Leaching of Iron, Controlling Factors and Implication to Arsenic Mobilization in an aquifer of the Brahmaputra Floodplain

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Abstract

To understand the process of iron leaching and arsenic (As) mobilization, three bore wells were drilled in suspected iron and arsenic enriched areas of Jorhat, Assam, India, to study possible release and mobilization process in the aquifer. Sediments and groundwater samples, collected from different depths in these boreholes were analyzed for different parameters. Combined Eh-pH stability diagram of iron and arsenic indicated the presence of Fe (II) and As (III) species in the groundwater. BCR three step sequential extraction method indicated relative mobility of Fe and As in a similar trend of decreasing order as: Residual fraction > Reducible fraction > Exchangeable fraction > Oxidizable fraction. The digestion of aquifer sediments by D 3974-81, (ASTM) showed Fe (106 mg/kg to 26991 mg/kg), Mn (7 mg/kg to 1588 mg/kg), As (0.16 mg/kg to 18.6 mg/kg). The morphology and mineralogy of the aquifer sediments, studied by scanning electron microscope/energy dispersive x-ray (SEM/EDX) and x-ray diffraction (XRD) analysis indicated the levels of Fe and As concentrations in the aquifer sediments. Sequential heating in the muffle furnace indicated organic content (0.01 % to 13.7 %) and carbonate content (0.15 % to 9.19 %) of aquifer sediments. Laser particle size analyser was used to find the specific surface area of the sediments (0.02 m^2/g to 0.19 m^2/g). The lithology of the soil consisted of silt, very fine sand, fine sand, medium sand and fine gravel. The relationship between Fe, Mn, As, organic content, carbonate content and specific surface area of the sediments along the depth for different bore holes was interpreted separately including with the help of Principal Component Analysis (PCA). In multiple linear regression models, the experimentally found and predicted concentrations of iron correlated as 0.83 for B bore hole and 0.87 for E bore hole, whereas correlation coefficients for arsenic concentration were 0.88 in B bore hole and 0.80 in E bore hole. With the help of the linear regression models, the correlation between these elements and the factors controlling their concentrations were evaluated.

Keywords: Arsenic; BCR Sequential Extraction; Multiple Regression Model; PCA

1 Introduction

Groundwater has been second major source after surface water in terms of its usage for drinking, agriculture, and other purposes. The groundwater quality plays a major role in the socio-economic condition of people dependent on it, and can have adverse effect due to its degradation. Both natural and anthropogenic sources can cause contamination of groundwater. The natural pollution of groundwater could be because of geochemical processes in which particularly release of heavy metals from rocks and salts into groundwater makes it unsafe and unfit for human use. Contamination of groundwater by iron and arsenic has been well observed in Bangladesh, India, China, Thailand, Taiwan, Vietnam and other parts of the world (Smedley and Kinniburgh, 2002; Bhattacharyya et al., 2003; Nickson et al., 2005; Nath et al., 2009). Iron exists naturally in the underground water in dissolved inorganic form of ferrous (Fe^{2+}) and arsenic in inorganic oxyanions of arsenite (As^{3+}) and arsenate (As^{5+}) (Smedley and Kinniburgh, 2002; Baig et al., 2010). Maximum Contaminant Limit (MCL) of Fe in groundwater is 0.3 ppm while that of arsenic is 0.01 ppm (IS 10500, WHO, 2004, USEPA, 1997). Consumption of groundwater with Fe contamination above the guideline values leads to Hemochromatosis (Franchini and Veneri, 2005) and arsenic consumption above the guideline values imparts Arsenicosis, Melanosis, Keratosis and related more serious health hazards (Majumder et al., 1988).

Groundwater contamination with iron and arsenic has been recently discovered in the state of Assam in India (Singh et al., 2004; Borah et al., 2009; CGWB, 2009; Chetia et al., 2010). Iron and arsenic found in the groundwater of Assam is geogenic in origin, which is being leached into the groundwater from sediments (Singh, 2004). Along the banks of the river Brahmaputra, ground water shows high concentrations of iron at shallow depths. About 95 % of the area of the north east India contains dissolved iron in excess of 2 mg/l and the iron concentration is as high as 15 mg/l (Singh, 2004). 19 districts out of a total of 23 districts in Assam were found to be contaminated with groundwater iron content of more than 1 mg/l (CGWB, 2009). Singh et al. (1999) had reported a study on the sediments having clay and organic compounds in high percentage, which may retain and release As in the groundwater aquifers. As contamination in flood plain aquifers derived from weathering of Himalayan bedrocks (e.g., Fe oxyhydroxides) which released As to surface waters was proposed in many studies (Mok and Wai, 1994; Nickson et al., 2000; Chatterjee et al., 2005; Saunders et al., 2005, 2008). Arsenic associated with the carbonaceous matter in Arunachal Pradesh, Assam, Nagaland and Meghalaya, had shown mean concentration of 95.1 mg/kg (Baruah, 2003). Chakraborti et al. (2004), based on their studies in the north eastern region of India observed dissolved arsenic concentration values to be as high as 0.490 mg/l. In a Rapid Assessment program carried out by the Public Health Engineering Department (PHED), Assam, 18 out of 23 districts in Assam were found to have groundwater arsenic contamination much above the BIS limits of 0.05 mg/l and WHO guidelines of 0.01 mg/l (JOPA, 2005). Chakraborti et al. (2004) observed that the arsenic concentration was maximum in the Jorhat district located on the southern bank of the river Brahmaputra in Assam, India, as compared to the other districts in the region. The iron concentration was found to be 2.36 mg/l in Jorhat which was above the safe drinking water limits of 0.3 mg/l (CGWB, 2009).

Particularly due to the widespread problem of arsenic enriched groundwater found in Bangladesh and West Bengal, there have been extensive studies performed to investigate the source and mobilization of arsenic in these areas (Ahmed et al., 2004; Bhattacharya et al. 1997, 2001; Nickson et al., 2000; Breit et al., 2004). In terms of spread and thickness of alluvial plains, the Brahmaputra valley in Assam is similar to that in Bangladesh. Therefore, the source and processes of arsenic mobilization and iron leaching may as well be similar in Assam as far as the depositional environment is concerned. The objective of the present study was thus to understand the process of iron leaching and its role in arsenic mobilization in an aquifer located in the Brahmaputra Floodplain in Assam, India and compare and contrast the findings with similar studies carried out in the lower Brahmaputra floodplains in Bangladesh.

2. Study Area

2.1 Physiographic setting

The study area forms an integral part of the upper floodplains of the Brahmaputra which consists of distributed young alluvial sediments. Lying between graticules 26° 45'N latitude and 94°13' E longitude, the Jorhat District lies on the southern bank of the Brahmaputra River in Assam covering an approximate area of 2,851 sq. kms (Fig.1). The area experiences a temperate climate along with heavy rainfall and humidity (temperature ranges between 6°C to 38° C, and mean relative humidity between 92 % to 98 %). Average annual rainfall in the study area is about 2818 mm (www.rainwaterharvesting.org). The Brahmaputra River, along with its tributaries like south Dhansiri, Bhogdoi and Kakodonga, drain the district (CGWB, 2008). The young alluvial soils of recent rivers characterized by light to dark grey colorization, are confined mostly in the floodplain areas of the Brahmaputra and its tributaries (CGWB, 2008).

