace and major elements. The work carried out includes analyses of core sediments and provenance study by rare earth element (REE) analysis. Results showed that the cores pass downward from silty clays and clays into fine to medium sands. The uppermost 3 m of the core sediments are oxidized [average oxidation reduction potential (ORP) + 230 mV], and the ORP values gradually become negative with depths (−45 to −170 mV), indicating anoxic conditions prevail in the Meghna sediments. The REE patterns of all lithotypes in the study areas are similar and are comparable to the average upper continental crust. Arsenic and other trace elements (Pb, Zn, Cu, Ni, and Cr) have greater concentrations in the silts and clays compared to those in the sands. Positive correlation between As and Fe was found in the sediments, indicating As may be adsorbed on Fe oxides in aquifer sediments.

Keywords Meghna River Delta · Arsenic · Sediment · Groundwater · Bangladesh

Introduction

Arsenic contamination of groundwater in sedimentary aquifers is a global concern. High concentrations of naturally occurring As have been reported in groundwater from many regions, including Bangladesh, India, Nepal, Thailand, China, Taiwan, Vietnam, Chile, Hungary, and parts of the USA (Smedley and Kinniburgh 2002; Garcia-Sanchez and Alvarez-Ayuso 2003). Among these, arsenic contamination of groundwater in large areas of Bangladesh and West Bengal, India has received much attention (Dhar et al. 1997; Mukherjee and Bhattacharya 2001). In that area, the most serious arsenic hazard occurs in Ganges and Meghna deltaic sediments in Bangladesh (Ishiga et al. 2000; Yamazaki et al. 2000; Ahmed et al. 2004).

Sediments act as both sources and sinks of As and other toxic trace elements (Guern et al. 2003), and the fate of trace metals is dependent on the biogeochemical transformations that occur in the sediments (Peltier et al. 2003). Arsenic is widely distributed as a trace constituent in rocks and soils, natural waters and organisms, and can be mobilized by weathering and microbial activity (Garcia-Sanchez and Alvarez-Ayuso 2003). Moreover, redox conditions and the availability of possible carrier phases also account for mobility and toxicity of As in natural environments (Fabian et al. 2003). It has been shown that Fe (oxy)hydroxides are a major carrier phase of adsorbed As in nature (Nickson et al. 2000; McArthur et al. 2001; Ravenscroft et al. 2001). Sullivan and Aller (1996) also noted that the diagenetic distribution of As in the geologic environment may be controlled by the redox behavior of Fe (oxy)hydroxide phases in sediments.

Over the last few decades, many geochemical studies have been directed at sediments to determine the extent

of contamination caused by As (e.g., Sullivan and Aller 1996; McArthur et al. 2001). Studies have shown that oxides and organic matter play an important role in elemental distributions in the sediments. The geochemistry of Holocene sediments is significant due to limited alteration during burial, diagenesis, and tectonic deformation, and may provide a continuous record of environmental changes (Ishiga et al. 2000). Geochemical analyses of the Holocene alluvial sediments have thus been carried out from several parts of Bangladesh to elucidate the behavior of As in differing sedimentary environments (Yamazaki et al. 2000; Akai et al. 2004).

The incidence of As contamination in Chandpur district is among the greatest in Bangladesh, as waters from 90% of the tube wells in the area exceed the Bangladesh As groundwater standard of 0.05 ppm (BGS and DPHE 2001; Smedley and Kinniburgh 2002; Ahmed et al. 2004). Such groundwater is used for drinking and extensive irrigation by many households, and thus constitutes a human health risk. Some 96% of the tube wells in Haziganj, 90% in Chandpur Sadar, and 80% in Matlab contain high levels of As (> 0.05 ppm), and over 3,000 patients affected by arsenic were identified in the Chandpur district alone (Islam 2003). Few studies, however, have considered the vertical distribution of major and trace elements in the Chandpur district. Such study is required to clarify the geological background of As contamination in the Meghna River Delta. Three sediment cores were collected from the Matlab North, Matlab South and Haziganj areas to determine geochemical compositions and distribution patterns, and to evaluate the provenance in the study areas. The results show that As concentrations are greater in the silts and clays than in the sands.

Materials and methods

Bangladesh is a low-lying country at the head of the Bay of Bengal, and occupies most of the Bengal Basin. Most of the country consists of low alluvial, coastal, and deltaic plains, and lies within an elevation of 20 m above sea level. The sediments are derived from three major rivers, the Ganges, the Brahmaputra, and the Meghna, and form the largest delta complex in the world. The study sites are in the Chandpur district of southeastern Bangladesh (Fig. 1). The district has a total area of about 1,671 km^2, and lies between 23°N–23°30′N and 90°35′E–91°E, about 65 km southeast of the capital, Dhaka. The Meghna River flows through the district from north to south, whereas the tributary Gumti River snakes through the middle part of the study area. The present deltaic Meghna, which combines the flow of the Ganges and the Meghna, is the largest river in Bangladesh, and discharges into the Bay of Bengal. The sampling area is characterized by sub-tropical climate. Deep tube wells were constructed for extensive irrigation and drinking water supply in the region, but shallow hand pump waters are also used for drinking water by many households.

Chandpur is composed of Holocene sediments of the Meghna River floodplain, deposited close to the present river course and downstream of its confluence with the Ganges (Fig. 1). The Meghna plain consists of alluvial sediments, mainly silt and clay, with lesser fine- to medium-grained sand. The sediments extend to variable depths, and are overlain by a shallow clay layer in the centers of some basins (Brammer 1996). The upper 60 m of exposed Holocene deposits consist mostly of yellow brown or gray silt and clay, and are more consolidated than the active floodplain sediments deposited at the mouth of the Ganges and Meghna rivers. Shallow aquifers are generally unconfined or semi-confined, whereas the deep aquifers are mostly confined by impervious clay layers.

