

CHAPTER 6

Phase distribution and mobility assessment using desorption and sequential extraction procedures

6.1. Introduction

Arsenic and fluoride are considered to be two of the most common geogenic inorganic pollutants in groundwater, in many regions of the world [1-3]. Arsenic is known to be carcinogenic in human beings [4], while F^- on the other hand cripples the body by causing fluorosis [5]. Distribution and occurrence of these two pollutants present a unique picture, although As has been reported from a number of different environments, yet it is most commonly associated with alluvial plains of major river systems [4, 6, 7]. Fluoride on the other hand has been mostly associated with arid/semi arid regions where recharge of the aquifers is very low promoting prolonged rock-water interactions [8, 9]. Of late some of the studies have pertained to the phenomenon of “co-occurrence” of the two contaminants as it represents a greater danger to human health and society [2, 3, 10]. How much As may be adsorbed or desorbed has been found to be controlled by the Fe content of the aquifer materials and the sediments [6, 11, 12]. Metals have often been separated out from their source materials like soils and sediments by using well established extraction procedures, however fractionation of trace elements like As which can exist as anionic forms is relatively new. Therefore the feasibility of extraction based techniques for different soil and sediments has to be established by newer databases.

Co-occurrence has been found to be more common in the arid parts of the world where rock-water interaction is ample and the groundwater condition is oxidising. Regions like Arizona and California in the USA [3, 13], Mexico [2, 3], Argentina [3, 6, 10, 11], China [14], Pakistan [1, 3] are some known cases of As- F^- co-occurrence. Although co-occurrence is more common in arid oxidizing conditions, yet some notable cases of As and F^- co-occurrence involving reducing aquifers include Hetao Basin [3, 15-17], Huhhot Basin [3, 18], Datong Basin [3, 19] and Montana in the USA [3, 20]. In India

although both As [7, 21-25] and F⁻ has been detected [26-28], yet co-occurrence studies are missing and more work needs to be done.

The partition coefficient (K_d) or the ability of a contaminant to separate out into the groundwater system depends on a number of factors. In many cases the total concentration of the pollutant in the soil/sediment is not an accurate indicator of the levels present in the groundwater. Total As content, pH, organic matter content, CEC, presence and the absence of Fe and Al oxides clay content, grain size, presence or absences of the parent material are some of the factors which can influence the leaching potential of contaminants like As [6, 29-33]. One of the primary factors which governs the mobilization of contaminants like As and F⁻ is their distribution in different soil/sediment phases [34]. Actual toxicity of many contaminants like As which occur in soils and sediments have been found to be dependent on the relative ease of the fractions to leach out of the solid phase rather than their total concentrations (soil/sediments or minerals) [35, 36]. Therefore in light of the above factors, it is essential to understand phase distribution of different fractions of “interest” in soil and aquifer materials.

Sequential extraction procedure (SEP), is one of the most well established methods for extracting and understanding these “operationally defined phases” or fractions of soils/sediments with the help of “reagents of increasing dissolution strength” under laboratory conditions [35]. However, field conditions present a completely different perspective than laboratory environment as the former is much more complex, and cannot be predicted or controlled. Although the examination of the aquifer materials provide a better understanding of the actual environment of the groundwater, yet the role of soil and sediment cannot be neglected, mainly because of two reasons, first of all, soils/sediments undergo deposition and compaction to form aquifers in the future, and secondly it provides a better insight into the role of anthropogenic activities in the particular region.

Physico-chemical parameters like pH and alkalinity have been found to positively affect the mobility of As and F⁻ in groundwater [3, 6]. Batch sorption/desorption and column

experiment based studies to understand As and F⁻ co-occurrence are few in number but present a much deeper understanding of release and co-occurrence mechanisms. Very few lab based works have pertained to understand the mobility dynamics and co-occurrence of As and F⁻ around the world and such works are lacking in India which ironically is a hotspot of As contamination. The BFP of Assam, India is a very large region and its population is at risk from drinking As and F⁻ contaminated groundwater as both these pollutants have been reported from this part [21]. However, no study has been conducted in this region to understand whether there is a possibility of co-occurrence or the likely mechanisms which could lead to such a phenomenon. Although groundwater and aquifers have been studied by many workers, yet works on naturally porous mediums like soil/sediment and the affect of infiltration on groundwater As and F⁻ levels are less in number. Soil types and conditions are therefore important considerations. Increasing trends of pesticide and fertilizer usage can also affect the groundwater As levels [37], therefore there is a need to understand the governing factors and the mass balance involved in the mobilization of As and F⁻ in the groundwater. Considering the above factors, an attempt was made in this study to understand: Distribution of the different phases in the soil and sediments of the region, correlation of Fe on total As, and on the leaching of As and F⁻ in the system and effect of pH change on the mobilization of As and F⁻ in the groundwater from porous medium.

6.2. Materials and methods

A total of 5 grab samples were collected along the BFP, the selected sampling points were Dibrugarh (Dibrugarh district), Borholla (Jorhat district), Bosasimalu (Sonitpur district), Barpeta town (Barpeta district) and Jogighopa (Bongaigaon district) (Fig. 6.1). Out of the above mentioned five grab samples, the first and the last are river sediment samples while the other three are soil samples. The soil/sediment samples were brought to the laboratory and dried initially at 50°C for 24 h and then stored at 4°C until further analysis [3]. Detection of the minerals and elements was done by powder XRD and SEM EDX. Physical and chemical characterization of the samples was done by analysing the TOC, EC, pH and grain size.

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Fractionation of As was done by the modified method for sequential extraction of As proposed by [35], while batch desorption was performed on the samples by adopting the procedure given by [3]. The methodology has been discussed in greater details in chapter 2 dealing with materials and methods. In order to observe the relation between the As content in the groundwater and the soil/sediments, immediate *in situ* analysis of groundwater As was performed in the soil/sediment sampling sites using a Merck portable As detection kit. Partition coefficient (K_d) was calculated for risk assessment. Correlation analysis was performed to observe the relation between the different physico-chemical parameters. Saturation indices were calculated using MinteqA2 version 3.1.

