

CHAPTER 2

Literature review

2.1. The problem and its background

With a rapid growth in human population, the pressures on the natural resources have spiked. Groundwater is one such resource; it is considered to be the most viable source of drinking water in most of the populated world. Apart from its usage as drinking water, groundwater has also found utility in various other fields like industries, agriculture etc. Groundwater holds a special importance because unlike surface water, it is reportedly very hard to pollute groundwater as it is impermeable by normal means; however it also has a very slow flow rate making it difficult for groundwater to be treated or cured once it is polluted. In the recent era of development and industrialization the threat to groundwater has been found to increase, incidences like the heavy metal pollution in the Aberjona watershed in the United States of America is a stark example of this. Advent of better detection techniques like atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP) etc. has made it possible for us to easily detect various pollutants in the groundwater. In recent times arsenic (As) and fluoride (F⁻) have been found to be two of the most important inorganic pollutants contaminating groundwater reserves throughout the world, both these pollutants have been found to originate from anthropogenic as well as geogenic sources. More emphasis should be given to the geogenic sources, as industrial or other anthropogenic sources are point sources and limited to developed areas; while geogenic sources can occur in any region in different types of settings and are generally very difficult to detect.

2.2. Groundwater arsenic across the world and India

The problem of naturally occurring As pollution in groundwater is a burning issue which has now been recognized as one of the greatest environmental hazards, threatening the lives of millions across the globe [1-16]. The most widespread As enrichment in groundwater has been documented from parts of Asia, including Bangladesh, India, Nepal,

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Cambodia, Thailand, Vietnam, China, and Taiwan. This region has been called “South and Southeast Asian As Belt (SSAAB)” [6,17-23]. In terms of the clinical manifestation due to As induced diseases and percentage of tube wells with high As concentration, Bangladesh has been found to be the worst affected nation in the world [1, 3, 24-27]. In the recent decades, occurrence of elevated concentration of As in groundwater has been reported extensively from different parts of India namely the Middle Gangetic Plains (MGP) (Bihar, Uttar Pradesh, Jharkhand), lower Ganga (West Bengal) [15, 28-33] and several states of North East India [34-38]. However, in India the worst cases of As related health problem have been reported from the state of West Bengal where the As problem is endemic. The first case of chronic As poisoning due to drinking water was diagnosed from the state way back in 1983 [6, 9, 15,18, 22, 38, 39, 40-44].

Occurrence of geogenic As in excess of the permissible limit of $10\mu\text{L}^{-1}$ in potable groundwater resources of North East India was first reported in the year 2004 [36, 34]. The scale of the problem is potentially large in the state of Assam where 21 of the total 27 districts are reported to be severely affected by groundwater As contamination [36]. The highest levels of As were found in the flood plain of Jorhat, Lakhimpur, Nalbari, and Nagaon districts [36, 45-50]. Most of the As affected groundwater in Assam and Manipur have been reported from the floodplains of Brahmaputra and Barak Rivers respectively [34, 51, 52]. All the As affected districts of Assam [18 from BFP and 3 in the Barak Valley Plains (BVP)] have been found to be overlain by successions of alluvial Quaternary sediments. The source of the As enriched sediments is widely believed to be the mountainous rocks. Himalayas towards the north has been reported to be the source of As in the BFP; and the Barail hills in the south has been reported to be the source of the As in the BVP [13, 34, 38, 49]. Iron (hydr)oxides coatings which are commonly found on sand, silt and clay particle have been found to undergo reductive dissolution under the anoxic conditions promoted by bacterial oxidation of organic matter. This mechanism has been proposed as the process of As mobilization in the two flood plains [1, 2, 6, 15, 17, 22, 33, 53-57].