Analytical procedures

Sample collection and preservation

Sediment cores were taken at three locations (Cp1, Panchani; Cp2, Nabakalash and Cp3, Tungirpar; Fig. 1), using the rotary drill Percussion Reverse Circulation (PRC) method. Depths of the cores ranged between 35 and 54 m. About 200 g of wet sediments were collected for each sample and packed in zip-Lock bags. A total of 41 sediment samples were collected from the cores, and ORP was measured, using a Horiba U-23 ORP meter. The samples were stored at 4°C in a cooler box for transport to the laboratory. These cores were logged, photographed and the layers were visually classified during sampling.

Sample preparation and analysis

Approximately, 50 g of each sediment sample were dried in an oven at 110°C for 24 h. The dried samples were then ground for 20 min in an automatic agate mortar and pestle. The powdered samples were later compressed into briquettes using a force of 200 kN for 60 s.

X-ray fluorescence analysis

Selected major oxide [Fe_2O_3*(total iron is expressed as Fe_2O_3*), TiO_2, CaO, and P_2O_5], total sulfur (TS) and trace element (As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, and U) concentrations were determined by X-ray fluores-

Fig. 1 Location of the study sites in Chandpur, Bangladesh
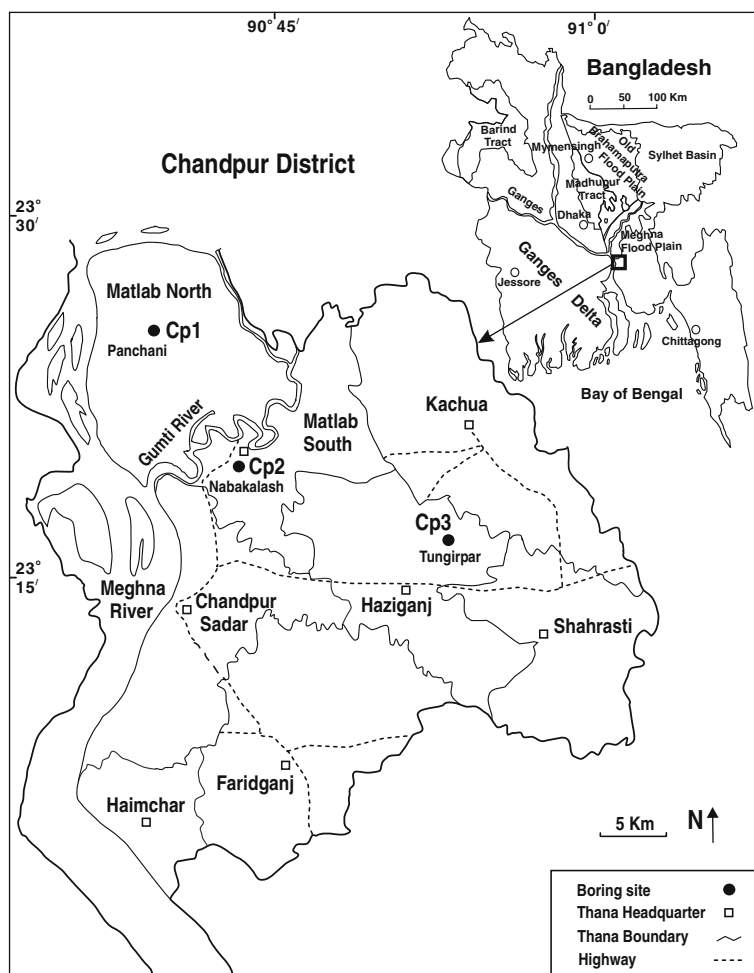
cence (XRF) at Shimane University, using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd.) equipped with a Rh-anode X-ray tube. All analyses were made on pressed powder briquettes, following the method of Ogasawara (1987). Average errors for all elements are less than ± 10% relative. Analytical results for USGS standard SCo-1 (Cody Shale) were acceptable compared to the proposed values of Potts et al. (1992).

Instrumental neutron activation analysis

Rare earth element (REE: La, Ce, Sm, Eu, Gd, Tb, Yb, and Lu) and other trace element concentrations (Sc, Hf, Ta, Th, Cs, Sb, and Rb) in 13 selected samples were determined by instrumental neutron activation analysis (INAA) at the Research Reactor Institute, Kyoto University. Sample preparation, analytical methods and precision are described by Musashino (1990). Average errors for these elements are less than ± 10%, and the results are acceptable when compared with values for the Geological Survey of Japan standard JA2 as given in Potts et al. (1992). The

Eu anomaly (Eu/Eu*) was calculated following the formula given by Condie (1993): $Eu/Eu* = Eu_N/(Sm_N \times Gd_N)^{1/2}$, where $Gd = (Sm \times Tb^2)^{1/3}$ and N = chondrite normalized concentrations.

Results

Sediment characteristics

Areas in Bangladesh affected by arsenic are mainly confined to the Holocene alluvial aquifers at shallow and intermediate depths (BGS and DPHE 2001; Mukherjee and Bhattacharya 2001), as reported by Acharyya et al. (2000) for West Bengal, India. The Meghna sediments in Bangladesh are rich in quartz, mica, feldspar, calcite, and dolomite (Anawar et al. 2002). Characteristics of the core sediments (Cp1, Cp2, and Cp3) from surface to depths of 35 and 54 m are shown in Fig. 2. The stratigraphic sequence consists of silty clays and clays at top, passing downward into light to gray fine- to medium-grained sands. The fining upward sequence seen in all three cores
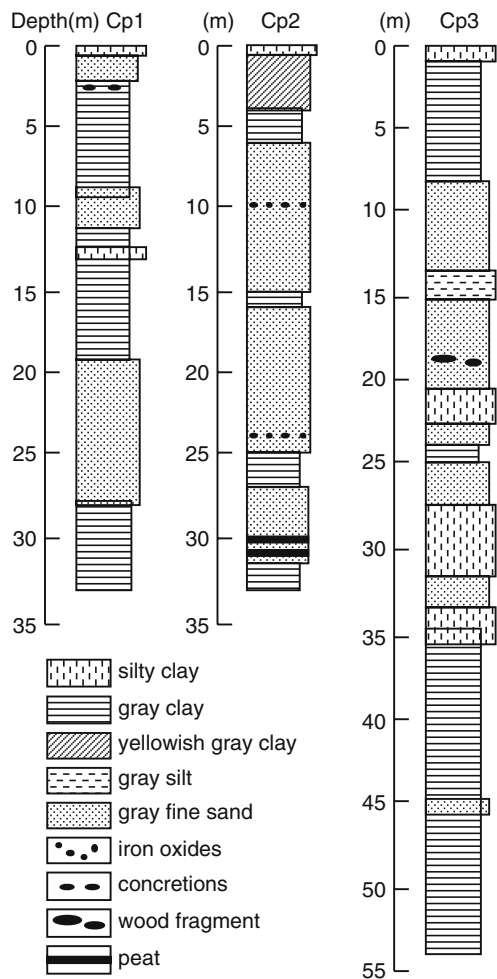
Fig. 2 Columnar sections of Holocene sediments in Chandpur (Cp1, Cp2, and Cp3)

