Adsorption-Desorption Characteristics of Arsenic on Agricultural Soil

by

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December, 2006

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A thesis submitted to the Department of Civil Engineering of Bangladesh University of Engineering and Technology, Dhaka, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING

DECEMBER 2006

The thesis titled "**Adsorption-Desorption Characteristics of Arsenic on Agricultural Soil**" submitted by Sultana Rebeka Akhter, Student No. 040204103P, and Session: April 2002 has been accepted as satisfactory in partial fulfillment of the requirements for the degree of M. Sc. Engineering (Civil and Environmental) on 27th December 2006.

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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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Sultana Rebeka Akhter

Dedicated

To

My Mother

ACKNOWLEDGEMENT

First of all I want to pay my gratitude to the Almighty Allah for helping me in preparing this thesis paper successfully. Secondly, I want to express my gratefulness to my thesis supervisor, Dr. Ashraf Ali, for providing me continuous support and guideline to prepare a collaborative formal paper. His contribution to me can only be acknowledged but never be compensated.

I would like to express my deepest gratitude to the Department of Civil Engineering, BUET, and Head of the Department of Civil Engineering and all the members of BPGS committee to give me such a great opportunity of doing my M.Sc and this wide spread research work.

I would also like to convey my heartiest thanks especially to Dr. Ganesh Chandra Saha, Assistant Professor, DUET, who has helped me a lot with his kind views, assistance, cordial cooperation and help and encouragement.

Furthermore, I want to thank Mr. Ehsan and Mr. Mithu of Environmental Engineering Laboratory for frequent technical support in field and laboratory work through out whole thesis work. I would like to thank also all the staffs of environmental laboratory who in various ways eased the task of myself.

I would also like to covey my gratefulness and thanks to all my family members and friends specially my husband and parents for their patience, cordial cooperation and help. There support and coordination during the thesis period was generous and indispensable.

At last I want to thank my department, all the members of the defense board and respected supervisor Dr. Ashraf Ali once again for giving me such an opportunity, which has obviously enhanced my environmental background related knowledge and skills to a great extent.

ABSTRACT

Accumulation of As on paddy field soils as a result of irrigation with As contaminated groundwater and its introduction into the food chain are major concerns. Adsorption is the principal mechanism by which As is accumulated on soils. In this study, adsorption characteristics of arsenic on paddy field soils from three As affected areas (Munshiganj, Faridpur and Brahmanbaria) and one unaffected area (Naogaon) were assessed in laboratory batch experiments.

As adsorption on paddy field soils has been found to increase with increasing oxalate-extractable iron content (as well as total iron content) of soil; thus amorphous iron oxyhydroxides appear to be the principal adsorbent of As. Iron content of paddy field soil, in turn, has been found to increase with increasing dissolved Fe content in irrigation water. Thus, As adsorption onto paddy field soil depends not only on the characteristics of soil, but also on the characteristics of (e.g., iron content) of irrigation water. For some paddy field soils, very high adsorption densities, approaching 200 mg/kg, have been recorded under the laboratory experimental conditions. If As is present in such high concentrations in paddy field soils throughout the year, it could have significant adverse effects on growth and yield of crops. On the other hand, As adsorption by soil may play an important role in reducing As availability to plant and its introduction into the food chain. The high adsorption capacity of soils could reduce the bioavailability of arsenic to plant and also retard its transport through the subsurface.

Arsenate adsorbs much more strongly onto soil than arsenite. For same initial concentration of arsenic, arsenate adsorption is almost 3 times greater than arsenite adsorption. Phosphate was found to adsorb quite strongly on paddy field soils and, like As, its adsorption appear to increase with increasing iron content of soil. Arsenite adsorption was found to decrease with increasing phosphate concentrations due to its higher affinity for sorption sites than As; but since the batch experiments were carried out with low sorbate to sorbent ratios, the effects were apparent only when concentrations of both As and phosphate were high. Effect of pH on adsorption of both arsenate and arsenite appear to follow the same trend; adsorption as a function of pH followed a concave downward profile with the maximum adsorption occurring at pH between 4 & 6.

Some recent studies suggest that significant amount of As (that is accumulated in the paddy field soils during the irrigation season) is mobilized/released from paddy field soil in the wet season (that immediately follow the irrigation season) during inundation with flood/rain water. Desorption from soil and reductive dissolution of iron oxyhydroxides, the principal adsorbent is the soil matrix, are thought to be responsible for the phenomenon. Results obtained from this study confirm that significant amount of As could be mobilized from paddy field soils by desorption, especially over longer time periods, and through reductive dissolution. Desorption of As from paddy field soils have been found to be a strong function of time. Under the experimental conditions, about 10% of As initially present in soil was desorbed within a period of about one month. Since paddy fields are often inundated under a significant depth of water for about three months during the wet season, As release/mobilization from soil by desorption could be significant. Significant As release from As-rich paddy field soils was recorded under reducing condition created by addition of a carbon source (glucose) and nutrients. Such

mobilization of As through reductive dissolution of iron oxyhydroxides has also been found to be a strong function of time. Both desorption and reductive dissolution of iron oxyhydroxides appears to be important processes that govern the fate of As in irrigated paddy fields. Results from this study suggest that these natural processes play a major role in preventing As concentration in soil to reach toxic levels.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Awareness about the presence of arsenic has been growing since late 1993 when arsenic was first tested and detected in groundwater samples from the district of Chapai Nawabgonj bordering the West-Bengal district of India. Since then, high levels of arsenic have been detected in 270 out of 465 Upazilla; the southern, south- western and north-eastern regions of the country are worst-affected. Arsenic contamination has primarily affected the shallow aquifers, which are widely used for both domestic water supply and irrigation purposes. Eight to twelve million wells across the country constitute the backbone of the rural water supply system, presenting a growing danger to their lives. This has created major problems, especially among the rural people. It is estimated that about 85 million people in Bangladesh are at risk of arsenic toxicity.

Besides domestic use, groundwater is also widely used for irrigation during dry season, particularly for growing the dry-season paddy called boro, which requires about 1 m of irrigation. A total of 925,125 shallow tube wells and 24,718 deep tube wells were used for irrigation during the 2004 dry season (BADC, 2005) and groundwater irrigation covered about 75 percent of the total irrigated area. The contribution of groundwater to total irrigated area has increased from 41 percent in 1982-83 to 71 percent in 1996-97 and to about 75 percent in 2004. During the last five years, the rate of increase has leveled off, probably due to the unavailability of additional cultivable land. Much of this increase has been accomplished through installation of irrigation wells in shallow aquifer. In 2004, shallow irrigation wells covered about 60 percent of total irrigated area (Harvey et al., 2005).

Widespread use of groundwater for irrigation suggests that ingestion of irrigated crops could be another major exposure route for arsenic. Possible adverse effect of high

concentration of arsenic in agricultural soil on crop yield is another concern. Due to its affinity for metal oxides/hydroxides in soil, higher accumulation of arsenic in irrigated surface soils is expected and a number of studies (e.g., Saha, 2006; Ullah, 1998; Jahiruddin et al., 2000; Meharg and Rahman, 2003; Huq et al., 2003; Ali et al., 2003b; Panuallah *et al.*, 2003; Masud, 2003; Islam et al., 2005; Ahmed, 2005; Farid et al., 2005; Jahiruddin et al., 2005) have reported relatively higher levels of arsenic in paddy field soils irrigated with arsenic bearing groundwater.

The arsenic pumped into an agricultural land with irrigation water may go through the following processes:

(i) undergo adsorption and precipitation and thus become retained onto soil;
(ii) be transported back into the aquifer with percolating water;
(iii) be taken up by plants, and enter into the food chain,
(iv) volatilize into the atmosphere as a result of different bio-geochemical transformations into volatile forms;
(v) arsenic initially retained on soils may undergo desorption/ dissolution and partition back into aqueous phase (e.g., flood water/ rainwater) and subsequently transported away from the site with runoff or percolating water.

In an agricultural land, arsenic may undergo photo-oxidation in presence of sunlight. Limited data suggests the presence of both As(III) and As(V) as well as MMA (monomethylarsenic acid) and DMA (dimethylarsenic acid) in agricultural soil. Adsorption-desorption, volatilization as well as plant uptake of arsenic depend to a large extent on chemical forms/transformations of arsenic. Some recent works (e.g., Saha, 2006; Saha and Ali, 2006) showed that arsenic concentration in top soils within a paddy vary significantly both spatially and temporally. Arsenic concentration of topsoil in paddy field soils irrigated with As contaminated groundwater has been found to increase significantly at the end of the irrigation season, but then decreases after the wet season. Adsorption of arsenic onto the topsoil appears to be the principal mechanism with arsenic in irrigation water accumulates in the topsoil; whereas desorption and reductive

dissolution of iron oxyhydroxides appear to the principal mechanisms responsible for lowering of arsenic concentration in the topsoil during inundation by floodwater.

Adsorption-desorption of arsenic onto soil are key to the understanding its fate in the environment. For example, among the different arsenic species, arsenate is most strongly adsorbed and retained onto soil. Available information on adsorption-desorption of arsenic on soil and metal oxy-hydroxides are mostly concentrated on adsorption of arsenate [As(V)] and the effect of phosphate on arsenate adsorption-desorption. Relatively limited data is available on adsorption-desorption characteristics of arsenite, the principal chemical form of arsenic in groundwater. There appears to be a lack of information on desorption kinetics of arsenic from agricultural soil. Virtually no study has been carried out to assess adsorption-desorption characteristics of arsenic on agricultural soils of Bangladesh.

1.2 OBJECTIVES OF THE PRESENT RESEARCH

The overall objective of this study is to assess the effects of different processes and parameters controlling accumulation of arsenic in agricultural soil of Bangladesh. More specifically, adsorption-desorption characteristics of arsenic on agricultural soil of Bangladesh and effects of different water quality and soil parameters on adsorption-desorption characteristics have been assessed. Specific objectives include:

(a) Development of adsorption isotherm of arsenic on agricultural soil collected from different regions of Bangladesh.

(b) Assessment of the effects of selected water quality parameters (pH, phosphate content) on adsorption of arsenic in agricultural soil.

(c) Assessment of the effect of soil parameters (iron content, grain size and clay content) on adsorption of arsenic on agricultural soil.

(d) Assessment of the desorption characteristics of arsenic from arsenic-rich agricultural soil under different geochemical conditions.

(e) Assessment of mobilization of arsenic from arsenic-rich agricultural soil under reducing environment (e.g., that created during inundation of agricultural land by floodwater).

The proposed research is expected to improve understanding of different issues related to the dynamics of arsenic concentration in agricultural soil of Bangladesh, including: (i) Understanding of the role of adsorption on accumulation of arsenic in agricultural soil, (ii) Understanding of the important factors, including water quality and soil characteristics, affecting adsorption of arsenic on agricultural soil, (iii) Understanding the role of desorption in the regulation of arsenic content of top-soil of agricultural lands, and (iv) Understanding of the role of reductive dissolution of arsenic from agricultural soil in the regulation of arsenic content of topsoil, as no such studies have conducted before in respect of agricultural soil of Bangladesh.

1.3 ORGANIZATION OF THE THESIS

Apart from this Chapter, the remainder of the thesis has been divided into four chapters. Chapter 2 presents literature review concerning the history, uses and behavior of arsenic in the environment. This Chapter briefly reviews the situation of arsenic contamination in Bangladesh, arsenic in the environment and adsorption desorption of arsenic in agricultural soil. There is also a short overview of arsenic contamination of drinking water and the chemistry in soil and past studies on arsenic adsorption desorption characteristics.

Chapter 3 represents the results of laboratory experiments designed to assess the adsorption characteristics of arsenic onto paddy field soils and effect of various parameters, e.g., pH, phosphate concentration of water, and soil grain size. The implications of the results on arsenic accumulation in paddy field soils have also been discussed in this Chapter.

