ARSENIC AND OTHER TOXIC ELEMENTAL CONTAMINATION OF GROUNDWATER, SURFACE WATER AND SOIL IN BANGLADESH AND ITS POSSIBLE EFFECTS ON HUMAN HEALTH

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Abstract. The problems of contamination caused by arsenic (As) and other toxic metals in groundwater, surface water and soils in the Bengal basin of Bangladesh have been studied. Altogether 10 groundwater, seven surface water and 31 soil samples were collected from arsenic-affected areas and analysed chemically. The geologic and anthropogenic sources of As and other toxic metals are discussed in this paper. The chemical results show that the mean As concentrations in groundwater in the Char Ruppur (0.253 mg As L^{-1}), Rajarampur (1.955 mg As L^{-1}) and Shamta areas (0.996 mg As L^{-1}) greatly exceed the WHO recommended value, which is 0.01 mg As L^{-1}. The concentrations of As in groundwater are very high compared to those in surface water and in surface soil in the three (As-affected) areas studied. This indicates that the source of As in groundwater could be bedrock. The relatively high concentrations of Cr, Cu, Ni, Pb and Zn in surface water, compared to world typical value, are due to the solubility of metal ions, organometalic complexes, coprecipitation or co-existance with the colloidal clay fraction. In the soil, the elevated concentrations of As, Cr, Cu, Ni, Pb and Zn are due to their strong affinity to organic matter, hydrous oxides of Fe and Mn, and clay minerals.

Key words: Arsenic, Bangladesh, groundwater, soil, surface water, toxic elements

1. Introduction

Arsenic (As) is ubiquitous in the environment, being present usually in small amounts in all rocks, soil, dust, water and air (Onishi, 1969). The element is common in pyrite, galena, chalcopyrite and more rarely in sphalerite (Goldschmidt, 1954). The most common As mineral is arsenopyrite, $FeAsS_2$. The average concentration of As in igneous and sedimentary rocks is approximately 2 mg As kg^{-1}, and common concentrations in most rocks range from 0.5–2.5 As kg^{-1} (Kabata-Pendias and Pendias, 1984). The average concentration of As in soil of about 5–6 mg As kg^{-1} is higher than that of rocks but may vary from region to region (Peterson *et al.*, 1981). Weathering of rocks may mobilise As as salts of arsenous acid and arsenic acid (Irgolic *et al.*, 1995).

Intermittent incidents of As contamination in groundwater and the subsequent ill health of people from As poisoning have been widely reported (Das *et al.*, 1996).

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There are many clinical manifestations, among which the most common symptoms of chronic As poisoning are conjunctivitis, melanosis and hyperkeratosis. In severe cases, gangrene in the limbs and malignant neoplasm have also been observed (Das *et al.,* 1996). Epidemiological studies undertaken in southwest Taiwan in the 1960s clearly showed a relationship between high concentrations of As in drinking water and skin cancer, keratosis and Blackfoot disease or a type of gangrene (Tseng *et al.*, 1968; Tseng, 1977). Further investigations in Taiwan have established relationships between high As exposure and cancers of the bladder and other internal organs (Chen *et al.,* 1988, 1992). Hepatic effects have been recorded in India (Mazumder *et al.,* 1988) and vasoconstriction and acrocyanosis in Chile (Borgono *et al.,* 1977). Other metals, i.e., Al, Cr, Pb, Cu, Ni, Zn etc. could also be ecotoxic if the concentrations of those metals are higher than the expected levels in the soil and surface water bodies.

Bangladesh has been experiencing As contamination of its water and land resources as well as other toxic elemental contamination such as Al and Cr (Islam, 1996; Ratan *et al.,* 1997). The extremely high concentration of As in groundwater in the affected areas has caused skin leisons such as melanosis, leucomelanosis, keratosis, hyperkeratosis, drosum, non-peting oedema, gangrene and skin cancer (Ratan *et al.,* 1997). However, the sources of the higher concentration of arsenic in groundwater in Bangladesh are unknown. The main objectives of the study are to know (1) the degree of arsenic contamination in groundwater, surface water and soil in the study area, (2) sources of the arsenic and other toxic metals in water and soil, and (3) the factors controlling the release of arsenic as well as other toxic metals into the groundwater, surface water and soil.

The problem of As and other toxic metal (Al, Cr, Cu, Ni, Pb and Zn) contamination of groundwater, surface water and soils in Bangladesh is described in this paper. The geologic and anthropogenic sources are evaluated and discussed on the basis of the chemical results of surface water, groundwater and soils. Also other applicable geological information is presented.

2. Geology of the study area

2.1. LOCATION AND PHYSIOGRAPHY

Bangladesh extends from latitude 20°43′ to 26°36′N and longitude 88°3′ to 92°40′E (Figure 1). Bangladesh occupies the greater part of the Bengal basin and covers part of the Himalayan piedmont plain and the eastern and southeastern hill ranges of the Sylhet, Chittagong and Chittagong Hill Tracts (Paul and Lian, 1975). The Bengal basin is enclosed to the west, north and east by the Indian shield, the Shillong shield and the Naga–Lustral orogenic belt, respectively; but opens to the south into the Bay of Bengal (Sengupta, 1966).