indicates a fluvial environment of deposition, as suggested by Ahmed et al. (2004). The uppermost layers commonly consist of yellowish brown silty clays. Color typically changes from yellowish brown to dark gray and olive gray within the shallow depth of the aquifers. The aquifer sediments become gray when reduction of Fe (oxy)hydroxides is complete and the entire load of sorbed As is released to solution (McArthur et al. 2004).

The fine-grained sediments prevalent in the Cp1, Cp2, and Cp3 cores are relatively rich in organic matter, representing over-bank facies. Clay layers occur from 2–9, 12–19 and 28–33 m in core Cp1; from 1–6, 15–16, 25–27 and 32–33 m in Cp2, and at 1–8, 24–25 and 35–54 m in Cp3. The uppermost 3 m of the sediments in Cp1 and Cp3 are oxidized (average ORP + 180 and + 220 mV, respectively), and ORP values gradually become negative with increasing depth (Cp1, −60 to −140 mV; Cp3, −100 to −150 mV). These low ORP values indicate anoxic conditions in the sediments.

Fine sands are more abundant in the aquifers at depths of about 6–30 m in Cp2 and 8–35 m in Cp3. The upper silty clay layers (0–3 m) of core Cp2 were oxic (average ORP + 290 mV). Below this layer, the oxic sands (ORP + 40 to + 230 mV) extend down to a depth of 15 m. However, intercalated anoxic clay (ORP −45 and −170 mV) and fine sand layers were observed from 15 to 33 m depth. In the same core, thin black peat bands were present at 30 and 31 m below surface in the anoxic zone. The sections immediately above and below the peat were fine sands. However, the peat samples were not analyzed in this study.

The aquifer in the investigated area is composed of well-sorted quartz sands containing mica flakes, and is occasionally enriched in biotite. Oxide and carbonate concretions rich in ferruginous minerals (e.g., Fe-coated quartz and Fe oxide) were observed mainly in the sandy layers.

Major and trace elements

Elemental compositions of the core sediments analyzed by XRF are given in Table. 1 and 2. Abundances of Fe_2O_3 (6.19–9.46 wt%) and TiO_2 (0.60–0.82 wt%) in the silts and clays are greater than those in the sands (Fe_2O_3 4.01–7.72 wt%; TiO_2 0.47–0.67 wt%, except sample Cp3-6). In contrast, CaO contents tend to have slightly greater concentrations in sands (1.36–2.22 wt%) than those of the clays (1.08–2.05 wt%). Anomalously high Fe_2O_3 (15.4 wt%) and TiO_2 (0.92 wt%) concentrations were found in a blackish sand sample (Cp3-6) is rich in biotite. TS concentrations generally ranged from 0.05 to 0.11 wt%, though some samples have lower values (< 0.05 wt%). Abundances of P_2O_5 were generally low (0.09–0.16 wt%). The highest P_2O_5 value (0.21 wt%) was observed in the same blackish sandy layer (Cp3-6) at a depth of 13 m.

Most trace elements are enriched in the clays relative to the sands, e.g., As (ranging from 6.2 to 26 ppm in the clays; 3.6 to 8 ppm in the sands, excluding Cp3-6), Pb (19–27 ppm; 18–21 ppm), Zn (64–143 ppm; 41–76 ppm), Cu (17–48 ppm; 6–16 ppm), Ni (39–84 ppm; 26–50 ppm), Cr (72–126 ppm; 83–111 ppm), and V (116–194 ppm; 83–140 ppm). In contrast, Sr is enriched (148–177 ppm) in the sands relative to the clayey sediments (111–163 ppm). The Cu contents show large fluctuations (range 8–48 ppm) within the core Cp2. Ni averages 56 ppm, with a range of 26–75 ppm in the same core. Exceptionally, sand sample Cp3-6 has greater concentrations of As (15 ppm), Pb (24 ppm), Zn (127 ppm), Cu (25 ppm), Ni (78 ppm), Cr (101 ppm), V (243 ppm), Nb (14 ppm), Y (38 ppm), and U (6 ppm) at 13 m depth, possibly because it consists of blackish very fine micaceous sand rich in biotite.