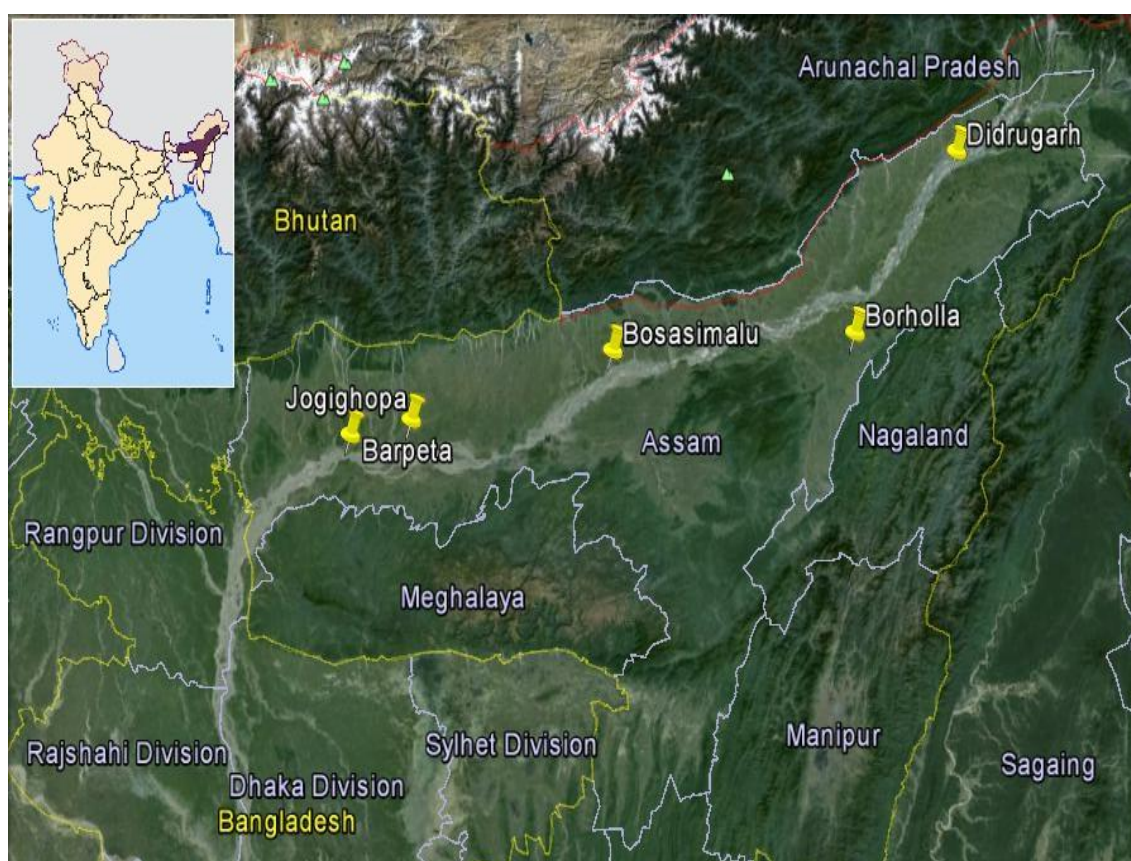


Figure 6.1: Map depicting the soil/sediment sampling points

6.3. Results and discussion

6.3.1. Physico-chemical characterization of the soil and sediment samples and its implication

The values of the different parameters have been displayed in Table. 6.1, while Table. 6.2 show the correlation between the parameters. The groundwater samples which were extracted from the vicinity of the soil samples were found to have As level in excess of the drinking water limit ($10 \mu\text{gL}^{-1}$) prescribed by the World Health Organization [38]. High groundwater As was found to be associated with elevated levels of organic matter, CEC and clay (Table. 6.1), the same was also reflected in the strong positive correlation of groundwater As with organic matter, CEC and clay (Table. 6.2, $r = 0.93, 0.94$ and 0.97 respectively). Some other studies have also reported the aforementioned trend [6, 12, 33]. Microbial degradation of organic matter has been found to consume oxygen and create anoxic condition suitable for As release in groundwater by reductive hydrolysis of metal (hydr)oxide [11, 12]. Clay fraction has been found to bind more metal (hydr)oxide due to its higher surface area and innate negative surface charge, [39, 40] which in turn has been found to hold higher amounts of As. Higher clay content has also been reported to affect the CEC of soils and sediment positively due its ability to hold more cations [39, 40]. These cationic fractions are reported to bind As in the soils and sediments resulting in their positive correlation [6, 35].

Out of the 5 samples, the river sediment samples were found to have alkaline pH while the three soil samples had pH close to neutral (Table. 6.1), this could be due to leaching away of the base cations and retention of salts due to rain in the soil samples as they were collected from regions far from the influence of the river [41]. Soil samples in the present study had much lower EC than the sediment samples. Higher CEC and clay content has been linked with higher EC in the soils [42], but in our case the opposite was observed (Table. 6.1). The probable reason could be that the soil samples were far from the influence of the river and were older. In older soils regular exposure to rains has been reported to cause leaching out of base cations as well as anions ultimately leading to the lowering of EC [42].

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Table 6.1: Descriptive data for the different parameters of the soil and sediment samples

Sample location	GW As (μgL^{-1})	pH	TOC (mgKg^{-1})	EC (μScm^{-1})	CEC (meq100g^{-1})	Grain size analysis (%)			F-I	F-II	F-III	F-IV	F-V	Sum of fractions 1–5	Total As (raw sample)	Recovery percentage	K_{d1}	K_{d2} (Lkg^{-1})
						Sand	Silt	Clay										
Dibrugarh	0.65	8.50	0.44	318	3.50	92.5	1.35	6.15	7.77	2.69	60.6	53.1	141	265	411	64.4	25.33	803
Jorhat	110	6.87	16.6	68.0	15.1	37.1	32.5	30.2	7.96	12.8	170.	167	120	478	533	89.8	23.02	4.33
Sonitpur	62.1	7.01	2.28	62.0	7.35	51.4	30.2	18.2	7.31	2.68	137	132	19.4	299	390	76.8	29.92	4.82
Barpeta	132	6.91	15.2	63.0	19.6	24.4	29.4	45.4	10.7	28.0	189	164	141	521	600	86.9	13.46	2.01
Bongaigaon	3.16	8.20	0.58	689	7.10	91.9	0.75	7.40	8.92	5.17	93.6	87.18	118	313	472	66.3	22.21	99.1