Quaternary sediments, deposited mainly by the Ganges (Padma), Brahmaputra (Jamuna) and Meghna rivers and their numerous distributaries, cover about three

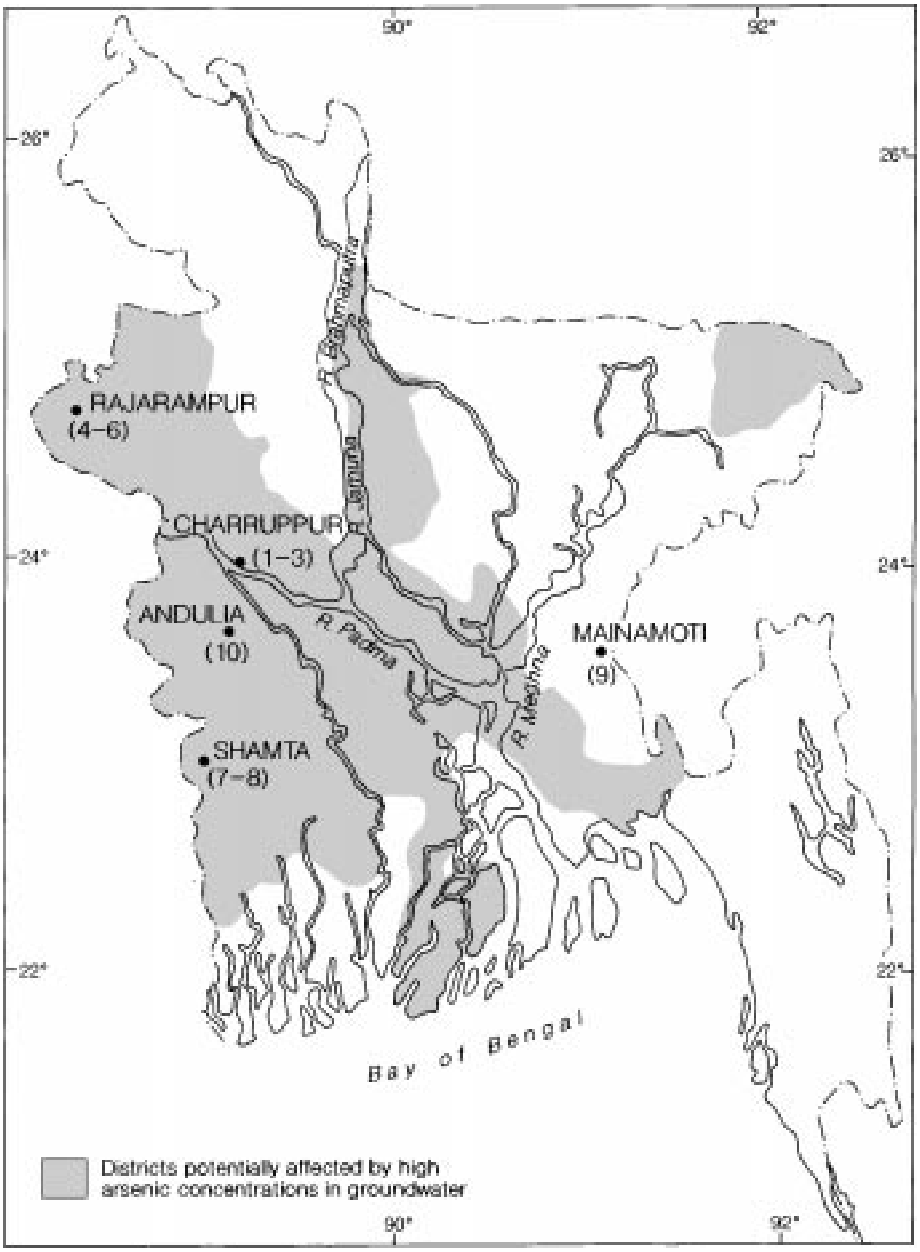

Figure 1. Location map of the sampling sites in Bangladesh: 1 – Charruppur, Ishurdi; 2 – Rajarampur, Chapai Nawabgonj; 3 – Shamta area, Jessore; 4 – Mainamoti area, Comilla and 5-Andulia area, Jhenidah. Highly arsenic affected areas are marked according to Dhar *et al*. (1997).

quarters of Bangladesh. Hillocks and hills are confined to a narrow strip along the southern spur of the Shillong plateau, to the eastern and southern portions of the Sylhet district and to the Chittagong Hill Tracts in the south–east of the country bordering upon the Indian states of Tripura and Mizuram and the Union of Burma (Reimann, 1993). Rashid (1977) has subdivided Bangladesh into 24 physiographic ‘subregions and 54 units’ by refining previous attempts, as for example those of Morgan and McIntire (1959). The major subdivisions are described in detail by Reimann (1993).

2.2. CLIMATE

Bangladesh has a tropical climate characterised by two main seasons, a dry season from November to March and a rainy (monsoon) season from June to October. In addition to the summer monsoon, winter depressions originating from the Mediterranean and the so-called ‘Nor’Westers’ in April and May contribute to annual precipitation. The climatic features of Bangladesh vary region to region and season to season. During the monsoon, the average rainfall varies from about 890 mm in the western districts to more than 2030 mm in the southeastern and northeastern parts of the country (Reimann, 1993).