Table 1 Major and trace element compositions of the cores Cp1 and Cp2, Chandpur

Sample no.	Depth (m)	Lithology	Major oxides (wt%)				Trace elements (ppm)											TS (wt%)
			TiO_2	Fe_2O_3	CaO	P_2O_5	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Y	Nb	U	
Matlab (North)																		
Cp1-0	0	Silty clay	0.70	7.21	1.19	0.14	6.2	20	81	28	51	99	139	158	33	13	4	0.05
Cp1-1	3	Clay	0.78	7.89	1.89	0.13	8.0	20	89	32	58	102	164	151	38	15	4	0.05
Cp1-2	5	Clay	0.71	7.22	2.05	0.14	6.8	20	79	27	51	111	144	163	35	14	4	0.05
Cp1-3	9	Sand	0.66	5.59	2.22	0.15	5.0	18	57	14	37	111	118	174	31	12	4	< 0.05
Cp1-4	12	Clay	0.77	8.22	1.86	0.14	9.1	21	95	36	64	107	168	148	38	15	5	0.05
Cp1-5	14	Clay	0.79	7.99	1.87	0.14	8.4	21	92	38	63	107	162	150	38	15	4	0.05
Cp1-6	18	Clay	0.76	8.02	1.93	0.13	8.7	19	90	34	57	105	160	152	36	15	4	0.05
Cp1-7	28	Clay	0.69	6.89	1.62	0.09	11.0	20	82	32	57	93	152	147	36	14	5	0.05
Cp1-8	29	Clay	0.76	7.79	1.70	0.12	9.5	22	86	34	52	93	149	134	39	15	5	0.06
Matlab (South)																		
Cp2-0	0	Silty clay	0.70	7.22	1.71	0.15	9.6	21	143	33	56	89	146	140	35	13	5	< 0.05
Cp2-1	1	Clay	0.77	7.47	1.42	0.14	7.2	22	101	40	66	105	161	132	38	15	5	< 0.05
Cp2-2	2	Clay	0.74	7.70	1.55	0.10	8.2	21	86	31	59	102	158	138	36	15	5	< 0.05
Cp2-3	3	Clay	0.74	8.55	1.46	0.11	11.0	23	99	38	67	112	170	127	39	15	5	< 0.05
Cp2-4	4	Clay	0.71	8.43	1.47	0.16	26.0	23	92	33	60	105	166	129	38	15	5	< 0.05
Cp2-5	9	Sand	0.47	4.20	2.15	0.13	3.6	19	42	9	26	98	84	177	24	8	3	< 0.05
Cp2-6	13	Sand	0.51	4.01	2.02	0.14	3.6	19	41	8	26	89	83	176	25	8	3	< 0.05
Cp2-7	16	Clay	0.72	7.29	1.77	0.12	8.1	22	83	29	57	98	140	139	36	14	4	0.06
Cp2-8	22	Sand	0.54	5.86	1.60	0.09	6.2	20	62	13	44	92	99	163	26	9	5	< 0.05
Cp2-9	26	Clay	0.81	9.10	1.83	0.13	11.0	23	100	44	63	113	182	134	40	16	5	0.08
Cp2-12	32	Clay	0.76	9.28	1.48	0.11	9.6	24	107	48	75	117	194	135	39	14	5	0.06
Cp2-13	33	Clay	0.73	8.89	1.53	0.11	8.6	24	103	42	71	114	185	141	38	14	5	0.05

Rare earth elements

Analyses of REE (La, Ce, Sm, Eu, Gd, Tb, Yb, and Lu) and other minor elements (Sc, Hf, Ta, Th, Cs, Sb, and Rb) were made in selected samples to evaluate the possibility of change in source materials. The REE data were normalized to chondrite (Taylor and McLennan 1985) and compared with average upper continental crust (UCC). All samples show enrichment in light rare earth elements (LREE; average $La_N/Sm_N = 3.4$) over

Table 2 Major and trace element compositions of the core Cp3, Chandpur

Sample no.	Depth (m)	Lithology	Major oxides (wt%)				Trace elements (ppm)											TS (wt%)
			TiO_2	Fe_2O_3	CaO	P_2O_5	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Y	Nb	U	
Haz4ganj																		
Cp3-0	0	Silty clay	0.74	7.41	1.36	0.15	12.0	21	99	20	50	90	141	126	37	15	5	0.05
Cp3-1	1	Clay	0.65	6.45	1.39	0.10	9.1	19	70	17	39	72	121	133	33	14	4	< 0.05
Cp3-2	4	Clay	0.75	8.34	1.56	0.11	14.0	22	88	33	54	97	162	131	39	15	5	0.10
Cp3-3	5	Clay	0.60	6.19	1.57	0.12	6.9	21	64	17	40	87	116	141	30	10	4	0.05
Cp3-4	6	Clay	0.71	7.69	1.60	0.11	10.0	22	84	28	49	91	142	140	36	14	5	0.07
Cp3-5	10	Sand	0.55	4.52	1.76	0.11	5.8	18	43	6	26	83	89	149	26	9	4	< 0.05
Cp3-6	13	Sand	0.92	15.4	1.36	0.21	15.0	24	127	25	78	101	243	114	38	14	6	< 0.05
Cp3-7	14	Silt	0.78	8.52	1.68	0.13	17.0	24	90	40	55	92	157	142	39	15	5	0.11
Cp3-8	19	Sand	0.56	5.69	1.76	0.10	6.2	21	57	15	37	94	100	155	26	9	4	0.08
Cp3-9	20	Sand	0.67	7.72	1.68	0.14	8.0	20	76	16	50	88	140	148	28	10	4	0.08
Cp3-10	22	Silty clay	0.82	8.32	1.84	0.12	10.4	22	91	37	55	98	163	135	40	16	5	0.07
Cp3-11	25	Clay	0.77	8.46	1.51	0.11	11.1	23	98	35	61	106	164	129	39	16	5	0.07
Cp3-12	29	Silty clay	0.79	8.48	1.57	0.11	10.3	23	93	40	63	110	167	133	39	16	5	0.06
Cp3-13	31	Silty clay	0.80	8.73	1.55	0.11	10.6	24	98	42	66	112	175	134	40	16	5	0.06
Cp3-14	35	Clay	0.81	9.01	1.50	0.11	10.4	23	103	42	72	118	180	133	40	16	5	0.06
Cp3-15	38	Clay	0.80	8.49	1.35	0.11	10.7	25	97	39	75	118	177	124	37	15	5	0.07
Cp3-16	43	Clay	0.79	8.50	1.42	0.11	11.5	26	98	38	73	119	180	127	38	15	5	0.08
Cp3-17	49	Clay	0.71	8.75	1.12	0.09	11.0	25	103	40	80	122	176	116	37	14	5	0.06
Cp3-18	52	Clay	0.75	9.15	1.08	0.13	11.3	27	108	39	84	125	193	111	38	14	5	0.07
Cp3-19	54	Clay	0.74	9.46	1.11	0.09	11.0	27	106	41	83	126	194	114	39	14	5	0.07

heavy rare earth elements (HREE; average Gd_N/Yb_N = 1.3) with negative Eu anomalies (average Eu/Eu^* = 0.62). Results are shown in Table 3.

