Bull. Environ. Contam. Toxicol. (2002) 69:538–545

DOI: 10.1007/s00128-002-0095-5

Bulletin of Environmental Contamination and Toxicology

Arsenic in Groundwater of the Bengal Delta Plain Aquifers in Bangladesh

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Received: 7 August 2001/Accepted: 26 April 2002

Arsenic (As) is a common contaminant in groundwater that affects human health adversely at levels as low as 10 μg/L (WHO 1999). Arsenic occurs widely in the Bengal Delta Plain (BDP) aquifers in Bangladesh and India (Bhattacharya et al. 1997; Nickson et al. 2000). Traditionally surface water was used for drinking purposes in this region, which led to widespread gastrointestinal problems. Consequently people started using groundwater resources. Groundwater exploitation of has increased dramatically in Bangladesh and nearly 4-5 million tubewells have been installed to provide safe drinking water to nearly 97% of the population. Unfortunately, high As levels in groundwater has raised a serious threat to public health. Arsenic levels in groundwater is typically above the drinking water standard of Bangladesh (> 50 μg/L) in 44 districts, above the WHO limit (> 10-50 μg/L) in another 7 districts, and lastly < 10 μg/L in only 11 districts (Mukherjee and Bhattacharya, 2001). In addition, the use of As rich groundwater in agriculture has resulted in bioaccumulation of As, and elevated As levels have been reported in vegetables and rice (Mukherjee and Bhattacharya 2001). As of today, nearly 33-75 million people in Bangladesh are at a potential health risk due to high As in groundwater (Mukherjee and Bhattacharya 2001).

The BDP comprises of a thick sequence of sediments deposited by the meandering Ganges-Brahmaputra (Jamuna)-Meghna river system and their tributaries during the Late Quaternary or Holocene age (Mukherjee and Bhattacharya 2001). The lithological succession is dominated by coarse to medium sand representing channel facies and predominantly fine grained sediments representing the overbank facies and exhibits a fining upward character (Bhattacharya et al. 1997). The overbank sediments are rich in organic matter and often indicate well developed peat in several cut-off meander segments. This paper focuses on the chemical characteristics of arseniferous groundwater in Bangladesh, their spatial variation and inter-relationships, and possible mechanisms involved in mobilization of As.

MATERIALS AND METHODS

Groundwater samples discussed in this paper were collected from existing domestic tubewells in nine As affected districts of Bangladesh during January 1999 and 2000 (Fig. 1; Table 1). pH, Eh, temperature and conductivity were measured in the field. pH was measured using a Radiometer Copenhagen PHM 80 instrument equipped

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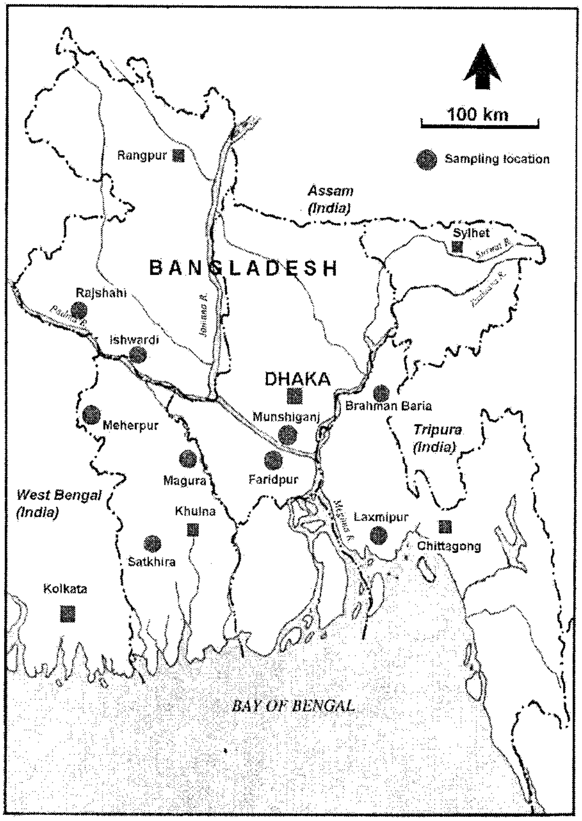

Figure 1. Map of Bangladesh showing the network of major rivers Ganges (Padma)-Brahmaputra (Jamuna)-Meghna and the groundwater sampling locations.