**F stands for fraction and the unit for the As extracted from the soil/sediment samples is μgKg^{-1}*

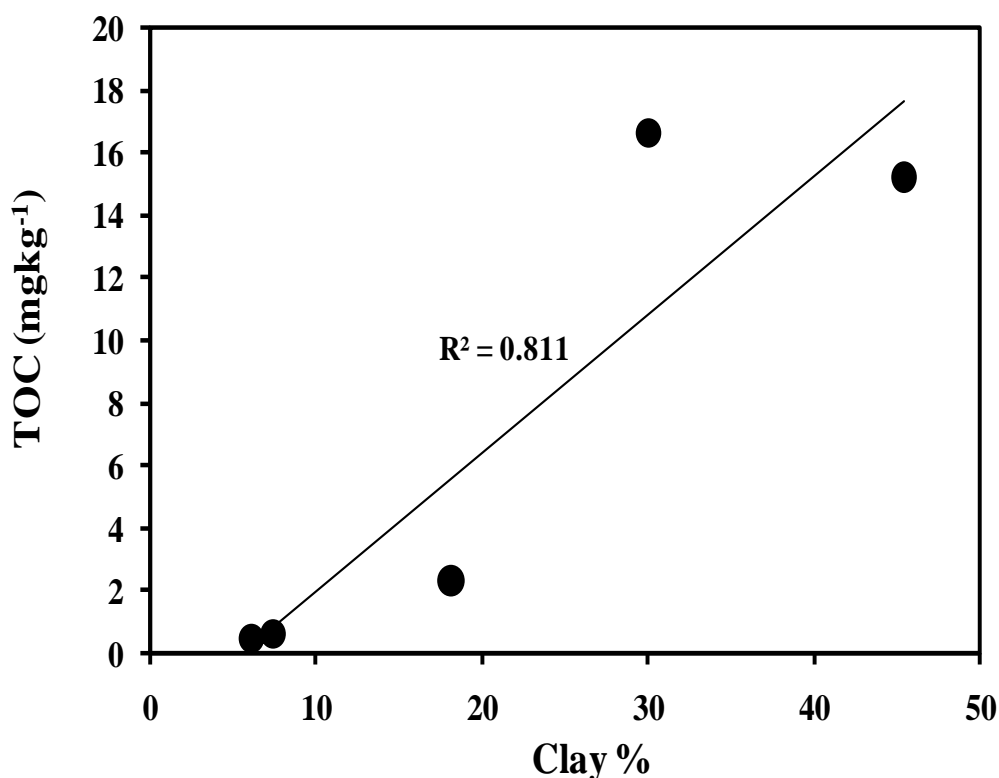


Figure 6.2: Scatter plot for clay percentage versus total organic carbon shows a highly linear relationship, indicating that clay content determines the organic carbon content of soils and sediments to a great extent

TOC of the soil/sediment samples was found to relate well with the clay content (Table. 6.2) (Fig. 6.2). Clay particles being fine provide charged binding sites for organic matter, which slows down the decomposition process of the organic matter [40]. Moreover soils with higher clay content have been found to have increased potential for formation of aggregates. These aggregates protect the organic matter from further decomposition [40]. Results of the EDX showed that the soil and sediment samples had high amounts of Fe and Mn, moreover As was found to be associated with Fe, Mn, Si and Al, indicating its state as a co-precipitated or adsorbed phase in the soil and the sediments of the region (Fig. 6.3). Similar results were obtained by [23], in core soil samples collected from Titabar area, Jorhat district, Assam, India, where As was found to be present in co-precipitated form along with Si, Al, Fe and Mn.

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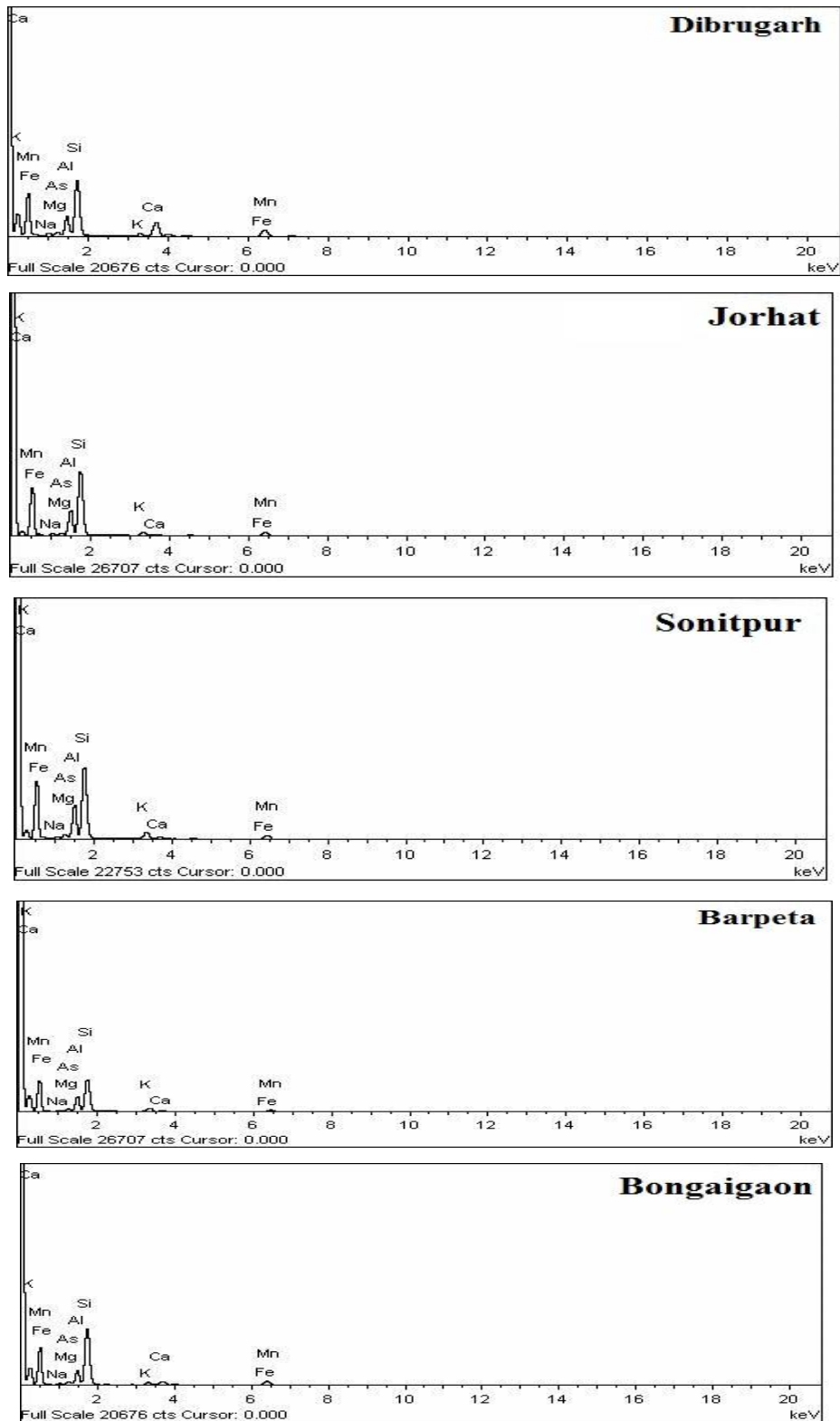


Figure 6.3: Energy dispersive X-Ray (EDX) spectroscopy of the soil and sediment samples illustrating As as a part of the mineral phases in all the sample