Discussion

Evaluation of provenance

REE patterns have been used extensively in recent years for evaluation of provenance (Taylor and McLennan 1985; Condie 1993; McLennan et al. 1993; Roser 2000). The patterns of the analyzed samples are characterized by steep inclination from middle to light REE (average La_N/Sm_N = 3.4), clear depletion in Eu (av. Eu/Eu^* = 0.62) compared to other middle REE to heavy REE and gentle inclination from middle to heavy REE (av. Gd_N/Yb_N = 1.3). These values are comparable with those of average UCC (Fig. 3, La_N/Sm_N = 3.2, Eu/Eu^* = 0.59 and Gd_N/Yb_N = 1.7; Condie 1993). All samples exhibit similar REE patterns, reflecting the homogeneous composition of Holocene sediments in the Ganges delta (Rahman and Ishiga 1999). Th/Sc ratios

(average 2.17) greater than the value of UCC (0.97; Condie 1993, about 1.0; Taylor and McLennan 1985) indicate a felsic source.

Vertical profiles of major and trace elements

Distributions of major and trace elements are mainly controlled by a variety of factors including sediment texture, source-rock mineralogy, and geochemical process (Abraham 1998). Fine-grained clays are enriched in trace metals, as they possess higher surface areas than coarser grains (Padmalal et al. 1997; Singh et al. 2005). Factors controlling the spatial sediment composition can be broadly considered in terms of source effects, processes that occur during transport and deposition, and post-depositional processes (Norman and De Deckker 1990).

Depth-wise variation of trace elements shows moderate trend in core Cp1 (Fig. 4). Vertical distribution of As in this core is similar to that of iron, while from 15 m downwards it shows a less consistent trend. Cu and Zn decrease sharply at 9 m depth, and concentrations of

Table 3 Distribution of REE and other trace elements in the cores Cp2 and Cp3, Chandpur

Sample no.	Cp3-0	Cp3-1	Cp3-3	Cp3-4	Cp3-5	Cp3-6	Cp3-7	Cp3-11	Cp3-13	Cp3-15	Cp3-17	Cp3-19	Cp2-4
REE (ppm)													
La	47.0	51.0	33.0	44.0	49.0	23.0	47.0	47.0	55.0	47.0	43.0	41.0	40.0
Ce	96.0	101.0	66.0	89.0	94.0	45.0	88.0	92.0	109.0	100.0	91.0	77.0	80.0
Sm	8.3	9.1	6.2	8.5	8.1	4.9	9.2	8.5	10.1	8.9	8.1	7.8	6.4
Eu	1.4	1.5	1.1	1.4	1.2	1.1	1.4	1.4	1.7	1.5	1.4	1.3	1.2
Gd	1.7	1.8	1.2	1.6	1.8	1.4	1.8	1.7	2.0	1.8	2.0	2.1	1.4
Tb	0.8	0.8	0.5	0.7	0.9	0.7	0.8	0.8	0.9	0.8	1.0	1.1	0.7
Yb	4.1	4.4	2.9	4.0	2.8	2.7	3.7	4.2	4.7	4.4	3.0	2.8	3.5
Lu	0.5	0.6	0.4	0.5	0.4	0.4	0.5	0.5	0.6	0.5	0.6	0.5	0.4
Chondrite normalized													
La	128.0	139.0	90.0	120.0	135.0	63.0	128.0	127.0	149.0	127.0	116.0	113.0	109.0
Ce	100.0	106.0	69.0	93.0	99.0	47.0	92.0	96.0	114.0	105.0	96.0	81.0	83.0
Sm	35.7	39.3	27.0	36.7	35.3	21.4	39.7	36.8	43.8	38.6	35.0	34.0	27.6
Eu	15.9	16.7	13.0	16.2	14.0	12.3	16.2	16.1	19.2	17.3	15.8	15.3	13.8
Gd	18.4	20.1	13.3	17.8	19.9	14.9	19.3	18.8	22.1	19.1	21.3	22.7	15.4
Tb	13.2	14.4	9.3	12.4	14.9	12.5	13.5	13.4	15.7	13.4	16.6	18.6	11.5
Yb	16.7	17.6	11.8	16.0	11.2	10.7	14.8	16.9	18.8	17.6	12.2	11.5	14.2
Lu	13.1	14.7	9.5	14.3	10.6	11.0	14.4	13.5	16.5	13.7	14.5	12.6	10.2
Eu/Eu^*	0.62	0.60	0.69	0.63	0.53	0.69	0.59	0.61	0.62	0.64	0.58	0.55	0.67
Th/Sc	2.6	2.6	2.2	2.9	1.9	0.8	2.3	2.3	2.3	2.2	1.6	1.4	3.2
La_N/Sm_N	3.6	3.5	3.3	3.3	3.8	2.9	3.2	3.4	3.4	3.3	3.3	3.3	4.0
Gd_N/Yb_N	1.1	1.1	1.1	1.1	1.8	1.4	1.3	1.1	1.2	1.1	1.7	2.0	1.1
La_N/Yb_N	7.7	7.9	7.6	7.5	12.0	5.9	8.6	7.5	7.9	7.2	9.5	9.9	7.7
Trace elements (ppm)													
Sc	8.4	8.6	7.0	7.4	13.1	11.6	9.4	9.9	12.1	10.6	14.4	15.0	5.7
Hf	7.6	8.6	5.1	7.2	8.5	3.4	6.4	6.1	7.4	7.3	5.1	3.7	5.4
Ta	1.5	1.3	1.1	1.4	1.1	1.5	1.5	1.4	1.6	1.4	1.3	1.1	1.4
Th	21.7	22.6	15.1	21.3	24.7	9.6	21.4	22.8	28.2	23.5	22.8	20.9	18.2
Cs	9.3	7.4	7.3	10.5	5.1	21.7	10.0	11.0	12.4	12.3	15.0	14.0	10.5
Sb	0.6	0.7	0.7	1.0	0.4	1.1	0.7	0.8	0.7	0.7	1.0	1.0	0.7
Rb	174.0	154.0	162.0	209.0	144.0	301.0	186.0	202.0	222.0	192.0	231.0	215.0	167.0