Bangladesh experiences two distinct temperature conditions, a cool and a warm season, with the former lasting from November to January and the later from March to October. The average January temperature is about 19°C in the south and 17°C in the north. The average July temperature ranges country-wide from 27°C to 29°C. The maximum temperatures recorded from the western districts, which reach 36°C in April, occasionally exceed 38°C (Islam and Mia, 1981). The average annual humidity in the northeastern, eastern and southeastern districts is 78.66%, 80.74%, and 76.91%, respectively (Statistical yearbook of Bangladesh, 1991). The humidity in the western, northwestern and southwestern districts is generally slightly lower.

Chittagong and Cox’s Bazar districts are situated in the southeastern part of Bangladesh. In Chittagong the annual average maximum temperature is 31°C and minimum temperature 20°C. Mean annual humidity is 76% and rain fall 3,022 mm. The annual average maximum and minimum temperature of Cox’s Bazar district is 31°C and 21°C, respectively, and the humidity 79% (Statistical year book of Bangladesh, 1991). The mean annual rainfall of this area is 3,663 mm (Samad, 1986).

2.3. STRATIGRAPHY AND ROCK TYPES

The stratigraphy of Bangladesh is mainly based on the lithologic interpretation of Khan and Muminullah (1980). Bangladesh has a thick stratigraphic succession of mostly Tertiary sediments and occasionally Quaternary sediments (Table I). Sandstones, siltstones, shale and claystones are the main rock types existing all over the country. Tectonically, the basin can be subdivided into a stable area to the west and northwest, and the geosynclinal Bengal foredeep to the east and southeast.

On the stable shelf, between 1 and 8 km of sediments of Permian to recent age have accumulated. The Pre-cambrian Archean basement complex consists mainly of gneisses. The main minerals are orthoclase, quartz, muscovite, biotite and hornblende (Khan and Muminullah, 1980). By contrast, in the more tectonically active Bengal Foredeep, more than 16 km of mainly Tertiary sediments have been laid down (Paul and Lian, 1975). The weathered sandstones, siltstones, shales and claystones in the geosynclinal foredeep region contain mainly quartz together with minor amounts of muscovite, plagioclase, K-feldspar, biotite, carbonate, epidote and clay minerals such as chlorite and illite (Islam, 1996). The geochemistry of the geosynclinal foredeep region is described in detailed by Islam (1996).

Lithostratigraphic units and lithology of the stable shelf region and geosynclinal foredeep regions are shown in Table I.

2.4. STRUCTURE

The structure of the Bengal basin has been discussed by several authors, including Bakhtine (1966), Sengupta (1966), Raju (1968), and Guha (1978). The Bengal basin is a double-fronted asymmetrical basin with the flanks sharply dipping to the west and gently sloping to the east. The western flank borders the Pre-cambrian crystalline massifs near longitude 88°E (Banerjee, 1981). The Bengal exogeosyncline is one of the world’s largest and is part of the Bengal geosyncline. The latter includes the Bengal basin and the Bay of Bengal (Alam, 1989).

2.5. PALAEOTECTONIC AND BASIN EVOLUTION

The evolution of Bengal basin started in the Permo-Carboniferous with the sedimentation in the faulted Gondwana basins. The break up of Gondwana land in the Cretaceous period led to the eventual separation of peninsular India from the southern continents with counterclockwise rotation and northward drift, permitting a cretaceous marine transgression and sedimentation in the Bengal basin (Alam, 1989). The Bengal basin has undergone two successive phases of evolution. The first, a marine transgressive phase (with minor regression) lasting up to the end of the late Eocene, was followed by a regressive phase with an intermediate transgressive phase stage which resulted in a series of continental, fluviodeltaic to marginal marine sedimentations during the Oligo-Miocene. The great Himalayan uplifts dominated towards the northeastern and eastern parts during the Miocene, Pliocene and Pleistocene (Banerjee, 1984). During these epochs, huge amounts of clastic sediment were deposited into the basin from the northeast and the major Mio-Pliocene delta complex started to be built in the northeast side. A considerable amount of sediment was also coming into the basin from the northwest and small deltas were building on the western side of the basin (Alam, 1989).

TABLE I
Stratigraphic sequence in Bangladesh

Geologic age	Stable shelf		Bengal foredeep		Lithology
	Group	Formation	Group	Formation	
Holocene		Alluvium Uncomformity		Alluvium Unconformity	Silt, sand, gravel and clay
Pleistocene late Pliocene	Madhupur	Dihing Unconformity	Madhupur	Madhupur clay Unconformity	Pebbly sandstone, sticky clay
Mid Pliocene – early Pliocene		Dupi Tila Unconformity		Dupi Tila Unconformity	Sandstone, coarse quartz, pebbles, petrified wood
		Jamalgonj		Girujan clay	
Miocene	Surma		Tipam	Tipam	Claystone with sandstone
					Sandstone, coarsegrained cross-bedded, pebbles of granite, quartzite, shale and lignite. Clay mostly at base
			Surma	Boka bil Bhuban	Marine shale, pyritic gray marine fossils; Sandy shale, sandstone, breccia interbeds
Oligocene	Barail	Bogra	Barail	Jenam	Siltstone, fine-grained sandstone, Carbonaceous shale
Late Eocene		Kopili		Unconformity	Sandstone, locally glauconitic: shale, highly fossiliferous: thin calcareous beds; limestone, nummulitic: sandstone interbeds; Sandstone, coal, and shale