Chapter 4 presents the results of laboratory experiments designed to assess mobilization of arsenic from arsenic-rich paddy field soils under different conditions. The conditions (e.g., reducing environment) likely to exist in paddy field soil during inundation by

floodwater were simulated in the laboratory. Based on the results of these laboratory experiments, possible mechanisms of arsenic mobilization from paddy field soils have been discussed.

Finally, Chapter 5 presents the major conclusions of the study and also provides recommendations for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Arsenic compounds have been mined and used since ancient times. The "King of Poison" is presently a mystery and myth with a synonym "toxic" having being colorless, tasteless and odorless. Arsenic is widely distributed throughout the earth's crust. Arsenic (As) is a member of the Nitrogen Family with both metallic and nonmetallic properties, and the cycling of arsenic in the environment is regulated by natural processes and human activities. It is the twentieth most common element in the Earth's crust. Arsenic occurs in many forms, but is most toxic as an ion because it reacts with sulfur-containing groups on certain enzymes. Exposure to non-lethal levels of arsenic over a long period of time may result in chronic poisoning and carcinogenic (cancer-causing) effects. For this reason, arsenic remains a work-safety issue in industries where it is still used, such as in the manufacture of weed killers and insecticides, the preservation of wood, and in the extraction of lead and copper ores. The symptoms of acute arsenic poisoning occur in two forms. In the paralytic form, a severe paralysis develops within 1-2 hours, often accompanied by signs of delirium. In the gastrointestinal form, symptoms such as nausea, headache, intense pain, vomiting and diarrhea are dominant. It may have been introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks. The extraction of the element from arsenic compounds as a human poison was first reported by Albertus Magnus in 1250 A.D. Arsenic is naturally found at concentration levels of about 0.4 to 30 ng/m^3 in the atmospheric air, about 0.4 to 120 µg/kg in food and at concentrations from undetectable level to a few µg/L in natural water. Thus, humans all over the world are exposed to small amounts of arsenic, mostly through food, water and air. Groundwater contamination by this toxic element has been reported from several countries viz. Argentina, Mongolia, China, Taiwan, Thailand, Mexico, Chile, Hungary, Greece, Ghana, and some parts of USA, but the extent of groundwater arsenic

contamination in Bangladesh is by far the most severe arsenic contamination, both in terms of area and population exposed.

Arsenic contamination was first detected in Bangladesh in late 1993 in the district of Chapai Nawabganj in the western Bangladesh. Since then high concentrations of arsenic have been detected in 270 out of 465 upazilas of the country, mostly in the water from the shallow aquifer. Since water from shallow aquifer is also widely used for irrigation during the dry season, accumulation of arsenic in agricultural soil and its introduction into the food chain is also a major concern. This Chapter briefly summarizes the status of arsenic contamination in groundwater of Bangladesh. It also describes the irrigation practices in Bangladesh and summarizes the available information on arsenic concentrations in agricultural soils. This Chapter then describes the possible fate of arsenic that is added to agricultural soils with arsenic contaminated irrigation water. This Chapter also summarizes the available information on adsorption-desorption characteristics of arsenic on different sorbents.

2.2 ARSENIC CONTAMINATION OF GROUNDWATER IN BANGLADESH

In Bangladesh arsenic was first detected in late 1993 in groundwater samples from the district of Chapai Nawabgonj bordering the West-Bengal district of India. Since then higher levels of arsenic (exceeding the WHO standard of 0.01 mg/L and Bangladesh standard of 0.05 mg/L) have been detected in many regions of the country. The most comprehensive study on distribution of arsenic in groundwater of Bangladesh was carried out by the British Geological Survey (BGS) in cooperation with the Department of Public Health Engineering (DPHE) (BGS/DPHE, 2001). In this study, water samples from 3534 tubewells from 61 out of 64 districts and from 433 out of the 496 upazilas were analyzed. Recently, the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) carried out a detailed screening of tubewells and survey of arsenicosis patients in 270 arsenic-affected upazilas of the country (BAMWSP, 2005). In this study, every household of these arsenic-affected upazilas was surveyed and all tubewells were tested using field test kits. A total of 4,946,933 tubewells were screened for arsenic and over 66 million people surveyed for arsenicosis.

The regional pattern of arsenic distribution obtained from the BGS/DPHE and BAMWSP surveys are very similar, with the greatest contamination in the south and south-east (except Chittagong and Chittagong Hill Tracts) region and least in the north-west and in the uplifted areas of the north-central Bangladesh. Figures 2.1 shows the distribution of arsenic concentration in Bangladesh based on the nationwide survey carried out by BGS/DPHE. According to BGS/DPHE (2001) arsenic concentration exceeding the Bangladesh standard of 50 ppb was detected in 53 out of 61 districts, and in 249 *upazilas* out of 433 sampled upazilas. Of the 3534 samples, only 9% were from deep (>150 m) tubewells and the rest were from shallow wells. Among the shallow tubewells, 27% contained arsenic in excess of 50 ppb (Bangladesh standard) and 46% in excess of WHO guideline value of 10 ppb. For the deep tubewells, the corresponding figures are 1% and 5%, respectively (BGS/DPHE, 2001). The survey results revealed some 'hot spots' with high arsenic concentration in some least contaminated regions (e.g., Chapai Nawabganj in western Bangladesh). It was recognized that the sample density in the BGS/DPHE survey was not sufficient to ensure detection of all such 'hot spots'. An important observation from this and other arsenic surveys is the significant variation of arsenic concentration in well waters within short distances. Neighboring wells within a village have been found to contain quite different concentrations of arsenic and other water quality parameters (BGS/DPHE, 2001). In the vertical dimension, high concentrations have been detected within tens of meters of low concentrations.

Estimates of population exposed to arsenic concentration above the Bangladesh drinking water standard of 0.05 mg/L vary from about 20 million to over 36 million (DPHE/BGS/MML, 1999; EES/DCH, 2000; Begum, 2001; BGS/DPHE, 2001). According to BGS/DPHE (2001), 35 million people of Bangladesh are exposed to an arsenic concentration in drinking water exceeding the national standard of 50 μg/l and 57 million people exposed to a concentration exceeding the WHO guideline value of 10 μg/l.

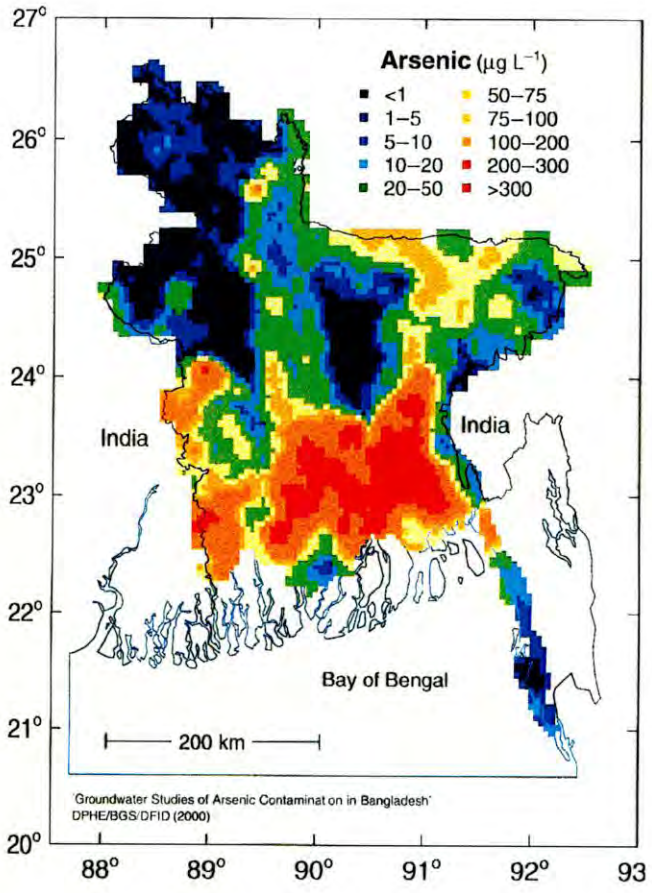

Figure 2.1: Distribution of As in groundwater of Bangladesh according to the BGS/DHPE survey (Source: BGS/DPHE, 2001)

Yu et al. (2003) estimated that if consumption of contaminated water continues, the prevalence of arsenicosis and skin cancer in Bangladesh will be approximately 2,000,000 and 1,000,000 cases per year, respectively, and the incidence of death from cancer induced by arsenic will be approximately 3,000 cases per year. In the nationwide screening program carried out by the BAMWSP, over 66 million people of every household of 270 arsenic-affected upazilas were surveyed for arsenicosis patients. Figure 2.2 shows the distribution of arsenicosis patients in the survey areas. A total of 38,430 arsenicosis patients were identified in this survey. Results from all previous surveys show poor correlation between the percentage of contaminated groundwater in a particular area and the density of patients (BGS/DPHE, 2001). Although the BAMWSP survey shows relatively low prevalence of arsenicosis, many fear it to be the 'tip of the iceberg', considering the usual delayed effect of arsenic on exposed population.

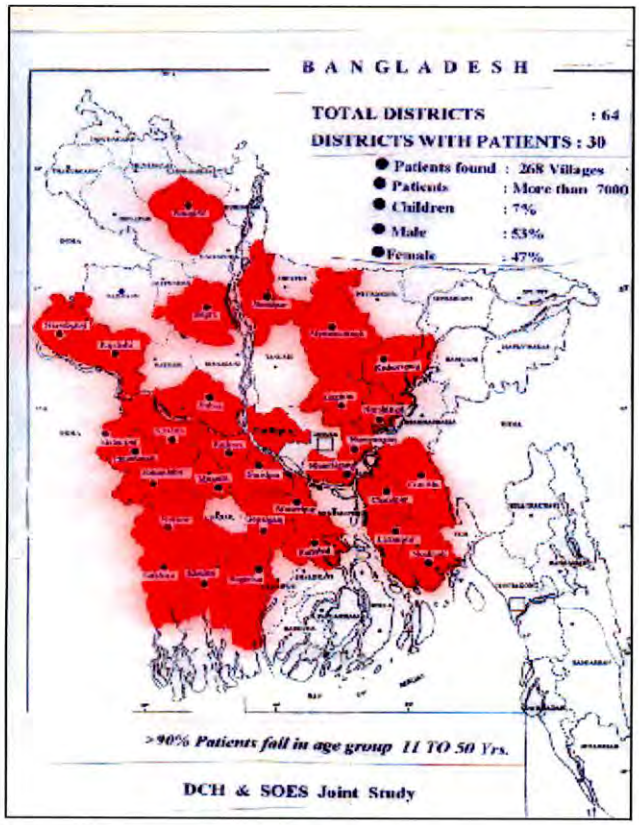

Figure 2.2: Distribution of arsenicosis patients in Bangladesh (DCH and SOES, 2002)

2.3 IRRIGATION PRACTICES AND ARSENIC IN AGRICULTURAL SOILS IN BANGLADESH

2.3.1 Irrigation practices in Bangladesh

The existence of high arsenic content has been first reported in Bangladesh in shallow hand tube well in 1993 when arsenic was first tested and detected in groundwater samples from the district of Chapai Nawabgonj bordering the West-Bengal district of India. Bangladesh belongs to South Asia and lies between $20^0 34'$ and $26^0 38'$ N, and $88^0 01'$ and $92^0 41'$ E. The area of the country is 147570 square mile. Of which Hilly areas cover 18% (26562.6 square mile). Water in the aquifers of the Pleistocene and older sediments, which are these eastern and northeastern hill regions, are arsenic free. Barinda - Modhupur cover 10% area (14757 square mile). Besides this, 1405 square mile of Panchagar district and 1809 square mile of Thakurga district of Rajshahi division were find arsenic contamination free according to BGS report. The Arsenic distribution map

(BGS and DPHE, 2001) shows that, the greater concentration is within the deltaic and flood plain areas of the country. In terms of aquifer condition, the mid and upper Holocene aquifers are severely affected while the lower Holocene, Pleistocene and older aquifers are not affected.

