

CHAPTER 5

Assessment of arsenic and fluoride co-contamination perspectives in the natural settings

5.1. Introduction

The sources of both the As and F⁻ are found to be mainly geogenic in nature. Arsenic has been found to be released from a number of minerals like arsenopyrite, scorodite, orpiment, realgar, etc. [1], while minerals like fluorapatite, hydroxyapatite, fluorspar, cryolite etc. are known to release F⁻ in groundwater [2-4] which have been found to occur mainly in volcanic rocks [5]. Oxidation of sulphides like arsenopyrite; and reductive hydrolysis of (hydr)oxides of various metals like Fe, Mn and Al have been reported to be the two most common mechanism of As release in groundwater [1]. Groundwater with high F⁻ is generally found to be associated with high pH and NaHCO₃, and low Ca²⁺ and Mg²⁺ concentration [5]. The release mechanisms of F⁻ have been reported to involve weathering and dissolution and depend on the contact time between the groundwater and the aquifer minerals [5].

Both As and F⁻ on the virtue of existing as anions in the groundwater has been found to be adsorbed on positively charged surfaces like various oxides and hydroxides of Fe, Mn and Al [6]. The prospect of co-contamination due to both As and F⁻ is a serious threat to groundwater quality and human health. Co-contamination of As and F⁻ has been studied by a handful of workers. Kim et al [6] reported that both As and F⁻ was associated with Fe (hydr)oxides in the groundwater, and was influenced by an increase in pH. Under reducing condition, reductive hydrolytic processes were found to be dominant, while under oxidizing conditions it was the increase in pH which was found to mainly lead to the release of As and F⁻. Workers in this field have reported that the process of co-contamination is common in arid and semi-arid regions, like Arizona and California [6, 7], Mexico [6, 8], Argentina [1, 6, 9, 10], China [11], Pakistan [4, 6]. Most of these aquifers are reported to be oxidizing in nature. Under such conditions dissolution of Fe (hydr)oxides has not been observed and the main pathway of

mobilization appeared to be desorption motivated by an increase in pH [6]. The phenomenon of co-contamination has been found to be less prevalent in reducing aquifers. Examples of regions where As and F⁻ co-contamination has been reported under reducing conditions are Hetao Basin [6, 12-14], Huhbot Basin [6, 15], Datong Basin [6, 16] and Montana in the USA [6, 17]. Under reducing conditions, reductive hydrolysis of Fe (hydr)oxides is reported to be the process which is responsible for the release of these two contaminants [6].

In India, As has been detected in a number of different regions like the Middle Ganga Plains [18- 22], the State of West Bengal [23- 30] and the North Eastern part of the country including Assam [31]. In most of the above mentioned works, As was detected in an alluvial setting and reductive hydrolytic processes were the cause of As mobilization in groundwater. Fluoride has also been reported from different parts of India like Andhra Pradesh, Rajasthan, Gujarat and Assam [31-34]. On closer examination it is found that that semi-arid, crystalline igneous rocks and alkaline soils were the most affected [35-37]. The Brahmaputra River and its tributaries gave rise to the Brahmaputra Flood Plain (BFP) by depositing alluvium extensively; the region is very fertile and is the life line for the people of Assam. Both As and F⁻ had been detected in the BFP [31]. In many of the districts like Nagaon and Karbi Anglong, both the contaminants have been found to contaminate the groundwaters [31]; however no study has been undertaken to assess the behaviour of these two contaminants in the BFP.

The objective of this study is to characterize the behaviour of As and F⁻ in the groundwater of the BFP, by understanding (i). The processes and the sources of As and F⁻ in the groundwater of the region. (ii). Delineating the complex relations and controls between the different species including As and F⁻ in their natural settings by the use of multivariate tools like PCA and HCA and (iii). To evaluate the future of co-contamination in the BFP region based on speciation and calculation of saturation indices.

5.2. Materials and method

A total of 164 groundwater samples and 8 sediment samples were collected over a two year period (2011 and 2012) in the Brahmaputra Flood Plains (BFP) (Fig. 3.4) for the present study. Cation, anion, trace metal and DOC analyses were performed using the standard methods described in chapter 2. SPSS 20 was used for multivariate statistical analysis namely hierarchical cluster analysis (HCA) and principal components analysis (PCA). Speciation modeling was done by using the software MINTEQA2 v 3.1.

5.3. Results and discussion

5.3.1. General hydrogeochemistry and water type

Table 5.1: Summary of descriptive statistics for different variables. The unit for TDS, DO, Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, Cl⁻, SO₄²⁻, PO₄³⁻ and Fe is mgL⁻¹, while the units for EC, ORP and As are μScm⁻¹, mV and μgL⁻¹ respectively

Parameters	Range	Average±SD	Co-efficient of Variance
pH	10.12-5.04	6.99±0.81	0.12
EC	1789-43.4	258.49±197.7	0.76
TDS	851-21.5	160.10±111.71	0.70
ORP	185 -(-135.7)	-4.90±51.24	-10.45
Na ⁺	49.6-0.96	15.78±9.88	0.63
K ⁺	14-0.1	3.34±2.78	0.83
Ca ²⁺	118.5-3.12	23.71±16.18	0.68
Mg ²⁺	35.5-2.38	9.18±6.37	0.69
HCO ₃ ⁻	400-50	177.66±83.68	0.47
Cl ⁻	332.28-5.68	28.53±29.8	1.04
SO ₄ ²⁻	142.36-.03	12.18±16.14	1.33
PO ₄ ³⁻	2.56-0.16	0.45±0.38	0.84
NO ₃ ⁻	2.10-0 (ND)	0.45±0.53	1.18
F ⁻	1.31-0 (ND)	0.23±0.29	3.70
Fe	5.70-0.01	1.24±1.37	1.10
As	25.10-0.80	3.49±3.91	1.12

**ND represents not detectable*

The study area, the BFP, is a very large region and a wide variation is observed from the chemical analysis of the different physico-chemical parameters. The summary of the

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chemical parameters has been shown in table 5.1. The pH in the aquifers of the region ranges from 5.04 to 10.12 with a mean of 6.99, indicating that a near neutral condition is common. While highly alkaline and acidic incidences are rare. Electrical conductivity values range from 1789 to 43.4 μScm^{-1} , with a mean of 258.49 μScm^{-1} . The high values of EC indicate the prevalence of weathering and dissolution processes in the study area. TDS ranges from 851 to 21.5 mgL^{-1} , with a mean of 160.1 mgL^{-1} , this shows that groundwater quality is fresh [38, 39].