2.3. Health hazards associated with consumption of arsenic contaminated water

Arsenic has been known to cause a variety of health hazards in humans like melanosis, hyperkeratosis, restrictive lung disease, gangrene, hypertension, various vascular diseases; the most severe however are cancers of different types [58]. The two forms of As, i.e. As (III) and As (V) have been found to affect the biochemistry of the human body in different ways. Arsenite or As (III) has been found to attack the thiol groups (SH) of enzymes thereby inhibiting their activity. At very high concentrations As (III) has been found to attack sulphur bonds which effectively destroys the secondary and tertiary structures of proteins [59]. Due to its similarity with P, As (V) has been found to affect processes involving P like ATP generation [59].

2.4. Sources and pathways of arsenic in groundwater

The sources and pathways of groundwater As has been studied by a number of workers around the world. Groundwater As has been found to origin mainly from the minerals, rocks, sediments and soils. As has been found to occur in more than 200 minerals, which include elemental As, arsenides, sulphides, oxides, arsenates and arsenites [6]. Arsenic has been found to exist in mineralized areas, and exhibit close relations with transition metals like Cd, Pb, Ag, Au, Sb, P, W and Mo [6]. Arsenopyrite (FeAsS), realgar (AsS) and orpiment (As₂S₃) are dominant As bearing minerals in the ore zones; but the most important mineral source of As appears to be arsenian pyrite [(Fe(S,As)₂] [6]. Arsenic has been found to be more common in the ore minerals than in the rock forming minerals. Pyrite, chalcopyrite, galena and marcasite are examples of such minerals [6]. Pyrite a sulphide mineral has been found to be stable only under intense reducing conditions and decompose under oxidizing conditions. Many oxide minerals and hydrous oxides of metals either have been found to have As in their mineral structures or have sorption sites on which As is adsorbed. Arsenate has been found to have very high affinity for these metal oxides and hydroxides [6, 60- 62]. Calcite and clay minerals could also act as adsorption sites for As, although the adsorption efficiency on such surfaces are reported to be lower than in oxides and hydroxides of metals [6].

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Arsenic and phosphorous have similar chemical properties and form very similar ions in water. Therefore As has been found to occur in phosphate minerals; very high values up to 1000 mgkg⁻¹ of As has been detected in minerals like apatite [Ca₅(PO₄)₃(F,Cl,OH)] [6]. Also As has been found to easily substitute for a number of cations like Si⁴⁺, Al³⁺, Fe³⁺ and Ti⁴⁺ in different mineral structures [6]. Apart from ore minerals and rock forming minerals, As has also been found in different rocks, soils and sediments. Typically undistinguished igneous rocks have been found to have an average As value of around 1.5 mgkg⁻¹ [6, 63]. Igneous rocks distinguished by silica content can have higher As content but not more than 5 mgkg⁻¹ as reported by [6]; while volcanic glass have been reported to contain higher As content up to 5.9 mgkg⁻¹ [6]. The As levels in metamorphic rocks have been found to depend on the As content of the source rocks, while sedimentary rocks were found to have a wider range of As content and are reportedly more As enriched than igneous rocks [6]. Argillaceous sediments can have As content as high 13 mgkg⁻¹, while certain sedimentary rocks like Fe-rich iron stones and phosphorites were found to have very high As values of up to 2900 and 400 mgkg⁻¹ respectively. Higher amount of As has been reported from finer unconsolidated sediments like mud and clays, typically in the range of 3-10 mgkg⁻¹, depending on texture and mineralogy [6]. Arsenic has also been detected in lake sediments ranging from 0.9 to 44 mgkg⁻¹ and glacial tills with a range of around 13 mgkg⁻¹.

The level of As in soils differ based on the prevalent minerals. Base line concentration of As has been found to be around 5-10 mgkg⁻¹ [6]. This value can however vary as [63] gave a higher average value of 11.3 mgkg⁻¹. Increase in sulphide minerals in the soil has been found to lead to elevation in the level of As; concentrations as high as 45 mgkg⁻¹ has been detected in acid sulphide soils [64]. Anthropogenic activities like mining have also been found to affect or impact geogenic As levels. Mining activities have been reported to increase the availability of primary As rich sulphide minerals [6, 65]. Mining of metals like Au has been found to release significant amount of As from the mine tailings as the ores of Au have As impurities [6, 66]. Acid mine drainage from abandoned mines can oxidize minerals like pyrite which hold As and release huge amounts of the trace element based on the volume of drainage generated from the mines [6, 66-69].