Besides domestic use, groundwater is also widely used for irrigation during dry season, particularly for growing the dry-season paddy called boro which requires about 1 m of irrigation. There are two major sources of irrigation water in Bangladesh - surface water and groundwater. During dry season the availability of surface water is very low. So groundwater is extensively used as a source of irrigation. The tendency of increase of groundwater irrigation and at the same time, decrease of surface water irrigation during 1970-2004 is shown in Figs. 2.3 and 2.4 and Table 2.1. As shown in Fig. 2.4, during 1970 to 1982, the contribution of surface water was more than that of groundwater; during 1985-86 the contribution from the two sources was almost similar. During the last two decades, the area irrigated by groundwater increased significantly (Fig. 2.3). For example, according to BADC (2005), in *boro* season of 2004, the total irrigated area was 4043859.09 hectares, of which 3031948.85 ha or about 75 percent was irrigated by groundwater and 1011910.24 ha or about 25 percent was irrigated by surface water. The contribution of groundwater to total irrigated area has increased from 41 percent in 1982-83 to 71 percent in 1996-97 and to about 75 percent in 2004. During the last five years, the rate of increase has leveled off, probably due to the unavailability of additional cultivable land. The contribution of surface water has declined from 59 percent to less than 25 percent during this period.

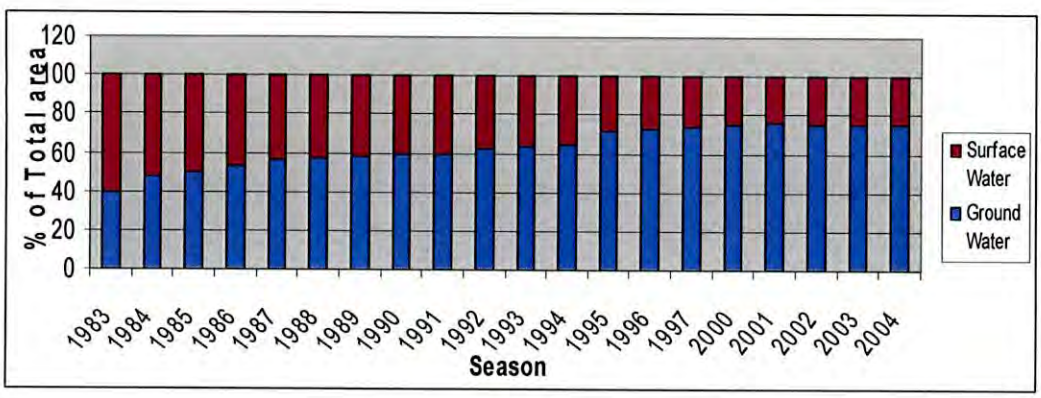

Figure 2.3: Percent of area irrigated by surface and groundwater sources (Data Source: WARPO 1999, GoB, 1998, Harvy et al., 2005, and BADC, 2005)

Table 2.1: Area irrigated by surface and groundwater in Bangladesh
(Data Source: BADC, 2001; BADC, 2002; BADC, 2003; BADC, 2004 and BADC, 2005)

	Irrigated Area (ha)				
Source of Water	Year 2000	Year 2001	Year 2002	Year 2003	Year 2004
Ground Water	2670802	2874354	2900215	3012058	3031948

Due to the increase of population, the surface water sources like ponds, lakes, and beels are being filled for various purposes like building construction, road construction, and extension of agriculture land. At the same time collection and distribution of groundwater from shallow aquifer have become easy and less costly. Hence, as a source of irrigation water, use of surface water has decreased and that of groundwater has increased.

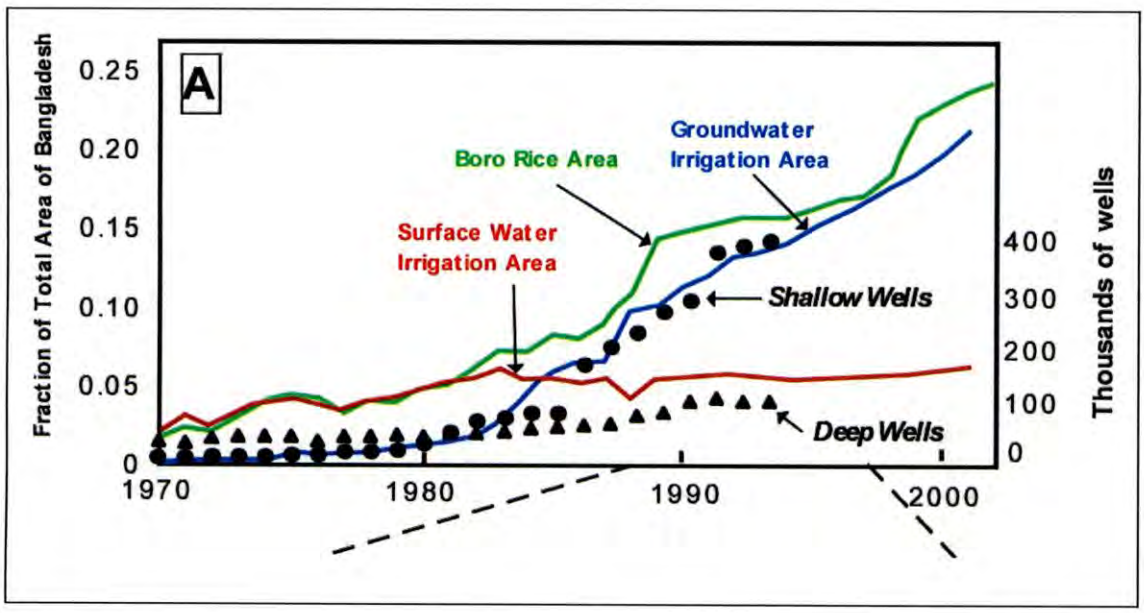

Figure 2.4: Source of water, irrigation equipment and irrigated area in Bangladesh.
(Source: Harvey et al., 2005)

So, shallow tubewells are widely used in Bangladesh for irrigation. A total of 924,023 shallow tubewells and 23,434 deep tubewells were used for irrigation during the 2003 dry season (BADC, 2003). Thus, groundwater irrigation greatly increased agricultural production in Bangladesh. Since we are increasingly depending on shallow aquifer (a large part of which is arsenic contaminated) for irrigation water, a huge quantity of arsenic is being added in the agricultural fields each year with irrigation water. Saha

(2006) showed that close to 1000 metric tons of arsenic is cycled each year with irrigation water. Arsenic in irrigation water poses a potential challenge to the agricultural sector. Ingestion of food items irrigated with arsenic contaminated groundwater may be a major route of human exposure to arsenic. Thus, accumulation of arsenic in paddy field soil and its introduction into the food chain through uptake by paddy plants are major concerns.

2.3.2 Arsenic in soils

Due to its affinity for metal oxides/hydroxides in soil, higher accumulation of arsenic in irrigated surface soils is expected and a number of studies (e.g., Alam and Sattar, 2000; Huq et al., 2003; Meharg and Rahman, 2003; Ali et al., 2003; Ahmed, 2005; Farid et al., 2005; Islam et al., 2005; Jahiruddin et al., 2005, Saha, 2006) have reported relatively higher levels of arsenic in paddy field soils irrigated with arsenic bearing groundwater. In a study conducted in five *upazilas* of the country, Islam et al. (2005) found wide variation in total As concentrations in soil samples. The arsenic concentration at these locations varied from 0.3 to 48.8 μg/g with a mean of 12.3 μg/g. The soils of the Ganges river floodplain had higher soil As levels compared to those of Meghna river floodplain. Of the 456 samples, 53 percent had total As from 0-10.0 μg/g, 26 percent between 10.1-20.0 μg/g, 17 percent between 30.1-40.0 μg/g, and the remaining 1 percent of the soils had arsenic exceeding 40.0 μg/g.

Based on analysis of soil samples (top 15 cm) collected from 161 sites, Shah et al. (2004) reported that 65% of soil had arsenic concentration exceeding 10 mg/kg. Lower soil As levels were reported by Huq et al. (2003) for a study covering 24 upazilas. Arsenic level exceeding 10 mg/kg were reported for only 3 upazilas, while 18 upazilas had arsenic level in soil below 5 mg/kg. Ali et al. (2003) and Saha (2006) showed that in paddy fields soil arsenic level at the beginning and at the end of the irrigation season could vary by a factor of over two. Some or much of the variation of soil arsenic concentrations reported in the literature may be attributed to the variation in sampling time.

2.4 FATE OF ARSENIC ON AGRICULTURAL SOILS

The arsenic pumped into an agricultural land with irrigation water may go through the following processes (Fig. 2.5):

(i) Undergo adsorption and precipitation and thus become retained onto soil;
(ii) Be transported back into the aquifer with percolating water;
(iii) Be taken up by plants, and enter into the food chain,
(iv) Volatilize into the atmosphere as a result of different bio-geochemical transformations into volatile forms;
(v) Arsenic initially retained on soils may undergo desorption/ dissolution and partition back into aqueous phase (e.g., flood water/ rainwater) and subsequently transported away from the site with runoff or percolating water.

In an agricultural land, arsenic may undergo photo-oxidation in presence of sunlight. Limited data suggests the presence of both As (III) and As (V) as well as MMA and DMA in agricultural soil. Adsorption of arsenic depends to a large extent on chemical forms/transformations of arsenic.

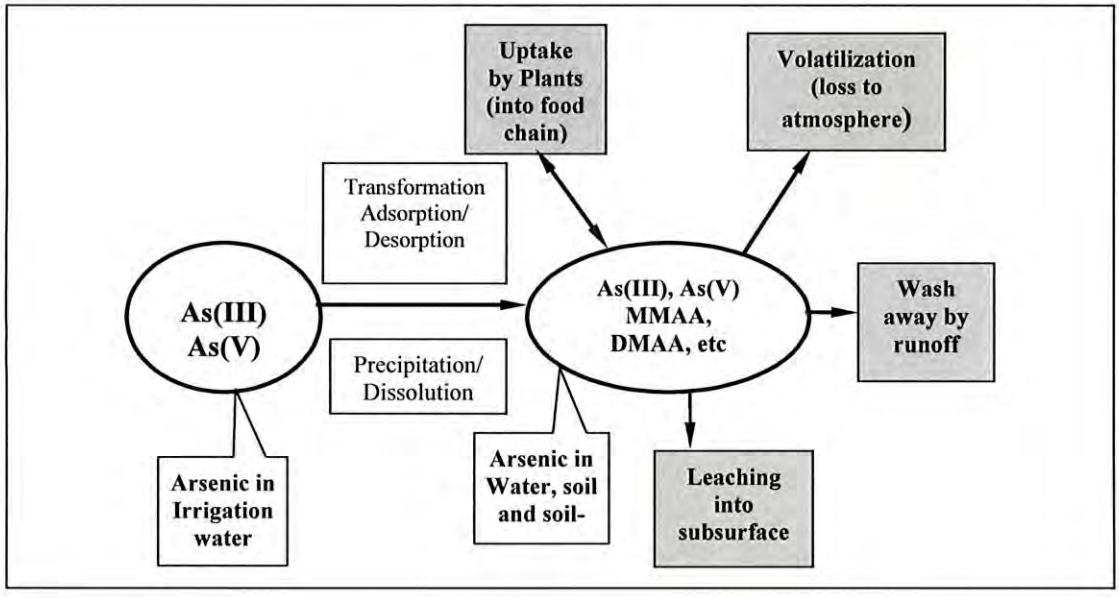

Figure 2.5: Fate of arsenic in soil-water-plant environment

Adsorption of arsenic onto soil are key to the understanding its fate in the environment. Among the different arsenic species, arsenate is most strongly adsorbed and retained onto soil. Available information on adsorption of arsenic on soil and metal oxy-hydroxides are mostly concentrated on adsorption of arsenate [As (V)] and the effect of phosphate on arsenate adsorption. Relatively limited data is available on adsorption characteristics of arsenite, the principal chemical form of arsenic in groundwater.