Although the ORP values in the groundwater range from 185 to -135.7 mV, it is observed that most of the groundwater samples had a negative value indicating the presence of a reducing environment. The cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} have ranges of 49.6-0.96 mgL^{-1} , 14-0.1 mgL^{-1} , 118.5-3.12 mgL^{-1} and 35.5-2.38 mgL^{-1} respectively. The anions HCO_3^{-} , Cl^- , SO_4^{2-} , PO_4^{3-} and NO_3^- range from 400-50 mgL^{-1} , 332.28-5.68 mgL^{-1} , 142.36-0.03 mgL^{-1} , 2.56-0.16 mgL^{-1} and 2.1-0 mgL^{-1} respectively. Low values of NO_3^- could be due to the reducing environment resulting in the reduction of NO_3^- . Extreme range of Cl^- was observed due to the unusually high Cl^- value in a single groundwater sample from the north bank; the probable reason appeared to be the use of bleaching powder [$\text{Ca}(\text{ClO})_2$] in the locality. The range of F^- is very wide; the highest detectable value was 14.4 mgL^{-1} which is well above the [40] prescribed level for F^- in drinking water i.e., 1.5 mgL^{-1} ; while in all other samples the F^- was within the WHO prescribed limit. The maximum F^- value however was detected in Tekelangjun, Karbi Anglong district, which fell outside the spread of the BFP and was omitted from the results and discussion section on account of being an outlier. Iron was found in excess of the WHO prescribed limit for Fe in drinking water [40], with a range of 5.7 to 0.01 mgL^{-1} and a mean of 1.24 mgL^{-1} . Presence of reducing environment could influence the dissolution of various oxides and hydroxides of Fe. In this study the highest level of groundwater As detected was 25.1 μgL^{-1} which is in excess of the WHO prescribed limit for As in drinking water i.e., 10 μgL^{-1} [40]. However the As limit was within limit in most of the samples.

Different graphical tools have used to delineate the various phases or facies in the groundwater. These facies are indicative of the hydrochemistry of the groundwater of

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the region. Interaction of various minerals determines the hydrochemistry of the aquifers of a region [39, 41, 42, 43]. The major cations and anions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} and Cl^-) were plotted in the Piper [39, 44] diagram. It can be observed from the Piper diagram (Fig. 5.1) that most of the groundwater samples fall into the category of Ca^{2+} - Mg^{2+} - HCO_3^- type water. This shows a dominance of alkaline earth metals (Ca^{2+} and Mg^{2+}) over alkali metals (Na^+ and K^+), and the dominance of weaker carbonic acid over stronger acids (SO_4^{2-} and Cl^-). Abundance of Ca^{2+} , Mg^{2+} and HCO_3^- indicates the prevalence of weathering of carbonate minerals like calcite and dolomite, while silicate weathering may be of occasional occurrence. Closer observation of the Piper diagram reveals that high As ($10 \mu\text{gL}^{-1}$) is associated with HCO_3^- (Fig. 5.1), the facies associated with high As are Ca^{2+} - HCO_3^- , Ca^{2+} - Mg^{2+} - Na^+ + K^+ - HCO_3^- and Na^+ + K^+ - HCO_3^- . Thus it can be inferred that alkalinity and high As in the groundwater are related, in fact high HCO_3^- could be one of the factors that affect As mobilization in the groundwater of the region.

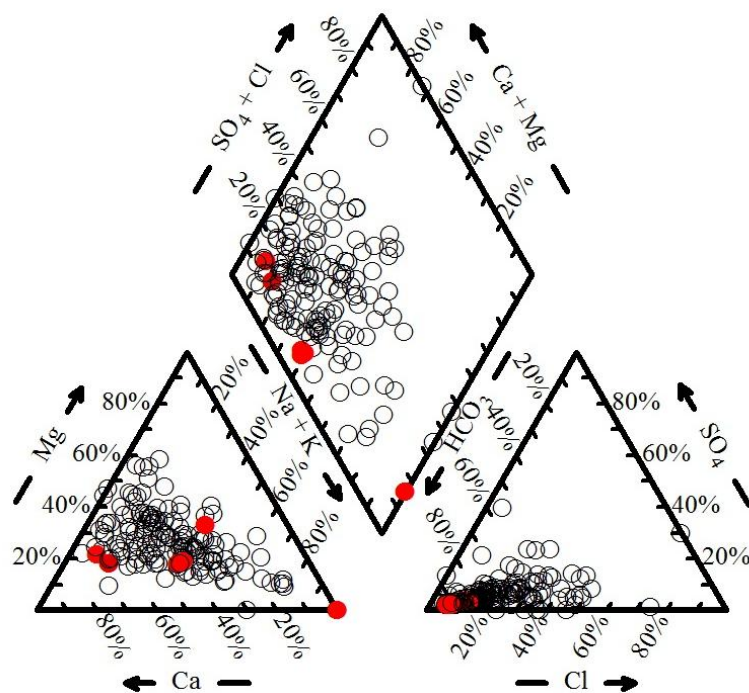


Figure 5.1: Piper plot depicting water type, the red dots represent samples with As $> 10 \mu\text{gL}^{-1}$

5.3.2. Characterization of Arsenic and Fluoride

Previous studies report the occurrence of both As and F⁻ in groundwater of Assam. The highest value of groundwater As was detected from the Jorhat district (657 µgL⁻¹), other districts which also reported high groundwater As are Golaghat, Lakhimpur, Barpeta, Dhemaji, Dhubri and Darrang district [31, 45]. Fluoride on the other hand has been found to occur more commonly in drier regions like Nagaon and Karbi Anglong districts, both of which have been identified as rain shadow zones of Assam [31]. High F⁻ levels have also been reported from Guwahati, the largest city of North East India [46]. In our study however much lower values of both the contaminants were noted. It was observed that both As and F⁻ values were well within the permissible limit for drinking in most of the groundwater samples. The probable reasons could be that, (i) most of the previous studies were done intensively and involved much smaller areas; while the BFP is a very large region and the groundwater sampling sites are scattered. (ii) instead of collecting samples from previously known hotspots, we collected the samples from areas which were not sampled previously or didn't have a past record of high groundwater As and F⁻ in order to observe the status of As and F⁻ contamination in previously unreported sites and see the occurrence of As and F⁻ in flood plain conditions under the light of world reports on As and F⁻ in the vicinity of floodplains like Gangetic Flood Plains (MGP) and others. The highest level of groundwater As and F⁻ detected in the BFP were 25.1 µgL⁻¹ and 1.31 mgL⁻¹ respectively.