with a combination electrode (pH C2401-7). Eh was measured in a flow-through cell using a combined platinum electrode (MC408Pt) with a calomel reference electrode. Water samples were taken in replicates: i) filtered samples (Sartorius 0.45 µm online filter) for anion analyses; ii) filtered and acidified samples (14 M HNO_3) for major and trace element analyses. Speciation of As(III) was carried out in the field using disposable cartridges. Anions such as Cl^- and SO_4^{2-} were analyzed by a Dionex 120 ion chromatograph, whereas NO_3^- and PO_4^{3-} were analyzed using Tecator AQUATEC 5400 analyzer at wavelengths 540 nm and 690 nm, respectively. The major and trace metals were analyzed on a Perkin Elmer Elan 6000 ICP-MS. As(V) was calculated as a difference between total As and As(III) in the samples. Organoarsines were not analyzed in this study. Certified standards, SLRS-4 (National Research Council, Canada) and GRUMO 3A (VKI, Denmak) and synthetic chemical standards prepared in the laboratory, and duplicates were analyzed after every 10 samples during the runs. Trace element concentrations in standards were within 90-110% of their true values. Relative percent difference between the original and duplicate samples were within ±10%. Dissolved organic carbon (DOC) in the water samples were determined on a Shimadzu 5000 TOC analyzer (0.5 mg/L detection limit with a precision of ± 10 % at the detection limit.

RESULTS AND DISCUSSION

Results of the chemical analyses of the BDP groundwater are presented in Table 1. The water samples were near-neutral to slightly alkaline (pH 6.5-7.6). Eh varied between +0.59 to -0.44 V suggesting mildly oxidizing to moderately strong reducing conditions. The water samples were of predominantly Ca-HCO_3 or Ca-Mg-HCO_3 type. However, Ca-Na-HCO_3 and Na-Cl type waters also occurred in some areas. Electrical conductivity in groundwater varied between 307-1970 µS/cm. HCO_3^- was the dominant anion (320-600 mg/L). Cl^- (1.9-794 mg/L), SO_4^{2-} (< 2 mg/L) and NO_3^- (< 0.2 mg/L) were low, whereas PO_4^{3-} was generally high (0.05-15.3 mg/L). The major cations such as Ca (20.7-122 mg/L), Mg (13.8-41 mg/L), Na (7.4-150 mg/L), and K (1.5-13.5 mg/L) levels were variable (Table 1). Total arsenic (As_{tot}) levels varied between 2.5-846 µg/L, whereas total Fe (Fe_{tot}) and Mn varied between 0.4-15.7 mg/L and 0.02-1.86 mg/L, respectively. As(III) was the dominant species representing about 67-99% of As_{tot}.

The variations in groundwater chemistry were plotted against depth (Fig. 2). HCO_3^- levels were high between 13-67.5 m and consistent with the elevated pH and mildly reducing conditions (Fig. 2a-c). Moreover, HCO_3^- concentration also coincided with high Ca and Mg levels (data not plotted; Table 1). DOC in BDP groundwaters were between 1.2-14.2 mg/L, and concentrations > 5 mg/L occurred at depths of 36.6, 42.7, and 67.1 m (Fig. 3c). It is interesting that high As concentration in the deep well at Faridpur at 228.6 m coincided with the high DOC value (Fig. 2c,i). SO_4^{2-} was predominant at 13.7-15.2 m in Faridpur and at 36.6 m in Rajshahi. NO_3^- was high in the Meherpur and Satkhira wells (28-29 m), and Cl^- peaked at 67.1 m in Munshiganj. High PO_4^{3-} levels occurred at 22.9-67.1 m in Munshiganj, Brahman Baria, and Satkhira (Fig. 2e-h). Interestingly, a well in Munshiganj district (254.3 m), yielded water with high Cl^- (797 mg/L), SO_4^{2-} (8.5 mg/L), and NO_3^- (0.8 mg/L), but low HCO_3^- (209 mg/L) levels. The water also indicated high levels of Na (105 mg/L), Ca (211 mg/L), and Mg (110 mg/L) (Fig. 2c,e,f). The brackish chemistry probably results from relict seawater entrapped in these sediments during the Holocene transgression.