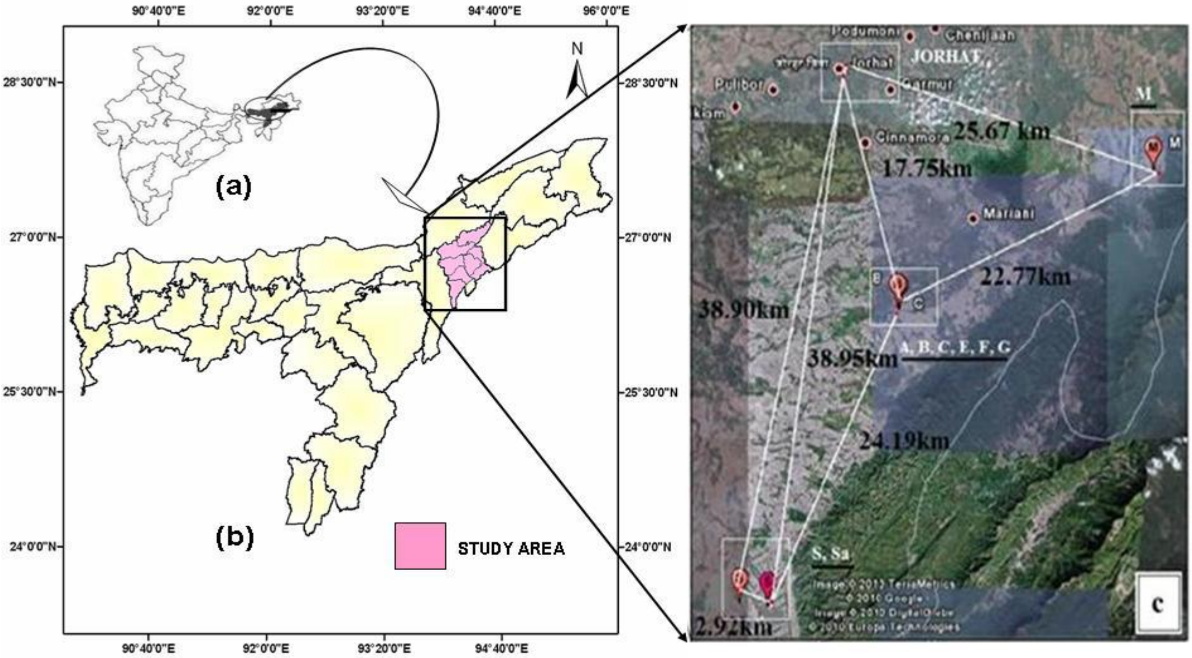


Fig. 1 Map showing the study area (a) Map of India (b) Map of Assam (c) Map of the Study Area highlighting the three studied boreholes, B, C and E.

2.2 General geology of the foothills of the major floodplain

The Brahmaputra Basin is an integral feature of the landform in Assam, a state located in the northeastern part of India. The basin is bounded by the Eastern Himalayas in its north and east, the Naga and Patkai range in the north eastern part, with Shillong Plateau on its south (Sharma, 2005). Geologically, the basin is characterized by sediments of both the Paleozoic and Cenozoic era, comprising of gneisses, high and low grade schists, ultrabasic rocks, shales, sandstones, mottled clays and conglomerates (Sharma, 2005). Resent alluvial deposits in the basin occur in the form of alluvial fans and floodplain sediments of the Brahmaputra River and its tributaries. The Brahmaputra River and its tributaries flowing through the Himalayas carry most of these alluvial sediments disturbed by tectonism and landslides (Sharma, 2005). The northern tributaries of the river are braided together creating the flood plain of Brahmaputra Valley, made up primarily of Holocene sedimentary aquifers. These sedimentary aquifers are thought to be the key repositories of arsenic enrichment in the Brahmaputra Floodplain in Assam. Predominant geologic formations in the study area include unconsolidated alluvial sediments of Quaternary age characterized by Older and Younger alluvium. The Older alluvium occupies the upland areas with sediments of oxidized and relatively compact nature, while the younger alluvium occurs along the low lying tracks of the area along the river course (CGWB, 2008). Superficial blanket of clay belonging to Younger alluvium occurs further in the southern part (CGWB, 2008). The district is blessed with enormous thickness of aquifer in the central and northern parts comprising medium to coarse sand within the explored depth of 450 m (1476 ft), capped in the upper parts by 30 to 50 m (98 ft- 164 ft) of clay beds and varied thickness of clay intercalations in between (CGWB, 2008).

2.3 Sedimentology of the alluvial aquifers

The Brahmaputra basin in Assam is underlain by a 200 – 300 m (656 ft - 984 ft) thickness of recent alluvium (Mahanta and Subramanian, 2004). The alluvial soils can further be divided into two main sub types-young alluvial and old alluvial soils (Talukdar et al, 2004). The alluvial sediments of the Brahmaputra comprise mostly of silt, clay, sand and gravels (CGWB, 1995). The recent alluvial soils carried by recent rivers are light grey to dark grey in colour and are confined to the flood plain area adjacent to the Brahmaputra River and its tributaries, while the older alluvial soil is sandy loam to silty and clay loam characterized by light yellowish brown to light brown in colour (CGWB, 2008). These alluvial soils are further characterized by organic matter and available phosphorus and low potash . The soils in the southern part are residual in origin, derived from the semi consolidated rocks underlying these areas. Brought down by the Brahmaputra and its numerous tributaries draining the Himalayas, these materials act as arsenic sink in the floodplain areas. Similar lithological set up of the Brahmaputra Floodplain in Bangladesh comprising alluvial silt and clay, peat and clay units are also reported to be some of the highly arsenic affected areas in Bangladesh (Reza et al., 2010). In terms of colour, the dominant hue of the colour of the soils of the Brahmaputra basin is 10YR, with a change of greyness of the soils of the eastern part of the basin to yellowish brown along with reddish mottles in the western part of the basin being a characteristic feature of the soil colour of the Brahmaputra Basin (Talukdar et al., 2004). Based on the characteristic features of drainage, wetness and chemical processes associated, soil colour may vary within locations (Talukdar et al., 2004). The bulk density of the soils of the Brahmaputra Basin range from 1.36 to 2.10 gm/cm^3 , with upland soils of the basin having a relatively higher bulk density than other soils (Talukdar et al., 2004).

3. Materials and Methods

3.1 Sample Collection and Characterization

Based on the results of a rapid assessment study for arsenic monitoring in the Brahmaputra Floodplain in Assam, the present study area i.e the Jorhat district in Assam had been chosen for this study. Evaluating the results of the rapid assessment study, the high arsenic contaminated areas were deciphered and drilling around a few of these highly arsenic contaminated wells was proposed. Three bore wells were drilled out by personnel hired through PHED (Fig.1). Drilling was done by percussion technique and combined with reverse circulation as describe by Horneman et al., (2004). The subsurface sediments and the groundwater samples from different depths of the three bore holes B, C and E were collected in January 2010. Groundwater table depth in the study area was observed to be in the range of 2.13 m (7 ft) to 2.59 m (8.5 ft). The groundwater obtained by reverse circulation was collected from 3.05 m (10 ft) and increasingly deeper levels and was transferred to 150 ml polypropylene tubes after filtering it by clean cotton cloth and Whatman filter paper to separate the minute suspended particles. In situ measurements of Eh and pH were done using a precalibrated portable pH/ORP meter (WD-35650-10 Waterproof pH/ORP tester). The sediment samples were collected from depths ranging upto 46 m (150 ft). Samples were packed in zipped polyethylene bags and then in black polyethylene in order to avoid direct contact with the sun and oxygen, before being brought back and stored in the laboratory.

3.2 Sediment analysis

The sediment samples after being brought to the laboratory at the Indian Institute of Technology Guwahati were analysed geochemically for Fe, Mn, As concentrations, organic content, carbonate content, specific surface area and particle sizes. The elemental analysis was performed according to standard practices for extraction of trace elements from sediments [D3974-8, (Reapproved 2003) by ASTM]. The organic content and the carbonate contents were evaluated by loss on ignition method by Bengston and Enell (1986) and Dean (1974). For particle size analysis, 4g of each soil sample was first made into solution of 10ml with distilled water and were added to the 1L of distilled water glass jar which was analysed by laser diffraction principle in the particle size analyser (Mastersizer 2000, Malvern, UK).