Arsenic and F⁻ behaviour in the BFP was studied by comparing with Secondary data on groundwater As and F⁻ obtained from selected studies, the details of which have been given in table 5.2. The secondary data obtained from the other studies were used for plotting a scatter diagram which was then compared with the scatter diagram generated from our data. . For [47] mean values were used, while for [10] and [49] mean, maximum and minimum values were used as per availability of data. For the [4] entire data set was available and used accordingly.

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Table 5.2: Reported concentrations of As and F⁻ from selected studies around the world

Sampling location	pH range or character	Range of As (μgL^{-1})	Range of F ⁻ (mgL^{-1})	R ²	Prevailing environmental conditions	Reference
Lahore and Kasur districts, Pakistan	7.3-8.7	10-530,	0.16-21.1 Mean=6.92	0.123	Oxidising Alluvial Plains Semi Arid Conditions	[4]
Lahore and Kasur districts, Pakistan	7.3-8.8	1-398, Shallow aquifers	0.3-5.19, Shallow aquifers	0.020	Oxidising Alluvial Plains Semi Arid Conditions	[47]
Lahore and Kasur districts, Pakistan	7.1-8.8	1-398, All aquifers	0.3-11.40, All aquifers	0.013	Oxidising Alluvial Plains Semi Arid Conditions	[47]
Coronel Moldes, Argentina	7.31-8.85	0-250 Mean=70	0.5-12 Mean=3.5	0.999	Arid highly oxidising	[10]
Chihuahua, Mexico	7.22-7.82	4-39	1.06-4.55	0.673	Arid highly oxidizing	[48]
Yuncheng Basin, Northern China	6.24-9.16	0.24-154 Mean=8.38	0.31-14.1 Mean=2.4	0.991	Semi arid	[49]

A strong positive correlation was observed between As and F⁻ from aquifers with arid oxidizing conditions (Table. 5.2), especially in Yuncheng Basin, Northern China [49] and Chihuahua, Mexico [48] (Fig. 5.2a). It has been reported that F⁻ mobilization is highly dependent on contact time and rock-water interaction; and high groundwater recharge rates have been found to be a deterrent in the said process [36, 37]. As arid and semi-arid conditions provide the aforementioned conditions therefore, such areas have been found to have very high F⁻ levels [5]. Groundwater As on the other hand has been reported to occur in both reducing and oxidizing conditions [1, 6]. In arid and semi-arid aquifers where oxidizing condition predominates it has been observed that As exists mainly as the oxyanion arsenate, the release of which was found to be motivated by an increase in alkalinity [1, 6, 50].

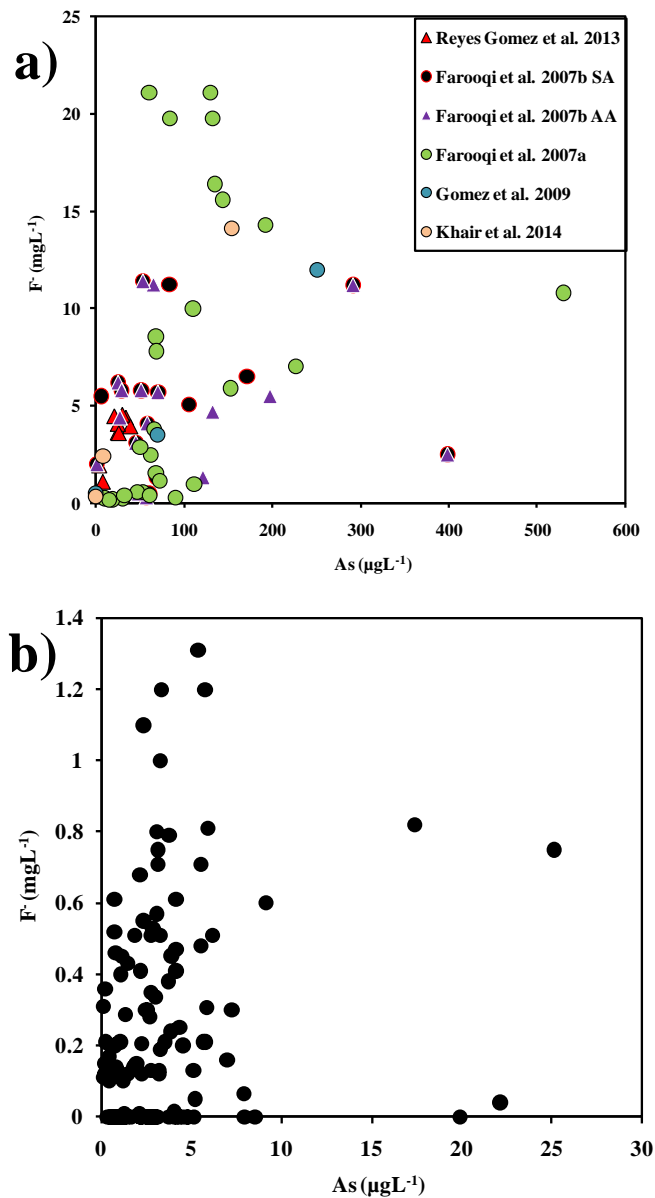


Figure 5.2: Scatter plots of As versus F⁻ for (a) selected previous studies and (b) BFP. SA and AA represent “shallow aquifers” and “all aquifers” respectively

Metal (hydr)oxides have been reported to adsorb negatively charged anions due to their innate positive surface charge; however conditions of increasing alkalinity have been found to promote the accumulation of negative charge on their surface, leading to the desorption of the adsorbed anions [1, 6]. In fact it has been reported that As, whether it originates from geogenic or anthropogenic sources, is absorbed on Fe (hydr)oxides at acidic conditions and desorbed under alkaline conditions [47]. The secondary data in table 5.2 shows that the condition in all the aquifers were highly alkaline, therefore it is

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likely that the high co-contamination incidences of As and F⁻ were observed due to desorption from positive surfaces like metal (hydr)oxides. The level of As and F⁻ correlation in the Lahore and Kasur districts of Punjab, Pakistan was found to be quite low even though the regions had oxidizing and alkaline conditions (Fig. 5.2a, Table 5.2). This occurrence was reported because F⁻ was found to originate through more than a single pathway one of them being the dissolution of fluorite (CaF₂), while anthropogenic sources like fertilizer usage and air pollutants derived from kilns were also cited as secondary sources.