Processes (e.g., adsorption-desorption, reductive dissolution of iron oxyhydroxides, microbial transformation of arsenic) that may govern fate of arsenic in agricultural soil are not clearly understood. Although considerable work has been done on microbial methylation (and volatilization) processes of arsenic, primarily as it applies to bioremediation of arsenic-contaminated soils, the importance of such processes in determining the fate of arsenic in agricultural fields is not clearly understood.

2.5 ADSORPTION-DESORPTION OF ARSENIC ON AGRICULTURAL SOIL

The solubility of arsenic in water is usually controlled by redox condition, pH and adsorption reactions. Adsorption is the principal mechanism by which arsenic in irrigation water accumulates in the topsoil; whereas desorption and reductive dissolution of iron oxyhydroxides are the mechanisms through which arsenic concentration in the topsoil may decrease during inundation by floodwater. However, limited information is available the literature on adsorption characteristics of arsenite, As(III) (the principal chemical form of arsenic in groundwater) on agricultural soil. Also, soil and water quality parameters affecting adsorption-desorption characteristics are also not clearly understood. Phosphate, which is naturally present in the groundwater in many areas of the country and which may also come from addition of phosphate fertilizer, may compete with arsenic for adsorption on soil. Thus, it is important to assess the effect of phosphate on arsenic adsorption on paddy field soil.

Most of the available information in the literature are on adsorption of arsenate [As(V)] and effect of phosphate on arsenate adsorption. The major oxidation states of As in the soil environment are As(III) or As(V). As(III) can be oxidized in soils by manganese oxides to form As(V) which is the dominant species under non-reducing conditions in

soils. The primary sorbent phases for arsenate are hydr(oxides) of Fe and Al (Livesey and Huang, 1981; Pierce and Moore, 1982).

2.5.1 Previous Studies on Arsenic adsorption

Available information suggest that arsenate sorption on soils increases with pH until maximum sorption is reached and then sorption decreases with further pH increase (Goldberg and Glaubig, 1988; Xu et al., 1988). At lower pH values, metal ions solubilize from the sediments with concurrent release of arsenic species. At high pH levels, the increased hydroxide concentrations cause displacement of arsenic species from their binding sites (Mok and Wai, 1994). For example, arsenate sorption on montmorillonite and kaolinite increased at low pH, displayed a peak near pH 5, and decreased at higher pH values (Goldberg and Glaubig, 1988). Researchers have shown that arsenate is specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism (Fendorf et al., 1997; Grossl et al., 1997; Hsia et al., 1994; Sun and Doner, 1996).

Since PO_4^{3-}, like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism, it is likely to compete with arsenate for goethite surface sites (Parfitt, 1978; Persson et al., 1996; Tejedor-Tejedor and Anderson, 1990). Lumsdon et al. (1984) determined that arsenate might be sorbed more strongly because, unlike PO_4^{3-}, the arsenate ion is larger in size and interacts more strongly with some of the OH^- groups that remain on the surface. Additionally, Barrow (1992) concluded that PO_4^{3-} becomes more competitive over time since it is capable of slow sorption.

Many researches have shown that phosphate reduces arsenate adsorption (Barrow, 1974; Hingston et al., 1971; Livesey and Huang, 1981; Melamed et al., 1995), but the extent of the suppression varied between soils. Woolson et al. (1973) found that when the P and As concentrations were similar, P was sorbed in preference to As. Phosphate is stable over a much wider range of Eh and pH conditions than arsenate. The consensus of most investigators is that arsenate and phosphate are sorbed in soils by the same mechanism (Roy et al., 1986). Similarly charged As and P species compete for sorption sites on the soil components. Phosphate anions are smaller than arsenate anions and have a higher

charge and therefore, phosphate binds more strongly than arsenate. However, if the arsenic: phosphorus concentration ratio was increased then P could be desorbed and the solution concentration of P increased.

Darland and Inskeep (1997) found that PO_4^{3-} effectively competed with arsenate for adsorption sites on sand in batch isotherms as well as in saturated transport studies. The phosphate competition was not, however, sufficient to desorb all of the applied arsenate either in simultaneously applied pulses, or in a column where arsenate was applied before a concentrated pulse of phosphate. Pierce and Moore (1982) found that once arsenate was sorbed to a natural surface in an aqueous system, the sorbed arsenate was not affected by the post addition of PO_4^{3-} and SO_4^{2-}; however, sorbed arsenate was affected, at low concentrations, by the prior addition of PO_4^{3-} and SO_4^{2-} to the system. Elkhatib et al. (1984) found that arsenite adsorption was not reversible, with only small amounts of sorbed arsenite released during subsequent desorption procedures. No significant correlation was found between arsenic adsorption and soil organic carbon or cation exchange capacity (CEC) (Elkhatib et al., 1984).

There have been many studies of the effect of phosphatic fertiliser additions to soils contaminated with As with respect to the possible mobilisation of As by competitive adsorption (e.g., Peryea, 1991; Peryea and Kammereck; 1997). However, in areas of the world where soils are irrigated with water contaminated with As, for example West Bengal, Bangladesh, Chile, Taiwan (Islam et al., 2000) there are potential implications for the phosphate status of soils due to mobilization of P and subsequent losses by leaching. It is rare that arsenic accumulation on plants reach levels that are harmful to animals and man because, invariably, growth is reduced arsenate-induced phosphate release from soils 43 before the As content reaches toxic levels (Peterson et al., 1981). However, reduced phosphate availability or arsenic toxicity could affect crop yields.

The adsorption and desorption capacity of soil also depends on the soil characteristics (grain size characteristics, water content). Two grades of particle size are recognized, the silt grade, in which the particle range in size from 1/16-1/256 mm, and clay grade, with particles of less than 1/256 mm. Arsenic is strongly adsorbed by clay and shale. Sorption of arsenate is increased with increasing clay particles. Arsenite adsorption by clay

minerals increases with pH up to maximum of around pH 7. The pH of clay and shale is believed to be the same as that of the waters of the depositional environment. The fresh water shales are said to have a mean pH of about 7.8.

The amount of As sorbed from solution increases as the free iron oxide, magnesium oxide, aluminum oxide or clay content of the soil increases (Livesey and Huang, 1981). Adsorption of As on soil colloids depends on the adsorption capacity and behaviors of these colloids (clay, oxides/hydroxides of Al, Fe, Mn, calcium carbonates or organic matter). In general, Fe oxides/hydroxides are the most commonly involved in adsorption of As in both acidic and alkaline soils (Sadiq, 1997). Manning and Goldberg (1997) studied the adsorption of As in three arid-zone soils. They found that the soil with the highest citrate–dithionite extractable iron and percentage of clay had the highest affinity for arsenite and arsenate and displayed adsorption behavior similar to that of pure ferric oxide. Adsorption isotherms indicated that arsenate species adsorbed more strongly than arsenite.

2.5.2 Previous Studies on Arsenic Desorption

There appears a lack of information on desorption kinetics of arsenic from agricultural soil. Soil and water quality parameters affecting desorption characteristics are also not clearly understood.

Precipitation is another mechanism of As removal from soil. Thermodynamic calculations showed that in acidic oxic and suboxic soils, iron arsenate may control arsenic solubility, whereas in anoxic soils, sulfides of arsenite may control the concentrations of the dissolved arsenic in soil solutions. In alkaline, acidic, oxic and suboxic soils, precipitation of both iron arsenate and calcium arsenate may limit arsenic concentrations in soil solutions (Sadiq et al., 1983; Sadiq, 1997).

Arsenate is not easily desorbed or removed. Johnston and Barnard (1979) tested many soil extractants (such as 0.5 M NH4F, 0.5 M $NaHCO_3$, 0.5 M HCl, 0.5 M KH_2PO4, and 0.25 M H_2SO_4), however, none of the extractants removed more than 80% of the As after 18 h of shaking. Woolson et al. (1973) showed that arsenate could be leached from soil by

PO_4^{3-}, and Melamed et al. (1995) and Davenport and Peryea (1991) showed that arsenate mobility was vastly enhanced by treatments with increasing amounts of PO_4^{3-}.

Sparks (1995) monitored surface runoff of arsenic from fine montmorillonitic clay after application of arsenic acid for desiccation of cotton. They calculated that approximately 7% of the amount applied As were transported from the watershed by runoff and erosion, 38% in solution and 62% attached to sediment. Tammes and de Lint (1969) calculated an average half-life of 6.5 ± 0.4 years for arsenic persistence on two Netherlands soils after application of arsenite.

There exists hysteretic behavior resulting from discrepancy between adsorption and desorption isotherms in view of the kinetic retention behavior of As(V) in soils (Selim and Amacher, 1997). Several studies indicated that observed hysteresis in batch experiments may be due to kinetic retention behavior and slow release and/or irreversible adsorption conditions. Adsorption-desorption isotherms indicate that the amount of irreversible or nondesorbable phases increased with time of reaction. As(V) may be retained by heterogeneous type sites having a wide range of binding energies. At low concentrations, binding may be irreversible. In groundwater, arsenate and arsenite are the two common forms of arsenic. Arsenate is present under oxidizing conditions whereas arsenite is present under more reducing conditions. In the natural pH range of groundwater, arsenate exists with a negative charge whereas arsenite is neutral. Therefore, the desorption reactions between a variety of aquifer contents, such as iron oxides, are stronger for arsenate than arsenite. However, as the pH of the water increases (i.e. water becomes more alkaline), desorption of arsenate from materials like iron oxides increase.

2.5.3 Effect of Sorbent Phases

The distribution of As is virtually ubiquitous in the environment. The major oxidation states of As in the soil environment are As(III) (arsenite) or As(V) (arsenate). As (III) can be oxidized in soils by manganese oxides to form As(V) which is the dominant species under non reducing conditions in soils. The primary sorbent phases for arsenate are hydr(oxides) of Fe and Al (Fordham and Norrish, 1974, 1983; Huang, 1975; Livesey and

Huang, 1981; Pierce and Moore, 1982). Arsenate can also sorbs to micron-size particles of rutile and anatase, but it does not sorb significantly to pure clay minerals or soil organic matter (Fordham and Norrish, 1979, 1983; Jacobs et al., 1970).

Goethite the most common iron oxide in soils, has double bands of $FeO_3(OH)_3$ octahedra which share edges and corners to form 2 by 1 octahedra tunnels (only large enough to accommodate the passage of protons) partially bonded by H bonds (Cornell and Schwertmann, 1996; Schwertmann and Cornell, 1991; Sparks, 1995). Goethite exhibits needle-shaped crystals with grooves and edges (Sparks, 1995). Researchers have shown that arsenate is specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism (Fuller et al. 1993; Fendorf et al., 1997; Grossl et al., 1997; Hsia et al., 1994; Lumsdon et al., 1984; Parfitt, 1978; Sun and Doner, 1996; Waychunas et al., 1993). Sun and Doner (1996), using Transmission-Fourier Transform Infrared (T-FTIR) and Attenuated Total Reflectance-FTIR (ATR-FTIR) spectroscopy, found that arsenate replaced two singly coordinated surface OH groups to form binuclear bridging complexes. Lumsdon et al. (1984), using infrared spectroscopy, discovered that the $HAsO^{2-}_4$ ion participated in ligand exchange reactions displacing singly coordinated surface hydroxl groups to adsorb as a binuclear species. EXAFS studies by Fendorf et al. (1997), Waychunas et al. (1993), and Manceau (1995) found that bidentate binuclear complexation was the major bonding mechanism for arsenate adsorption on goethite.