Table 1. Summary of BCR sequential extraction procedure followed in the study

Extraction step	Reactive/ concentration/ pH	Solid phase
1	Acetic acid: CH_3COOH (0.11 mol/L) , pH 2.85	Exchangeable, water and acid soluble(e.g. carbonates)
2	Hydroxyammoniumchloride: $NH_2OH.HCl$ (0.1 mol /L) at pH 2	Reducible(e.g. iron /manganese oxides)
3	Hydrogen peroxide: H_2O_2 (8.8 mol/L) followed by ammonium acetate: CH_3COONH_4 (1.0 mol/l) at pH 2	Oxidizable (e.g. organics substances and sulfides)
Residual	Aqua regia: 3 HCL+ HNO_3	Remaining non Silicate bound metals

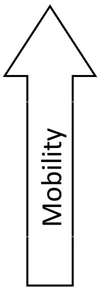
3.3 BCR Extraction Scheme

A modified BCR three-stage sequential extraction method (Zemberyova et al., 2004, Baig et al., 2009) was performed on the aquifer sediments from different depths to determine the presence of Fe, Mn, As in different phases namely exchangeable, reducible, oxidizable while the remains were considered as a residual phase analysed by aqua regia method (ISO 11466:

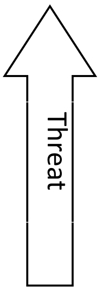
1995) to find the elements bonded in silica matrix (Table 1). 1 gm of dry soil sample was extracted with 40 ml of 0.11 mol L^{-1} acetic acid to estimate the elements bound to carbonates (Tessier et al. 1979; Filgueiras et al. 2002, Hasan et al, 2007). The residue was then extracted by using 40 ml of 0.1 mol L^{-1} hydroxylammonium chloride to quantify the elements in reducible phases i.e. poorly crystalline and amorphous oxyhydroxides (Bhattacharya et al. 2001; Wenzel et al. 2001) followed by extraction with hydrogen peroxide to estimate the oxidizable phases i.e. elements bound to the organic matter and sulphides (Quevauviller et al. 1993; Filgueiras et al. 2002). Finally the residue was extracted using aqua regia to estimate the residual phase which generally is immobile phase (Ahmed et al. 2004; Bhattacharya et al. 2006). The extract was filtered through filter paper by adding 1 mol L^{-1} HNO_3 solution in small amounts on the last residue in the centrifuge tube. The tube walls were carefully rinsed using the same acid solution and then the dregs were collected in a beaker. The extracts acquired after the different extraction stages applied sequentially, were evaporated to near dryness. Extracts were completed to 5 mL with 1 mol L^{-1} HNO_3. The determinations of Fe, Mn, in the extracts were performed using Flame Atomic Absorption Spectra (FAAS) and As by Vapour Generation Assemblage (VGA) attached to FAAS. Table 2 shows the sequential extraction steps and the mobility of the elements.

The modified BCR extraction protocol was chosen over other methods as it has simplified three steps for extraction of elements in forms of carbonates, Fe-Mn oxides and organic complexes. Sequential extractions are the most frequently applied analytical method for studying the solid phase speciation of environmentally relevant heavy metals (Tack and Verloo, 1995). The BCR scheme was selected due to its widespread use and easiness of application. The BCR three stage methods has only three sequential states of analysis, where the elements could be in the form of carbonates, Fe-Mn oxides, organic complexes bonded in the silica matrix following the corresponding BCR protocol phases.

Table 2. Association of different phases extracted and their mobility potential in the sediments



Metal species	**Association**
Exchangeable (Available) Fraction	Metals sorbed on the surface, Carbonate bound
Reducible Fraction	Metals associated with Fe-Mn Oxides
Oxidizable Fraction	Metals bound with Organics and Sulfide
Residual fraction	Metals fixed in Crystalline phase



3.4 Mineralogy

Mineralogy was studied combining optical petrography, X-ray diffraction, SEM coupled with an energy dispersive X-ray analysis on the residuals obtained from each BCR protocol step. The mineralogical study (MAC Science XXP 18) was conducted on the residuals obtained from each BCR protocol step by using x-ray powder diffraction with Cu Kα radiation and a position-sensitive detector. The accelerating voltage was kept at 30 kV and the current at 20 mA. A divergent slit (1^0), a scattering slit (1^0) and a receiving slit (0.2 mm) were used to produce the best spectrum. Scans were conducted from 4^0 to 80^0 at the rate of 1^0-2θ/min. Data were digitally recorded and identification of compounds was made by manual search of the Joint Committee on Powder Diffraction Standards (JCPDS) – with International Centre for Diffraction Data (ICDD) as a reference database. A morphological investigations was also carried out on the residual obtained from each phase of BCR protocol by scanning electron microscopy (SEM) coupled with an energy dispersive x-ray (EDX) where the accelerating voltage of SEM was kept at 30kV, and the EDX was run with a lithium drifted silicon detector at a resolution of 133 eV. The images were taken with maximum magnification. The BCR sequential steps were coupled together with the XRD and SEM/EDX because the results were expected to support each other regarding the concentrations of Fe, As and other controlling factors.

4. Results and Discussion

4.1 Groundwater chemistry

The pH of groundwater was of acidic nature with values ranging between 4.8 and 6.92 with all corresponding values of Eh being negative (Table 3). The pH value of 4.8 was observed for one sample with corresponding values for the rest of the samples ranging between 5.25 and 6.92. Some other low values were also observed in the boreholes irrespective of depth. The low pH value of 4.8 can be attributed to possible localised influence considering that they are independent of depth or perhaps to the lithological variations in the aquifers. Gypsum dissolution was believed to have occurred in some parts of the aquifer, thus contributing Ca^{2+} and SO_4^{2-} leading to precipitation of calcite at few places and thus increase CO_2, which leads to lowering of pH and super saturation or near equilibrium of groundwater with calcium. Anaerobic decay of organic matter and SO_4^{2-} reduction (both reactions release CO_2) controls the SO_4^{2-} concentration in groundwater and subsequent increase in HCO_3^- leading to decrease in pH. A study of the Central Groundwater Board (CGWB, 2008), Assam have reported that the general pH range of the study area is between 4.5-6.0 indicating that the pH range observed during the present study is consistent with that of the CGWB report. Plots of the measured Eh and pH values in the combined Eh-pH stability diagram show that most of the Fe and As occurred as Fe (II) and As (III) (Fig. 2).

Table 3. pH of the groundwater samples from the three boreholes i.e. B, C and E.

Depth (in ft)	**pH**		
	B	**C**	**E**
0	6.07	6.92	5.25
10	6.65	6.58	5.87
30	6.17	5.29	5.81
50	6.1	6.03	6.1
70	6.23	6.11	5.86
90	5.31	6.37	4.8
110	5.56	6.24	6.06
130	5.4	6.41	6.22
150	6.1	5.54	6.3