In our study we could not find any significant correlation between As and F⁻ in the BFP (Fig. 5.2b). The BFP is a vast alluvial region and in the previous chapter 4, we found that the conditions in the aquifers were mostly reducing in nature. More over as the BFP is known to receive very high rainfall annually therefore groundwater recharge rates are also expected to be high. The aforementioned conditions have been found to be unsuitable for F⁻ occurrence in the groundwater as mentioned earlier, which is also indicated by the extremely low groundwater F⁻ values recorded in our own study. At the same time, such an environment has been reported to be suitable for the mobilization of groundwater As through the process of reductive hydrolysis of Fe (hydr)oxides which was reported based on our results in chapter 4. Therefore the plotting of As and F⁻ failed to show any conclusive results in this study.

In order to get a better insight into the hydrogeochemical influences on As and F⁻ co-contamination, both contaminants were plotted against a number of other hydrogeochemical parameters. Arsenic and F⁻ were plotted against pH (Fig. 5.3a); it was observed that both acidic and alkaline pH was prevalent in the BFP and both the contaminants were found to increase with pH. Increase in alkalinity has been found to elevate As level due to dissociation of adsorbed As oxyanions from Fe (hydr)oxides [1, 6, 50], the mechanism of which has already been discussed earlier, while minerals like fluorite are known to undergo dissolution under alkaline condition to release F⁻ [36, 37]. Dependence of F⁻ release on pH also suggests the involvement of adsorptive/desorptive processes as explained earlier.

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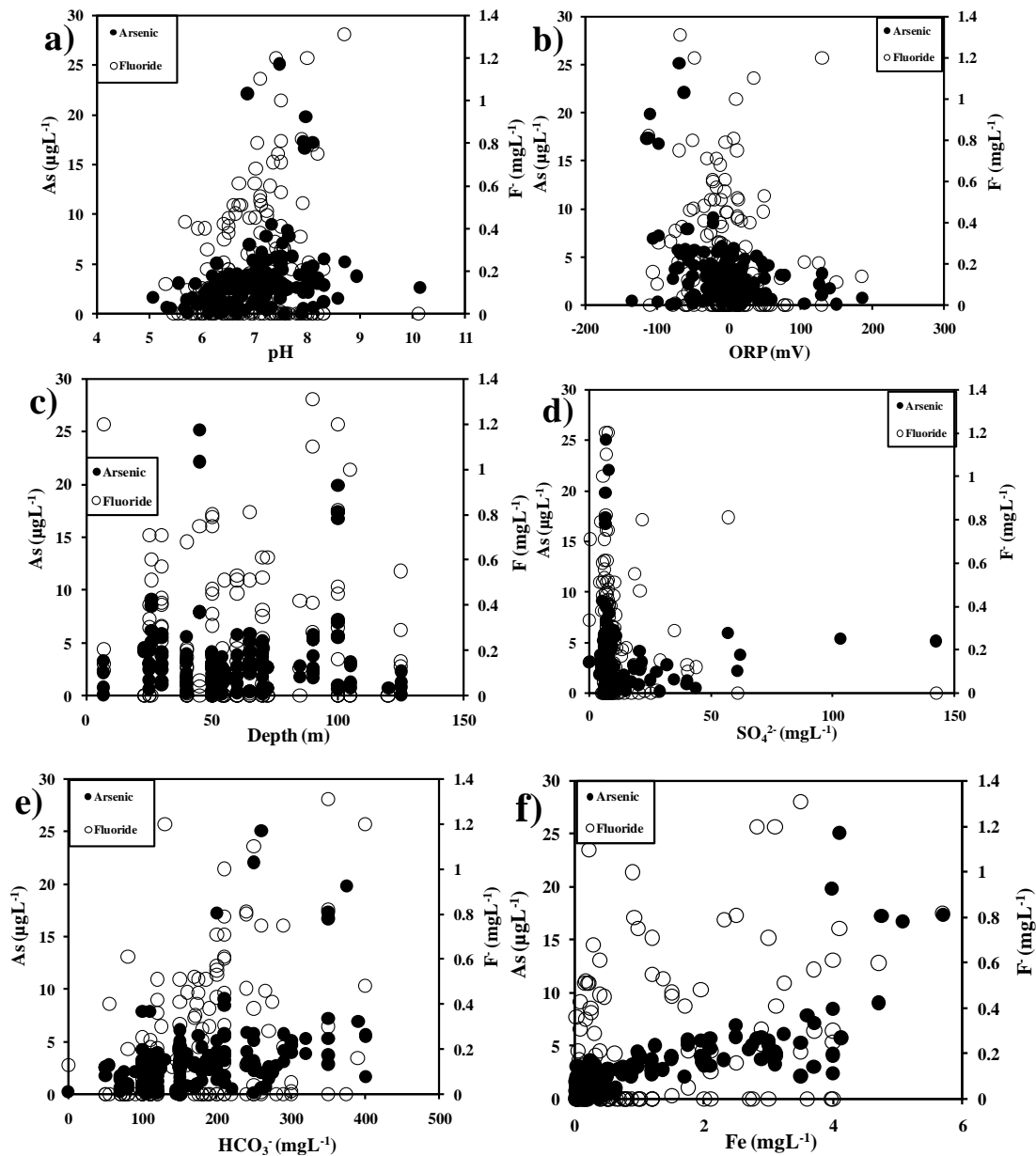


Figure 5.3: Scatter plots showing the behaviour of As and F^- with (a) pH, (b) ORP, (c) Depth, (d) SO_4 , (e) HCO_3 and (f) Fe

Previously in chapter 4, a reducing condition was found to dominate in the BFP, and a positive correlation was observed between As and Fe indicating the occurrence of reductive hydrolysis of Fe (hydr)oxides. However the role played by reductive hydrolytic processes in controlling F^- mobilization was still not clear. Therefore As and F^- were plotted against ORP (Fig. 5.3b). It is seen that both groundwater As and F^- share a negative correlation with ORP, although the relation was much weaker in case of F^- .