TABLE I
(*continued*)

Geologic age	Stable shelf		Bengal foredeep		Lithology
	Group	Formation	Group	Formation	
Middle Eocene	Jaintia	Sylhet limestone	?	?	
Early Eocene		Tura sandstone	?	?	
Paleocene			?	?	
Late-middle Cretaceous		Unconformity Shibgong Trapwash			Sandstone, coarse yellow-brown; clay, white; volcanic ash
Early Cretaceous–Jurassic	Upper Gondwana	Unconformity Rajmahal Traps	?	?	Basalt, amygdaloidal; andesite, serpentinized; shale, agglomerate
Late Permian	Lower Gondwana	Unconformity Paharpur	?	?	Sandstone, feldspathic graywacke; coal, shale. Sandsone-coarse-grained; shale; coal thick seams
Early Permian	Lower Gondwana	Kuchma			
Precambrian		Unconformity Basement Complex			Gneiss and schist

Source: Based on Khan (1980) and Zaher and Rahman (1980).

3. Methodology

3.1. WATER AND SOIL SAMPLING

The study areas were selected to represent the arsenic-affected regions. The affected areas have been primarily reported by health workers on the basis of the diseases related to As poisoning and has been confirmed by the limited groundwater analyses. The sampling sites are marked on the location map (Figure 1). Three groundwater samples and four soil samples (depth ranges from 0.33 to 1.35 m) were collected from Char Ruppur, of Pabna district (alluvial sand). From Rajarampur village of the northwestern Chapai Nawabgonj district (alluvial sand), two groundwater, three surface water and 11 soil samples (0.10–1.00 m) were collected. Two groundwater, two surface water and six soil samples (0.25–2.25 m) were collected from Shamta village, of Jessore district (deltaic silt). Two groundwater, one surface water and six soil samples (0.15–8.00 m) were collected from the Mainamoti area of the eastern district of Comilla (Pleistocene Madhupur Clay Residum); and two groundwater, one surface water and four soil samples (0.20–1.50 m) were collected from Andulia, Harinakundu of the southwestern Jhenidah district (Deltaic silt).

Groundwater samples were taken from drilled tube wells, which have been constructed using hand augers. After drilling the wells were cased in perforated steel-screens against the aquifer. The depth of tube wells ranges between 20–30 m. The pumping rate or yield of a tube-well is approximately $2\,\mathrm{L\,min^{-1}}$. Water samples were collected in 100 ml acid-washed polythene or polypropene bottles, immediately preserved with concentrated HNO_3 ($1\,\mathrm{ml\,L^{-1}}$), and preserved in a cool place. A total of 10 groundwater samples were collected from the three extremely high As-affected areas, and, for comparison, two of them from the area of low arsenic concentrations. Both nonfiltered and filtered surface water samples were taken in 500 ml acid washed polythene or polypropene bottles from the ponds and lakes close to the groundwater sampling sites. The natural lakes in the locations studied vary from 2 to $4\,\mathrm{km^2}$ in area and their mean depth is 4 m. The lakes receive water from precipitation, river inflow, and runoff from surrounding agricultural lands and densely populated villages. Some of the lakes have outlets during the rainy season. Artificial reservoirs are typically 100 m length and 70 m in width and have an average depth of around 7 m. Surface water was filtered with disposable membranes ($< 0.45\,\mu\mathrm{m}$) and were acidified with concentrated HNO_3 (0.500 ml/500 ml).

Soil samples were collected (about 500 g each for different analyses) from the arsenic affected areas in the vicinity of the groundwater and surface water sampling sites. The soil samples were taken into polythene bags from pits (from bottom upward to avoid contamination) with minimum 0.10 m interval depending on the variation of lithology and were closed immediately in order to avoid the loss of moisture. The soil sampling spot was selected having similar geomorphological as well as lithological feature with the regional stratigraphy. From each sampling spot a composite water and soil sample was collected for further investigations.

3.2. ANALYSES

3.2.1. *Water*

Filtered ($< 0.45\ \mu$m) and acidified surface water and groundwater samples were analysed for Al, As, Cr, Cu, Ni, Pb and Zn with ICP-MS/ICP-AES technique in the chemical laboratory of Geological Survey of Finland (GSF), Espoo. In order to know the influence of organic matter and colloidal clay fraction, non-filtered surface water was also analysed.

3.2.2. *Soil*

The collected soil samples were air-dried at < 40°C and sieved to the < 2 mm fraction (ISO/DIS 11464). The soil samples were analysed in the chemical laboratory of the GSF in Kuopio according to the following procedures.

Aqua regia-leachable elements: 12 ml of *aqua regia* (1 HNO_3 : 3 HCl) and 60 ml of water were added to dried soil samples weighing 1.2 g. Arsenic, Al, Cr, Cu, Ni, Pb and Zn concentrations of the soil were determined after digestion in 90°C *aqua regia* for 1 h time by ICP-AES (ISO/DIS 1146). Most of the minerals in soils are silicates that dissolve only slightly in mineral acids. Therefore, the *aqua regia* leach resulted in only partial dissolution for the majority of the soil samples. However, the *aqua regia* leach dissolves selectively carbonates, most of the sulphides, sulphosalts, arsenides, arsenates, phosphates, vanadates, tungstates, molybdates and sulphates, trioctahedral micas, clay minerals and precipitates on mineral grains (Kähkönen, 1996).