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Although the sources of As are numerous however the pathways of groundwater As release are complex and depend on a number of different variables and the environmental settings of the aquifers. The pH and the redox condition of the aquifers have been found to be two of the most important factors controlling the availability of As in the groundwater. The availability of the As phases under different redox conditions and pH ranges has been discussed by [6]. It was found that As had a tendency to exist as oxyanions at higher pH and lower Eh. Similarly the two oxyanions were found to be differently affected by the pH range [6]. Arsenite was found to exist as a charge less species in a pH range from about 6 to 9, at greater pH it is replaced by H_2AsO_3^- or dihydrogen arsenite, while arsenate was reported to occur as a negatively charged species over a wide range of pH [6]. The Eh-pH diagram (Fig. 2.1), and the diagrams of As species versus pH (Fig. 2.2a and b) [6] show the availability of different As phases based on the redox and pH conditions of the groundwater.

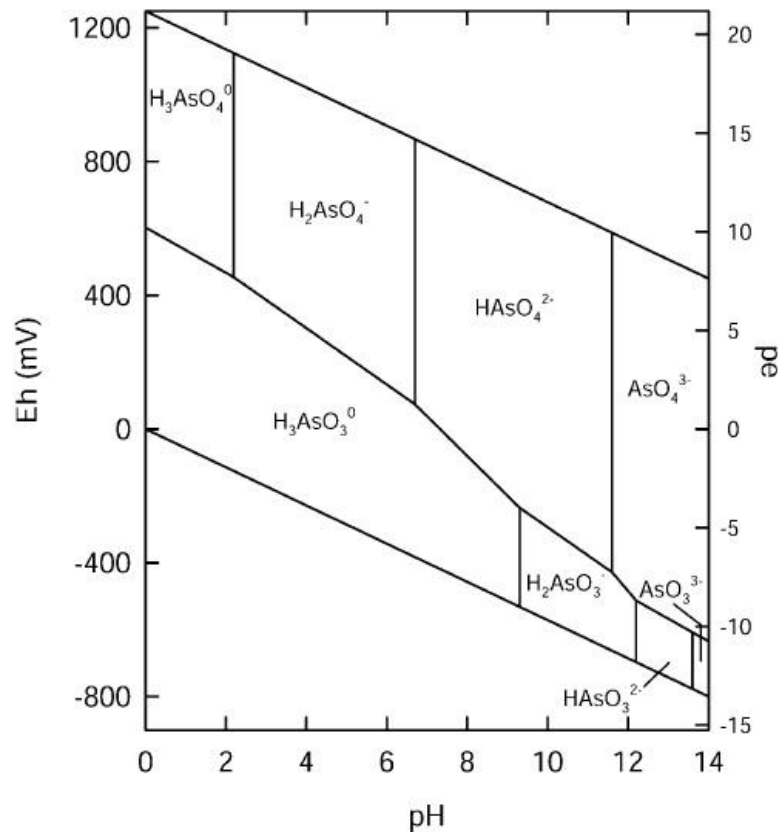


Figure 2.1: Distribution of As species in different ranges of Eh-pH [6]