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The most likely reason for the negative relation between F^- and ORP is that, F^- being an anion has been found to be adsorbed on positively charged surfaces like Fe (hydr)oxides and dissolution of these (hydr)oxides by reductive hydrolysis has been known to increase F^- levels in groundwater [6]. This showed that reductive hydrolysis of Fe (hydr)oxides played a role in the mobilization of F^- in the BFP to some extent.

The role of depth on mobilization of As and F^- was observed by plotting the two contaminants against depth (Fig. 5.3c). No significant trend could be observed from the plot of As and F^- versus depth. The SO_4^{2-} level in our study was found to be low and the relationship of As and F^- with SO_4^{2-} was found to be slightly negative but not very significant (Fig. 5.3d). This indicates the dominance of reductive hydrolytic processes or else SO_4^{2-} level would have increased with Fe [1, 51]. Although F^- and SO_4^{2-} have different pathways for mobilization, however the weak negative correlation suggests the probability that the two might act as competitive anions for sorption sites on surfaces like Fe (hydr)oxides.

Alkalinity was found to positively affect the mobilization of both As and F^- in groundwater although the relationship was not observed to be very strong (Fig. 5.3e). Fluoride dissolution has been found to increase under alkaline conditions due to dissolution of primary F^- minerals like fluorite [36, 37]. Also it has been reported that bicarbonate is released as a product during both carbonate and silicate weathering. Available literature shows that weathering of silicate rocks is one of the probable mechanisms of F^- release [52, 53]. Increase in alkalinity has also shown to release anions like As oxyanions and F^- from Fe (hydr)oxides as already discussed [6].

Strong correlation of As with Fe confirms the existence of reductive hydrolysis of Fe (hydr)oxide as the prime mode of As mobilization in the groundwater of BFP (Fig. 5.3f). Dissolution of Fe (hydr)oxides appears to be a minor contributor in the release of F^- in the BFP as the process has been linked to arid conditions where oxidizing conditions prevail [1, 5, 6]. This could explain the low correlation observed between F^- and Fe in the BFP (Fig. 5.3f). The relationship of F^- and Fe has been further studied

using principal components analysis (PCA) and hierarchical cluster analysis (HCA) in the statistical section.

5.3.3. Statistical analysis

Multivariate statistical techniques, PCA and HCA were performed on the standardized data to observe relations which could not be studied by simple bivariate techniques like linear regression and correlation.

5.3.3.1. Principal components analysis

Principal components analysis was performed on the standardized data to obtain 5 components with eigen values > 1 which represented 67.78 % variance (Table 5.3 and Fig. 5.4). The difference in the variance of component 1 and 2, and 3 and 4 is very less, therefore PCs 1 and 2 have been considered to be a single component with a variance 36.3%. This combined component represents an alkaline condition as shown by the positive loadings from pH and HCO_3^- . This PC also has high loadings due to Fe and As which can be inferred as the involvement of reductive hydrolysis of Fe (hydr)oxides in releasing As in the BFP. The association of alkalinity with Fe and As could indicate mobilization of As from Fe (hydr)oxides through desorptive processes at high pH, the mechanism of which has already been explained earlier [1, 6, 50]. Salt dissolution also appears to be an important process as seen from the positive loading on this PC due to EC, TDS and Cl⁻. The combination of components 3 and 4 give a single component (PC2) with a variance of 22.4 %. Positive loading on PC2 from Ca^{2+} and Mg^{2+} is indicative of a common origin for both the cations. Carbonate weathering especially dolomite could be the process responsible for the release of both the cations. Fluoride and SO_4^{2-} also displayed positive loadings on PC2 which could be due to the fact that both anions were mobilized due to desorption from substrates like Fe (hydr)oxides. Earlier a slight negative correlation was also observed between F^- and SO_4^{2-} implying the competitive nature of the adsorption and desorption processes. Sodium and K^+ account for the last component with 9.1 % variance, the probable process involved could be silicate weathering.

Table 5.3: Principal component analysis with three principal components

Parameters	PC 1	PC 2	PC3
pH	0.68		
EC	0.90		
TDS	0.92		
ORP			
Na ⁺			0.84
K ⁺			0.79
Ca ²⁺		0.89	
Mg ²⁺		0.90	
HCO ₃ ⁻	0.67		
Cl ⁻	0.88		
SO ₄ ²⁻		0.82	
PO ₄ ³⁻			
F ⁻		0.81	
Fe	0.79		
As	0.83		
% Variance	36.3	22.4	9.1

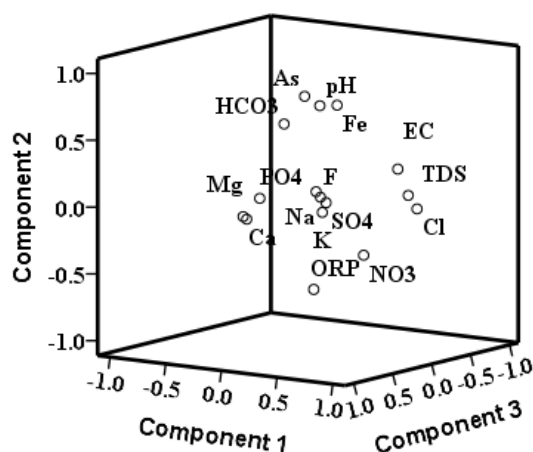


Figure 5.4: Three dimensional representations of the PCs in a loading plot obtained from PCA using Varimax rotation. The loadings are shown for the three components

5.3.3.2. Hierarchical cluster analysis

After performing the HCA (Fig. 5.5), we obtained two clusters, in cluster 1 three sub clusters are observed; the first includes EC, TDS and Cl⁻ indicating that salt dissolution

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is one of the most important processes and is responsible for the majority of conductivity and dissolved solids in the groundwater. The second sub cluster is composed of SO_4^{2-} and F^- , the similarity could arise from the fact that both are adsorbed and desorbed on similarly natured positively charged surfaces. Arsenic and Fe form a sub cluster which points to the involvement of Fe (hydr)oxides as the source of both the contaminants. The sub cluster of Fe and As also shows a close relation pH and HCO_3^- implying that an alkaline environment with high pH influences As and Fe mobilization.