Total arsenic (As_{tot}) in the BDP wells was above the Bangladesh drinking water standard (< 50 µg/L) as well as the WHO guideline for drinking water (<10 µg/L). Arsenic concentrations as high as > 500 µg/L was observed at 13.7, 15.2, and 16.8 m in Faridpur, and at 28.5 m in Ishwardi. Arsenic levels between 250-500 µg/L occurred at 21 m in Faridpur, and between 36.6-42.7 m in Sonarampur and Brahman Baria. Groundwater with 100-250 µg/L As occurred at 7.9-36.6 m in wells located in Rajshahi, Meherpur, Brahman Baria, Satkhira, and Laxmipur, and at > 50 m in Munshiganj, Satkhira, and Brahman Baria. Tubewells at depths > 150 m indicated < 10 µg/L As, except the deep well in Faridpur at 228.6m. Fe_{tot} concentrations peaked intermittently up to 67.5 m, and high Mn levels were noted between 21-36.6 m and in wells > 67.5 m (Fig. 2i-k). Fe_{tot} indicated a weak correlation with As_{tot} ($r^2 = 0.42$; $p < 0.001$), PO_4^{3-} ($r^2 = 0.48$; $p < 0.001$), and HCO_3^- ($r^2 = 0.57$; $p < 0.001$; Fig. 3a-c). A weak correlation was also noted between HCO_3^-

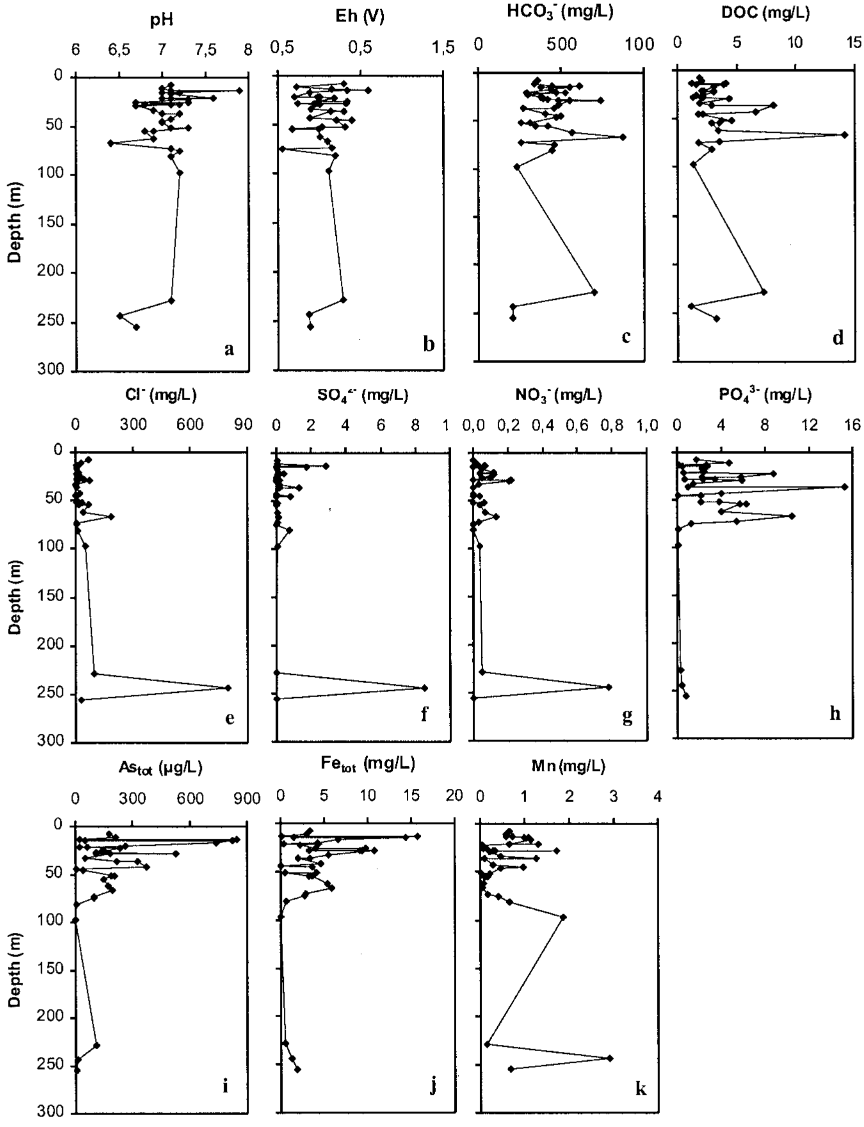

Figure 2. Profiles showing the variation in groundwater chemistry with depth in the BDP groundwater.

