

## CHAPTER 7

# Conclusion and recommendation

### 7.1. Conclusion

Arsenic and  $F^-$  have been detected in groundwater across the world including India. Studies of their co-contamination perspective are rare and lacking, in India no effort has been made to study this phenomenon. A pilot attempt was made to study the same, for which the Brahmaputra flood plains (BFP) were selected as the study area. The present study was an attempt to understand (i) the co-contamination behaviour of As and  $F^-$  in a natural settings and controlled conditions, (ii) how As and  $F^-$  are released into the groundwater from solid/adsorbed phases and their governing factors, (iii) what would be the fate of their aqueous species and (iv) how proximity to river affected As and  $F^-$  distribution and enrichment.

Hydrogeochemistry of the BFP appear to be controlled by natural weathering processes rather than anthropogenic activities which were found to be minor occurrences based on the land use patterns across the BFP. Bicarbonate ( $HCO_3^-$ ) type water with mixed cation ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) dominance was found out to be a common occurrence in the region. The BFP region also appears to have a multiple aquifer system consisting of both reducing and oxidising aquifers. This was indicated by the detection of both positive and negative ORPs in the groundwater samples. It is likely that anthropogenic activities like groundwater withdrawal and agricultural return flow leads to oxidising conditions while geogenic processes and microbial degradation induced reducing conditions. Reducing conditions were found to be more dominating of the two. A strong correlation was observed between Fe and As both spatially and seasonally indicating that Fe (hydr)oxides could be the phase associated with As mobilization. Depth was found to influence the mobilization of As but not  $F^-$ .

Fluoride was found to be positively correlated to Fe in the north bank, at the same time a weak negative correlation was also observed between  $F^-$  and  $SO_4^{2-}$ . This indicates

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towards the possibility of Fe (hydr)oxides as a source of anions like  $F^-$  and  $SO_4^{2-}$ . The weak negative correlation between  $F^-$  and  $SO_4^{2-}$  could arise due to the competitive interaction between the two for positively charged surfaces like Fe (hydr)oxides. Hierarchical cluster analysis grouped  $F^-$  and  $SO_4^{2-}$  close to As and Fe, which confirms that such anions could be released from Fe (hydr)oxides by desorptive processes. Mineralogical studies by XRD analysis of soil/sediment samples showed the presence of As bearing minerals like arsenopyrite ( $FeAsS$ ) and walpurgite [ $(BiO)_4UO_2(AsO_4)_2 \cdot H_2O$ ] indicating their role as the primary source of As in the BFP. While SEM analysis, revealed the association of As with Fe, Mn, Si and Al, indicating its presence in a co-precipitated form. Iron and Mn especially were found to be high in the sediment and soil samples.

Proximity to the river was found to play a very crucial role in distribution and occurrence of As and  $F^-$ . Groundwater As appeared to be directly influenced by proximity to the river as higher levels of groundwater As were detected closer to the Brahmaputra River, while  $F^-$  distribution was found to be inversely affected by river proximity. In fact the extremely low values of  $F^-$  in the BFP suggest that fluvial environment with high sedimentation and groundwater recharge rates were unsuitable for the occurrence of  $F^-$ . It is therefore likely that  $F^-$  occurs at greater distance from the river, in drier regions where the groundwater recharge rates are low prompting more rock-water interaction. Both As and  $F^-$  mobilization were found to be affected by alkalinity and pH all round the year.

The impact of anthropogenic activities on As mobilization can be inferred from the detailed study of the groundwater in the Jorhat district. A weak correlation was observed between As and Fe, while  $PO_4^{3-}$  showed a good correlation with As. Moreover a high seasonal variation was observed in the groundwater As levels of the Jorhat district, indicating the dependence of As mobilization on groundwater recharge. Presence of sulphide oxidation is suggested by the positive correlation between As and  $SO_4^{2-}$ . Intrusion of oxygen during the pre-monsoon season due to the lowering of water table could create the oxidizing condition needed for As release by sulphide oxidation. Sulphide oxidation appears to be a minor occurrence when compared to the overall

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trend observed in the BFP, i.e. reductive hydrolysis of Fe (hydr)oxides. The groundwater of the BFP is under-saturated with respect to As and F<sup>-</sup> bearing minerals as indicated by the speciation studies, therefore there is a strong likelihood of As and F<sup>-</sup> enhancement in the groundwater of BFP in the near future.

Due to the absence of significant correlation between As and F<sup>-</sup> under natural settings, an effort was made to understand the same using As phase distribution and batch desorption experiments. Clay content was found to determine the As content of soil and sediments to a great extent. A strong correlation of organic matter and clay suggest that clay content determined the organic matter content of the soil and sediments, which in turn highly affected the amount of As in the soil/sediment samples. The Fe (hydr)oxides associated fraction of As i.e.  $\Sigma$  fraction (III+IV) was found to be particularly affected by the organic matter content. This confirms that the presence organic matter enhances the process of As release and mobilization. This is due to the fact that bacterial decomposition of organic matter consumes oxygen resulting in a highly anoxic condition favourable for release of As through reductive hydrolysis of Fe (hydr)oxides. Out of the 5 “operationally defined phases” of As, fraction I and II (physisorbed and chemisorbed fractions respectively) were found to have very low percentage share of the total As.