$Eu/Eu^* = Eu_N(Sm_N \times Gd_N)^{1/2}$, where $Gd = (Sm \times Tb^2)^{1/3}$ and N = chondrite normalized concentrations (after Taylor and McLennan 1985)

Fig. 3 Chondrite-normalized REE patterns for sediments from cores Cp2 and Cp3, Chandpur, Bangladesh. UCC and Chondrite normalizing factors from Taylor and McLennan (1985)
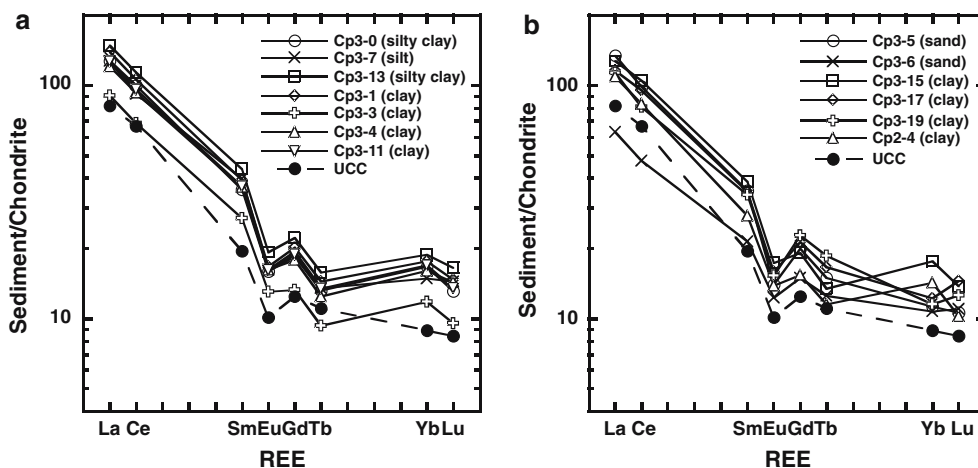
both metals then increase to maxima of 36 and 95 ppm at 12 m depth, respectively. CaO and Sr show similar trends in core Cp1.

As and Fe exhibits similar vertical distribution in core Cp2 (Fig. 5). From the bottom of the core to the surface, Zn increases irregularly upward, and reaches its highest value (143 ppm) in the uppermost sample. Cr also displays an irregular trend from base to the top core. Cu, Ni, and Zn have strong affinity to organic matter, Fe oxides and clay minerals (Tessier et al. 1994; Tribovillard et al. 1994; Singh et al. 2005). Therefore, the vertical profiles of As, Fe, Cu, Zn, and Ni have similarities throughout the cores. The sandy character of sediments reduces their adsorptive properties, leading to

reduction of metal levels in sediments from the Cp2 core.

Arsenic and iron are distributed randomly, with general increase in the upper part of the core Cp3 (Fig. 6). A suite of trace elements (Zn, Ni, and V) are enriched in the blackish micaceous sand sample rich in biotite at 13 m, just above the silt layer. The trends of these traces are similar to Fe, which shows a strong spike in concentration at the same depth. Trace metals are probably controlled by the presence of Fe oxides (Preda and Cox 2002) as Fe (oxy)hydroxides have high affinity for trace metals (Tessier et al. 1994).

Trace element concentrations in core samples collected from the Old Brahmaputra River plain in

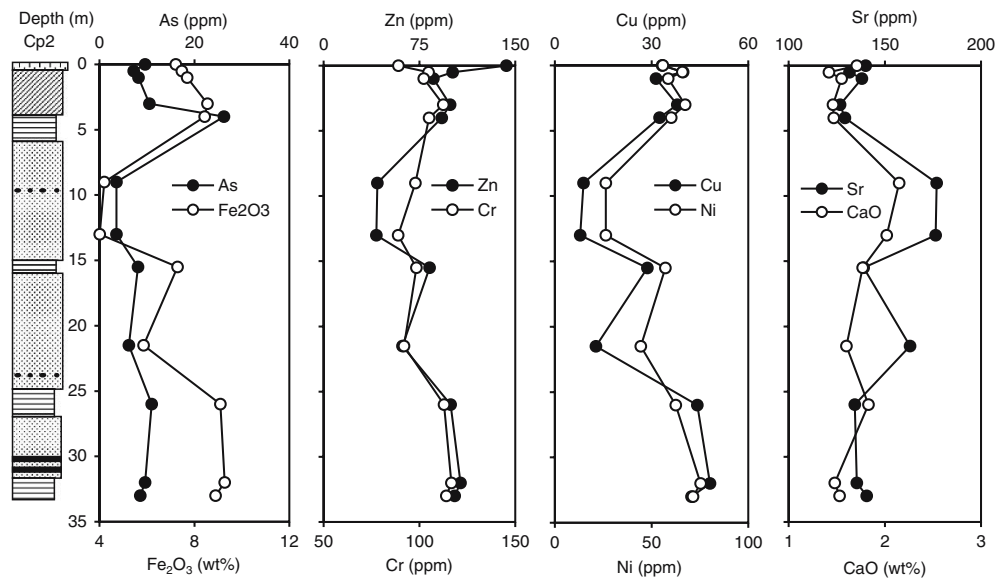**Fig. 4** Vertical distribution of As, Fe$_2$O$_3$, Zn, Cu, Sr, and CaO in core Cp1, Chandpur
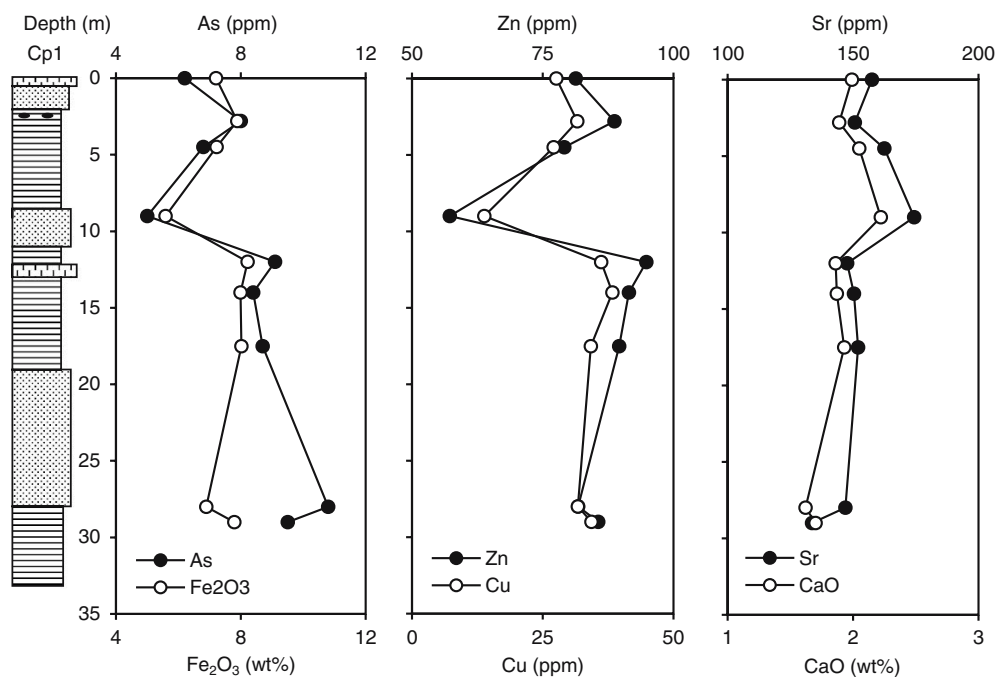
Fig. 5 Vertical distribution of As, Fe2O3, Zn, Cr, Cu, Ni, Sr, and CaO in core Cp2, Chandpur