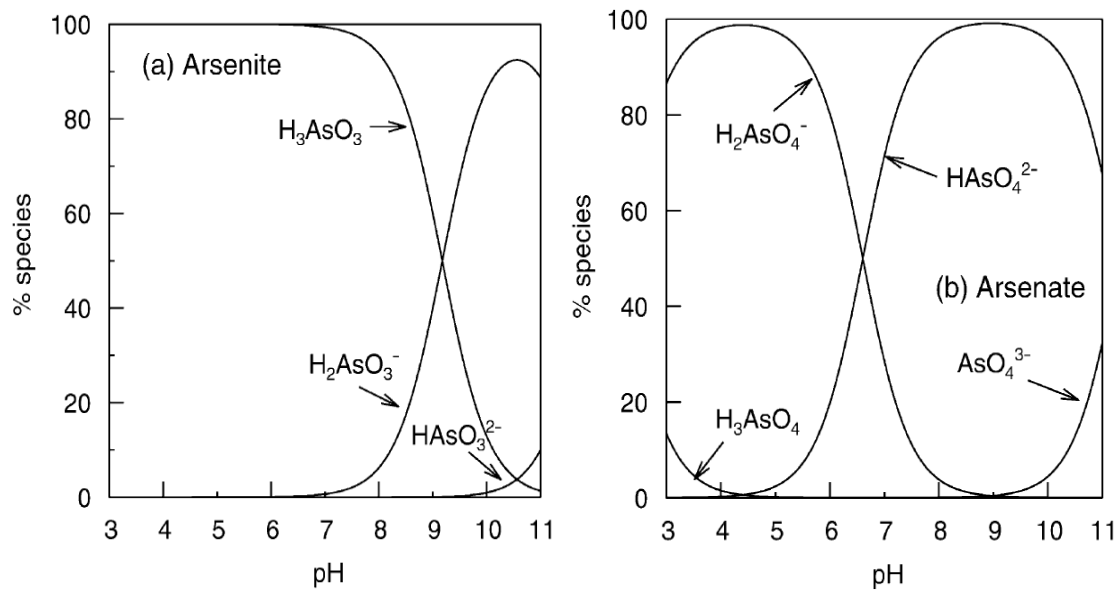


Figure 2.2: (a) Arsenite species versus pH and (b) arsenate species versus pH [6]

Innate properties of the soil and the sediments have been found to play important roles in determining their own As content and moderating the amount of As released into the groundwater. Grain size is one of the most important aspects in this regard. Grain size and As content of soils and sediments have been found to be inversely related i.e., higher As has been detected in the finer fractions of the soils and the sediments [2, 70]. The probable reason has been proposed to be that finer particles have higher surface areas and thus can hold more metal (hydr)oxides which in turn hold higher amount of As [2]. Grain size is also related to the organic matter content of the soils; the latter is another parameter which has been found to affect the content and the mobility of As in the soils. It has been reported by many workers that finer soil fractions like clay can hold more organic matter; this is due to their smaller size and higher surface area [71]. Clay particles have been found to contain two to four times more organic matter than coarser fractions like sand [72]. Speaking of organic matter, it has been found and reported by many workers that higher organic matter leads to evolution or release of more As from the sediments to the groundwater. The reason for the above observation as reported by scientific workers is that organic matter acts as a bacterial fuel during reductive processes which release As [73-75].

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High groundwater As has been found to occur in both reducing as well as oxidizing aquifers. However reducing conditions have found to be more commonly associated with elevated groundwater As levels [6]. Generally regions which have an alluvial environment with abundance of recent Holocene sediments have been found to have reducing environments [6,76-81]. Bangladesh, India, China, Vietnam, Hungary and Romania are some of the countries where such reducing aquifers have been found [4, 6, 82-96]. The aquifers of these regions have been found to have high organic matter and neutral to alkaline pH [6]. Under the above mentioned conditions reductive hydrolysis of oxides and hydroxides [(hydr)oxides] of metals like Fe, Mn and Al have been found to release As [1, 2, 15, 17, 22, 53, 54, 79]. The above process in turn is reported to be fueled by the bacterial oxidation of organic matter [73- 75] which create highly anoxic condition in the aquifers. Moreover of all the metal (hydr)oxides, Fe (hydr)oxides have been found to be the most active in mobilization of As in the groundwater [6]. High As in the reducing environment has been reported mostly from shallow wells [6, 81]. The probable reason reported by many workers is that with increase in depth groundwater gradually becomes too anoxic resulting in the formation of sulphides which adsorb the mobile As [6, 81]. However deep wells have also shown incidences of very high As in many regions with reducing conditions [6, 94].