Exchangeable cations: The soil samples were analysed for exchangeable As, Al, Cr, Cu, Ni, Pb and Zn from the buffered 1 M NH_4Ac digestion method at pH 4.5, using the ICP-AES method (e.g., Halonen *et al.*, 1983; Page *et al.*, 1982; Erviö and Palko, 1984). Since pH 4.5 is roughly the same as the pH in podzols (e.g. in Finland) it can be assumed that the concentrations of exchangeable cations refer to the maximum concentrations of exchangeable cations in the soil (Räisänen, 1989). For analysis 3.0 g of soil sample was weighted. In the analysis, the ratio of soil samples to ammonium acetate solution was 1:10.

Total analyses: About 35 g of soil sample was crushed (Islam, 1996) by vibrating disk mills (Herzog, type: Hsm 100 A) to prepare XRF sample (button) and were used to determine the major (also trace elements) elemental composition by X-ray fluorescence (XRF). Analyses were carried out with a Siemens SRS-X-ray 303 As spectrometer with standard curves based on International Rock Standards at the Institute of Electron Optics, University of Oulu.

pH determination: The pH of soil samples was determined in unbuffered 0.025 M NH_4NO_3 solution, which characterises the type of binding capacity of the cations better than pH measured in water suspension (Räisänen and Lahermo, 1985).

4. Results

4.1. GROUNDWATER

The results of the chemical analyses of groundwater, surface water and soil are given in Tables II–IV, respectively. The chemical analyses of groundwater show that the mean As concentration in Char Ruppur, Ishurdi (0.253 mg As L^{-1}); Rajarampur, Chapainawabgonj (1.955 mg As L^{-1}) and the Shamta, Sharsha area (0.996 mg As L^{-1}) exceeded the WHO (1993) guide line which is 0.01 mg As L^{-1}. Only in the Mainamoti area (0.0002 mg As L^{-1}) and the Andulia area (0.009 mg As L^{-1}) was it below the guide value. The highest and lowest As concentrations were recorded in the Rajarampur (2.190 mg As L^{-1}) and Mainamoti (0.0002 mg As L^{-1}) area, respectively. The concentrations of Al, Cr, Cu, Ni, Pb and Zn in groundwater of all the five sampling sites are below the WHO (1993) guide values.

4.2. SURFACE WATER

The results of the chemical analyses of surface water is given in the Table III. The elemental concentrations in surface water were compared with the data for world lake and river waters (Wedepohl, 1969–1979). The elemental concentrations in surface water show that the level of As, Al, Cr, Cu, Ni, Pb and Zn is higher in samples collected in the four study areas in Bangladesh than in world surface waters. The highest As value was recorded in the Rajarampur area (0.176 mg As L^{-1}). The highest Al value was recorded in the Andulia area (2.050 mg Al L^{-1}) and the lowest in the Shamta area. The highest Cr concentration (0.009 mg Cr L^{-1}) is from the Shamta area. The highest value of Cu was analysed from nonfiltered sample in the Shamta area (0.018 mg Cu L^{-1}) and also Ni from Shamta area (0.006 mg Ni L^{-1}). The highest Pb concentration was recorded in the Shamta area (0.023 mg Pb L^{-1}). The average values of Zn exceed the typical value (0.015 mg Zn L^{-1}) in all the study areas.

4.3. SOIL

The results of the chemical analyses of soil is given in the Table IV. The elemental concentrations in soil have been compared with the worldwide soil analyses published by Wedepohl (1969–1979) and the data from marine clays from Finland by Salminen *et al.* (1997). The total concentrations of the elements, analysed by XRF method have been taken mainly into consideration for comparison. The As concentrations in soil from Bangladesh show that the values of As exceeded the typical world concentrations (5 ppm).

Aluminium concentration analysed in the total analyses (XRF) show that the level of Al values is lower than the typical value elsewhere. The highest Cr concentrations in Rajarampur (94 mg Cr kg^{-1}) and Andulia (115 mg Cr kg^{-1}), exceeded the typical values, respectively. Also the average concentrations of Cu val-

TABLE II

The average elemental compositions of groundwater mg L^{-1}

Elements	Char Ruppur	Rajarampur	Shamta	Mainamoti	Andulia	Standard value*
Al	–	0.004	0.021	0.023	0.049	0.2
Ranges	< 0.001–0.003	0.001–0.008	0.009–0.034	0.012–0.033	0.036–0.063	
As	0.253	1.955	0.996	0.0002	0.009	0.01
Ranges	0.0004–0.6	1.72–2.19	0.152–1.84	0.0002–0.0002	0.008–0.01	
Cr	0.0004	–	< 0.0002	0.0031	–	0.05
Range	0 0002–0.0006	–	–	0.003–0.003	< 0.0002–0.0003	
Cu	0.0008	0.0002	–	0.0006	–	2
Ranges	0.00004–0.0001	0.0–0.0004	< 0.0–0.0001	0.0005–0.0008	0.0–0.0002	
Ni	0.0002	< 0.00006	< 0.00006	0.001	< 0.00006	0.02
Ranges	0.0–0.0004	–	–	0.001–0.001	–	
Pb	0	0.0002	0.0005	0.001	0.0007	0.01
Ranges	< 0.0–0.0002	0.0001–0.0004	0.0003–0.0008	0.001–0.002	0.0002–0.012	
Zn	0.012	0.03	0.027	0.053	0.078	3
Ranges	0.0002–0.023	0.011–0.050	0.003–0.052	0.042–0.064	0.07–0.086	
No. of sample	2	2	2	2	2	–

*Standard value is WHO (1993) guide value for drinking water.