Mymensingh district (average As 10 ppm, Cu 29 ppm, Zn 74 ppm, Ni 48 ppm, and V 137 ppm; Ishiga et al. 2000) are similar to those in Chandpur district (average As 10 ppm, Cu 31 ppm, Zn 88 ppm, Ni 57 ppm, and V 154 ppm). However, these concentrations are greater than that of UCC (average As 1.5 ppm, Cu 25 ppm, Zn 71 ppm, Ni 20 ppm, and V 60 ppm; Taylor and McLennan 1985). As there are no industries in the vicinity of the study areas and no known point sources for trace element enrichment in the sediments, it is therefore likely the sources of elements are the sediment matrix (e.g., weathering of bedrock) homogenized by

transport as well as aquifer conditions (oxic or anoxic). Singh et al. (2005) also noted that mineral sorting during fluvial transportation and deposition controls major and trace elements distribution in the Ganges alluvial plain weathering products.

Characteristics of As in sediments

The clays contain 6.2–26 ppm As, while contents in the sands (3.6–8 ppm) are half to one-third lower (Tables 1, 2). These results are comparable to data for samples

Fig. 6 Vertical distribution of As, Fe2O3, Zn, Cr, Cu, Ni, V, and P2O5 in core Cp3, Chandpur
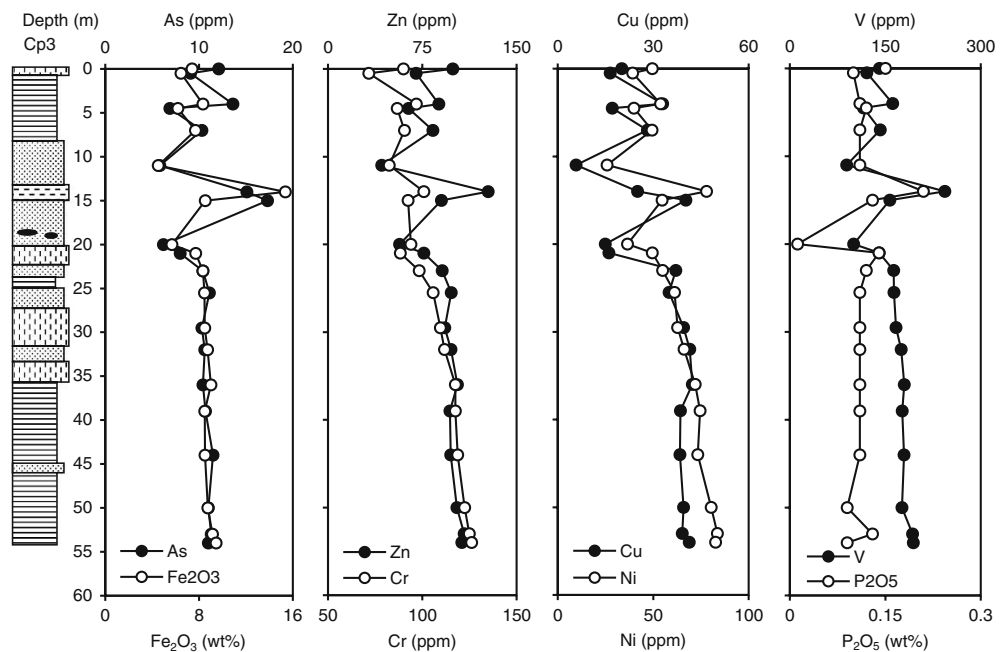
from the Ganges Delta in Jessore region (4–18 ppm in clays; 3–7 ppm in sands; Yamazaki et al. 2003). The Jessore region is one of the most As contaminated areas of Bangladesh. This contrasting distribution of As between clays and sands in the Ganges–Meghna–Brahmaputra (GMB) River system is also consistent with other reports (e.g., Yamazaki et al. 2000; Anawar et al. 2002). Arsenic may be scavenged by clay minerals (Yan et al. 2000) and the high dissolved As might result from the pH-dependent adsorption characteristics of As(V) onto the clay mineral surfaces (Pierce and Moore 1982), following desorption under reducing conditions. One clay sample (Cp2-4) from 4 m depth has a comparatively high As concentration (26 ppm). The sand sample Cp3-6 also has slightly greater concentrations of As (15 ppm), reflecting irregular distributions of As. However, As concentrations in the shallow groundwater of these areas are significant (0.11–0.93 ppm; data not shown), despite the relatively low As concentrations (average 10 ppm) within the aquifer sediments.