and As_{tot} (r^2 = 0.23, Fig. 3d), but a definite trend for increasing As_{tot} with accompanying HCO_3^- levels was noted (e.g., the wells along array I; Fig. 3d). The data indicated a strong correlation between As(III) and DOC (Fig. 4). Interestingly, variations were observed in terms of As(III) concentration and DOC if depths were taken into account, particularly, at 7.9-28.5 m and 29-62.5 m (Fig. 4a-c). The source for DOC in the BDP groundwater is not well known. However, Routh et al. (2000) indicated that BDP sediments are enriched in organic carbon (TOC = 0.1-5%), degradation of which may add DOC to groundwater. A trend indicating increasing

Table 1. Groundwater chemistry of selected wells in the BDP aquifers of Bangladesh.

Location	Depth (m)	pH	Eh (V)	EC (µS/cm)	DOC	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Ca	Mg	Na	K	CBE (%)	Fe_{tot}	Mn	As_{tot}	As(III)	As(III) (%)
					mg/L											µg/L				
Rajshahi																				
Harian (D)	26.0	7.3	+0.34	738	1.6	392	30.6	0.10	bdl	2.3	96	21.4	18.3	3.4	0.4	9.7	0.14	152	133	87.4
Harian (D)	28.0	6.8	+0.33	742	2.2	421	14.3	bdl	0.03	3.4	66	22.5	17.8	2.4	0.4	9.1	0.29	106	99	93.1
Charghat (D)	36.6	7.0	+0.30	798	2.9	460	3.8	bdl	1.32	1.0	112	25.2	22.5	1.5	2.4	3.4	1.27	220	143	64.9
Charghat (D)	45.0	7.0	+0.40	840	2.1	501	6.3	0.04	0.81	0.07	112	25.6	13.7	1.9	-0.5	0.04	0.98	5.3	2.6	49.1
Ishwardi																				
Char Ruppur (D)	28.5	7.1	-0.06	1312	2.1	739	47.1	bdl	0.12	0.7	174	41.0	15.5	1.72	-2.3	3.3	4.6	530	476	89.9
Char Ruppur (D)	81.1	7.1	+0.19	760	2.9	445	8.8	bdl	0.76	0.08	102	23.4	9.0	2.9	-0.5	0.6	0.66	4.38	3.8	86.3
Meherpur																				
Ujalpur (D)	28.5	7.2	-0.25	812	1.3	484	3.3	0.22	0.18	2.4	100	24.3	13.1	3.8	-3.0	9.4	0.33	111.5	111	99.2
Ujalpur (I)	75.1	7.2	-0.44	767	1.7	462	3.7	bdl	0.02	1.3	102	20.8	11.7	4.1	-2.0	2.8	0.40	96.9	88	90.9
Faridpur																				
Dhuldi Rajapur (D)	13.7	7.9	+0.16	860	4.1	611	5.9	0.06	0.04	2.6	122	36.4	20.7	6.1	-0.7	15.7	0.73	846	812	96.0
Komarpur (D)	15.2	7.0	+0.59	630	1.6	379	12.9	0.04	1.77	0.5	84	18.1	11.0	3.3	-3.1	1.48	1.00	54	51	94.1
Dhuldi Rajapur (D)	15.2	7.2	+0.34	810	3.9	552	8.1	bdl	bdl	2.7	114	31.7	17.1	6.1	-0.9	14.4	1.10	825	816	98.9
Majhch. Kourpur (D)	16.8	7.1	-0.12	700	3.1	442	3.9	0.05	0.07	2.3	91	20.9	11.1	4.0	-4.1	6.68	1.13	738	681	92.3