Arid regions where high As groundwater has been detected have been found to have oxidizing conditions in their aquifers. High As in oxidizing aquifers have been detected in countries like Argentina (Chaco-Pampean Plain), Northern Chile (Antofagasta) and South-west USA [6, 65, 97-101]. Under oxidising conditions the primary mode of As release in groundwater is reported to be oxidation of As bearing sulphide minerals, leading to the formation of secondary As minerals like metal (hydr)oxides, which later remobilize to release As (102). In oxidising environments the groundwater pH has been found to be mostly alkaline (> 8) (6, 103). As (V) phase has been found to show high dependence on alkaline pH and predominate in the above mentioned conditions. Arsenic in oxidising aquifers have also reported to show a high level of correlation with other anionic species in the groundwater like HCO_3^- , F^- , H_3BO_4 and H_2VO_4^- (6, 103).

2.5. Groundwater fluoride around the world and in India

Endemic fluorosis has been reported from many countries around the world, in African countries like Morocco, Tunisia, Algeria, Sudan, Egypt, Uganda, Somalia, Kenya, Tanzania, Senegal, Ghana, Nigeria, and South Africa [104-108], in India [108, 109], China [108, 110], Japan [108, 111], Canada [108, 112], Turkey [108, 113] and even developed countries like the USA [108, 114]. Fluoride along with some trace elements like iodine and selenium which are otherwise beneficial for the human body have been reported to be harmful when taken in excess amounts [108, 115, 116]. In India alone, 60-65 million people are expected to drink F^- contaminated groundwater. Those that are suffering from fluorosis are reported to number up to 2.5-6 million [117]. Fluoride is actually required by the human body for maintenance of bones and the teeth; a daily dose of 1.5mgL^{-1} has been recommended by the World Health Organization [118]. However the daily recommended value is subject to change based on the amount of water that is consumed by an individual [119]. Therefore hotter, arid and semi arid regions of the world where water consumption is high, should have much lower permissible limits for F^- in the drinking water [108, 120]. The equation given by [119] has been found to provide a more acceptable value for F^- in drinking water for the different countries based on the amount of fluid consumed and the temperature of the region.

We have already discussed that endemic fluorosis is prevalent in India. Out of the 29 states in the country, 177 districts in 19 states are reported to have F^- in their groundwater [117]. The states which were found to be the worst affected are Andhra Pradesh, Rajasthan, Gujarat, Uttar Pradesh, and Tamil Nadu [121, 122]. Most of the regions mentioned above are arid to semi arid regions. Of late high F^- in the groundwater has also been reported from the North Eastern region of the country which consists of the eight states, of Assam, Arunachal Pradesh, Manipur, Meghalaya, Mizoram, Nagaland, Sikkim and Tripura [36]. However unlike the other mentioned states, the climate and the environmental conditions in the North East are pretty much different. The region, especially Assam, is dominated by alluvial deposits from the river Brahmaputra and its tributaries. Also the region gets much higher rainfall than any other region in India. In the state of Assam, high F^- in groundwater was reported from the districts of Karbi Anglong and Nagaon in the last decade of the 20th

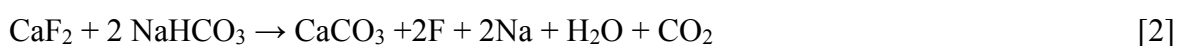
century [36, 121, 123]. High groundwater F^- has also been detected in Guwahati, Assam, the largest city of the region [124]. The study in Guwahati found that F^- increased with depth and shared positive correlations with Na, K and alkalinity; while negative relation was observed with Ca, Mg and hardness. Overall there is a lack of published work and proper research on F^- pollution and hydrogeochemistry in the region.