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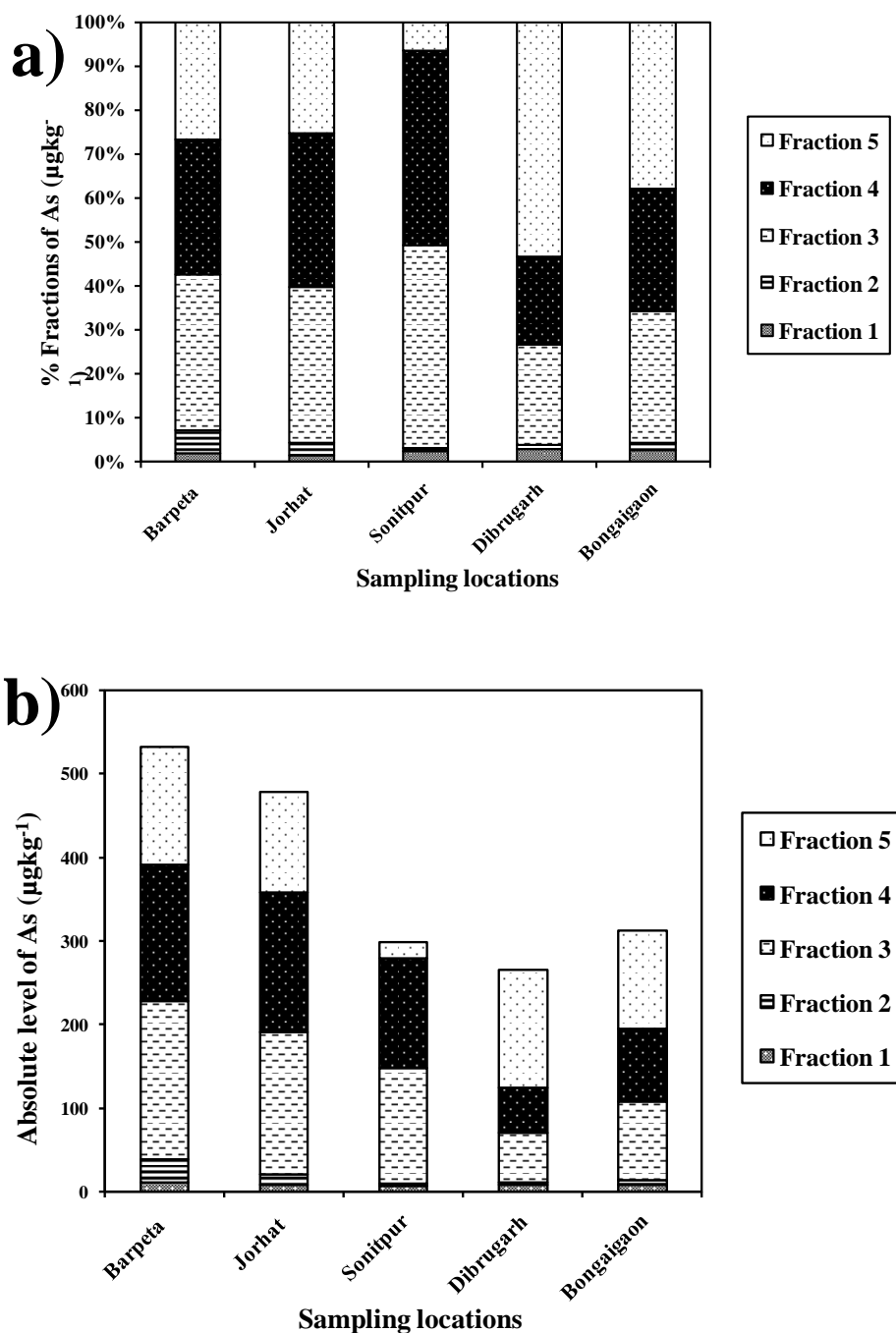


Figure 6.4: (a) Percentage and (b) absolute As content in soil and sediment show Fe (hydr)oxide phase as the most dominant contributor of groundwater As

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Table 6.2: Correlation matrix for the soil/sediment parameters and the As fractions extracted by the sequential extraction procedure.

	GW As	GW pH	TOC	EC	CEC	Clay	F-I	F-II	F-III	F-IV	F-V	Total As	K _{d1}
pH	0.92												
TOC	0.93	-0.77											
EC	-0.79	0.80	-0.63										
CEC	0.94	-0.78	0.94	-0.54									
Clay	0.97	-0.83	0.90	-0.70	0.97								
Fraction-I	0.45	0.19	0.47	0.04	0.70	0.64							
Fraction-II	0.82	0.58	0.82	-0.43	0.94	0.93	0.86						
Fraction-III	0.98	0.95	0.88	-0.70	0.93	0.94	0.47	0.79					
Fraction-IV	0.96	0.97	0.87	-0.70	0.88	0.89	0.34	0.69	0.99				
Fraction-V	0.02	0.35	0.32	0.27	0.28	0.16	0.56	0.45	-0.08	-0.16			
Total As	0.92	0.73	0.97	-0.52	0.99	0.94	0.66	0.92	0.90	0.86	0.37		
K_{d1}	-0.53	0.21	-0.62	0.04	-0.77	-0.69	-0.96	-0.91	-0.51	-0.39	-0.70	-0.76	
K_{d2}	-0.65	0.79	-0.52	0.27	-0.65	-0.59	-0.31	-0.44	-0.80	-0.83	0.38	-0.58	0.24

6.3.2. Arsenic fractionation

Arsenic fractionation was done in the soil/sediment samples to investigate the distribution of the different “operationally defined phases” of As in the soil/sediment samples. The details of the different fractions in each of the samples have been presented in Table. 6.1. The distribution of the different As fractions in the soil/sediment samples have been graphically represented in Figure.6.4. In the succeeding section we discuss the different fractions of each of the samples.

Physisorbed As: Due to the weak nature of the Van Der Waals forces, As in this fraction is highly labile and has been found to be easily replaceable by other anions like SO_4^{2-} , therefore this phase has also been termed the “physisorbed fraction” [35, 43]. Low values of As extracted from this fraction (Table. 6.1) suggest that this fraction is not the prime source of As contamination in the groundwater of the BFP. This is also evident from the low correlation observed between this fraction and the groundwater As level. Also a positive correlation observed between fraction I and CEC could be due to weak attractive forces between the oxyanions of As and the cations.

Chemisorbed: This fraction of As has been also been termed “chemisorbed” fraction because As in this phase appears to be chemically bonded primarily to the cations, as observed from the high correlation between fraction II and CEC (Table. 6.2) [35, 43]. This fraction is less labile than fraction I, and is removed by anion exchange with PO_4^{3-} [35, 43]. Presence of high phosphates in the soil and the use of phosphate fertilizers can affect the mobilization of this fraction. Higher correlation observed between groundwater As and this fraction indicates the more dominant role played by this phase in groundwater As contamination.

As associated with amorphous and poorly crystalline Fe (hydr)oxides: A huge increment was observed in the amount of As extracted as fraction III (Table. 6.1). The combined contribution of fractions I and II to the cumulative amount of As extracted from the soils and sediments was found to have an average value of 4.71 % while fraction III accounted for 34.08 %.The amount of As extracted in this fraction was

found to be more for soil samples compared to the sediment samples (Table. 6.1). Soil samples were also found to have higher TOC than the sediment samples. Moreover the correlation between fraction III and TOC was observed and found to be significant (Table. 6.2. $r = 0.88$) suggesting that organic matter content strongly appears to influence the mobilization of As. The probable reason could be that microbial oxidation of organic matter creates a reducing environment suitable for hydrolysis of Fe (hydr)oxide thereby releasing the associated As [11, 12]. A very high correlation ($r = 0.94$) is observed between fraction III and the clay content of the soil/sediments (Table. 6.2). This could be due to the fact that clay fractions provide greater surface area for binding of (hydr)oxide which ultimately complexes with the As [6]. This observation can be supported by the fact that the sediment samples which had very low clay content were also found to have lower levels of As associated with fraction III. EDX results suggest that overall Fe (hydr)oxide is present in high amounts in the soil and sediments samples (Fig. 6.3). This indicates that this fraction plays a very important role in occurrence of high groundwater As in the BFP, which is further proved by the high correlation between groundwater As and fraction III (Table. 6.2, $r = 0.98$). This fraction of As is reported to be associated with amorphous and poorly crystalline Fe (hydr)oxide like ferrihydrite, because of which this fraction was reported to be less labile than previous fractions (I and II) [35, 43]. Its mobilization has been reported to be associated with action of hydroxamated ligands and reducing conditions [35, 43,44].