Pourasabha (D)	21.0	7.6	-0.30	538	2.2	290	16.4	0.12	0.15	2.4	65	14.4	8.0	2.4	-4.6	4.2	0.65	266	259	97.4
Majhch. Kourpur (D)	21.3	7.1	-0.02	630	2.0	475	8.7	0.12	0.17	0.6	108	21.4	11.3	3.3	-2.3	4.42	0.65	22	21	96.0
Komarpur (D)	228.6	7.1	+0.28	1180	7.3	697	99.5	0.05	bdl	0.3	77	28.8	150	5.9	-5.0	0.55	0.15	110	100	91.3
Munshiganj																				
Srinagar (D)	54.9	6.9	-0.33	620	3.5	345	16.3	0.04	0.01	6.4	40	27.2	34.0	6.7	-3.5	3.19	0.16	148	145	98.1
Maowa (D)	67.1	6.4	+0.10	1300	14.2	874	186.0	0.13	0.11	10.4	58	25.5	325	7.7	-1.5	5.85	0.06	197	188	94.0
Srinagar (D)	243.8	6.5	-0.12	1970	1.2	209	797.4	0.78	8.52	0.4	211	110	105	6.3	-3.7	1.20	2.92	10	2.6	25.4
Magura																				
Pourasabha (D)	33.5	6.9	-0.11	740	1.8	487	1.9	0.03	0.20	1.5	107	21.7	11.0	2.7	-2.9	5.53	0.45	54	47	88.4
Pourasabha (D)	45.7	7.0	+0.20	710	1.8	476	2.0	bdl	bdl	2.2	105	20.2	10.0	2.5	-3.3	3.60	0.47	40	nd	-
Brahman Baria Sadar																				
Sonarampur (D)	22.9	7.3	+0.18	510	3.1	297	4.8	0.12	0.05	8.8	22	32.1	16.2	9.5	-6.0	2.28	0.06	235	227	96.6
Sonarampur (D)	36.6	7.2	+0.14	520	8.1	275	6.1	bdl	0.20	15.3	12	12.6	54.5	8.9	-9.7	2.04	0.09	328	321	97.9
Kuttapara (D)	51.8	7.1	+0.31	620	4.5	314	31.8	bdl	bdl	2.2	26	19.9	63.7	5.1	-2.2	4.13	0.22	208	196	94.6
Medda (D)	73.2	7.1	+0.15	430	3.5	261	5.8	0.03	0.07	5.5	32	16.5	21.5	4.6	-7.0	2.90	0.16	100	nd	-
Haldarpara (D)	97.5	7.2	+0.12	550	1.3	235	53.6	0.04	0.06	0.05	31	31.7	16.2	13.5	-1.6	0.01	1.86	2.3	nd	-
Satkhira																				
Tala (D)	25.9	6.7	-0.01	611	2.1	377	15.1	0.05	bdl	5.8	76	18.8	14.9	4.1	-5.4	3.97	0.08	137	106	77.3
Tala (D)	29.0	6.7	+0.01	941	4.3	554	72.6	0.21	bdl	5.9	126	28.8	17.8	4.8	-8.4	10.7	0.21	183	135	73.7
Tala (D)	54.9	6.8	-0.01	752	2.9	423	67.6	0.04	bdl	5.7	77	22.2	38.5	4.9	-9.4	3.6	0.09	146	98	67.1
Tala (D)	62.5	6.9	+0.01	900	3.4	567	41.1	0.07	0.07	4.1	105	41.2	30.2	5.6	-2.4	5.4	0.08	171	125	73.2
Laxmipur																				
Shamsherabad (D)	7..9	7.1	+0.30	739	1.9	362	70.5	bdl	0.05	1.8	48	35	48.9	9.6	-2.2	3.38	0.66	175	165	94.4
Hazirpara (P)	11.7	7.0	-0.27	640	2.0	343	26.3	0.02	0.04	4.8	32	37.9	25.0	8.5	-3.9	2.97	0.59	211	153	72.7
Hazirpara (D)	255.3	6.7	-0.11	307	3.3	207	6.0	bdl	bdl	0.8	21	13.8	23.7	3.3	-4.4	1.84	0.67	5.1	0.7	12.9