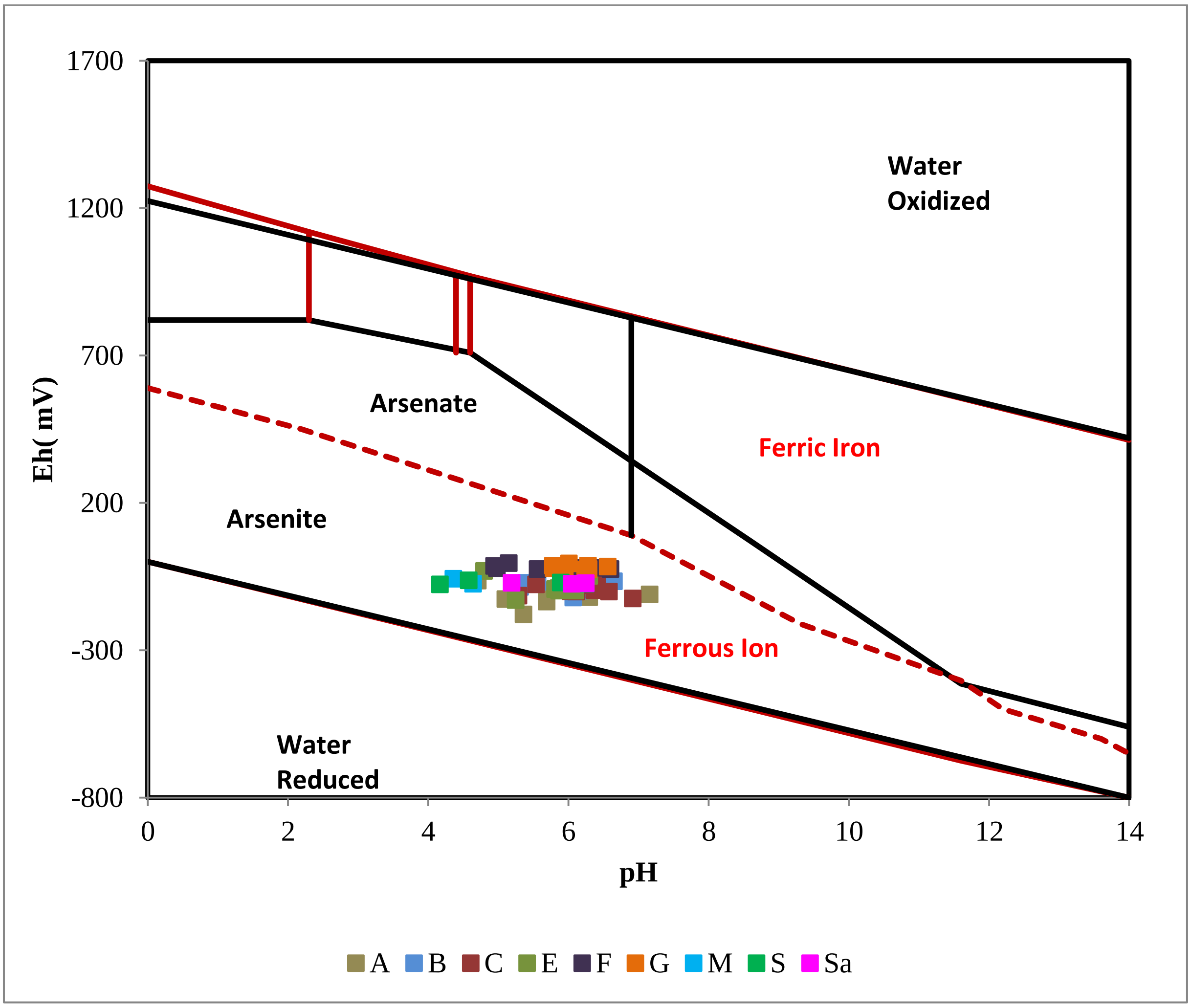


Fig. 2 Combined Eh-pH stability diagram depicting the groundwater samples collected from all the three bore holes

4.2 Sediment geochemistry

Geochemical characteristics of the sediment samples from the three boreholes are described in Table 4. Variation in the concentration of Fe, As, organic content, carbonate content, specific surface area and lithology has been observed along different depths within each borehole. Arsenic concentration ranged between below detection limit to 18.6 mg/kg with higher concentration ranges being predominant in the fine sand and very fine sand fractions. The concentration of arsenic fractions being confined mainly to the fine sand and very fine sand fractions is apparently due to the greater surface area, adsorbing the bulk of arsenic onto their surfaces (Anwar et al, 2003). The concentration of Fe was found to be maximum in the silt fraction for all the three boreholes, with maximum Fe concentration of 2699 mg/kg being measured at a depth of 21.3m (70 ft) in the C borehole. Mn concentration values ranged between 7.35 to 1588 mg/kg were found to be maximum in the fine sand fraction while the concentrations of organic content (0.3 to 13.7 mg/kg) , carbonate content (BDL to 9.2 %) and specific surface area (0.1 to 0.19 m^2/g) being highest in the silt and very fine sand fractions. Occurrence of Fe, Mn and As in each of these different lithological set up indicates the possibility of adsorption of iron oxide or iron hydroxide on the fine sediment surface. Arsenic in the dissolved state, is expected to have mobilized from aquifers lying above the fine sand. The occurrence of Fe and Mn in the aquifer sediments indicates the presence of ferro - manganese compounds in the aquifers.

Table 4. Geochemical characteristics of sediments collected from bore holes B and E

Design.	Depth (ft)	Fe (mg/kg)	Mn (mg/kg)	As (mg/kg)	OC (%)	Carbonate (%)	SSA (m^2/g)	Lithology
B	Surface	11806.79	22.79	2.26	5.18	1.15	0.11	Fine sand
	10	1190.02	51.92	0.35	2.29	0.56	0.19	Silt
	30	280.93	103.28	1	0.3	1.51	0.05	Silt
	50	9713.7	308.57	0.8	0.91	0.77	0.08	Fine sand
	70	16708.6	56.3	8.7	12.76	0.32	0.18	Silt
	90	8039.31	7.35	5.26	11.29	0.6	0.11	Very Fine sand
	110	7905.65	13.95	5.59	10.52	0	0.16	Very fine sand
	130	12508.9	177.1	18.6	5.29	1.13	0.11	Fine sand
	150	12290.38	173.7	16.73	10.05	1.36	0.11	Very fine sand
C	Surface	6625.6	136.56	13.57	5.31	0.25	0.11	Fine sand
	10	7835.2	129.3	1.71	7.69	9.19	0.19	Very fine sand
	30	8616.16	90.55	15.03	10.17	0.15	0.12	Fine sand
	50	6836.82	78.72	5.58	13.68	0.19	0.11	Fine sand
	70	26990.73	382.86	11.3	10.56	1.85	0.16	Silt
	90	21256.86	805.86	7.27	0.8	0.9	0.16	Fine sand
	110	106.2	738.98	13.71	6.52	0.5	0.13	Very fine sand
	130	1262.	583.	15.33	BDL	0.37	0.13	Fine sand
	150	230.79	116.61	2.37	3.67	1.	0.18	Very fine sand
E	Surface	198.96	23.32	0.27	0.3	2.25	0.07	Fine sand
	10	1700.86	29.9	0.6	2.38	1	0.02	Medium sand
	30	18780.82	1588.25	0.9	2.3	6.37	0.1	Silt
	50	832.6	288.6	0.23	6.65	3.55	0.19	Very fine sand
	70	8519.61	123.07	7.07	6.9	0.69	0.16	Fine sand
	90	3018.55	23.67	BDL	7.2	0.55	0.11	Fine sand
	110	806.67	358.65	0.68	0.5	0.87	0.07	Medium
	130	7752.99	92.3	0.8	0.01	1.1	0.1	Fine sand
	150	962.03	223.1	0.16	3.88	1.31	0.11	Fine sand

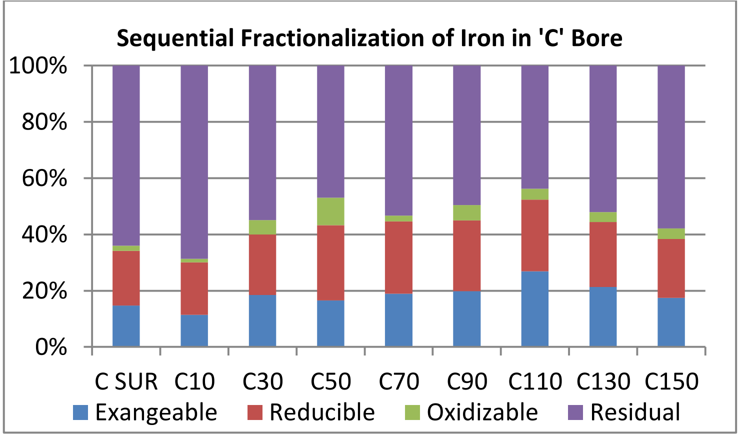
* BDL – Below Detection Limit

Subsurface sediments act as the key repositories of the precipitates of iron oxides, carbonates and mostly heterogeneous mixtures of organic matter and minerals (Smedley and Kinniburgh, 2002; McArthur et al., 2004). Metal oxides such as that of iron have been found to be major sorbents for As because of their high reactivity and high surface area (Fendorf et al, 1997). These amorphous iron oxides (ferric oxide) are capable of adsorbing 0.5 milli moles of ionic material per gram, of which oxyanions of arsenic could be one (Drever and Vance, 1994). Due to adsorption or co-precipitation, As concentration is found to be in natural iron oxide or oxyhydroxide forms in the subsurface sediments (Robins et al., 2001). Arsenate adsorbs on Fe (III) oxide or hydroxides by forming inner sphere surface complexes by exchange with hydroxyl group (Waychunas, 1993; Quicksall et al., 2008). Generally Fe and As are most often found to coexist together (McArthur et al., 2004). Ferromanganese oxides, manganese oxides and carbonates could also act as a sink for arsenic deposition (Edmunds 1986; Nickson et al., 2000; Pal et al., 2002; Bhattacharyya et al., 2003).