As associated with well crystalline Fe (hydr)oxides: This phase has been found to be associated with more crystalline (hydr)oxide of Fe like goethite [FeOOH] [35, 43] and therefore is less labile than the previous fractions (I, II and III). The average contribution of this fraction to the total As extracted was 31.69 % compared to 4.71 % contributed by the combined values of fraction I and II. High correlation of this fraction with TOC supports the involvement of bacterially mediated As release by consumption of oxygen in a reducing environment (Table. 6.2, $r = 0.87$) [11, 12]. This fraction like the previous fraction was also found to be strongly influenced by the pH of the soil/sediment (Table. 6.2, $r = 0.97$). This fraction also showed a very high correlation with clay content (Table. 6.2, $r = 0.89$) due to the fact that clay provides greater surface area for binding of Fe (hydr)oxide [6]. This observation can be supported by the fact

that the sediment samples which had lower As levels than the soil samples also had much lower clay content (Table. 6.1). Most importantly, this and the previous fraction appear to control the As contamination in the groundwater of the BFP. This is evident from the high correlation observed between fractions III and IV, and groundwater As levels (Table. 6.2). The principal mode by which this fraction appears to mobilize is reductive hydrolysis [3, 35, 43,44]. Other factors which also affect the mobilization of this fraction are pH, alkalinity and the presence or the absence of ligands [3, 35, 43,44].

As associated with residual minerals: This is the residual or the non-labile fraction which has been reported to be associated with sulphides like orpiment [35, 43]. Though the As level in this fraction represents an average 29.92 % of the total As (Table. 6.1), yet it shows no significant correlation with groundwater As (Table 6.2, $r = 0.02$), indicating that this fraction has no contribution in the process of groundwater As mobilization. This is because fraction V has been found to be unaffected by normal conditions. Instead extreme conditions of oxidation or anthropogenic activities like mining which releases highly oxidizing acidic discharges have been suggested as key processes capable of mobilizing this fraction [6, 18], however such activities have been found to be nonexistent in the vicinity of the sampling locations of this study. This fraction also showed no correlation with clay content (Table. 6.2), indicating that the As bearing sulphides formed discrete structures and were not found as coatings or layers on soil/sediment particles. Moreover the very low correlation with TOC suggests that microbially created reducing condition had no effect in its mobilization (Table. 6.2).

6.3.3. Evaluation of leaching potential of As through partitioning coefficient

Partition coefficients (K_{d1} and K_{d2}) were found to negative correlate with groundwater As (Table. 6.2, $r = -0.53$ and -0.65 respectively), a negative correlation implies higher leaching potential of soil and sediment bound As. The decrease in the relative ease of the successive As fractions to leach out is well depicted by their correlation with K_{d1} (Table. 6.2), the only exception being fraction V which depicts a lower correlation with K_{d1} compared to fractions III and IV. Correlation coefficients of the different fractions with K_{d2} was observed to study the relative contribution of each fractions to the

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groundwater As (Table. 6.2); it was found that Fe (hydr)oxides bound As accounted for maximum As in the groundwater (Table. 6.2, $r = -0.80$ and -0.83 for fractions III and IV respectively). The above observations show that although fractions I and II are capable of leaching out into groundwater system quite easily, yet it is the combined contribution of fractions III and IV or the Fe (hydr)oxides phase which accounts for maximum As pollution in the groundwater. Organic matter (TOC), CEC, clay and Fe (hydr)oxide content were found to influence the partition coefficients to a great extent indicating their roles in As mobilization which has already been discussed earlier. The residual fraction appears to have no correlation with K_{d2} indicating that this fraction has no role in mobilization of As in the BFP. The soil samples had the lowest K_{d2} values indicating maximum potential for As leaching compared to the sediment samples (Fig. 6.5). Some of the studies pertaining to elevated levels of As and F^- in reducing aquifers have explained the cause to weathering and dissolution of minerals like fluoroapatite $[Ca_5(PO_4)_3F]$ and fluorite (CaF_2) [3, 17, 28]. The reason was explained as ion exchange with OH^- in clay minerals or micas like muscovite and biotite at high pH by [3, 45]. Fluorite dissolution is also associated with precipitation of calcite [26, 27], in our study however the calculation of the saturation indices revealed that fluorite as well as calcite were under-saturated in the groundwater of the soil and sediment sampling sites (Table. 6.3).

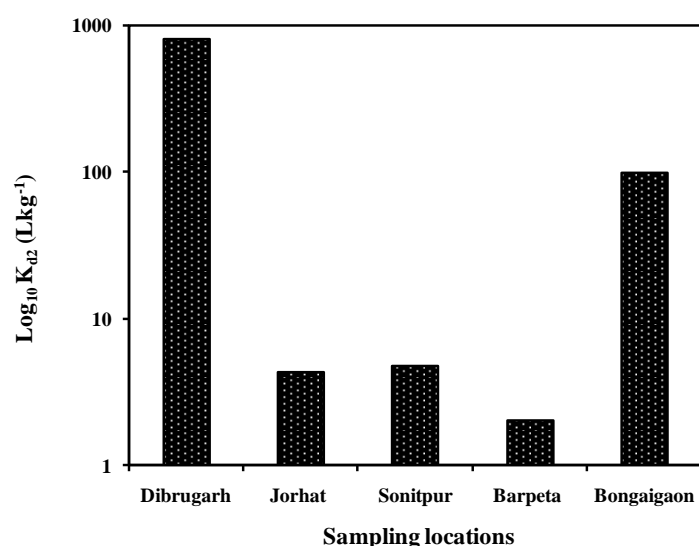


Figure 6.5: Bar diagram showing K_{d2} of each of the five samples indicate low mobilization of As from the sediment samples compared to the soil samples