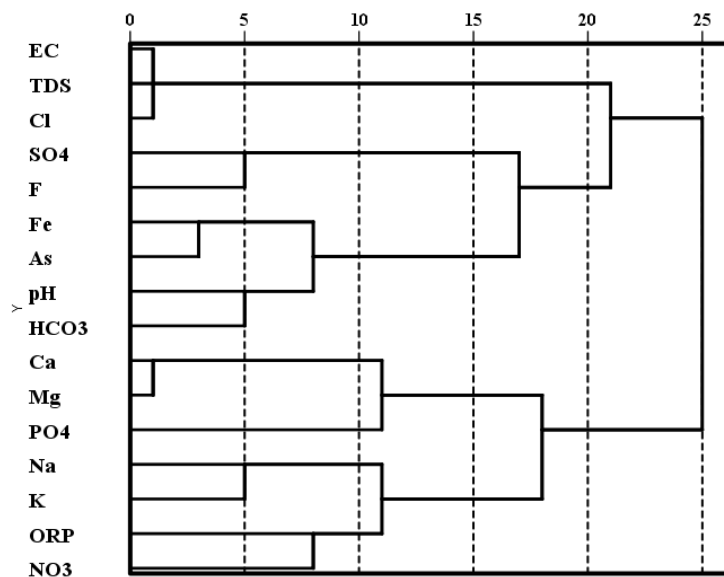


Figure 5.5 Dendrogram from HCA obtained by Ward’s linkage show the proximity of the different parameters to each other

The sub clusters of As and Fe, and pH and HCO_3^- share a relationship with SO_4^{2-} and F^- . This proves that Fe (hydr)oxides controls the mobilization of anions like F^- and SO_4^{2-} through desorption process under the influence of alkaline conditions. In cluster 2 it is observed that Ca^{2+} and Mg^{2+} forms a sub cluster with PO_4^{3-} . Association of Ca^{2+} and Mg^{2+} together could imply role of carbonates as their sources. Phosphates of Ca^{2+} and Mg^{2+} could act secondary minerals resulting in the clustering of Ca^{2+} and Mg^{2+} with PO_4^{3-} . Sodium and K^+ are clustered together, as this sub cluster do not appear to show any relation with HCO_3^- . The probable source of Na^+ and K^+ could be silicate weathering. The oxidation of NO_3^- under a reducing environment has already been

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discussed in the previous chapter; this could explain the close relation between the two in the dendrogram. Low levels of NO_3^- could also be an indicator of the low level of anthropogenic activities in the overall hydrogeochemistry of the BFP.

5.3.4. Mineralogical evidence

The mineralogy of the study area was obtained by performing XRD and SEM. Illite, kaolinite and chlorite were found to be the dominant clay fractions in the sediments of BFP. Previous study by Jain et al [54] also show that illite, kaolinite and chlorite percentages were in the order of 62.5%, 18.81% and 18.85% respectively. Arsenic rich minerals like arsenopyrite and walpurgite were detected in the sediments after powder X-ray diffraction was performed (Table. 5.4). This indicates that the original source of As in the BFP could be the aforementioned As bearing mineral which undergo dissolution. Arsenic released from such minerals have been found to become associated with (hydr)oxides of metals like Fe which later mobilize them under reducing conditions [1].

Table 5.4: Results of XRD analysis showing the mineralogy of the sediments

Serial	Sampling sites	Sediment type	Minerals
BRS-1	Guijan	Sand	Delhayelite, Anorthoclase, Inyoite , Paragonite & Troilite.
BRS-2	Rohmoria	Loam	Rutile, Anorthoclase, Sanidine.
BRS-3	Dibrugarh	Sand	Rutile, Opal & Silica.
BRS-4	Nimatighat	Clay loam	Rutile, Opal & Quartz
BRS-5	Dhansirimukh	Loamy sand	Rutile, Opal, Quartz & Arsenopyrite
BRS-6	Tezpur	Loam	Rutile & Opal.
BRS-7	Guwahati	Loam	Rutile, Riebeckelite, Walpurgite, Biotite & Vermiculite
BRS-8	Jogighopa	Sand	Labradorite, Troilite

Presence of fine clay particles has been found to be conducive for As and F^- contamination as these particles provide good surfaces for many chelating agents which

could adsorb and release the two contaminants in the groundwater [1]. More over in most cases the organic matter content of such clay minerals has been reported to be high. Presence of high organic matter can trigger the process of As release by creating a reducing environment [9, 55, 56].

5.3.5. Speciation modeling

The groundwater quality of a region has been reported to depend on the type of minerals, their reactivity and the extent of equilibrium that these minerals have attained [57, 58]. The equilibrium condition of the study region was studied by calculation of the saturation indices (SI), which was done by using the software Visual MINTEQA2 v 3.1. The SI can be expressed as: $SI = \log(IAP/K_{sp})$, where IAP is ion activity product of the solution and K_{sp} is the equilibrium constant of reaction at temperature T. The source of F^- in the region appears to be $Ca_5(PO_4)_3F$ Apatite (Table. 5.5), as the mineral is oversaturated in all the samples. However fluorite and sodium fluoride are under-saturated. The overall low levels of F^- in the groundwater of the region could mean that F^- is under-saturated in the groundwater of the region. The As minerals are under-saturated in all the samples, as are the hydroxides of Fe. As both As and F^- bearing minerals appear to be under-saturated in the groundwater, therefore there is a great possibility for the two contaminants to undergo further enhancement. The same can be observed from comparison of groundwater As and F^- levels from the BFP in two consecutive years (2011-2012) (Fig. 5.6). Concentrations of both As and F^- were found to be higher in the succeeding year proving that there is a high probability of continuous increase in groundwater As and F^- levels with time. The carbonate minerals aragonite, calcite and dolomite are also found to be under-saturated.