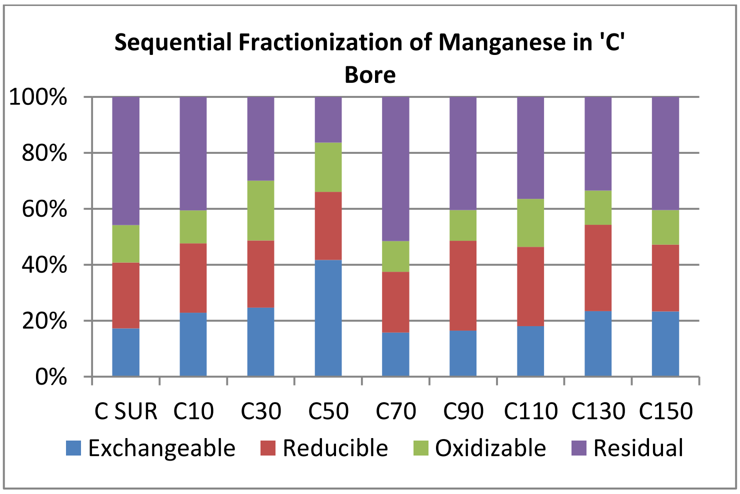
Dissolved mineral phases are usually formed in anoxic sediments by microbial decomposition of organic matter (Suess, 1979). The organic matter present in the groundwater aquifers is used as a substrate by the microorganisms present in the groundwater aquifers, where the anaerobic microorganisms consuming the organic matter releases carbon dioxide (McArthur et al., 2004). This carbon dioxide may get converted into carbonic acid responsible for reducing conditions leading to mobilization of arsenic from iron oxyhydroxides (Cummings et al., 1999; Solaiman et al., 2009). A high groundwater arsenic concentration was observed associated with extensive reduction of iron oxyhydroxides (McArthur et al., 2004). It is believed that the weathering of carbonaceous matter may have produced As-rich iron oxyhydroxides, which in turn released arsenic (after reduction) to the existing sedimentary environment (Nickson et al., 2000). Reductive dissolution of ferric hydroxides is believed to be the release mechanism for controlling the mobility of arsenic in Assam (Mahanta et al., 2008). The reducing condition by microbial activities controls the dissociation of iron from its compounds (iron oxyhydroxides, ferromanganese compounds), which is responsible for the leaching of iron into the groundwater from the aquifer sediments (Roden, 2006). As the arsenic is adsorbed on these iron oxides or oxyhydroxides, the leaching of iron facilitates arsenic mobilization.

4.3 Sequential extraction

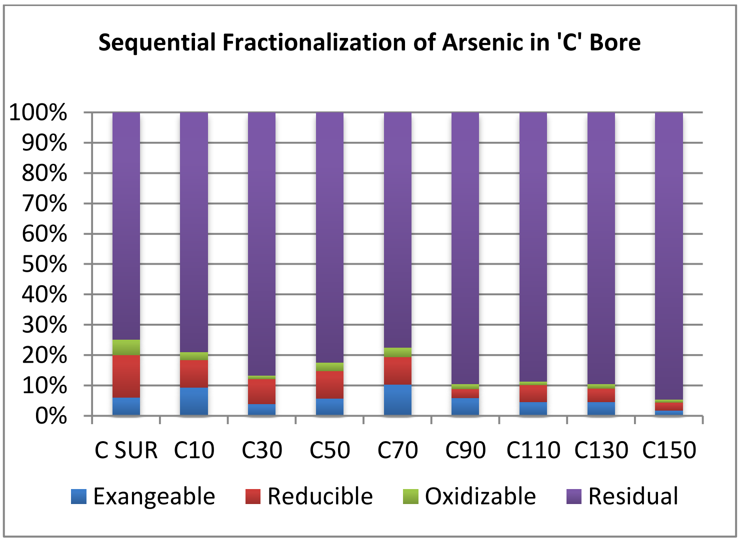
A higher concentration of Fe was observed in the C borehole at 21.33m (70 ft). As the study was focused on Fe leaching, this sample was further taken up for BCR sequential fractionation of Fe, Mn and As. The relative percentile quantification of the iron shows that hydroxyammonium chloride extractable Fe, which estimates the Fe bound to poorly crystalline and amorphous metal that (Fe, Al, Mn) oxyhydroxides dominated the crystalline phase (46 %) followed by Fe-Mn oxides (22 %), surface and carbonate bound (20 %) and minimum (13 %) bound to organics and sulfide [Fig. 3(a)]. The relative percentile quantification of the manganese shows that it is bound to crystalline phase in (55 %) followed by surface and carbonate bound (26 %) then in Fe-Mn oxides (16 %) and minimum (6 %) Fe was bound to organics and sulfides [Fig. 3(b)]. The relative percentile quantification of arsenic showed that it was bound to the crystalline phase (89 %) followed by Fe-Mn oxides (6%) then surface and carbonate bound (5 %) and minimum (2 %) bound to organics and sulfides [Fig. 3(c)]. Fe and As exhibited similar trend of occurrence in different fractions of sequential extractions. Sequential extraction studies conducted in the Bengal Delta plain showed that As present in oxyhydroxide phases of Fe and Mn was higher than that in the



(a)



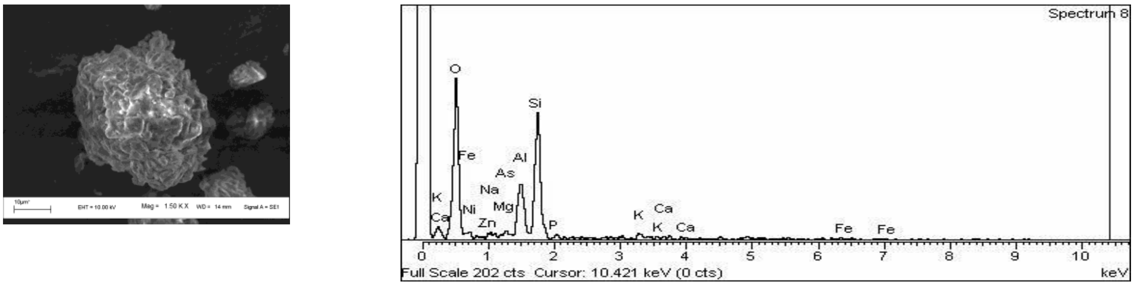
(b)



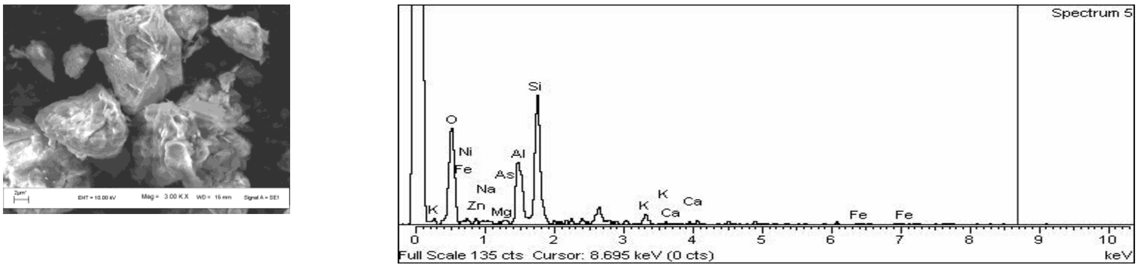
(c)

Fig. 3 Sequential extraction of Arsenic from C bore hole for (a) iron (b) manganese and (c) arsenic

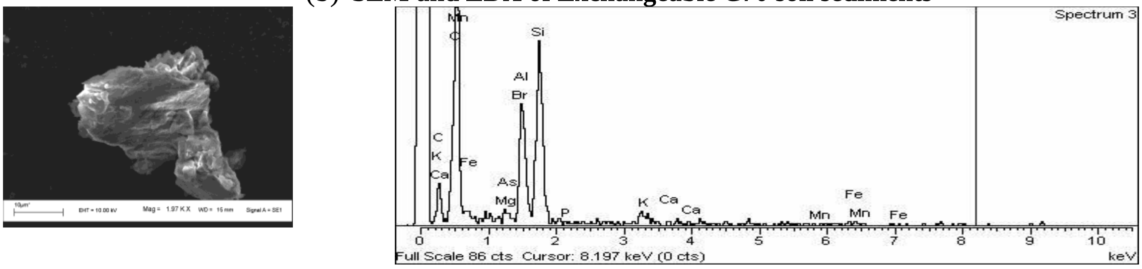
organic matter (Reza et al, 2010). The study area being predominated by alumino silicate minerals, the dominance of the residual phases can be justified because As and Fe are possibly bounded significantly to the mineral structures of the silicate minerals. The presence of aluminosilicate minerals was highlighted by the SEM/EDX and XRD analysis.