Table 6.3: Saturation indices of aqueous phases in the soil and sediment samples

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Aqueous Phase	Samples				
	Bongaigaon	Barpeta	Sonitpur	Jorhat	Dibrugarh
Aragonite	-2.17	-0.80	-1.3	-1.38	-1.10
Calcite	-2.03	-0.94	-0.65	-1.23	-0.96
Dolomite (disordered)	-4.91	-1.80	-3.06	-2.59	-2.63
Dolomite (ordered)	-4.36	-1.25	-2.51	-2.04	-2.08
Ferrihydrite	2.68	5.40	4.25	4.84	3.99
Ferrihydrite (aged)	3.19	5.91	4.76	5.35	4.50
Goethite	5.39	8.11	6.96	7.55	6.70
Gypsum	-2.68	-2.83	-3.15	-3.24	-3.05
Halite	-8.69	-7.88	-8.67	-8.85	-8.42
Mirabilite	-10.72	-9.84	-10.59	-10.35	-9.91
NaF	-19.44	-7.52	-19.24	-7.80	-8.02
Fluorite	-24.81	-2.02	-25.02	-2.47	-3.17

The relationship of As and F⁻ with pH was found to be slightly positive in the BFP (Fig. 6.6 from unpublished data), therefore other minerals like fluoroapatite could not be the source of F⁻, as the dissolution of fluoroapatite was found to decrease with increasing pH [3, 46]. Fluoride leaching experiments on biotite mica also revealed a negative correlation between F⁻ and pH [3, 47]. Therefore taking into account the findings of the fractionation, partition coefficient and saturation indices into account, the desorption experiments were designed to target the Fe (hydr)oxide phase of the soil and the sediment samples. The pH range of the experiment was a major consideration in the experiments, the details of which are provided in the succeeding section.

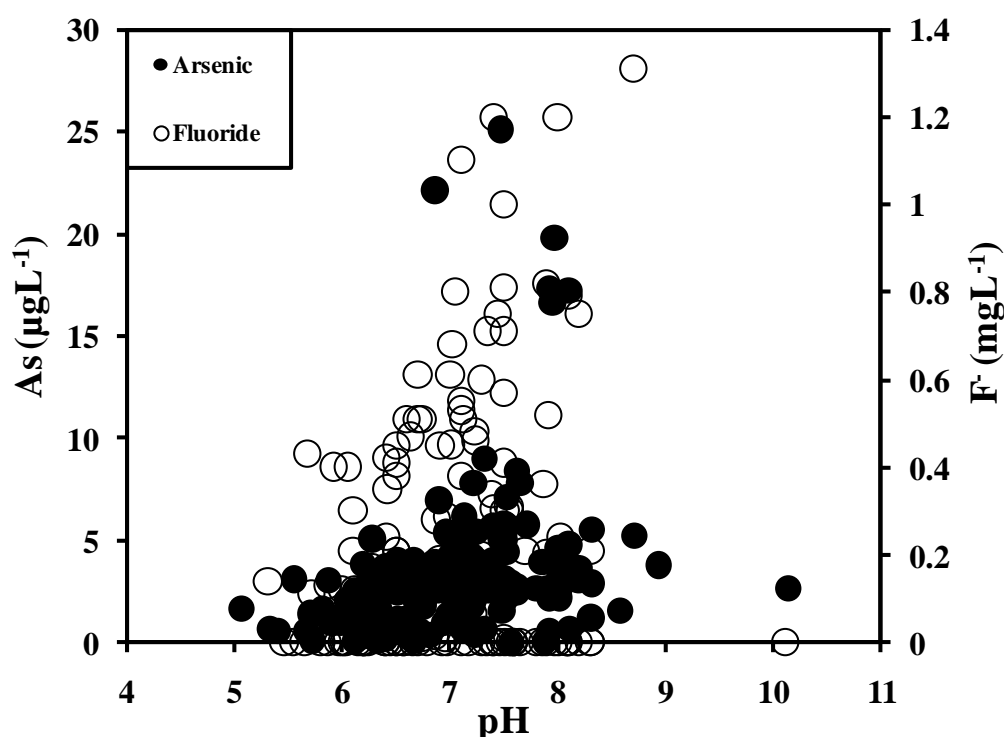


Figure 6.6: Scatter plot showing the behaviour of As and F^- with pH

6.3.4. Understanding As and F^- co-occurrence through batch desorption

Prior to conducting the batch experiments, the total F^- content of the soil/sediment and that of the Fe (hydr)oxide fraction was calculated by analysing the leachate of fractions III and IV (Table . 6.4 and 6.5). The amount of F^- extracted was found to be low (Table. 6.4 and 6.5), indicating that the sampled areas were not affected by high groundwater F^- . Although the overall F^- levels of the samples were found to be very low, yet the F^- extracted from fractions III and IV constituted a significant portion of the total F^- extracted (Table. 6.4 and 6.5). Examination of Tables. 6.4 and 6.5 revealed that the adsorptive capability of the soil and sediment samples were affected by the presence or absence of the Fe (hydr)oxide fraction. It was observed that the adsorptive capacity of the soil and sediment samples were greatly reduced after the removal of Fe (hydr)oxides. This supported the fact that the positively charged Fe (hydr)oxide surfaces could act as adsorptive substrates for negatively charged F^- anions and As oxyanions.

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Table 6.4: Details of the sorption and desorption experiment for raw samples at pH 5 and 10

Total As in the soil/sediment samples		As in Fe (hydr)oxide (fraction III+IV)	Adsorption	Spike [As in Fe (hydr)oxide + Adsorption]	Desorption	
					pH 5	pH 10
Dibrugarh	265000	113700	10300	124000	9375	10125
Jorhat	487000	337000	16400	353400	9625	15375
Sonitpur	299000	269000	19500	288500	4295	19313.75
Barpeta	521000	353000	23300	376300	3940	21215
Bongaigaon	313000	180780	11420	192200	9925	10237.5
Total F ⁻ in the soil/sediment samples		F ⁻ in Fe (hydr)oxide (fraction III+IV)	Adsorption	Spike [F ⁻ in Fe (hydr)oxide + Adsorption]	Desorption	
					pH 5	pH 10
Dibrugarh	260	157	995	1152	647.5	990
Jorhat	510	225	1510	1735	747.5	1445
Sonitpur	320	175	1390	1565	507.5	1375
Barpeta	710	295	1975	2270	589	1877.5
Bongaigaon	220	175	1260	1435	452.5	1205

** All the values have been normalized for a soil/sediment amount of 1 kg, the units for As is μgKg^{-1} and that for F⁻ is mgKg^{-1} .*

Table 6.5: Details of the sorption and desorption experiment for CBD treated at pH 5 and 10

Total As in the soil/sediment samples		As in Fe (hydr)oxide (fraction III+IV)	As in CBD leachate	As remaining in soil/sediment samples after CBD treatment	Spike [As in Fe (hydr)oxide + Adsorption]	Adsorption	Desorption	
							pH 5	pH 10
Dibrugarh	265000	113700	110000	3700	5850	2150	1955	2055
Jorhat	487000	337000	326000	11000	15790	4790	3264	3270
Sonitpur	299000	269000	251000	18000	21920	3920	1375	2772.5
Barpeta	521000	353000	325000	28000	36100	4300	3415	7130
Bongaigaon	313000	180780	162000	18780	21300	2520	2140	2175
Total F ⁻ in the soil/sediment samples		F ⁻ in Fe (hydr)oxide (fraction III+IV)	F ⁻ in CBD leachate	F ⁻ remaining in soil/sediment samples after CBD treatment	Spike [F ⁻ in Fe (hydr)oxide + Adsorption]	Adsorption	Desorption	
							pH 5	pH 10
Dibrugarh	260	157	129.5	27.5	29.06	1.56	10	17.5
Jorhat	510	225	205.2	19.8	27.72	7.92	15	20
Sonitpur	320	175	162.28	12.72	16.21	3.49	2.5	10
Barpeta	710	295	253.5	41.5	51.63	10.13	20	32.5
Bongaigaon	220	175	154.5	20.5	22.62	2.12	5	15