2.5.4 Effect of Equilibration Time

Adsorption of arsenate has been shown to be rapid initially and decrease with increasing equilibration time (Ferguson and Anderson, 1974; Fuller et al., 1993; Livesey and Huang, 1981; McGeehan et al., 1992; Pierce and Moore, 1982; Raven et al., 1998). In fact, Onken and Adriano (1997) found that As became more recalcitrant in soils over time; however, most kinetic studies have been conducted over very short time periods of minutes and hours. Fuller et al. (1993) found that slow adsorption of arsenate on ferrihydrite continued for a minimum of 192 h, and investigations with Co, Cd, Pb, N, and Zn have also shown continued slow sorption (Ainsworth et al., 1994; Backes et al., 1995; Bruemmer et al.,

1988). Longer term studies are more applicable to contaminated soils where the metal or metalloid may have reacted with the soil for months and years (Sparks, 1995). Hypotheses for the slow sorption mechanisms include diffusion, different sites of reactivity, or surface precipitation.

2.5.5 Effect of Extractants

Arsenate is not easily desorbable or removed. Johnston and Barnard (1979) tested many soil extractants (such as 0.5 *M* NH_4F, 0.5 *M* $NaHCO_3$, 0.5 *M* HCl, 0.5 *M* KH_2PO_4, and 0.25 *M* H_2SO_4), however, none of the extractants removed more than 80 percent of the As after 18 h of shaking, which was observed by other researchers (i.e., Waychunas et al., 1993; Woolson et al., 1973). Woolson et al. (1973) showed that arsenate could be leached from soil by PO^{3-}_4, and Melamed et al. (1995) and Davenport and Peryea (1991) showed that arsenate mobility was vastly enhanced by treatments with increasing amounts of PO_4^{3-} Phosphate-released As was not significantly resorbed in the presence of added PO_4^{3-} (Amacher and Amacher, 1994; Peryea, 1991). Misra and Tiwari (1963) showed that several mineral acids (0.05 *M* H_2SO_4 and 0.1 *M* HCl) and PO^{3-}_4 solution [0.1 M $(NH_4)_2HPO_4$ and 2.5 x 10^{-3} *M* Na-pyrophosphate] extract about the same amount of arsenate. Darland and Inskeep (1997) conducted transport studies using free iron oxides in a sand column and found that PO^{3-}_4 effectively competes with arsenate; however, the PO_4^{3-} was not able to desorb all of the applied arsenate, regardless of whether the arsenate was applied concurrently or prior to PO^{3-}_4 addition (as in a desorption study). Even when the applied PO^{3-}_4 surpassed the column adsorption capacity by twofold, some arsenate remained adsorbed to the free iron oxides in the sand. Similarly, when the authors applied a high concentration of PO^{3-}_4 perpetually to a column that had heretofore been spiked with arsenate, recovery of arsenate in the effluent did not exceed 60 percent, even though the total PO^{3-}_4 loading was greater than the calculated column capacity by more than two orders of magnitude (Darland and Inskeep, 1997). In contrast, Pierce and Moore (1982) found that once arsenate was sorbed to a natural surface in an aqueous system, the sorbed arsenate was not affected by the post addition of PO^{3-}_4 and SO^{2-}_4; however, sorbed arsenate was affected, at low concentrations, by the prior addition of PO^{3-}_4 and SO^{2-}_4 to the system.

2.5.6 Movement of Arsenic from Soil

Arsenic from soil may be transported by wind or water erosion. However, because many arsenic compounds tend to adsorb to soils, leaching usually results in transportation over only short distances in soil (Moore et al., 1988; Welch et al., 1988). However, rainwater or snowmelt may leach soluble forms into surface water or groundwater, and soil microorganisms may reduce a small amount to volatile forms (arsines) (Woolson, 1977a; Cheng and Focht, 1979; Turpeinen et al., 1999).

2.5.7 Effect of Soil Characteristics

The amount of arsenic sorbed from solution increases as the free iron oxide, magnesium oxide, aluminum oxide or clay content of the soil increases; removal of amorphous iron or aluminum components by treatment with oxalate eliminates or appreciably reduces the arsenic sorption capacity of the soil (Jacobs et al., 1970a; Galba, 1972; Wauchope, 1975; Livesey and Huang, 1981). Amacher et al. (1994) examined the adsorption characteristics of a forest soil profile. The greatest sorption capacity for arsenic occurred at a depth of 30 cm in the profile, in the B2 horizon where there was a predominance of clay and oxyhydroxides of iron and aluminum. Adsorption of arsenic on soil colloids depends on the adsorption capacity and behavior of these colloids (clay, oxides or hydroxides of aluminum, iron and manganese, calcium carbonates or organic matter). In general, iron oxides/hydroxides are the most commonly involved in adsorption of arsenic in both acidic and alkaline soils (Sadiq, 1997). Manning and Goldberg (1997) studied the adsorption of arsenic in three arid-zone soils. They found that the soil with the highest citrate–dithionite extractable iron and percentage of clay had the highest affinity for arsenite and arsenate and displayed adsorption behavior similar to that of pure ferric oxide. Adsorption isotherms indicated that arsenate species adsorbed more strongly than arsenite.

The surfaces of aluminum oxides/hydroxides and clay may play a role in arsenic adsorption, but only in acidic soils. Carbonate minerals are expected to adsorb in calcareous soils (Sadiq, 1997), and Goldberg and Glaubig (1988) concluded that carbonates play a major role in arsenate adsorption at pH > 9. Phosphate substantially suppresses arsenate adsorption by soil, with the extent of the suppression varying from

soil to soil (Livesey and Huang, 1981). Darland and Inskeep (1997) found that phosphate effectively competed with arsenate for adsorption sites on sand in batch isotherms as well as in saturated transport studies. The phosphate competition was not, however, sufficient to desorb all of the applied arsenate either in simultaneously applied pulses, or in a column where arsenate was applied before a concentrated pulse of phosphate. Approximately 40 percent of the applied arsenate remained sorbed to the sand even after the total phosphate loading exceeded the column capacity by more than two orders of magnitude. The authors concluded that rates of arsenate desorption play an important role in transport of arsenate through porous media. Elkhatib et al. (1984) found that arsenite adsorption was not reversible, with only small amounts of sorbed arsenite released during subsequent desorption procedures. No significant correlation was found between arsenic adsorption and soil organic carbon or cation exchange capacity (CEC) (Elkhatib et al., 1984).

Leaching does not appear to be a significant route of arsenic loss from soil. Arsenic as MMA was applied to three soil types over a 6-year period. Percentage recovery of applied arsenic averaged 67 percent, 57 percent and 39 percent in a fine sandy loam, a silt loam and a sandy loam soil respectively. All of the arsenic recovered in the soils was detected in the ploughed layer (< 30 cm) with no evidence of leaching into deeper zones Elfving et al. (1994). They monitored the movement of arsenic following the application of lead arsenate to fruit orchards for insect control. The rate of decrease in concentration of arsenic with depth was significantly greater in a sandy soil than in clay, suggesting that downward movement occurred less readily in the former. The use of phosphate fertilizers significantly increases the amount of arsenic leached from soil contaminated with lead arsenate pesticide residues (Davenport & Peryea, 1991).

Sparks, D.L. 1995 monitored surface runoff of arsenic from a fine montmorillonitic clay after application of arsenic acid for desiccation of cotton (*Gossypium hirsutum*). They calculated that approximately 7 percent of the amount applied would be transported from the watershed by runoff and erosion, 38 percent in solution and 62 percent attached to sediment.

2.5.8 Effect of Precipitation

Precipitation is another mechanism of arsenic removal from soil. Thermodynamic calculations showed that in acidic oxic and suboxic soils, iron arsenate may control arsenic solubility, whereas in anoxic soils, sulfides of arsenite may control the concentrations of the dissolved arsenic in soil solutions. In alkaline, acidic, oxic and suboxic soils, precipitation of both iron arsenate and calcium arsenate may limit arsenic concentrations in soil solutions (Sadiq et al., 1983; Sadiq, 1997). Moore et al, (1992) studied the sorption of arsenic in two free-draining sandy soils in New Zealand. They concluded that arsenate sorption occurred primarily through adsorption rather than a precipitation mechanism.

Masscheleyn et al. (1991a) found that at soil Eh levels of 200 and 500 mV arsenic solubility was low and the major part (65–98%) of the arsenic in solution was arsenate. Under moderately reduced soil conditions (at 0 and –100 mV) arsenic solubility was controlled by the dissolution of iron oxyhydroxides. Arsenic was co-precipitated as arsenate with iron oxyhydroxides and released on solubilization. On reduction to –200 mV the soluble arsenic content increased to 13 times what it was at 500 mV.

2.5.9 Effect of Soil Organisms

Many soil organisms are capable of converting arsenate and arsenite to several reduced forms; largely methylated arsines which are volatile. Woolson (1977b) proposed that about 12 percent of the arsenic applied and present in a soil is lost through volatilization of alkylarsines each year. As per this report total losses of 14–15 percent per year from soil treated with sodium arsenite, DMA or MMA. Most of the loss was through volatilisation, although some apparent loss was caused by movement to or mixing with subsoil. Sandberg & Allen (1975) estimated an arsenic loss of 17–35 percent per year through volatilization. They concluded that arsenic volatilization showed a direct relationship with nutrient levels and microbial growth in soil.

2.6 SUMMARY

Several research works have been carried out in the past on adsorption desorption characteristics of arsenic on different types of adsorbents. But very limited data are available on adsorption-desorption characteristics of arsenic on natural soils. Most of the studies conducted so far are focused on adsorption of arsenate. Very limited data are available in the literature on the adsorption desorption characteristics of arsenite, the dominant form of arsenic in groundwater of Bangladesh. Therefore, it is very important of carry out research works for better understanding of adsorption desorption characteristics of arsenic (both arsenate and arsenite) on natural paddy field soils. In this context, the effect of pH and phosphate on arsenic adsorption-desorption is of particular interest in the context of Bangladesh.

As noted earlier, available information suggest that arsenic is mobilized from the arsenic-rich top soil of paddy fields during inundation by rainwater/floodwater. But the mechanism of arsenic release form soil is not clearly understood. Desorption and reductive dissolution of iron oxyhydroxides (which adsorb arsenic) are thought to play important roles in the mobilization of arsenic from paddy field soils. Controlled experiments need to be carried out to better understand the processes leading to arsenic mobilization from natural soils during inundation by floodwater/rainwater.

CHAPTER 3

ADSORPTION OF ARSENIC ON PADDY FIELD SOIL

3.1 INTRODUCTION

The arsenic contamination of groundwater in the Bengal Delta plain represents a crucial problem, particularly for Bangladesh and West Bengal, India. Even when alternative water sources become more or less available for potable purposes, agriculture remains dependent mostly on groundwater and, to date; scant attention has been devoted to the fate of arsenic reaching soils with irrigation water. Adsorption characteristics on soil colloids are one of the main mechanisms controlling the mobility of arsenic in the water-soil system. In irrigated agricultural land, water lost by evaporation will leave arsenic along with other minerals in the topsoil. A large fraction of this arsenic is not likely to be washed out by flood or rainwater in oxidized condition due to its affinity for iron, manganese, aluminum and other minerals in soil. Due to its affinity for metal oxides/hydroxides in soil, higher accumulation of arsenic in irrigated surface soils is expected and a number of studies (e.g., Huq et al., 2001; Meharg and Rahman, 2003; Ali et al., 2003b; Masud, 2003; Ahmed, 2005; Jahiruddin et al., 2005, Saha, 2006) have reported relatively higher levels of arsenic in paddy field soils irrigated with arsenic contaminated groundwater. Saha (2006) reported that arsenic concentration in paddy field soils irrigated with arsenic contaminated groundwater varies significantly with time. Saha (2006) reported that average arsenic concentrations in the top 0-150 mm soil layer of paddy fields increase significantly at the end of the irrigation season (in May-June) compared to levels at the beginning of the irrigation season. However, after the rainy season and before the beginning of the next irrigation season, the arsenic concentrations in the top soil layer decrease significantly and come down to levels comparable to those found at the beginning of the irrigation season.