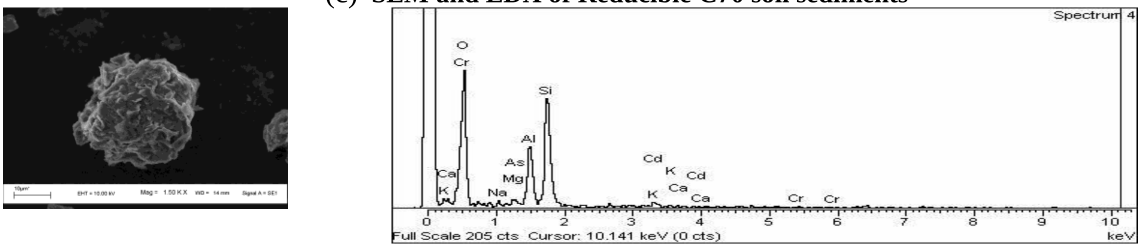
(a) **SEM and EXD of Untreated C70 soil sediments**



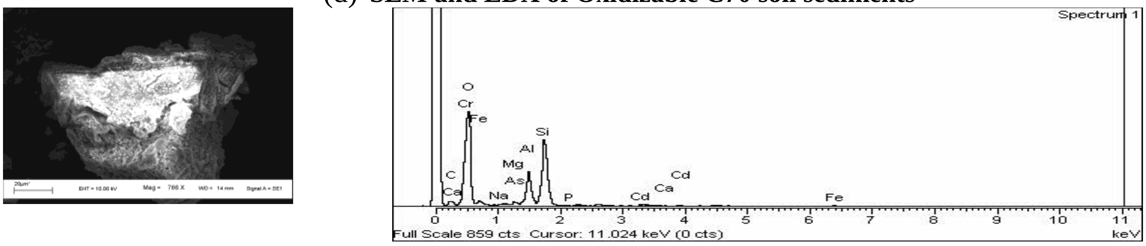
(b) **SEM and EDX of Exchangeable C70 soil sediments**



(c) **SEM and EDX of Reducible C70 soil sediments**



(d) **SEM and EDX of Oxidizable C70 soil sediments**



(e) **SEM and EDX of Residual C70 soil sediments**

Fig. 4 SEM and EDX of the C70 aquifer sediments through the BCR sequential extraction fraction

4.4 Aquifer sediment mineralogy

SEM/EDX and XRD analyses of the collected sediment samples from borehole C were carried out simultaneously at each step of the sequential extraction process in order to understand how the different medium of the Exchangeable, Reducible, Oxidizable and Residual fractions might have affected the sediment morphology and mineralogy (Fig. 4). SEM/EDX analysis profiles of the aquifer sediments showed that the mineralogy was dominated alumino-silicates of Na, K, Mg as well as that of Fe. EDX spectra further exhibited the peak for Cr in the oxidizable and residual phases of the C70 sediment sample. As EDX is sediment particle specific, there is not sufficient ground to consider Cr to be generally spread all over the aquifer. The presence of Cr in the aquifer sediments could possibly be due to the diagenetic processes involving iron oxides and aluminosilicate which appears to be the most important factor controlling the behaviour of As and Cr in sediments (Sompongchaiyakul and Sirinawin, 2007). The SEM and EDX analysis results further revealed that the extent of agglomeration decreased from the first to the last step, and the EDX supported the SEM images, where the amplitude of occurrence of the peaks representing respective elements decreased, suggesting reduction of their relative concentration in the corresponding phases. Results of the SEM analysis indicated that the sediment grains were moderately rounded to well rounded, suggesting that the sediments must have travelled some distance and the source of these sediments are located far away and hence are not local, hinting the Himalayas as a possible provenance.

XRD analysis profiles of the sediment samples confirmed the presence of Albite, Mica, Quartz, Gypsum, NaCl (Halite), $CaSO_4$ (Gypsum), $CaCO_3$ (Calcite), Feldspars, Hematite, MgO, Al_2O_3 , AsS and clay minerals (Illite), with the bulk composition being dominated by Quartz, Mica, Feldspars and Clay minerals (Fig.5). The amplitudes of the mineral peaks became diminished from the untreated soil to the residual step. Some of these minerals were the sources of iron, manganese and arsenic elements in the aquifer sediments. Results of the XRD analysis were in conformity with the BCR sequential extraction, as the XRD analysis showed the presence of quartz in high amount whereas the residual phase was mostly in crystalline phase. The lithology confirmed that the fine sands composed of Quartz, Gypsum and Illite as indicated by the XRD, SEM and EDX analysis as possible sources of iron, while $CaCO_3$ acts as a common mineral, which may lead to the formation of Fe-Mn carbonates & oxides in the investigated boreholes. The morphology of the different BCR sequential extraction phases shows that the state of agglomeration decreased from the untreated sediment followed by exchangeable phase to the residual state. Agglomeration of the sediment samples exhibited different textures in the different phases indicating that when these sediment come in contact with different chemical surrounding which may then release the adsorbed elements into the groundwater. A textural surface change in the sediments from the subsurface environment where the adsorption of Fe, Mn and As takes place is also indicated by the SEM and EDX analysis results obtained for the different stages of sequential extractions.

4.5 Multivariate statistics

Principal Component Analysis (PCA) is a powerful tool that attempts to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables (Kouras et al, 2007). Positive correlation observed between the depth, Fe & As indicates that both Fe and As increased with depth (Fig.6). Further, the positive correlation between Fe, Mn and As also indicates the possibility of presence of ferromanganese oxides associated with the