** All the values have been normalized for a soil/sediment amount of 1 kg, the units for As is μgKg^{-1} and that for F⁻ is mgKg^{-1} .*

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The soil and sediment samples were spiked with a standard solution of known strength ($1000 \mu\text{gL}^{-1} \text{As} + 100 \text{mgL}^{-1} \text{F}^-$) to observe sorption and desorption (Table. 6.6). Arsenic and F^- analysis of the leachate obtained after spiking the raw soil/sediment samples reveal substantial amount of adsorption (Table. 6.4 and 6.5), the adsorption of F^- was found to be higher compared to As (Table. 6.4). The aforementioned observation brings to light the capability of the Fe (hydr)oxide fraction to adsorb negatively charged species like F^- and oxyanions of As. Due to the relative under-saturation of F^- in the soil and the sediment samples, it is likely that comparatively higher amounts of F^- was adsorbed by the samples during the spiking step.

Table 6.6: Outline of desorption experiment in the soil and sediment samples

Soil pre treatment:			
Raw soils: 4 g of raw soil was pulverised and dried at 50°C for leaching			
CBD treated soils: Fe (hydr)oxide free soil was prepared by reacting the raw soil (4 g) with 40 mL of 0.3 M Na-citrate + 5 mL 1 M Na-bicarbonate + 1 g Na-dithionite (CBD) in a water-bath at 80°C for 0.5 h [48]. The treatment was repeated three times to ensure complete removal of Fe (hydr)oxide.			
Spiking: Both the raw and the CBD treated soils were spiked with a solution of known As and F^- concentrations ($\text{Na}_2\text{HAs(V)O}_4 \cdot 7\text{H}_2\text{O} - \text{NaF}$ (Himedia chemicals) solution ($\text{As } 1000 \mu\text{gL}^{-1}$, $\text{F}^- 100 \text{mgL}^{-1}$; 1:10)			
Experiment A (desorption at pH 5)		Experiment B (desorption at pH 10)	
Leaching was observed in raw samples for 4 hours	Leaching was observed in CBD treated samples for 4 hours	Leaching was observed in CBD treated samples for 4 hours	Leaching was observed in raw samples for 4 hours
Arsenic and F^- analysed in AAS and IC respectively			

The desorption of As and F^- from the samples were also found to correlate with the presence or absence of Fe (hydr)oxide. It was revealed that the amount of As and F^- desorbed from raw soil/sediments was much higher than that desorbed from CBD treated samples (Fig. 6.7). This shows that Fe (hydr)oxide which is quite ubiquitous in soils and sediments from BFP can act as a source for both As and F^- . The samples in which fractions III and IV i.e., the Fe (hydr)oxide phase was removed had lost the capacity to adsorb both As and F^- (Table. 6.5), therefore the observed desorption was much lower in the CBD treated samples compared to the raw samples. In order to

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explore the dependence of As and F^- desorption on Fe (hydr)oxide, we plotted the levels of As and F^- desorbed from the raw samples in the above experiment with the As fraction associated with Fe (hydr)oxide (sum of fractions III and IV of the sequential extraction process) (Fig. 6.8). At pH 10, the As and F^- desorbed from the raw samples had a significant positive correlation with the total As extracted from fraction III and IV (Fig. 6.8a and c). However As and F^- desorbed at pH 5 didn't show any relation with the As extracted from fractions III and IV (Fig. 6.8b and d). This proves that Fe (hydr)oxide are responsible for adsorption and desorption of both As and F^- from the soil and sediments in our study.

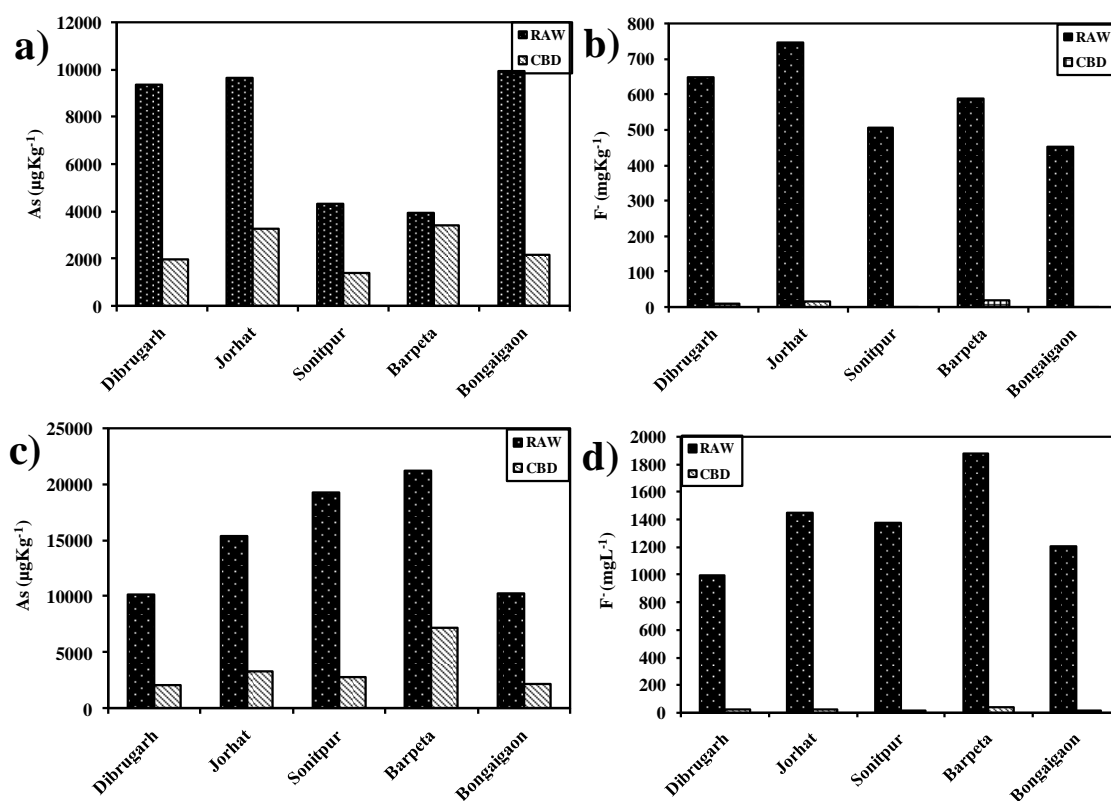


Figure 6.7: Results of desorption experiment at pH 5 for: (a) As and (b) F^- (b) at pH 5 from raw and CBD treated soil/sediment samples normalized to a weight of 1 kg, Experiment B: Desorption of (c) As and (d) F^- at pH 10 from raw and CBD treated soil/sediment samples