2.6. Fluoride hydrogeochemistry

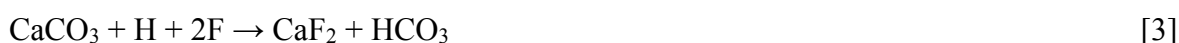
Fluorine is the most electronegative element in the periodic table. As a negative ion (anion) it has the ability to form a number of compounds and complexes [108, 125]. It is also highly abundant and is the 13th element in the order of abundance in the earth's crust [125]. The F^- contamination of the groundwater has been found to depend to a large extent on rock-water interaction [125, 126]. Moreover the process of F^- mobilization and its levels in the groundwater have been found to be determined by a number of factors like climate, host-rock composition, pH, anion exchange capacity of aquifer materials (OH^- for F^-), cation exchange capacity (Na^+ for Ca^{2+}) and the hydrogeochemistry [108, 125]. The sources of F^- in most natural waters are of geogenic origin, mostly from the host rocks, F^- has been found to be especially associated with silica rich rocks like granite [108]. Fluorite (CaF_2) has been considered to be the most important source of F^- in groundwater, "especially in granitic terrains" [108, 127]. However many researchers believe that other minerals like fluorapatite [$Ca_{10}(PO_4)_6F_2$], villiaumite (NaF), cryolite (Na_3AlF_6), and silicates could act as more ready sources of F^- as rate of dissolution of CaF_2 in water is quite slow [108, 128, 129]. Fluoride has been found to be higher in groundwater of arid regions than in regions with sufficient rainfall, mainly because arid regions offer more time for rock-water interaction without the involvement of recharge [108, 130]. Another interesting trend which has been observed in many regions with high F^- groundwater is that the level of F^- has been found to increase with depth; this could be due to an increase in temperature with increasing depth [108, 131]. Increase in the temperature could increase the equilibrium constant of fluorite (" $10^{-10.8}$ at $10^\circ C$ to $10^{-10.57}$ at $25^\circ C$ ") [108, 132], resulting in its higher dissolution. The above observation counters the observation for As, which has been found to initially increase with depth but decrease afterwards at greater

depths [81]. Workers like Farooqi et al [133] have reported that higher F^- occurred at shallow depths.

We have already mentioned about pH and the alkalinity of the environment. It has been observed in many regions with high F^- , that increase in the alkalinity and pH has a positive effect on the concentration of F^- in that region. Under acidic pH, F^- has been found to remain adsorbed on clay minerals, but with increasing alkalinity it has been observed to desorb from the substrates [134]. Dissolution of more F^- under alkaline conditions can be explained by the following equation [135].



Other minerals like calcite ($CaCO_3$) can also lead to enrichment of F^- in the groundwater, as shown in the equation below:



$$K = \frac{a(HCO_3^-)}{a(H^+) * a(F^-)^2}$$

“Where K is an equilibrium, and a is the activity” [135]. Due to the low solubility of CaF_2 , the activity of F^- is directly proportional to the level of HCO_3^- in the groundwater of the region.

2.7. Dangers associated with drinking fluoride contaminated water

Fluoride is necessary for normal bone growth and for maintenance of dental strength [136]. However excess amount of F^- in drinking water and diet has been found to cause severe disabilities collectively termed fluorosis: dental fluorosis if it affects the teeth and skeletal fluorosis if the bones are affected. The enamel of our teeth is composed of hydroxyapatite and carbonated hydroxyapatite; F^- in excessive amounts has been found to convert the two forms of hydroxyapatite to fluoroapatite which lead to weathering and weakening of the enamel of the teeth [137]. Excess F^- in our bodies has been linked to the formation of HF which is highly corrosive and reportedly found to act on the carbonated

hydroxyapatite of the bones leading to the formation of CaF_2 , an insoluble salt. This salt is useless for the body and results in weakening of the bones [138].