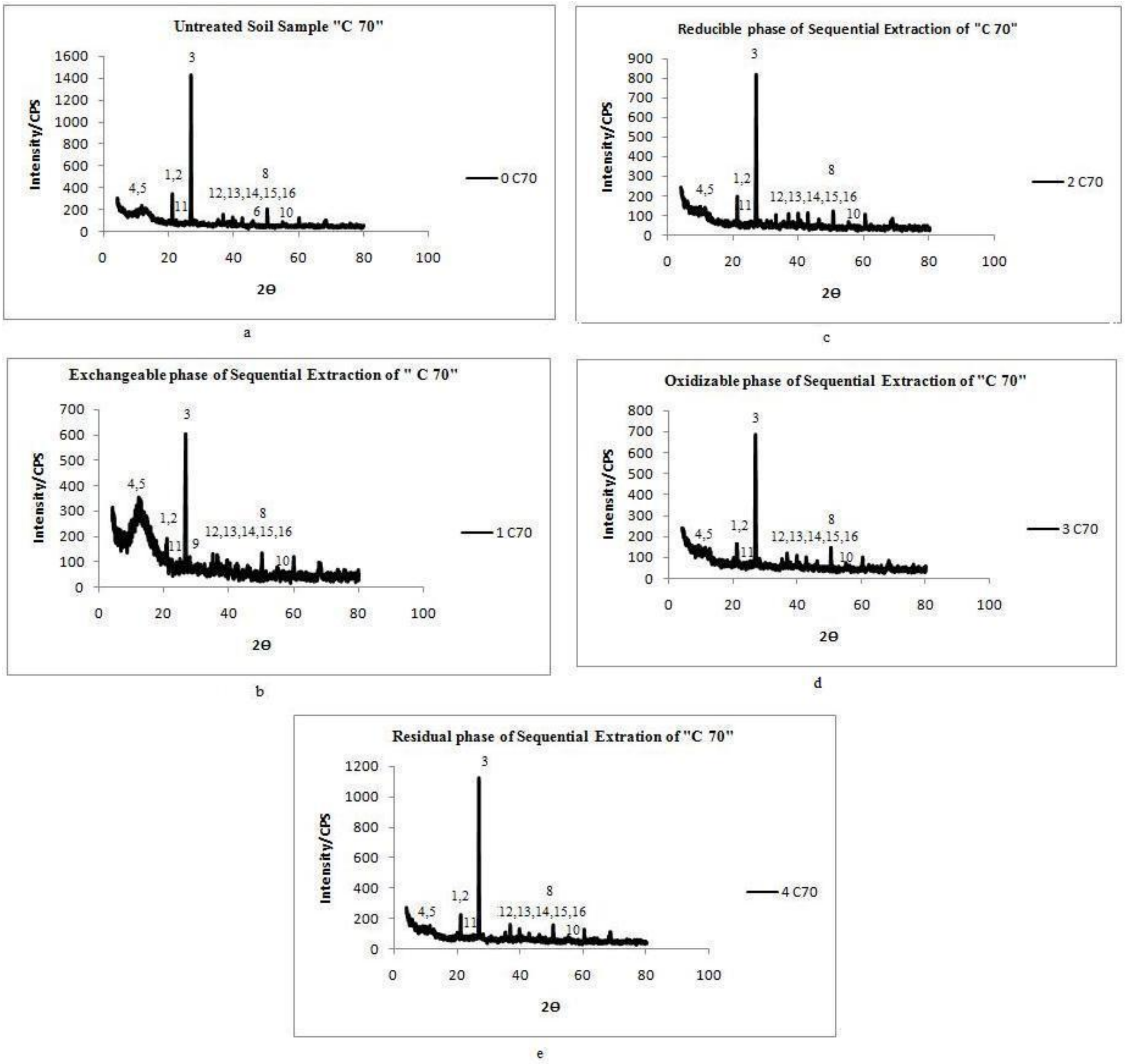
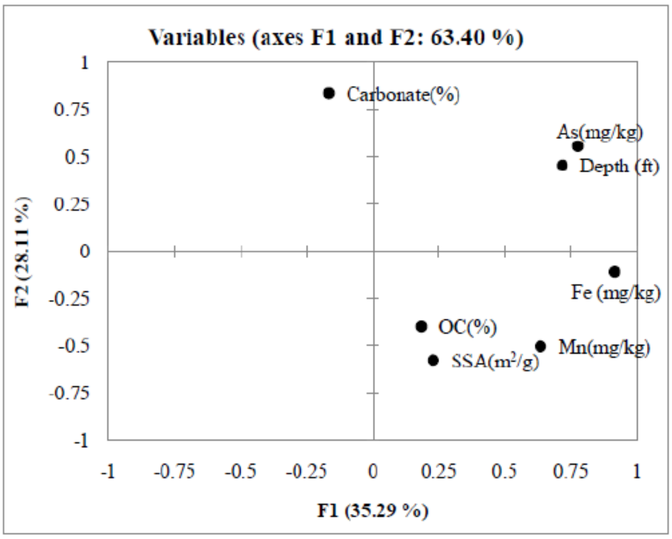
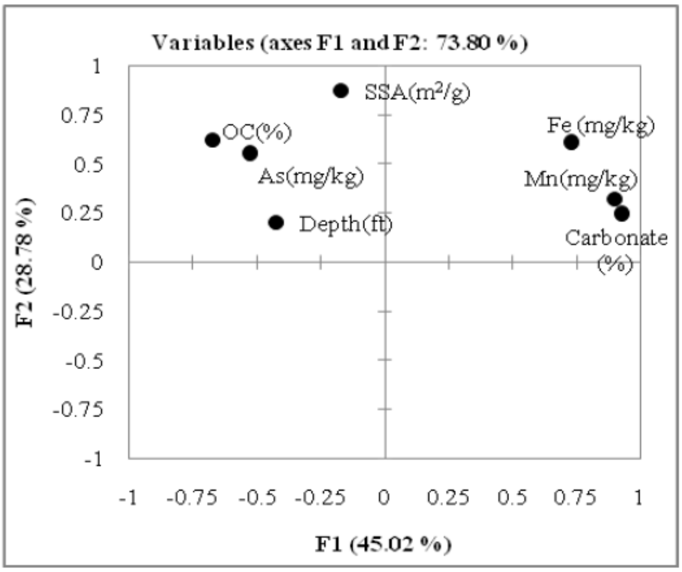


Fig. 5 XRD of the C70 aquifer sediments through the BCR sequential extraction fractions



(a)



(b)

Fig.6 PCA plots for (a) bore hole B (b) bore hole E

sediments (Pedersen et al., 2006). Results of sequential extraction analysis indicated that Mn- and Fe-hydroxides and organic matter were the major leachable As solid phases in the sediments. Positive correlation between manganese and carbonates for bore hole E indicated the likely presence of manganese carbonates, which has further been confirmed by the results of the sequential extraction. Correlation between iron & manganese and the carbonates is a strong reason to suspect that there may be predominance of carbonates with Fe co-precipitations (Deurer et al., 2003). However, with a negative correlation between As and carbonate in bore hole B, it is indicative that the carbonates may be predominantly constituted of coarse grain particles [Fig.6 (a)]. With manganese and carbonate contents positively correlated as observed in other studies (Varsanyi and Kovacs, 2006), the presence of manganese carbonates can be confirmed in the aquifer sediments, which has also been indicated by the results of sequential extraction analysis. Since the prevailing pH range is below 8.3, all carbonate species are expected to be present in the form of HCO_3 ions. Bi carbonate ions may form complexes on the surface sites of iron hydroxide and substitute arsenic from the surface of minerals and sediments, resulting in release of arsenic to groundwater (Anwar et al, 2004).

Arsenic and organic content has positive relations (Cullen et al., 1989) stating that arsenic can form bonds with organics. Presence of such organic matter has also been reported in the aquifer sediments of the Bengal basin (Ahmed et al. 2004; McArthur et al. 2001; Nickson et al. 2000), the degradation of which could drive the sequence of redox reactions in the aquifer thereby enhancing arsenic mobilization (Anwar et al. 2003; McArthur et al. 2004; Ravenscroft et al. 2001). Negative correlation between arsenic and carbonate indicates that the arsenic may not be of carbonate origin while a positive correlation between organic content and SSA indicates that organic matter got adsorbed to smaller particles (Schorer, 1997) [Fig. 6(b)]. Organic matter can act as an electron carrier via the humic substances to enhance microbial Fe reduction and control the rate and magnitude of microbially-mediated arsenic release in Bangladesh aquifers (Rowland et al., 2007; Mladenov et al., 2010, Reza et al, 2010). Organic matter can further influence the solubility and mobility of As mainly through competitive adsorption, complexation, and redox reactions (Wang and Mulligan, 2006). The presence of Fe, Mn and As fractions associated with organic content is thus supported both by the results of the PCA and the sequential extraction.

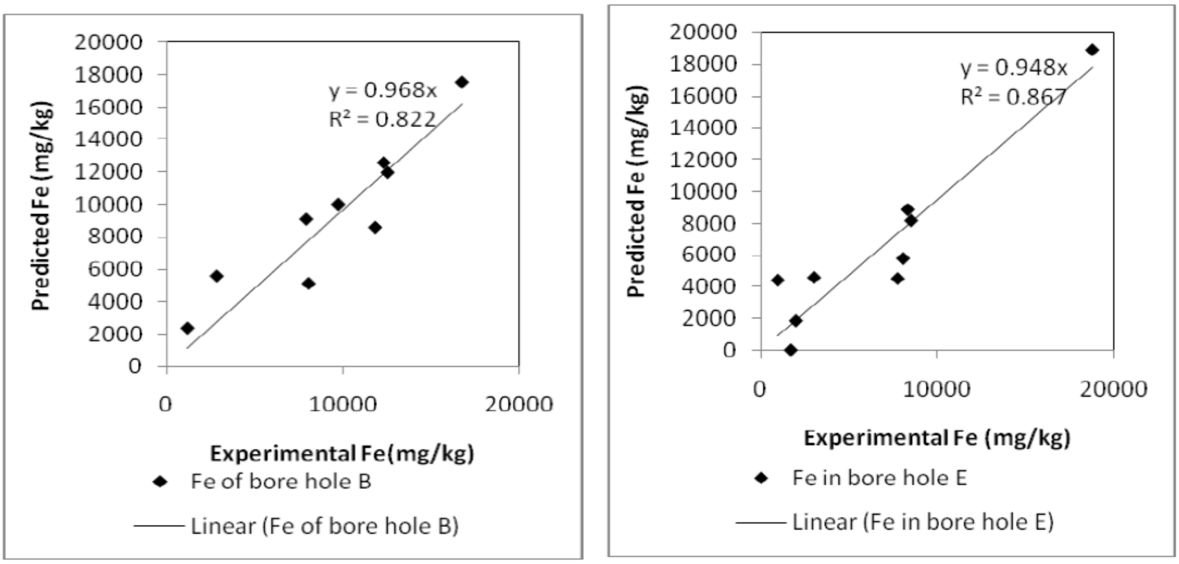
4.6 Multivariate regression analysis

Multiple regression analysis attempts to fit the independent variables for predicting a single dependent variable (Rahman et al, 2009). The general form of a model developed with multiple regression looks like [Rahman et al, 2009]:

$$Y = \beta0 + \beta1X1 + \beta2X2 + \beta3X3 + \ldots\ldots..+ \varepsilon \ (1)$$