The desorption process was also found to be affected by the pH of the system as higher amount of desorption was observed at pH 10 compared to pH 5 (Fig. 6.7). The

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dependency of As and F⁻ desorption on pH can be explained by the concept of “point of zero charge (PZC)”. Iron (hydr)oxides have been found to have a net positive charge at a pH range from 5 to 8. However when the pH increases beyond 8 (8.5 to 9.3) an equilibrium of positive and negative charge is observed. This is called the PZC when net charge on the surface of Fe (hydr)oxide is effectively zero [3, 49]. Arsenic in water exists mainly as the oxyanions arsenate and arsenite, the former especially is stable over a wide range of pH while the latter exists mostly as a charge less species, therefore with an increase in pH the As is released from the Fe (hydr)oxide [3, 6]. In both the experiments it can be observed that some amount of As and F⁻ are desorbed even from CBD treated samples at both pH 5 and 10. This desorption could occur from the clay minerals which are inherently present in the samples, clay minerals structure were found to be affected to very less extent by CBD treatment [3, 48]. The overall mechanism of As and F⁻ desorption from the soil and sediment samples appear to be weathering of Fe (hydr)oxide, the desorption process in turn appears to be controlled by the pH range of the system.

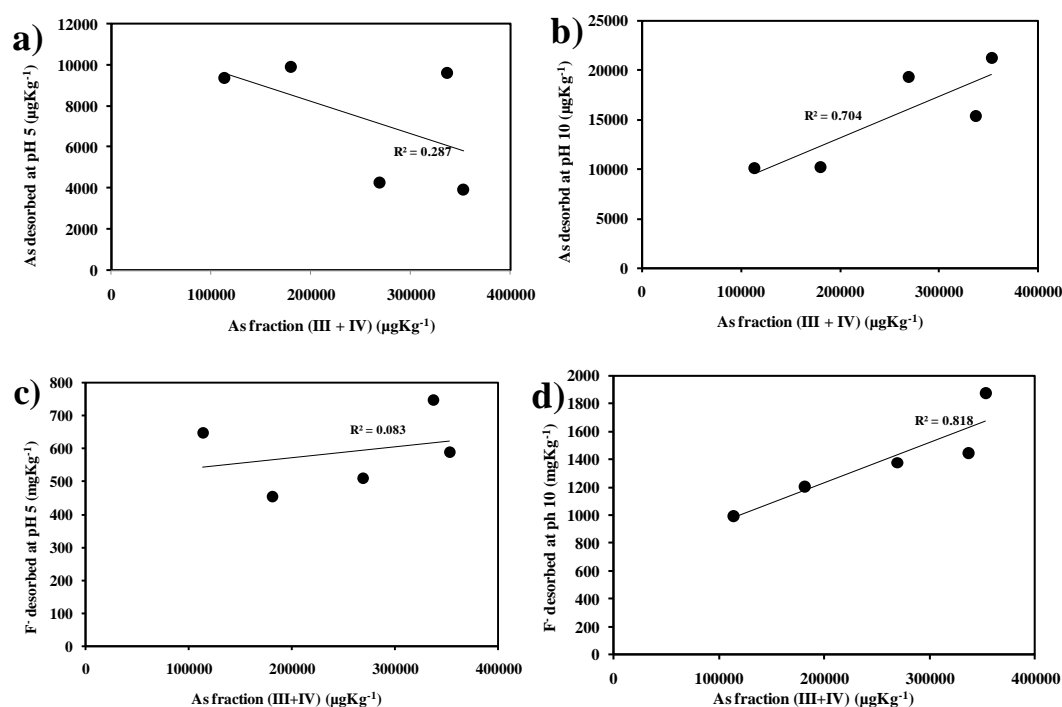


Figure 6.8: Presence of Fe (hydr)oxides positively affects the co-evolution of As and F⁻ from the sediments and the process is enhanced by increasing pH

6.4. Conclusion and recommendations

Co-occurrence of As and F^- in groundwater is a less understood subject, more over it is very difficult to replicate in laboratory the exact set of conditions found in the natural settings. The findings from the present study showcases the behaviour of As and F^- in reducing aquifers of the Brahmaputra Flood Plains (BFP). Significant correlation between total As and the As extracted from fractions III and IV [Fe (hydr)oxides] suggested that the main source of groundwater As was the Fe (hydr)oxide present in soils and sediments. Although the sulphide bound As fraction was significantly high (fraction V), yet its insignificant correlation with the partition coefficients suggested that it was not the immediate source of As in the groundwater. Grain size and organic matter content in the samples were found to be of particular importance in determining the groundwater As levels. Soil samples had much higher clay and organic matter content than the sediment samples which also correlated with the higher amount of total and groundwater As in the former. Clay minerals due to their charged nature can hold higher amounts of cations of metals like Fe, which in turn bind anions like As oxyanions and F^- , organic matter on the other hand plays a role in bacterial decomposition leading to the dissolution of Fe (hydr)oxides . Removal of Fe (hydr)oxides from the soil and sediment was found to drastically change the adsorptive and thus also the desorptive properties of the samples. Spiking was found to affect raw or untreated samples the most as a significant amount of As and F^- was found to be adsorbed by Fe (hydr)oxides. It was found that removal of Fe reduced the adsorptive capacity of the soil/sediments and subsequently very less As and F^- was desorbed from the CBD treated samples. On the other hand raw samples showed much greater adsorptive capacity therefore desorption was also very high. Hence Fe hydr(oxides) phase (fraction III+IV) was the main phase associated with the co-contamination behaviour of As and F^- in the laboratory settings. Desorption of both As and F^- was found to be affected by the pH of the groundwater. Increase in pH leads to reduction of net positive charge on the Fe hydr(oxides) substrates. Therefore the negatively charged F^- and oxyanions of As showed greater desorption at higher pH. It is unlikely that As and F^- will occur together in high concentration in the BFP under natural settings. The high precipitation and recharge rates together with the high sedimentation in the region

favours the occurrence of As, while F⁻ appears to occur mainly in isolated regions where higher rock-water interaction is possible. Incidences of high As and F⁻ co-contamination are expected to occur in isolated aquifers of the BFP where groundwater recharge would likely be low. Higher rock-water interaction and the probable existence of an oxidizing condition in such aquifers will favour the existence of both As and F⁻, and Fe hydr(oxides) are likely to play a dominant role in their co-evolution. Seasonal variation could be another factor which could result in observation of temporary co-contamination due to As and F⁻. Drier conditions in the pre-monsoon season could lead to the development of the aforementioned conditions favourable for mobilization of both As and F⁻ in some aquifers of the BFP.

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