TABLE III

The average elemental compositions of surface water mg L^{-1}

Elemental	Char Ruppur	Rajarampur	Shamta area		Mainamoti		Andulia		Typical value*
		Nonfiltered	Filtered	Nonfiltered	Filtered	Nonfiltered	Filtered	Nonfiltered	
Al	–	0.825	0.519	0.615	0.738	0.517	1.06	2.05	0.3
Ranges	–	0.033–1.19	0.472–0.567	0.492–0.738	–	–	–	–	–
As	–	0.097	0.013	0.015	0.005	0.005	0.007	0.014	0.004
Ranges	–	0.013–0.176	0.009–0.017	0.005–0.025	–	–	–	–	–
Cr	–	0.001	< 0.00002	0.005	0.009	0.006	0.0006	0.002	0.0007
Range	–	0.001–0.002	< 0.00002	0.001–0.009	–	–	–	–	–
Cu	–	0.007	0.005	0.018	0.018	0.004	0.008	0.011	0.003
Ranges	–	0.004–0.009	0.004–0.006	0.017–0.018	–	–	–	–	–
Ni	–	0.003	0.004	0.006	0.005	0.003	0.003	0.006	0.0003
Ranges	–	0.001–0.004	0.004–0.004	0.005–0.068	–	–	–	–	–
Pb	–	0.008	0.004	0.016	0.009	0.005	0.008	0.013	0.003
Ranges	–	0.00–0.013	0.003–0.005	0.009–0.023	–	–	–	–	–
Zn	–	0.018	0.01	0.073	0.067	0.018	0.013	0.02	0.015
Ranges	–	0.001–0.034	0.01–0.052	0.067–0.078	–	–	–	–	–
No. of sample		3	2	2	1	1	1	1	–

*Typical values taken from Wedepohl (l969–1979) for surface water.

TABLE IVa

Selected elemental compositions of soil samples by different methods: *Aqua regia* leached mg L^{-1}

	Al	As	Cr	Cu	Ni	Pb	Zn
Char Ruppur ($n = 4$)							
Mean	14900	< 10	25	27.25	22	11.75	45.5
Range	7800–20200	< 10	14–33	13–36	13–29	5–16	31–56
Rajarampur ($n = 11$)							
Mean	21330	< 10	33.54	40	28	16.18	57.72
Range	17700–25400	–	28–29	33–46	24–33	13–20	51–66
Shamta area ($n = 6$)							
Mean	12910	< 10	21.5	29.66	18.33	11.16	39.5
Range	8600–17400	–	15–29	16–42	12–25	5–16	29–67
Mainamoti ($n = 6$)							
Mean	17810	< 10	21.13	19.83	15.5	15.3	23
Range	4400–26800	–	7–34	9–24	4–19	< 5–24	10–28
Andulia ($n = 4$)							
Mean	25720	< 10	40.75	47.5	35.25	23.2	69
Range	16100–32000	–	29–39	30–59	25–43	14–29	58–77
Typical value *	13000	2	27.9	21.1	16.7	10	32

–: not analyised; < ‘number’: analyte below the determination limit given by the number.
*Typical value is according to Wedepohl (1969–1979).

ues exceeded the typical value both in the *aqua regia* leached results (21.1 mg Cu kg^{-1}) and in total (XRF) result (21.1 mg Cu kg^{-1}). The highest Cu concentration (47.5 mg Cu kg^{-1}) was recorded in the Andulia area. The average Ni concentrations in soil from all the areas exceeded the typical value both by *aqua regia* (16.7 mg Ni kg^{-1}) leached and total value (20 mg Ni kg^{-1}) by XRF. The highest value was recorded in the Andulia area (average 48.5 mg Ni kg^{-1}). The concentrations of Pb in soil from all the study areas in Bangladesh exceeded the typical values both in the *aqua regia* leached (10 mg Pb kg^{-1}) and total analysis (XRF) results (17 mg Pb kg^{-1}). The average Zn concentrations in the Andulia (92.5 mg Zn kg^{-1}) and Rajarampur areas (78 mg Zn kg^{-1}) exceeded the typical value both in *aqua regia* leached (32 mg Zn kg^{-1}) and in total analyses (70 mg Zn kg^{-1}).

Ammonium acetate leached results have been compared with the published data of Finnish clay (Salminen *et al.,* 1997) which contain more trace elements than in Bangladesh. As a result elemental concentrations in the study areas (containing mainly sandstone and siltstone) are lower than that of marine clay in Finland. The soil pH is highest in the Char Ruppur area (pH 8.83) and lowest in the Mainamoti area (pH 4.85).