2.8. The problem of co-contamination and its study

It can be observed that although great progress has been made in the fields of As and F^- hydrogeochemistry, yet the two fields have remained separated to a great extent. The initial studies in both the fields concentrated on the monitoring aspect and later more emphasis was laid on their hydrogeochemistry and biochemistry as their potential hazards became known. However with the discovery of both the contaminants together in the same locality the approach has started to change, the two areas are now merging. Different workers are now working on both the contaminants with different objectives like remediation of the two contaminants at the same time or studying the synergistic or the antagonistic effects of the two in the human physiology. Despite this however a lot has to be done as the number of studies where the co-contamination aspect has been studied is still rare. The very proposition of the existence of the two contaminants together can be more detrimental than either of them acting alone. We have already mentioned the carcinogenic effects of As and debilitating symptoms of fluorosis, but a new study has found that co-contamination can act up to a genetic level in the expression of genes [139]. A recent study reveals that As may be involved in F^- induced bone toxicity through “PTH/PKA/AP1 signalling pathway” [139]. Thus we can imagine the extent of harm the two can wreak together on the human physiology. Some earlier studies have also discussed the behaviour and distribution of the two contaminants in the groundwater in different parts of the world. Children in the Shanyin County, China who were exposed to elevated levels of both As and F^- in their diet through drinking water showed a reduction in their IQs and experienced stunted growth [140]. The study of [141] explores the prevalence of As and F^- co-contamination in the country of Mexico. It was reported that both the contaminants had geogenic origins. Arsenic in the previous study originated from volcanic rocks and As rich ores; desorption from clay minerals and Fe and Mn oxides along with evaporation were also suggested as pathways for As mobilization. Fluoride on the other hand was found to be released mainly due to dissolution of acidic volcanic rocks [141]. Another study conducted by [142] in Argentina revealed high correlation between the two.

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Both the contaminants also showed good positive correlation with the ratio of Na/Ca. The above study concluded that both As and F⁻ came from volcanic glass, and was positively affected by alkaline NaHCO₃ type water which was effective in dissolving the above mentioned volcanic glasses in the region. The releases of the two contaminants were also found to depend on the redox status of the aquifers. It has been found that higher correlation was observed between the two (As and F⁻) in arid and semi arid regions which had commonly oxidizing conditions, while the relation was lower in reducing aquifers [1, 6, 9, 73, 81, 133, 142-150].

The use of total concentration of a contaminant to assess its hazard potential has been found to be inefficient and also misleading [152]. The true hazard potential of geogenic groundwater contaminants has been found to be dependent on their ability to separate out of the source material for e.g. soil/sediment or minerals and enter the groundwater. It has been reported that geogenic contaminants occur in the form of different pools in sediments and soils, these pools or fractions are affected by the environmental conditions and have been found to have varying labilities [152]. Extraction of these individual fractions has been found to provide crucial information regarding the origin, mode of occurrence, mobilization and transport mechanisms of geogenic contaminants especially trace elements [152]. It has also been reported that uptake of trace metals by plants and their toxicity can be related to these separate fractions [153-155]. Therefore it can be said that mere speciation of groundwater As into As (III) and (V) is not sufficient and further study is needed for observation of the phase distribution of As in the soils and sediments.

In this regard sequential extraction has become a well established method for separating the different fractions of trace elements in soils, sediments and other related materials [156]. Different sequential extraction procedures have been developed for different trace elements based on their chemical properties and knowledge of soil chemical analysis [152, 157]. The basic method involves treating the material, for e.g. a soil sample, with reagents of increasing reactivity to leach out the fractions with decreasing lability or leaching potential [155]. The different fractions are termed “operationally defined” based on their method of extraction [152]. Different sequential extraction procedures (SEPs) have been

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used for the purpose of monitoring the partition and the temporal changes in the lability or mobility of added metals [155, 158-160].