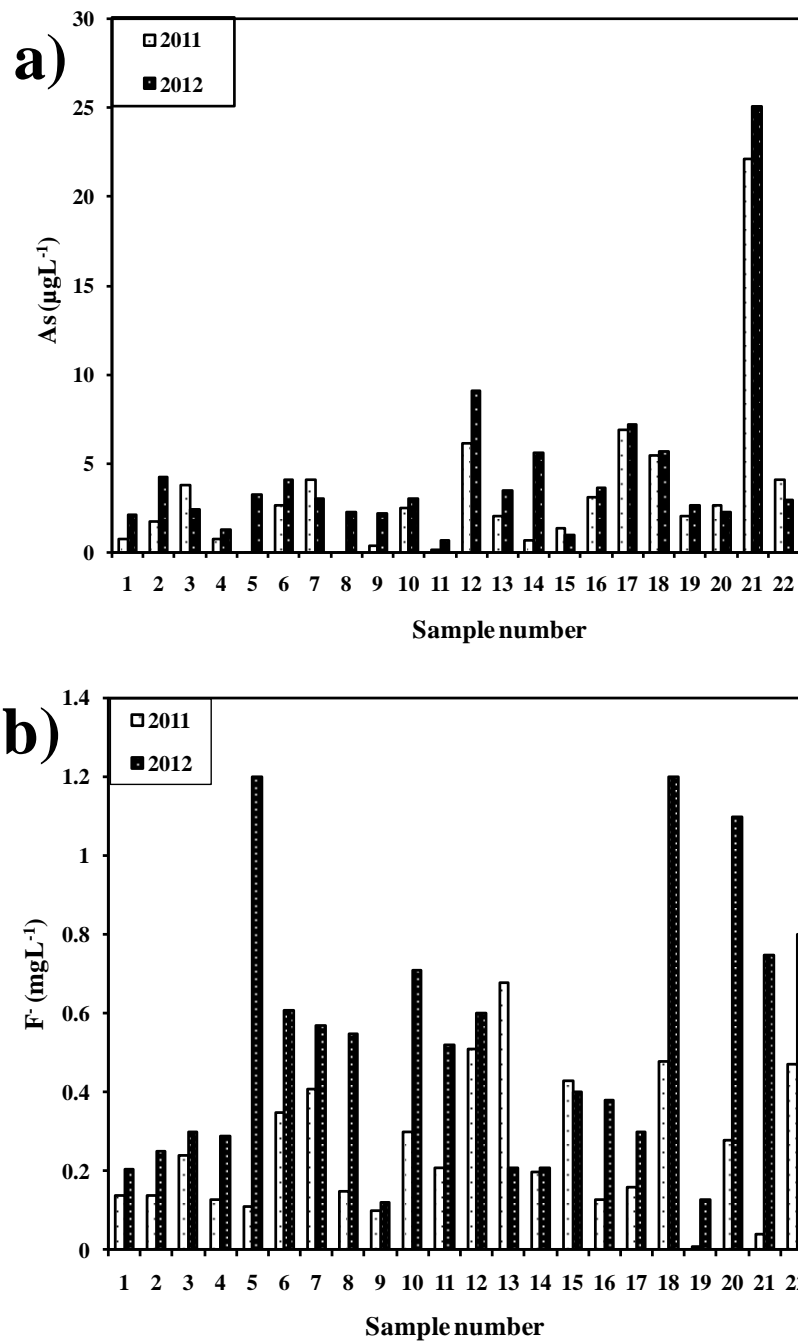


Figure 5.6: Concentration of (a) As and (b) F⁻ in groundwater from two different years

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Table 5.5: Saturation indices of selected aqueous phases in the monsoon season calculated by using MINTEQA2 v 3.1. am, c and s stand for amorphous, crystalline and solid respectively

Aqueous Phase	Samples												
	34	35	40	41	50	55	75	76	81	90	133	137	158
Aragonite	-1.08	-0.37	-0.77	-1.09	-0.99	-0.80	-0.34	-0.10	-0.10	-0.63	-0.34	-0.71	0.24
Arsenolite	-12.69	-13.36	-11.69	-13.15	-13.38	-13.71	-12.72	-13.54	-11.82	-15.31	-14.09	-13.74	-12.35
As ₂ O ₅	-38.95	-33.48	-35.20	-36.57	-34.94	-32.60	-35.99	-33.85	-33.40	-33.29	-32.62	-32.71	-34.99
Calcite	-0.94	-0.23	-0.62	-0.94	-0.85	-0.65	-0.19	0.04	0.05	-0.49	-0.20	-0.57	0.39
Claudetite	-12.73	-13.40	-11.73	-13.19	-13.42	-13.75	-12.76	-13.58	-11.86	-15.35	-14.13	-13.78	-12.39
Dolomite (disordered)	-2.34	-0.98	-2.17	-2.31	-2.99	-1.80	-0.84	-0.41	-0.90	-1.46	-1.10	-1.74	0.02
Dolomite (ordered)	-1.79	-0.43	-1.62	-1.76	-2.44	-1.25	-0.29	0.14	-0.35	-0.91	-0.55	-1.19	0.57
Fe(OH) ₂ (am)	-4.21	-3.67	-4.13	-4.95	-5.65	-3.64	-2.82	-3.15	-2.89	-3.10	-3.97	-3.11	-1.86
Fe(OH) ₂ (c)	-3.61	-3.07	-3.53	-4.35	-5.05	-3.04	-2.22	-2.55	-2.29	-2.50	-3.37	-2.51	-1.26
Gypsum	-3.43	-3.06	-2.86	-2.55	-2.97	-2.84	-3.27	-3.04	-2.88	-3.23	-2.94	-3.32	-1.26
Halite	-7.96	-8.24	-8.75	-8.08	-8.27	-7.88	-7.99	-8.16	-8.49	-8.29	-8.10	-7.61	-8.04
Mirabilite	-9.13	-9.68	-10.85	-9.84	-10.09	-9.82	-9.09	-9.54	-10.31	-9.96	-9.64	-9.43	-10.15
Siderite	0.42	0.63	0.34	-0.29	-1.15	0.34	1.14	0.96	1.00	0.74	0.33	0.84	1.71
NaF	-7.61	-7.41	-9.08	-7.72	-7.50	-7.52	-7.30	-6.91	-7.50	-7.73	-8.30	-7.11	-6.91
Fluorite	-3.49	-2.18	-4.15	-2.11	-1.86	-2.02	-2.77	-1.30	-1.54	-2.71	-3.87	-2.10	-1.69
FCO ₃ Apatite	4.19	11.38	6.69	6.01	7.78	10.87	11.30	14.28	15.09	12.47	8.99	8.46	15.81

Dissolution of a mineral may vary with depth, therefore we plotted As and F⁻ mineral phase SIs with depth values to observe any visible trend. Arsenolite SI values plotted against depth gave us no visible trend (Fig. 5.7a). The SI values remain constant with increase in depth; however when we plotted SI values of As₂O₅ against depth it was observed that the SI values of a number of samples decreased with depth (Fig. 5.7b). This shows that there is higher level of As saturation at shallow depths. With F⁻ phases, the results were different, it is seen that FCO₃⁻Apatite as well as NaF didn't show any observable trend with depth (Fig. 5.7c and d). The non-observance of any relation of the F⁻ phase SIs with depth could be due to local effects which we missed due to lack of an intensive sampling.