The adsorption of As in soil depends mostly on the nature of soil colloids, pH, and redox conditions. More toxic arsenite is also reported to be more mobile and thus more bio-

available than arsenate. Both forms of As can be found in water-soil environments in a wide range of redox conditions and their co-presence is particularly likely in paddy fields.

In this study, adsorption characteristics of arsenic (both arsenate and arsenite, which are the principal forms of As in groundwater) on agricultural soil has been assessed in batch experiments carried out with paddy field soil from three arsenic-contaminated areas and one uncontaminated area. Effect of soil composition and phosphate content of water on arsenic adsorption has also been assessed. This Chapter presents results of these laboratory investigations and their implications on arsenic accumulation in paddy field soils.

3.2 METHODOLOGY

3.2.1 Site Selection

Soil samples were collected from irrigated fields of four arsenic contaminated areas. Among these Munshiganj is a highly arsenic contaminated area, Faridpur and Brahmanbaria are moderately contaminated areas, and Naogaon is a relatively less contaminated area. These areas have been selected for detail characterization of soil samples.

3.2.2 Collection of Soil Core Sample

Soil samples from irrigated paddy fields in Faridpur, Brahmanbaria, and Naogaon districts were collected during May-June 2003; soil samples from a paddy field in Munshiganj were collected in May 2004. Soil sample were collected by inserting into the soil, a 37.5 mm diameter PVC pipe sampler, about 15 cm in height. A 3-pound hammer was used to insert the pipe sampler to the required depth. After withdrawing the sampler along with the soil core, its both ends were sealed with tapes to reduce contact with air and transported to the environmental Engineering Lab of BUET.

3.2.3 Laboratory Analysis

3.2.3.1 Arsenic and Iron Contents of Soil

Total (aqua-regia extractable) and oxalate-extractable arsenic and iron contents of the soil samples were determined following the procedure described below. For this purpose, soils of the top 0-75mm layer of the soil cores were used.

Digestion of Soil Sample for Determination of Total Arsenic and Iron:

For determination of total (aqua-regia extractable) arsenic and iron, the selected soil sample was taken in an aluminum bowl and kept in an oven at 110^0 C for 24 hours. After drying for 24 hours, the sample was ground in a grinder. The grinded soil sample was digested with aqua-regia for extraction of metal ions. For digestion, 2.5 ml concentrated nitric acid and 7.5 ml concentrated hydrochloric acid were added to 5 gm grinded oven dried sample taken in a 500 ml volumetric flask. The sample was kept overnight in the flask and then it was heated to boiling for two hours. Afterwards distilled water was added up to the 500 ml graduation mark. The contents of the flask were stirred for 5 minutes, then cooled and finally filtered using a filter paper (0.45 micron). The filtrate was stored in a plastic bottle for analysis of arsenic using an AAS attached with a graphite furnace (Shimadzu AA6800).

Determination of Oxalate Extractable Arsenic and Iron:

Oxalate-extractable iron provides an estimate of the amount of iron present as amorphous iron oxy-hydroxides, and oxalate extractable arsenic provide an estimate of the quantity of arsenic and iron associated with the amorphous iron oxy-hydroxides. The oxalate extraction was carried out with 0.2M oxalic acid following the method described in Keon et al. (2001). For extraction, 25 ml of 0.2 M oxalic acid solution was added to 2.5 gm of soil sample (taken from the selected segments of the soil cores) in a centrifuge tube and mixed for 2 hours in an end-over-end rotator. Then the tubes were centrifuged for 20 to 25 minutes. After decanting the supernatant, additional 25 ml 0.2 M oxalic acid solution was added to the tube and the whole procedure was repeated. The collected supernatant was analyzed for arsenic and iron using an AAS (Shimadzu, AA6800).

3.2.3.2 Analysis of Water Samples

Arsenic concentration of water samples was determined using an atomic absorption spectrophotometer (Shimadzu, AA6800) attached with a graphite furnace (GF). Iron concentration of water samples was measured with flame emission atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800); pH was measured using a pH meter (Hach), and electrical conductivity (EC) with a conductivity meter. Chloride was measured using $AgNO_3$ titrimetric method. Ammonia, nitrate and phosphate concentrations were measured with a spectrophotometer (Hach, DR4000U). Ammonia was measured using the Nessler method, nitrate by the cadmium reduction method and phosphate by the molybdenum blue method.

3.2.4 Batch Adsorption Experiments

3.2.4.1 Adsorption of As and PO_4

Adsorption characteristics of arsenic and phosphate on soil samples were assessed in batch experiments carried out in 15 ml centrifuge tubes. Adsorption characteristics of soil samples collected from paddy fields of the four different sites were assessed by equilibrating known mass of soil sample with aqueous solution containing varying arsenic (250 to 17000µg/l) and phosphate (2 to 22 mg/l) concentrations.

The batch experiments consisted of the following steps: (i) take 1 gm of soil from the top 0-75mm soil layer of the soil cores collected from the field in each of two 15 ml polyethylene centrifuge tubes, (ii) add 12.5 ml aqueous solution containing different concentrations of arsenite [As(III)] or phosphate to each tube; the resulting soil concentration in tube was 80 g/l; the aqueous solutions were prepared by adding required quantities of arsenic [As(III)] or phosphate stock solution to groundwater samples collected from Shahid Sarwardi Uddan pump station (adjacent to the Mazar of National Poet Kazi Nazrul Islam), (iii) equilibrate the contents of the centrifuge tubes in an end-over-end rotator for 24 hours or 7 days, (iv) centrifuge the tubes for separating the liquid from soil in the tubes, (v) measure arsenic concentration in the clear supernatant liquid collected from the tubes, (vi) estimate the amount of adsorbed arsenic by using the initial

and final concentrations of arsenic in the aqueous solution in contact with the soil. This test was performed for both arsenite and arsenate form of arsenic.

3.2.4.2 Effect of Phosphate on Adsorption of Arsenic

Effect of phosphate concentration on adsorption of arsenic on paddy field soils from the four field sites was assessed in similar batch experiments (described above) by varying phosphate and arsenic concentration of the aqueous solution in contact with the soil (80 g/l). In these experiments, arsenic concentration was varied from 150 to 2500 μg/l; and for each arsenic concentration, phosphate concentration was fixed at 2, 4, and 6 mg/l. Adsorption characteristics of Faridpur and Naogaon soils were also evaluated by varying phosphate concentrations over a wider range (2 to 42 mg/l) for a constant arsenic concentration of 1000 μg/l.

3.2.4.3 Effect of pH on Adsorption of Arsenic

Effect of pH on adsorption of arsenic on paddy field soils from Munshiganj and Naogaon was evaluated in similar batch experiments (described above) by varying pH of the aqueous solution in contact with the soil (80 g/l) using dilute hydrochloric acid (0.5M) or sodium hydroxide (0.5 M). In these batch experiments, arsenic concentration was fixed at 950μg/l.

3.2.5 Grain Size Analysis of Soil: Hydrometer Analysis

The hydrometer analysis is a widely used method of obtaining an estimate of the distribution of soil particle size from the No. 200 (0.075 mm) sieve to around 0.001 mm. The data is plotted on a semi-log plot of percent finer vs. grain diameters and combined with the data from a mechanical analysis of the material retained on the No. 200 sieve. The hydrometer analysis utilizes the relationship among the velocity of fall of spheres in a fluid, the diameter of the sphere, the specific weights of the sphere and of the fluid, and viscosity of the fluid as expressed by the Stokes' law. According to Stokes' law, larger particles will settle faster through the fluid than the smaller particles. To obtain the velocity of fall of the particles, hydrometer is used. Hydrometer analysis was carried out for the top 0-75 mm layer of soil samples collected from all four sampling sites.

Combined curves for soil of different sites were plotted and from these curves, sand (2.00-0.06 mm), silt (0.06-0.002 mm) and clay (percent finer than 0.002 mm) contents of the soil samples were determined.

3.3 RESULTS AND DISCUSSION

3.3.1 General Characteristics of Water and Soil Samples

Characteristics of Paddy Field Soil Samples

In this study, arsenic adsorption of arsenic on paddy field soil from four different sites was assessed. Table 3.1 shows composition of soil from the four sampling sitess, estimated from hydrometer analysis. It also shows the total (aqua-regia extractable) and oxalate-extractable arsenic and iron contents of the soil samples. The arsenic and iron concentrations of irrigation water used in the respective paddy fields are also shown in Table 3.1. Table 3.1 shows that silt comprises the major fraction of soil samples from all four areas. Silt content varies from 70.5% for Naogaon soil to 84.6% for the Munshiganj soil. Sand content was less than 10% for all samples, except the sample from Naogaon, which contained 19.1% sand. Clay content was highest for the Faridpur soil (23.2%), followed by Brahmanbaria (15.9%), Naogaon (10.5%), and Munshiganj (8.0%). But there was no significant correlation with arsenic content on soil sample. Figure 3.1(a) through 3.1(d) show grain size analysis curves for soil samples (top 0-75 mm) collected from Munshiganj, Brahmanbaria, Faridpur, and Naogaon, respectively.

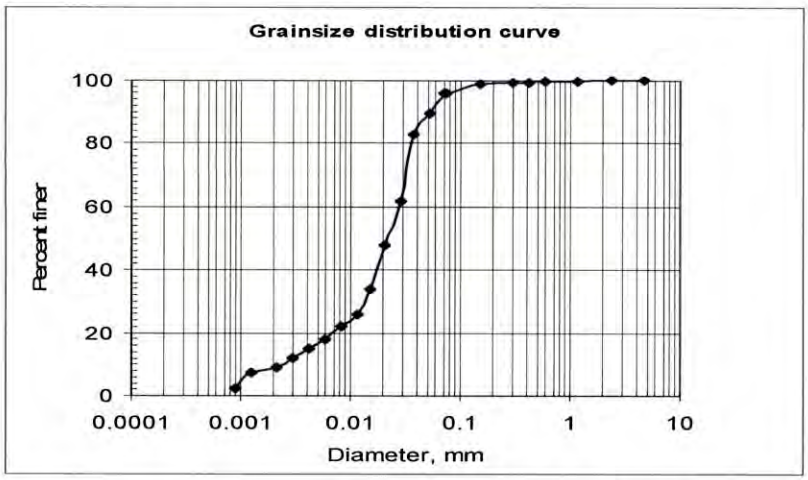

Fig. 3.1 a: Grain size analysis curve of soil sample from Munshiganj paddy field

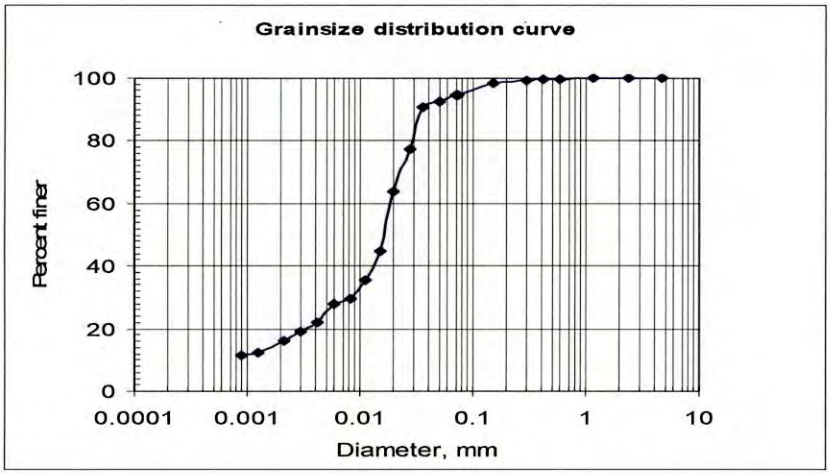

Fig. 3.1 b: Grain size analysis curve of soil sample from Brahmanbaria paddy field