D- domestic well, P- public well, I- irrigation well, bdl- below detection limit, nd- not determined, CBE- charge balance error

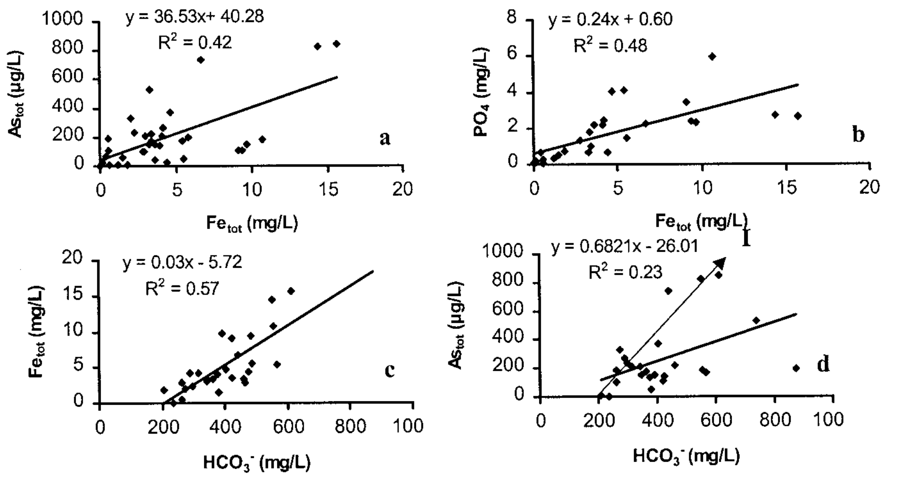

Figure 3. Relationship between: a) Fe_{tot} and As_{tot}, b) Fe_{tot} and PO_4^{3-}, c) HCO_3^- and Fe_{tot}, and d) HCO_3^- and DOC in the BDP groundwater.

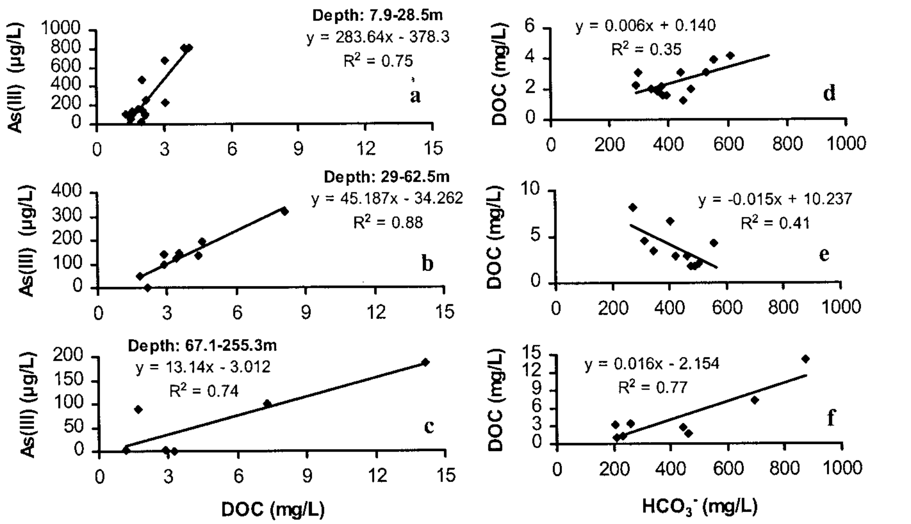

Figure 4. Relation between DOC-As (III) (a-c) and HCO_3^--DOC (d-f) in the BDP groundwater.

HCO_3^- with DOC levels was observed in the shallow wells (7.9-28.5 m; $r^2 = 0.35$) and a group of deep wells (67.1-255.3 m; $r^2 = 0.77$; $p < 0.05$). However, at depths of 29-62.5 m a negative correlation was observed between HCO_3^- and DOC ($r^2 = 0.42$, Fig. 4d-f). Fe_{tot} and Mn concentrations show a wide scatter if data for the entire population is plotted (Fig. 5). However Fe_{tot} versus Mn indicated specific trends if depth was accounted for in the plots. For example, a positive correlation ($r^2 = 0.84$; $p < 0.001$) was noted between 7.9-16.8 m, whereas at depth of 21.3-36.6 and 42.7-

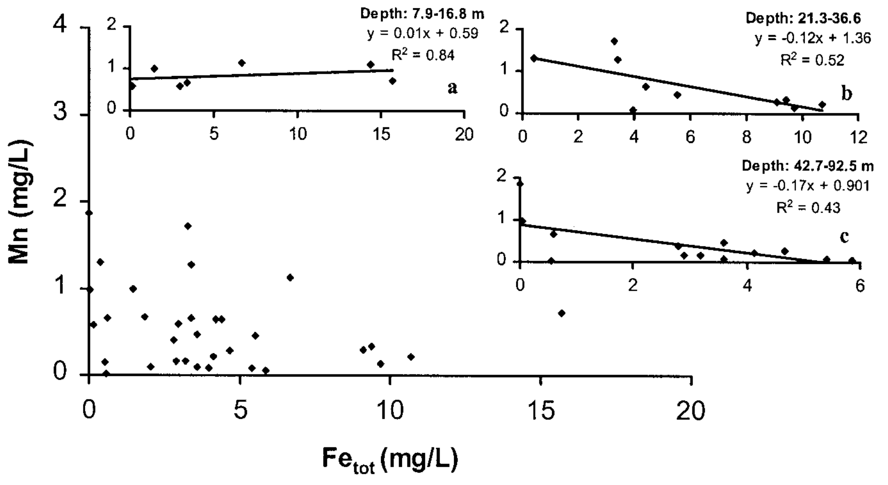

Figure 5. Relation between distribution Fe$_{tot}$ and Mn in the BDP groundwater. Note the data points grouped according to depth in insets (a-c).