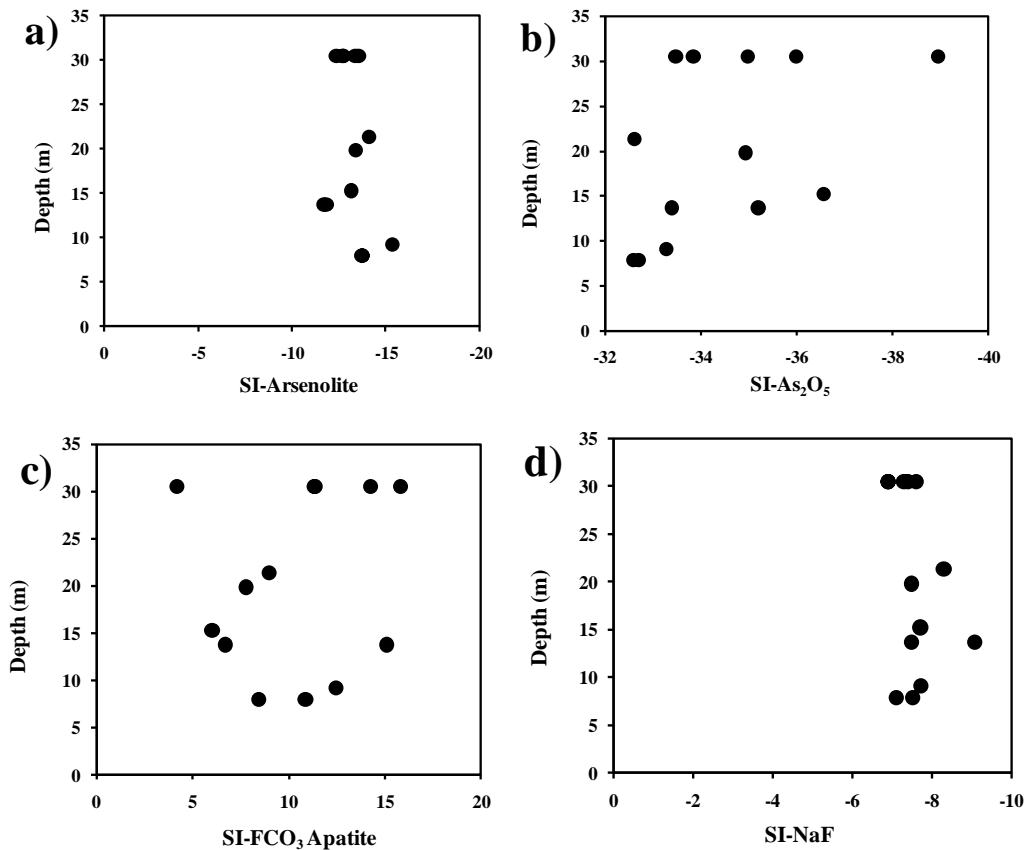


Fig 5.7: Plots of SI values of selected species versus depth. (a) SI-arsenolite versus depth (b) SI-As₂O₅ versus depth (c) SI-FCO₃ Apatite versus depth and (d) SI-NaF versus depth

5.4. Conclusion and recommendation

The relationship between As and F⁻ in the study area was not found to be very significant. The aquifers of the study area were found to be mostly reducing in nature and the decrease in ORP was found to positively affect both As and to some extent F⁻ mobilization in the groundwater. Reduction of Fe (hydr)oxides is the most likely mode of groundwater As mobilization in the study area as a strong relation was observed between As and Fe, and a negative relation was observed between As and ORP. The same was also shown by PCA and HCA where Fe and As were grouped together. Fluoride and SO₄²⁻ appear to be mobilized to some extent by desorption from Fe (hydr)oxides under an alkaline condition as shown by the close grouping of F⁻ and SO₄²⁻ with Fe and As in the HCA. PCA also reveal the association of F⁻ and SO₄²⁻ with each

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other. Moreover a slight negative correlation between the two anions could indicate their competitive nature. Previous studies have associated high F^- with drier arid conditions where the aquifers are mostly oxidizing. The conditions in the BFP were found to be the exact opposite which could explain the extremely low values of F^- . This along with sporadic distribution of the groundwater samples could be the reason why a defining trend was not observed between As and F^- . The SI values of the different mineral phases of As and F^- indicate that they are under-saturated, which implies that the hydrochemistry of the region's groundwater will change in the future resulting in an increase in the level of both As and F^- . This is also proved by the fact that higher levels of groundwater As and F^- were detected in 2012 compared to 2011. It is therefore very important to have a more detailed investigation of the trend by studying the phase distribution of As and co-contamination under laboratory settings.

We failed to observe a proper relationship between As and F^- over the vast extent of the BFP under natural conditions, therefore the sampling density should be increased. Studies by other workers have reported that both As and F^- mobilization is dependent on the depth of the aquifers. Multilayer sampling can be utilized for observing the influence of depth on As and F^- mobilization. Fluoride contamination of groundwater is reported to be highly dependent on rock-water interaction and groundwater recharge rates. Therefore seasonal variation is expected to play a major role in F^- mobilization especially during the drier months in aquifers with limited recharge. Arsenic has also been found to be mobilized under the aforementioned conditions if the environment becomes sufficiently oxidizing. Therefore As and F^- co-contamination should be studied in individual aquifers to investigate the influence of seasonal recharge, and the localized hydrogeochemistry.

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