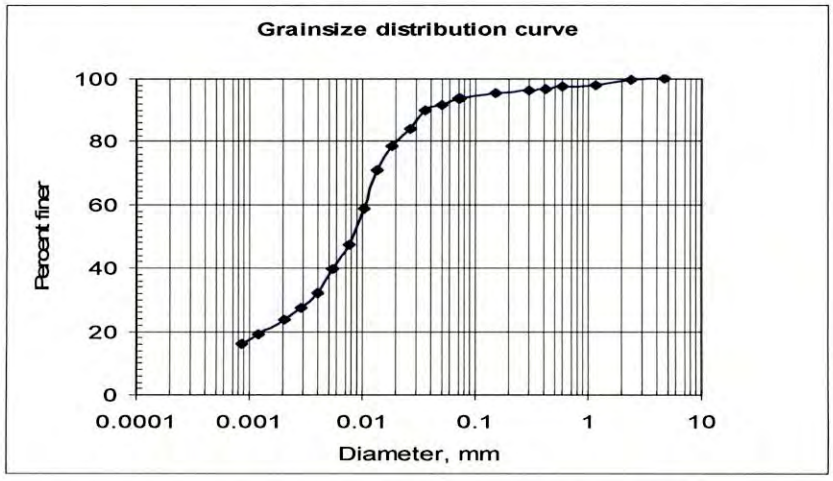

Fig. 3.1 c: Grain size analysis curve of soil sample from Faridpur paddy field

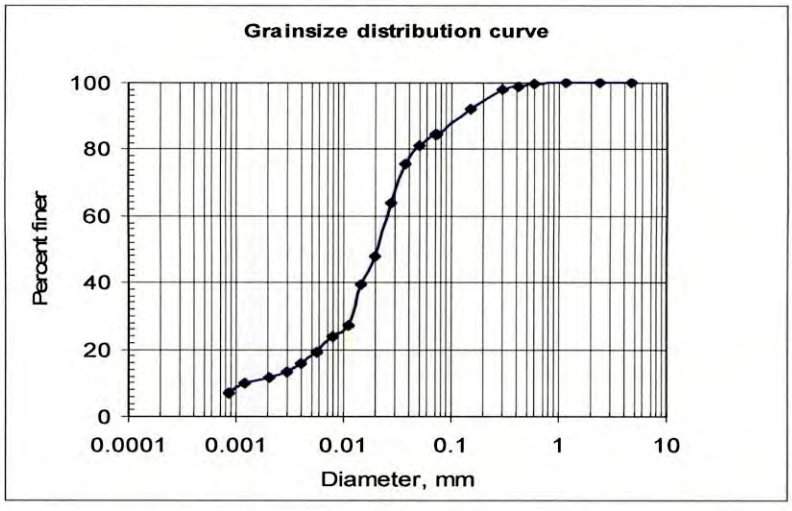

Fig. 3.1 d: Grain size analysis curve of soil sample from Naogaon paddy field

The total arsenic contents of soils samples collected from Munshiganj, Faridpur, Brahmanbaria and Naogaon are 26.98, 9.46, 5.28, and 1.68 mg/kg, respectively; the oxalate extractable arsenic contents are 18.58, 6.53, 3.85, and 0.78 mg/kg, respectively (Table 3.1). Arsenic concentrations of irrigation water of these four sites are 300, 96, 140 and < 1 μg/l, respectively. Thus, Arsenic contents of top soils appear to be strongly correlated to the arsenic contents of the irrigation water. High arsenic (366 μg/l) and iron (7.64 mg/l) contents of irrigation water appear to have contributed to the high As and Fe contents of Munshiganj top soil. In Naogaon, where irrigation water had low arsenic (<1 μg/l) and iron (0.46 mg/l) concentrations, the top soil was also found to have relatively low arsenic and iron. Similarly, iron content of soil samples also appear to be strongly correlated with iron content of irrigation water.

Table 3.1: Some selected soil parameters of different paddy field soil samples

Parameters	Munshiganj Soil	Faridpur Soil	Brahmanbaria Soil	Naogaon Soil
Soil composition	Sand = 7.4% Silt = 84.6% Clay = 8.0%	Sand = 7.4% Silt = 69.5% Clay = 23.2%	Sand = 6.6% Silt = 77.6% Clay = 15.9%	Sand = 19.1% Silt = 70.5% Clay = 10.5%
Total As	26.98 mg/kg	9.46 mg/kg	5.28 mg/kg	1.68 mg/kg
Oxalate-extractable As	18.58 mg/kg	6.53 mg/kg	3.85 mg/kg	0.78 mg/kg
Total Fe	42.35 g/kg	22.24 g/kg	24.25 g/kg	15.52g/kg
Oxalate- extractable Fe	22.05 g/kg	14.35 g/kg	16.73 g/kg	9.86 g/kg
As in irrigation water	366 μg/l	96 μg/l	149 μg/l	<1 μg/l
Fe in irrigation water	7.64 mg/l	3.62	3.38	0.46

Characteristics of Water Used in Batch Adsorption Experiments

Concentrations of selected chemical constituents of water used in batch adsorption-desorption experiments in this study are shown in Table 3.2. Arsenic concentration of this groundwater from a DTW pump station was below the Method Detection Limit (MDL) of 1 μg/l. The water also contained low concentrations of iron, ammonia, chloride and nitrate. Phosphate concentration (0.70 mg/l) was moderate.

Table 3.2: Concentration of selected chemical constituents of groundwater sample used in batch adsorption-desorption experiments

pH	Conductivity (μs/cm)	As (μg/l)	Fe (mg/l)	NH_3-N (mg/l)	PO_4 (mg/l)	Cl- (mg/l)	NO_3-N (mg/l)
6.88	352	<1	0.05	0.06	0.70	5.6	0.20

3.3.2 Effect of pH on Arsenic Adsorption

Effect of pH on adsorption of arsenate and arsenite on soil was assessed using paddy field topsoil (top 0-150 mm) from Munshiganj and Noagaon. Figure 3.2(a) and 3.2(b) show adsorption characteristics of arsenic for the Munshiganj and Naogaon paddy field soil, respectively. It may be noted that the initial As concentration in the Munshiganj paddy field soil was 26.98 mg/kg and that of the Naogaon soil was 1.68 mg/kg.

Figure 3.2 shows a plot of final pH of water in contact with the soil versus the quantity of As partitioned to soil (expressed as mg/kg, dry weight basis). Effect of pH on adsorption of both arsenate and arsenite appear to follow the same trend. Adsorption of arsenate was only slightly higher than that of arsenite. Usually arsenate adsorbs more strongly onto soil compared to arsenite. However, no such difference was apparent in Fig. 3.2 between adsorption of arsenite and arsenate. This is probably due to very high concentrations of adsorption sites (i.e., soil) compared to the concentration of arsenic in water. Adsorption of both arsenite and arsenate was significantly higher on the Munshiganj soil compared to that in the Noagaon soil. This is most likely related to the much higher oxalate extractable iron concentration (22.05 mg/kg) in the Munshiganj soil (which is the principal adsorbent of arsenic) compared to that in the Naogaon (9.86 mg/kg). Effect of pH on adsorption of arsenic was also more pronounced for the Munshiganj soil. Adsorption as a function of pH followed a concave downward profile with the maximum adsorption occurring at pH between 4 and 6. Both arsenate and arsenite sorption on soils increased with pH until maximum sorption is reached and then sorption decreased with further pH of increase. The variation of As adsorption for arsenite and arsenate is high at low pH range. For example, for Munshiganj soil at pH 3 arsenate and arsenite adsorption densities are 34 mg/kg and 28 mg/kg, respectively; at pH 7, the adsorption densities are is 31 mg/kg and 30 mg/kg; and at pH 11, the adsorption densities is 7.5mg/kg and 12 mg/kg, respectively. For Naogaon paddy field soil, there is no significant variation of arsenic adsorption in the neutral pH range; however, at higher pH (pH > 8), adsorption decreased.

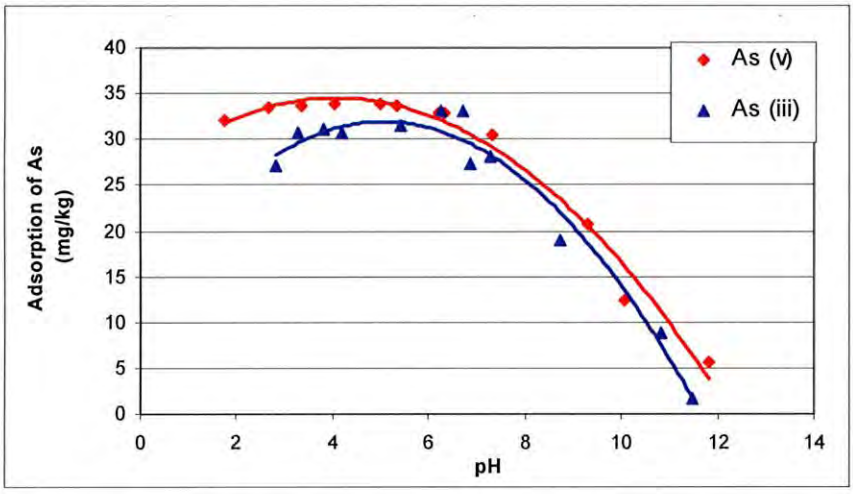

Fig 3.2(a): Effect of pH on adsorption of As on Munshiganj (26.98 mg/kg) paddy field soil (Initial As conc. in water was fixed at 950µg/l)

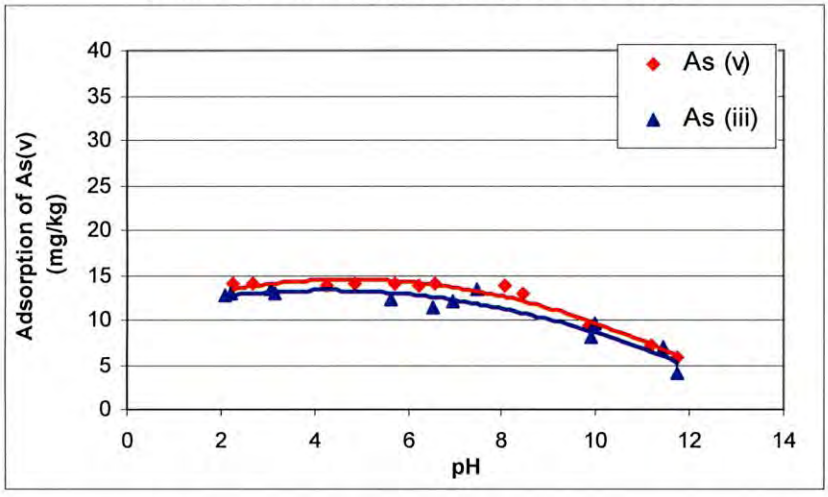

Fig 3.2(b): Effect of pH on adsorption of As on Naogaon (1.68 mg/kg) paddy field soil (Initial As conc. in water was fixed at 950µg/l)

The variation of arsenic adsorption with pH found in this study, especially for the Munshiganj soil, is similar to those reported by Goldberg and Glaubig (1988) and Xu et al. (1988). They found that arsenate sorption on montmorillonite and kaolinite increased at low pH, displayed a peak near pH 5, and decreased at higher pH values (Goldberg and Glaubig, 1988). Though Munshiganj soil had higher initial soil arsenic concentration than the Naogaon soil, the adsorption was higher for the Munshiganj soil. As explained earlier, this is most likely due to the higher sorption site on the Munshiganj site, as evidenced by the higher oxalate extractable iron content of this soil.