TABLE IVb

Selected elemental compositions of soil samples by different methods: Ammonium acetate leached (mg kg^{-1})

	Al_2O_3 Wt.%	As mg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Pb mg kg^{-1}	Zn mg kg^{-1}
Char Ruppur ($n = 4$)							
Mean	46.45	< 0.5	< 0.3	1.25	0.45	0.62	0.56
Range	31–69	–	–	0.5–1.6	0.4–0.5	0.6–0.7	0.34–1.56
Rajarampur ($n = 11$)							
Mean	58.09	< 0.5	< 0.3	1.18	–	–	0.26
Range	31.5–76.1	–	–	0.8–1.6	< 0.3–2.2	< 0.5–0.9	0.2–0.38
Shamta area ($n = 6$)							
Mean	15.28	< 0.5	< 0.3	1.21	0.35	0.5	0.94
Range	12.8–17.9	–	–	0.8–1.7	< 0.3–0.5	< 0.5–1	0.16–1.80
Mainamoti ($n = 6$)							
Mean	101.5	–	< 0.3	0.52	–	0.9	0.74
Range	7.7–206	< 0.5–0.6	–	< 0.3–0.9	< 0.3–0.6	< 0.5–1.09	0.15–1.55
Andulia ($n = 4$)							
Mean	90.67	< 0.5	< 0.3	0.82	< 0.3	1.06	0.34
Range	36.10–149	–	–	0.4–1.2	–	< 0.5–1.2	0.07–0.72
Typical value *	139	–	< 1.0	1.1	< 1	–	1.02

–: not analyised; < ‘number’: below the detection limit.

*Typical value is according to Salminen *et al.* (1997).

TABLE IVc

Selected elements compositions of soil samples by different methods: Total analyses by XRF

	Al_2O_3 Wt.%	As mg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Pb mg kg^{-1}	Zn mg kg^{-1}	pH
Char Ruppur ($n = 4$)								
Mean	11.05	19	67.5	26	31.2	29.8	60.8	8.83
Range	9–12	13–23	45–79	11–35	23–38	26–31	49–70	8.56–9.17
Rajarampur ($n = 11$)								
Mean	14	15.5	81.7	37.2	39.4	32.2	78.4	8.73
Range	12.5–15.4	8–21	69–94	29–43	32–47	28–35	66–92	8.49–8.94
Shamta area ($n = 6$)								
Mean	10.4	13.3	59.3	30	25.7	28	64.3	8.57
Range	8.8–12.0	6–14	42–73	13–15	20–41	23–31	37–93	7.91–9.24
Mainamoti ($n = 6$)								
Mean	10.3	18.8	61.5	16	34	35.5	40.3	5.52
Range	8.63–14.5	5–33	29–77	2–32	12–80	24–41	19–51	4.85–6.85
Andulia ($n = 4$)								
Mean	14.8	20.7	96.2	47.5	48.5	37	92.5	8.23
Range	12.2–16.4	12–28	67–115	27–61	36–60	29–42	71–105	8.09–8.41
Typical value*	15.1	5	80	21.1	20	17	70	–

*Typical value is according to Wedepohl (1969–1979).

5. Discussion

Arsenic is a mobile element in the environment and may circulate in various forms through the atmosphere, water and soil before finally entering into its ultimate sink, the bottom sediments and sea (Savory and Wills, 1984; Peterson *et al.*, 1981). From the chemical results of this study it can be concluded that the distribution of As between groundwater and surface water is quite improportional in the major As affected areas (Table V). The As concentration of soil, although somewhat higher than the typical As concentration of soils, remains rather constant in each of the study targets, being the lowest in the Shamta area (13 mg As kg^{-1}) and highest in the Andulia area (21 mg As kg^{-1}). The As concentration of groundwater, instead, varies very much in the study areas. Extremely high concentrations were detected in the Rajarampur (1.955 mg As L^{-1}), Shamta (0.996 mg As L^{-1}) and Char Ruppur (0.253 mg As L^{-1}) areas, but those in the Mainamoti (0.0002 mg As L^{-1}) and Andulia (0.009 mg As L^{-1}) areas were normal. The As concentration of surface waters does not vary as much as that of groundwaters, the highest concentrations being detected in Rajarampur (0.097 mg As L^{-1}) and the lowest in Mainamoti (0.006 mg As L^{-1}). However, the ratio of the As concentration in groundwater to the As concentration in surface water (Table V) shows that in Mainamoti and Andulia the share of As in surface waters is much higher than in the Rajarampur and Shamta areas. In the Rajarampur and Shamta areas there is an inconsistent relationship between As concentration of groundwater and surface water, and in general, also in the soil. There the higher As concentration of groundwater may be dependent on the bedrock and its As content with which the groundwater is in contact. In the surface water of the Rajarampur and Shamta areas there are also some possible anthropogenic sources of As. But in the Mainamoti and Andulia areas where the normal level of As concentration prevails, it is caused by leaching from surficial deposits.