The residual fraction V had a high percentage share in all the soil/sediment samples. However the difficulty of extracting this fraction under normal conditions, rule out the possibility of As contamination in the groundwater due to this fraction. This was also proved by the low correlation of fraction V with groundwater As. A very weak correlation between partition coefficient (K<sub>d</sub>) and fraction V also indicates that this fraction is very difficult to mobilize under normal conditions. The fractions III and IV or the Fe (hydr)oxides associated As was found to have a high percentage share of the total As content. At the same time very high positive correlation was also observed between groundwater As and the aforementioned As fraction. This shows that Fe (hydr)oxides are the main phase associated with mobilization of As in the BFP. This is also supported by the high negative correlations of fractions III and IV with K<sub>d</sub> which suggests that these fractions are easily leached into the groundwater.

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Results of the batch desorption experiment showed that Fe (hydr)oxide phase was responsible for the co-contamination behaviour of As and F<sup>-</sup>. Removal of Fe (hydr)oxides from soil and sediment was found to drastically reduce the As and F<sup>-</sup> adsorption capacity. Therefore even after spiking the soil/sediment with a known concentration of As and F<sup>-</sup>, very negligible leaching or desorption was observed. On the other hand raw or untreated soil/sediment samples were found to have a profound influence on As and F<sup>-</sup> mobilization. Presence of Fe (hydr)oxides in the raw soil/sediment were found to be responsible for the leaching of both the contaminants, and the process was found to be influenced by an alkaline condition. Increase in alkalinity leads to accumulation of higher negative charge on the surface of Fe (hydr)oxides which ultimately leads to the desorption of anions like F<sup>-</sup> and As oxyanions. The overall condition in the BFP is not very alkaline and high groundwater F<sup>-</sup> levels appear to be absent at close proximity to the Brahmaputra River. Therefore alkalinity induced co-contamination of groundwater by As and F<sup>-</sup> would likely be a rare occurrence in natural conditions of the BFP. However it is likely that, Fe (hydr)oxides will play a major role in co-contamination of groundwater by As and F<sup>-</sup> in isolated aquifers with low groundwater recharge, especially in the regions with lower amount of rainfall in the BFP. High rock-water interaction and the potential existence of an oxidizing condition due to intrusion of oxygen would be favourable for the release of both As and F<sup>-</sup> under an alkaline condition. Seasonal variation could also play an important role in this regard, as drier conditions in the pre-monsoon season could lead to the aforementioned conditions in some aquifers temporarily.

### 7.2. Recommendation

Our study was found to have many similarities with previously published works. Reductive hydrolysis of Fe (hydr)oxides was found to be the dominant mode of As mobilization in the BFP, as has been reported from other alluvial regions of the world. Previous studies have reported high F<sup>-</sup> in arid regions where aquifers are typically oxidizing in nature and more rock-water interaction is possible. Subsequently very low groundwater F<sup>-</sup> levels were recorded in the fluvial plains of the Brahmaputra River. The limited number of studies, that exists on As and F<sup>-</sup> co-contamination in groundwater

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have all proposed that semi arid to arid conditions with oxidizing aquifers were suitable for high As and F<sup>-</sup> correlation in the groundwater. The conditions in the BFP were found to be the exact opposite of the afore mentioned setting, and subsequently very poor correlation was observed between As and F<sup>-</sup> mobilization in our study. This study is unique in the sense that it attempts to address the As and F<sup>-</sup> hydrogeochemistry in the entire BFP, which has not been done earlier. Moreover the very study of As and F<sup>-</sup> co-contamination is lacking in the Indian context, this study was a maiden attempt to do the same in the context of the BFP. This study could have been augmented in a number of ways by including different dimensions. A more intensive sampling could have presented a better trend between As and F<sup>-</sup>, while techniques like isotope tracers can be used to identify As hotspots and F<sup>-</sup> enriched aquifers. This in turn can be used to delineate regions with safe drinking water. Multilayer groundwater sampling can be used to study As and F<sup>-</sup> co-contamination in natural setting at different depths. Column leaching experiments can be combined with batch desorption experiments for better observation of As and F<sup>-</sup> co-contamination. Although deeper aquifers are reported to be safe from As, yet excessive abstraction can lead to contamination of such aquifers. Moreover some studies have also reported higher F<sup>-</sup> levels at greater depths. Therefore it is recommended that the abundant surface water resources of the region are utilized for drinking by proper treatment and management options.