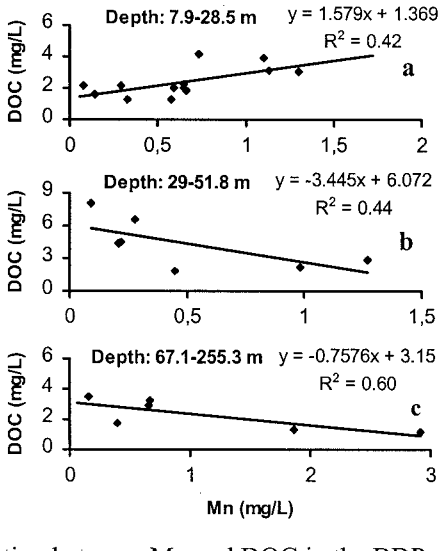

Figure 6. Relation between Mn and DOC in the BDP groundwater (some wells in Brahman Baria and Munshiganj with high DOC were excluded).

92.5 m a negative correlation was observed (r^2 values of 0.52 and 0.43; Fig. 5 insets a-c). Moreover, at shallow depths Mn and DOC correlated weakly (r^2 = 0.42; $p < 0.001$; Fig. 6a), whereas an inverse relationship was noticed for the deeper groundwater samples (Fig. 6b,c) which could be attributed to the reduction of Mn catalyzed by the DOC in the deeper anoxic groundwaters. Most BDP groundwaters with high Fe concentrations had high PO_4^{3-} and As levels, particularly up to 70 m. The weak correlation among Fe$_{tot}$ and As$_{tot}$ might be related to the precipitation of siderite ($FeCO_3$), while correlation between Fe$_{tot}$ and PO_4^{3-} may be controlled by vivianite ($Fe_3(PO_4)_2.8H_2O$). Both minerals act as a sink for Fe^{2+} ions in anoxic groundwater with high alkalinity and PO_4^{3-} levels. While the source for As is geogenic (Mukherjee and Bhattacharya 2001), the source for high PO_4^{3-} levels is not well understood. Phosphorous can be released during oxidation of organic matter, and may lead to elevated PO_4^{3-} levels in groundwater. Acharyya et al. (1999) speculated that PO_4^{3-} in BDP groundwater resulted from application of fertilizers, however, this is not convincing because the amount of dissolved and sorbed PO_4^{3-} over the aquifer volumes would exceed the amount of PO_4^{3-} applied as fertilizers (J.P. Gustafsson, *personal communication.*).

The most likely mechanism for mobilization of As seems to be oxidation of organic matter utilizing Fe-oxyhydroxides as electron acceptors. The dominance of Fe-oxyhydroxides in BDP sediments is revealed by the amount of oxalate extractable Fe (Fe_{ox}= 0.4-5.9 g/kg) over Mn (Mn_{ox}= 0.01-0.37 g/kg) or Al (Al_{ox}= 0.06-1.3 g/kg; Mukherjee and Bhattacharya 2001). High DOC levels and dominance of As(III) in groundwater suggests reduction of organic matter. The positive trends observed between HCO_3^- and Fe_{tot}, As_{tot}, as well as DOC imply that terminal electron accepting processes within the aquifers drive reductive dissolution. Mobilization of As may also be affected by bacterial reduction of Fe^{3+} to Fe^{2+} ions, which is known to convert As(V) to As(III). High Fe^{2+} and As(III) concentrations in groundwater supports this idea. Moreover, Fe^{2+} ions produced would further induce reduction of Mn causing precipitation of Fe-oxyhydroxides (Appelo and Postma 1993). The inverse relationship between Fe_{tot} and Mn in intermediate and deep wells coupled with low As_{tot} supports this idea. We believe that As(V) will be sorbed to Fe-oxyhydroxides retarding the mobility of As, unless redox reactions remobilize As.

Acknowledgments: The study was funded by Sida-SAREC (SWE-193/98) and Vetenskapsrådet. KMA and AAK thank SAREC for travel grants to visit KTH.

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