The chemical analyses of 11 core samples (sandstone, siltstone and shale) from a depth ranging between 973.5 and 3325 m in different parts of Bangladesh show the As concentrations ranging from 40 mg As kg^{-1} to 60 mg As kg^{-1}. These concentrations are higher than the As content in soil in the As-affected areas. This

TABLE V

The ratio of As concentrations between groundwater and surface water in the studied areas; and total As concentration in soil from same area

Name of the areas	Ratio	Soil (mg kg $^{-1}$)
Rajarampur	20.1	15
Shamta	72.1	13
Mainamoti	0.04	19
Andulia	0.67	21

suggests that the deeper bedrock is the likely source of high As concentration in groundwater. In a study of deep core sediments from As-affected West Bengal state of India, the School of Environmental studies, Jadavpur University (1991) concluded that As in groundwater did come from bedrock. The changes in geochemical environment due to heavy withdrawal of groundwater in the As-affected area in India had resulted in decomposition of pyrites to ferrous and ferric sulphate and sulphuric acid. The arsenic affected western part of Bangladesh is similar to the West Bengal regions in India in terms of surface and subsurface geology, geography and climate. Millions of cubic metres of groundwater was used for agricultural irrigation in Bangladesh. Due to the groundwater withdrawal, as well as due to the effect of the Farakka dam on the river Ganges in India, the groundwater level is being lowered markedly during the dry season in the northwestern and western regions of Bangladesh. Due to extensive lowering of the water table, the dry sediment layers become exposed to oxidation. As a result pyrites is being dissolved releasing As to groundwater. We have studied three deep core sediments (no more were available) by XRD (oriented glass slides) in order to detect pyrite. No pyrite was found through this limited study. Further study of more deep core samples would be needed to examine fully this question. Not only pyrite, but also feldspars, micas and some other accessory minerals in the sedimentary rocks in Bangladesh are also leached extensively due to intense chemical weathering (Islam, 1996); As can be released from those minerals too. Although this amount of As may not be the main source of high concentration of As in groundwater, it is possible.

The high concentrations of As in surface water in the Rajarampur and some extent in Shamta areas are presumably derived from agricultural practices as arsenic contaminated groundwater is used for irrigation purposes. In addition to As contaminated groundwater, chemical fertilisers and various pesticides are also used in the agricultural fields. In the pH values ranging 4.9–8.8 in the study area, arsenic is fairly immobile in soil profile. The overall increase of As in soil in the study areas is due to its adsorption on to Fe and Mn oxides and clay minerals. In Japan, the main thrust of the As pollution problem has been its toxicity to the rice plant (Takamatsu *et al.*, 1982). Irrigation of paddy fields with water contaminated by mining wastes or waste water from geothermal power stations has frequently produced growth depression of rice. The situation in Japan may be related to that in Bangladesh, since the regular use of groundwater for irrigation purposes in the arsenic affected areas in Bangladesh could lead to increase the As concentration in agricultural fields. Through contaminated agricultural land the products may be toxic and lead to human exposure to arsenic.

The human exposure to arsenic due to contamination of groundwater in Bangladesh has been reported by Dhar *et al.* (1997). According to the report, the arsenic-affected patients from 18 districts in western and southwestern part of Bangladesh, show arsenic skin lesions such as melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsum, non-peting oedema, gangrene and skin cancer.

5.1. OTHER METALS

In surface water the Al concentrations are much higher (highest value 2.050 mg Al L^{-1}) exceeding often the permissible value and typical values elsewhere. High concentrations of Al in surface water are significant in terms of human health since it is used by many people for drinking and cooking purposes. Al concentration of soil in the study areas is one source of aluminium in water. Low concentration of Al in the soil is due to the effect of organic acid released from soil organic matter or its secretion from the living organisms as stated by Islam (1996). In the study areas, pH of the soil profile varies from 4.85 to 9.24 which is not favourable for Al dissolution.

Chromium in surface water exceeded the typical value in all of the study areas. Factors affecting the mobility and availability of chromium include redox potential and oxidation state and availability of organic matter and hydrous oxides of iron and manganese. The surface water is also enriched in Cu, which is slightly more abundant than the typical values elsewhere (0.003 mg Cu L^{-1}). The solubility, mobility and availability of Cu to plants is largely dependent on soil pH. The concentrations of Ni in surface water and soil exceeded the typical values elsewhere due to co-precipitation with the organometallic complexes and colloidal clay fractions. In Bangladesh, the total Ni concentrations in soils is up to 60 mg Ni kg^{-1}. The concentration of Ni decreases with increasing % SiO_2 of the rock as has been indicated in the Mainamoti area where the lowest Ni concentrations among all soil profiles were recorded at the lowest pH value 4.85. Lead concentrations in surface water are higher than the typical value (0.003 mg Pb L^{-1}). The higher concentration of Pb analysed by total analyses is due to its incorporation in clay minerals and in Fe oxides during weathering (Islam, 1996). The higher concentration of Zn in surface water is due to the complexing effect of organic acids.

6. Conclusion

The source of exceptionally high concentration of As in groundwater in the Rajarampur, Char Ruppur and Shamta areas could be the bedrock. On the other hand, the high concentrations of As in surface water in the Rajarampur and some extent in Shamta areas are presumably derived from anthropogenic sources such as agricultural practices. The relatively high concentrations of As in soil in the studied areas are due to adsorption on to clay minerals and oxides of Fe and Mn formed during weathering. The regular use of As-contaminated groundwater for irrigation purposes on agricultural land may contaminate agricultural products and lead to human consumption of As.

The concentrations of Al, Cr, Cu, Ni, Pb and Zn in groundwater in all the study areas are much lower than the WHO (1993) guideline values, confirming safe water for drinking purpose apart from toxicity caused by As. However, the Al concentrations in surface water are much higher than the WHO guide line levels. This is very significant in terms of human health since many people use surface water for drinking and cooking purposes.

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