The distribution of As in the subsurface sediments is not solely controlled by a single mineral phase (Anawar et al. 2002). Fine-grained sediments favor deposition of Fe (oxy)hydroxides, and natural organic matter in the sediments is high (Padmalal et al. 1997), leading to high As concentrations. It is thus most likely the co-existence of As, Fe (oxy)hydroxides and organic matter is caused by the strong adsorption affinity of metal hydroxides for both As and organic matter in the finer sediments (Anawar et al. 2002). Positive correlation of As and Fe ($r^2 = 0.564$; $n = 41$; Fig. 7) is observed in Chandpur sediments, consistent with previous reports by Nickson et al. (2000) for Ganges sediments, Bangladesh and by Berg et al. (2001) for the Red River delta, Vietnam. This suggests that As may be associated with Fe (oxy)hydroxides in the sediments (Berg et al. 2001).
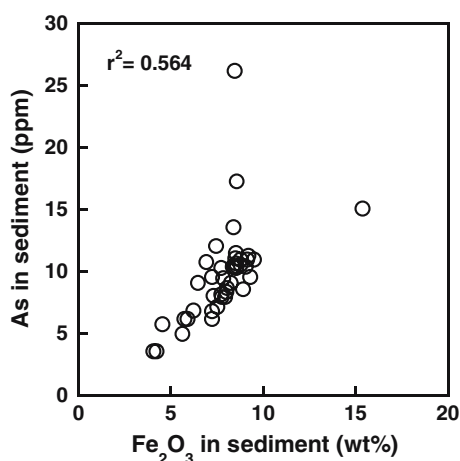

Fig. 7 Correlation between As and Fe_2O_3 in Chandpur core sediments (Cp1, Cp2, and Cp3; excluding one outlier; $n = 41$)

McArthur et al. (2001) and Ravenscroft et al. (2001) also reported that presence of arsenic-bearer phases, i.e., Fe (oxy)hydroxides is one of the major hosts of As in the Ganges sediments.

Existence of peat an important source of As

In the tropics, peat evolves in situ by accumulation of fallen trees, leaves and branches (Markgraf 1989). Rahman and Ishiga (1999) observed that the fluvial sediments supplied by the Ganges are rich in organic matter, derived from higher plants which grew in a humid and warm climate. Such natural organic matter (peat and peaty sediments) is one of the potential sources of As contamination of groundwater in Bangladesh (Ishiga et al. 2000; Yamazaki et al. 2000), which spread out widely in the Bengal lowland after ca. 5,000 years BP (Umitsu 1993). The extensive distribution of peat in the Meghna plain (Ahmed et al. 1998; Bibi et al. 2003) suggests that this area was exposed during a period of low sea level (Umitsu 1993).

The existence of thin peat bands at around 30 and 31 m depths in core Cp2 represents a reducing and marshy wetland in an anoxic environment. Appearance of these peat bands in the Holocene sediments accelerated the supply of organic matter, as evidenced by higher chemical oxygen demand (COD) values (about 50 ppm; data not shown) in Chandpur groundwater. High concentrations of NH_4^+ ((5 ppm; data not shown) in shallow tubewells are likely related to the burial of peat, as observed by McArthur et al. (2001) in the Ganges regions. Peat occurs extensively beneath the As-affected areas of Samta and Deuli villages in southwestern Bangladesh, and contains high concentrations of As (50–262 ppm), within which microbial degradation is high (Ishiga et al. 2000; Yamazaki et al. 2000). Thus, the peat is the driver for reduction of Fe (oxy)hydroxides in the Ganges plain (McArthur et al. 2004). Widespread occurrence of peat and peaty sediments, normally rich in As, has possibly enriched the transgressing seawater (Umitsu 1993), and is inferred to be one of the main sources of As in the Bengal basin.

The occurrence of CH_4 in combustible amounts at 36 m depth of the core Cp3 in Chandpur is due to the decomposition of organic matter. Although measurements of CH_4 were not made during drilling at this site, the occurrence of CH_4 was confirmed by the experience of the local drill team. This is consistent with the findings of Harvey et al. (2002) and Smedley and Kinniburgh (2002), and the presence of CH_4 in groundwater elsewhere in the Bengal basin (Ahmed et al. 1998). Harvey et al. (2002) noted the occurrence of CH_4 at around 30 m depth in the Munshiganj district. This could be due to the presence of subsurface organic matter in high concentrations (McArthur et al. 2004). Decomposed

wood fragments (ORP −75 mV; at 19 m in Cp3) as a source of carbon and organic matter in fine sands with detectable odor reflects simultaneous fermentation. Arsenic might have been deposited onto fine grained organic-rich sediments that were preferentially deposited under low energy conditions in the Ganges and Meghna floodplain during the Mid-Holocene sea-level rise (Acharyya et al. 2000). Presence of high concentrations of organic matter in the deltaic sediments (BGS and DPHE 2001) at subsurface depth may control reductive dissolution of As and Fe from sediments into groundwater.

Summary and conclusion

The results show that the stratigraphy in the study areas consists of yellowish brown silty clays and clays at top, passing downward into light to gray fine- to medium-grained sands within the shallow depth of the aquifers. The Meghna plain sediments have similar As contents as those in the Ganges and Old Brahmaputra plains,

Bangladesh. Abundances of As and other trace elements (Cu, Pb, Zn, Ni, and V) and Fe_2O_3 are greater in silts and clays than in the sands. Anomalously high concentrations of As, Pb, Zn, Cu, Ni, Cr, V, Fe_2O_3, and TiO_2 were found in a sample at 13 m depth, possibly because it consists of blackish very fine micaceous sand rich in biotite. The REE patterns of all types of sediments of the Meghna plain are similar and are comparable to the average UCC. The Chandpur aquifers are in reducing conditions, as indicated by negative ORP values in the core samples. A positive correlation between As and Fe was observed in the core sediments, suggesting As may be associated with Fe (oxy)hydroxides in the aquifers.

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