where,

$X1$, $X2$, $X3$ denote the independent variables, Y stands for the dependent variable, $\beta0$, $\beta1$, $\beta2$, $\beta3$ represent the correlation coefficients and ε designates the error term. The five selected independent variables Mn, Organic Carbon, Carbonate, Specific Surface Area (SSA) and Depth of the bore hole and one dependent variable Fe were used as the input data for fitting the multiple regression model (equation 1). Results of the regression analysis show that iron leaching is dependent on controlling factors like Mn concentrations, organic matter, carbonate content and SSA along with its depth. A coupled geochemistry exists between Fe and Mn in aquifer sediments (Taylor and Price., 1983). Organic matter provides the reducing conditions by microbial metabolism, which leads to the dissociation of the iron oxyhydroxides (Baalousha et al., 2009). The ferro carbonates leach iron at lower pH in anaerobic conditions (Vance 1994; Das et al., 2006) which further gets adsorbed on sediment particles with high SSA in natural conditions (Sarifuzzaman et al 2007). The multiple regression modelling was done with enabling the macros data analysis to perform regression in Microsoft Excel 2007. Fig. 7(a) and 7(b) shows that at the boreholes B & E, the equations satisfy iron leaching process as a function of other factors. Table 5 shows the combined equations explaining Fe leaching for bore hole B and E.

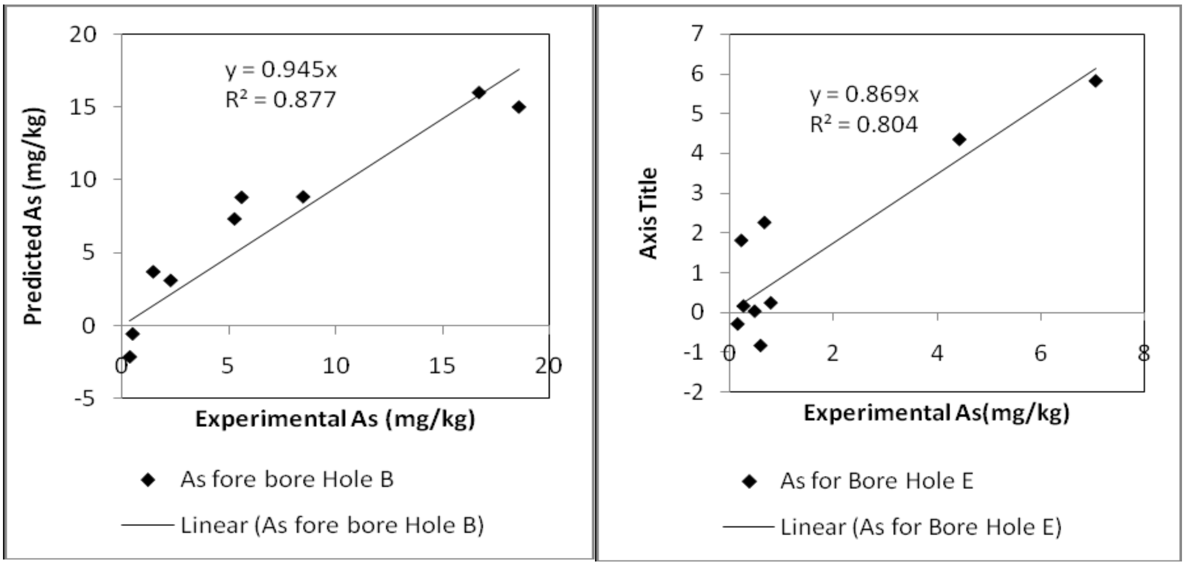


(a) **(b)**

Fig. 7 Graphical relation between the predicted and experimental values of Fe for (a) B bore hole and (b) E bore hole.

Table 5. Iron leaching dependent on various controlling parameters: regression analysis

Bore Hole	**Equation**	**R^2 between Experimental and Predicted Iron**
B	**Fe(mg/kg)** = 33.26 **Mn(mg/kg)** - 66.32 **OC(%)** +765.40 **Carbonate(%)** – 321.21 **SSA(m^2/g)** + 43 **depth(ft)**	0.8277
E	**Fe(mg/kg)** = 13.38 **Mn(mg/kg)** + 299.37 **OC(%)** - 1023.24**Carbonate(%)** + 40124.29 **SSA(m^2/g)** – 17.65 **depth(ft)**	0.8674



(a) **(b)**

Figure 8 Graphical relation between the predicted and experimental values of Arsenic (a) B bore hole (b) E bore hole.

Table 6. Arsenic mobilization dependent on various controlling parameters: regression Analysis

Bore Hole	**Equation**	**R^2 between Experimental and Predicted Arsenic**
B	**As(mg/kg)** = 3.43 x 10^{-4} **Fe (mg/kg)** +5.6 x 10^{-3} **Mn(mg/kg) -** 0.2 **OC(%)** + 0.76 **Carbonate(%) - 19.91 SSA(m^2/g)** + 0.09 **depth(ft)**	0.8771
E	**As(mg/kg)** = **-** 1.9 x 10^{-5} **Fe (mg/kg)** + 6.7 x 10^{-3} **Mn(mg/kg)** + 0.83 **OC(%)** - 2.06 **Carbonate(%)** + 16.78 **SSA(m^2/g) -** 0.02 **depth(ft)**	0.8041

The coexistence of Fe and As in arsenic enriched aquifers is well established (McArthur et al., 2004). The mobilization of arsenic from the iron oxyhydroxides, ferromanganese oxides, organic matter, carbonates takes place due to the reducing conditions caused by microbial factors (Nath et al., 2009; Duan et al., 2008; Guern, 2003; Varsanyi and Kovacs, 2006). The complexes formed by iron oxyhydroxides, ferro manganese oxides and carbonates with organic matter get adsorbed on surface area of the sediments, which is also responsible for arsenic mobilization along with depth (Xie et al., 2009; Sarifuzzaman et al 2007; Islam et al., 2000).

Predicted and experimental values obtained by multiple regression analysis co-relates at more than 0.8 for the aquifer sediments for both the bore holes B and E (Fig. 8) indicating that leaching of iron is a combined phenomenon consisting of reducing acidic conditions produced by organic matter, with desorption of iron from carbonates and its dissociation from ferromagnesian compounds, all of which were adsorbed on to the sediment surface.

5. Summary and Conclusion

The chemical characteristics and nature of As release into the groundwater from borehole sediments were investigated to refine our understanding of the role of Fe leaching in arsenic release to the groundwater. Groundwater in the study area was under a reducing condition as illustrated by the Eh-pH stability diagram, due to which the dominant species of iron and arsenic present was found to be Fe (II) and As (III). Concentrations of elevated arsenic in the sediment samples collected at variable depths of the three boreholes ranged between 1 mg/kg to 18.6 mg/kg, with maximum concentrations found in the fine sand fractions. Fe concentrations ranged between 106 mg/kg to 26991 mg/kg, with maximum concentrations present in the silt fractions. The silt and the fine sand sediment fractions seem to be the key repositories of high Fe and As concentrations in the study area, which is supported by the SEM/EDX and XRD analysis. Fractionation of Fe and As has shown the dominant phases as Residual (crystalline bound) fraction reinforcing the fact that the source of As in the sediments is geogenic as generally believed in case of such non-industrial terrain, followed by the Reducible (Fe Mn oxide bound) fraction; Exchangeable (surface and carbonate bound) fraction and Oxidizable (organic and sulphides bound) fractions. With similar trends of occurrence of Fe and As in all the fractions of the BCR phases, mobilization of arsenic seems to be an implication of iron leaching. Iron leaching is further found to be dependent upon the major controlling factors like the reduction of organic matter and the dissociation of iron oxyhydroxides, carbonates or other ferro manganese compounds adsorbed on the sediments, all of which may be variably responsible for enhancing arsenic mobilization. PCA plots confirmed a positive correlation between As, Fe, Mn and organic matter. This is also supported by the regression model analysis, where the correlation between the predicted and experimented values of iron were observed to be more than 0.8 for both the bore holes, indicating that the identified controlling factors play dominant roles in Fe leaching. The results of this study is found to be consistent with studies carried out in the Bengal Basin in Bangladesh, suggesting that the arsenic trail observed in the Brahmaputra Floodplains possibly extends finally to the Bengal Delta Plain.

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