Tessier et al [152] developed a SEP for extracting particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into five different fractions: “exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual”. The method was found to be quite accurate with an error margin better than 10±% standard deviation. However the “operational nature” of the SEPs used by different laboratories made it hard to compare their results. Therefore a unified SEP was devised under the “Commission of the European Communities, Community Bureau of Reference” (BCR, which now has been superseded by the Standards, Measurement and Testing Programme) [156, 161]. This SEP with three steps was found to be effective in fractionating trace elements in sediments [156]. The original BCR SEP has been modified by different workers and has been applied on other materials like sewage sludge [156, 162], marine sediment [156, 163], industrial “made ground” [156], ash [156, 164] and compost [156, 165].

Most of the SEPs including the ones mentioned above have been found to be effective on metal cations. Therefore in this regard the works on anions have been found to be “limited” [155]. Due to the similarities in the chemical properties of As and phosphorus (P) previous works on P fractionation have been used to lay the foundation for extraction of different fractions of As in soils and sediments. In this regard the SEP for P given by [166] has been modified by many workers for As fractionation [155]. Suitability of different SEPs in fractionating As and Se by using standard chemicals and minerals was also tested by [155, 167]. However a shortcoming was observed in majority of these SEPs. It was found that As desorbed from a particular phase was found to be re-adsorbed on other mineral phases decreasing the accuracy of the overall extraction. Wenzel et al [155] devised a modified SEP procedure for As in soil and sediment fractions by improving previous works of [166, 168-170]. The modified and improved SEP proposed by [155] has been found to extract 5 “operationally defined” fractions of As. Fraction I and II have been found to be easily leached by the action of sulphates and phosphates respectively, and have been termed as labile fractions. The fractions III and IV are As pools associated with amorphous and crystalline Fe (hydr)oxide phases respectively. The Fe (hydr)oxide

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associated fraction of As i.e. fraction (III+IV) has been found to be linked to ligand promoted dissolution and reductive hydrolysis [155, 177]. The last fraction i.e. fraction V or the residual As has been found to be associated with sulphide phases like orpiment (As_2S_3) and is extremely hard to remove under natural conditions, requiring extreme steps like acid digestion for extraction [155]. Outside of a laboratory environment, fraction V has been found to be mobilized under highly oxidising conditions like those generated by anthropogenic influences like acid mine drainage [155].

As mentioned earlier the hazard potential of a contaminant depends on its ability to separate out of the source materials. This capacity to separate can be assessed by the calculation of the partition coefficient (K_d). In terms of metal contamination, K_d has been found to be the ratio of the sorbed metal concentration to the dissolved metal concentration [172].

$$K_d = \frac{\text{sorbed metal concentration (mgkg}^{-1}\text{)}}{\text{dissolved metal concentration (mgL}^{-1}\text{)}}$$

Sequential extraction of trace elements like As has been found to reveal about the mobility of different fractions based on their ease of separation or extraction [155, 171]; this knowledge in turn can be applied for the calculation of K_d in different soils and sediments under laboratory settings.

Column leaching and batch sorption/desorption experiments can be used to study interaction and dynamics of contaminants based on the background information on trace element mobility from fractionation studies. Sorption and desorption procedures have been reported to be used for studying the leaching of contaminants and pollutants from waste soils, sludges and landfills [172]. These experiments have also been used in remediation studies of trace and heavy metals [174, 175] and for studying the leaching of contaminants from natural soils [176]. The same principle can also be applied to study the co-evolution of contaminants of geogenic origin like As and F^- from soils and sediments. Such studies are reported to be rare. One of most well documented studies on co-contamination perspectives of As and F^- has been conducted by Kim et al [81]. The batch sorption desorption experiment was used by Kim et al [81] to study the evolution of As and F^- in the river sediments obtained from the alluvial regions of the Mankyeong River, South

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Korea. The study observed the influence of the Fe (hydr)oxides phase of the soils/sediments on As and F⁻ mobilization under varying conditions of alkalinity. It was observed that Fe (hydr)oxides played a key role in adsorption and desorption of negatively charged species like F⁻ and oxyanions of As. While elevation in alkalinity was found to enhance the overall co-evolution of As and F⁻ from the soil and sediments.

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