3.3.3 Adsorption of As on Paddy Field Soil

In this study, adsorption characteristics of As(III) and As(V) on paddy field soils collected from four different sites have been assessed. Figure 3.3 shows adsorption isotherms of arsenite on paddy field soils from four different field sites and Fig. 3.4 shows adsorption isotherm of arsenate on paddy field sites from Munshiganj and Naogaon. These figures show quantity of arsenic partitioned to soil (expressed as mg/kg of soil) as a function of initial concentration of arsenic (μg/l) in water. Figures 3.3 and 3.4 show that in all cases arsenic partitioning to soil increases with increasing concentration of arsenic in water. These figures show that arsenate adsorbs much more strongly onto soil than arsenite. For same initial concentration of arsenic, arsenate adsorption is almost 3 times greater than arsenite adsorption.

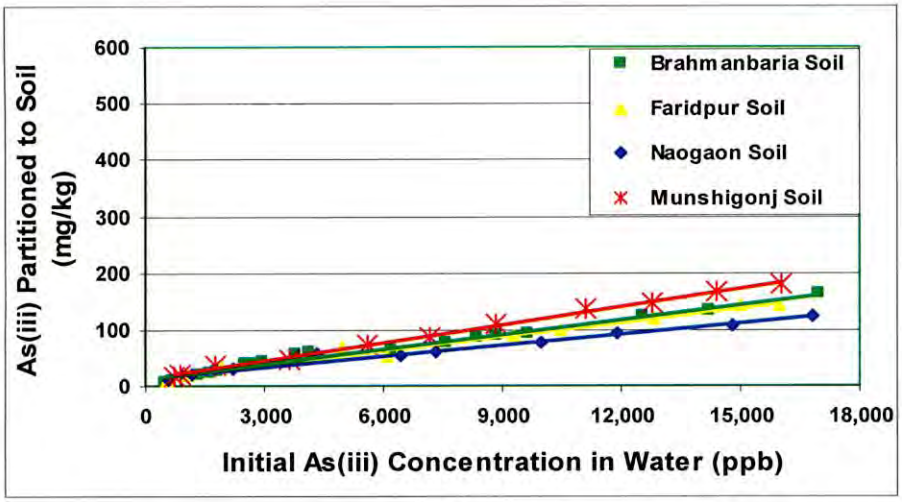

Fig. 3.3: Arsenic partitioning to paddy field soil in batch adsorption experiments as a function of initial As concentration in water

Figure 3.3 shows that for any initial concentration (up to 17000μg/l), partitioning of arsenite to soil is highest for Munshiganj soil and least for the Naogaon soil. Brahmanbaria and Faridpur paddy field soil lie in between. Figure 3.4 shows the same trend; arsenate adsorption on to Munshiganj paddy field soil is much more higher compared to Naogaon soil. This trend is consistent with total and oxalate-extractable iron concentrations in the paddy field soil (see Table 3.1). Soil samples with higher total and oxalate extractable iron have been found to adsorb higher amount of arsenic. Arsenic partitioning to soil at any particular initial arsenic concentration follows the same order as

the concentration of total / oxalate-extractable iron in soil – Munshiganj, followed by Brahmanbaria, Faridpur and Naogaon.

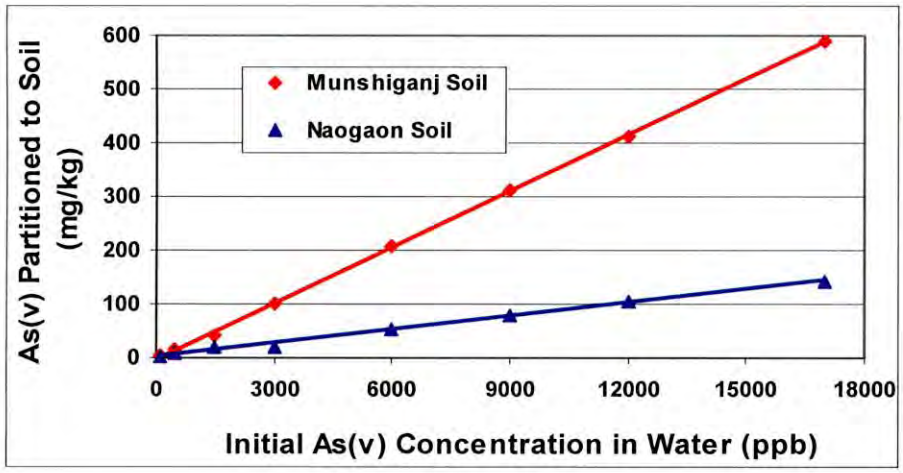

Fig. 3.4: Arsenic partitioning to paddy field soil in batch adsorption experiments as a function of initial As concentration in water

Figure 3.5 shows the correlation between calculated distribution coefficient for arsenite adsorption (i.e., slope of adsorption curves in Fig. 3.3) and total and oxalate-extractable iron concentrations of soil samples. It shows that the calculated distribution coefficients correlate very well with oxalate-extractable as well as total iron contents of soils. Initial concentration of As of soil does not appear to have any influence on limiting adsorption of arsenic onto soil. Also, other soil parameters including composition of soil do not appear to have any major influence on As partitioning to soil.

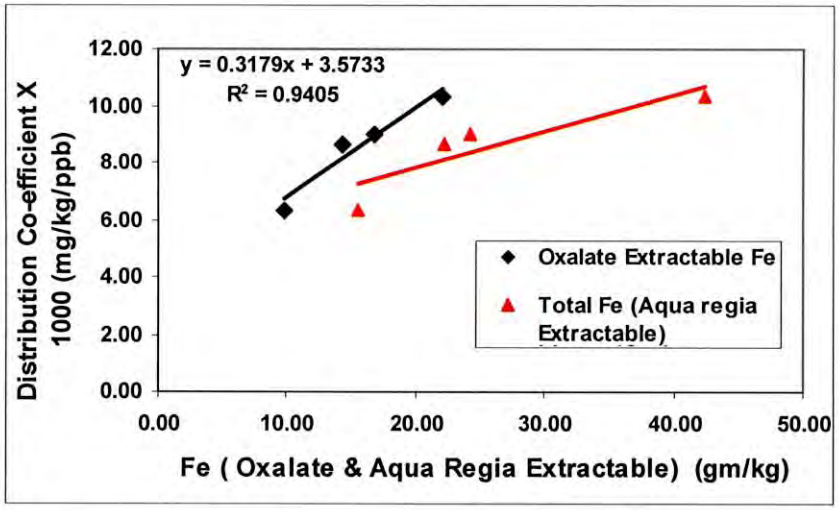

Fig. 3.5: Correlation between calculated distribution coefficient for As(III) adsorption and oxalate and aqua regia-extractable iron concentrations in paddy field soil

Iron and aluminum oxyhydroxides are the principal adsorbents in natural soil. The increasing adsorption of As to soil with increasing soil iron content suggests that iron oxyhydroxides are probably the principal adsorbent in soil. Though arsenite [As(III)] adsorbs onto iron oxy-hydroxides less strongly compared to arsenate [As(V)], relatively high adsorption of arsenite has been observed in the batch experiments conducted in this study (see Fig. 3.2). Figure 3.3 shows very high adsorption densities (~180 mg/kg for Munshiganj soil) of arsenic on paddy field soils. In fact, both field data (Dittmar et al., 2005) and estimated adsorption sites on amorphous iron oxyhydroxides are consistent with the observed adsorption densities of arsenic on paddy field soils. Dittmar et al. (2005) found arsenic concentration in the top soil of a paddy field in Munshiganj to be approaching 100 mg/kg.

If oxalate extractable iron (i.e., amorphous iron oxyhydroxide) is considered the principal adsorbent, then concentration of this adsorbent varies from 0.1766mol Fe/kg of soil for Naogaon to 0.395mol Fe/kg of soil in Munshiganj. Considering a site density of 0.2 mol/mol Fe, a value widely used for Hydrous Ferric Oxides (HFO) (Dzombak and Morel, 1990), this corresponds to a site concentration of $1.4x10^{-2}$ mol/l for Naogaon soil and $3.16x10^{-2}$ mol/l for Munshiganj soil (for batch experiments where concentration of soil was 80 g/l). Thus, the available surface sites of iron alone are about three orders of magnitude higher than the highest concentration of As used in the batch experiments (17000 μg/l or $2.7x10^{-5}$ mol/l).

As noted earlier, iron contents of paddy field soils are strongly related to the iron contents of irrigation water used in the paddy field. Hence it appears that adsorption of arsenic onto agricultural soil depend, not only on the characteristics of soil, but also on the quality (i.e., iron content) of irrigation water.

3.3.4 Adsorption of PO_4 on Agricultural Soil

Figure 3.6 shows adsorption isotherm of phosphate on paddy field soils from Brahmanbaria, Faridpur and Naogoan districts. It shows that in all cases adsorption on soil increases with increasing concentration of phosphate in water. Among the three soils, phosphate adsorption is highest for Brahmanbaria soil and least for Naogaon soil. Similar to the case for arsenic, it could be easily seen that phosphate adsorption on soil is strongly

related to the iron content of soil. Amorphous iron oxyhydroxides appear to be principal adsorbent of phosphate in the soil matrix. Calculated adsorption sites of oxalate-extractable iron are orders of magnitude higher than the highest concentration of phosphate used in the batch experiments.

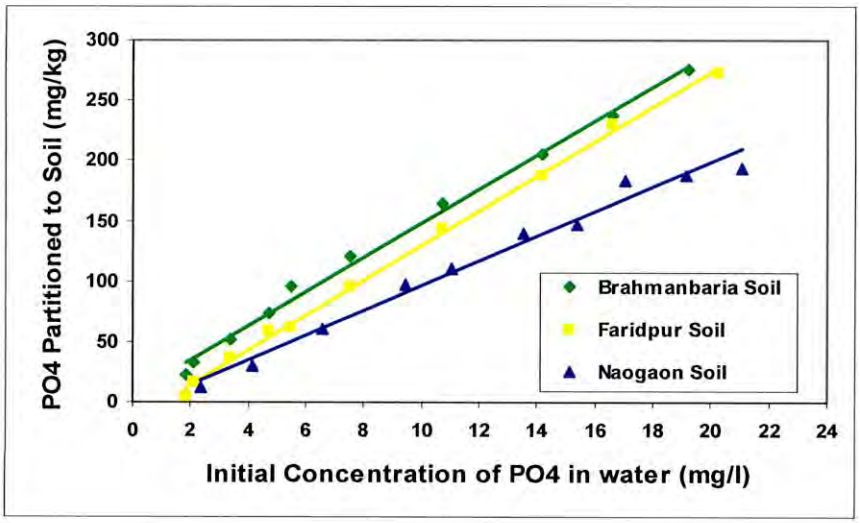

Fig. 3.6: Phosphate adsorption on paddy field soil in batch adsorption experiments as a function of initial phosphate concentration (pH of water 6.9)

3.3.5 Effect of Phosphate on Arsenic Adsorption

In this study, the effect of phosphate on adsorption of arsenic was investigated. Figures 3.7a-d show the arsenic adsorption on paddy field soil in the presence of phosphate for Munshiganj, Faridpur, Brahmanbaria, and Naogaon soils, respectively. In these experiments, initial As concentration was varied from 150 to 2500 μg/l and phosphate was varied from 0.7 mg/l (concentration present in groundwater used in this study) to 6 mg/l. These figures show that arsenic (arsenite) adsorption onto agricultural soil decreased in the presence of phosphate, but the effect of phosphate was significant only at high concentrations of both arsenic and phosphate. The reduced adsorption of arsenic in the presence of phosphate is due to occupation of adsorption sites by phosphate, which is known to have stronger affinity for iron oxyhydroxides compared to arsenite. Since the available adsorption surface sites are orders of magnitude higher than the combined concentrations of arsenic and phosphate for all batch experiments, effect of phosphate on arsenic adsorption was relatively less pronounced. Among the four different paddy field soils, more significant effect of phosphate on As adsorption was observed for Naogaon

and Faridpur soils, which have relatively less oxalate-extractable iron contents (and hence have relatively less iron sites for adsorption).

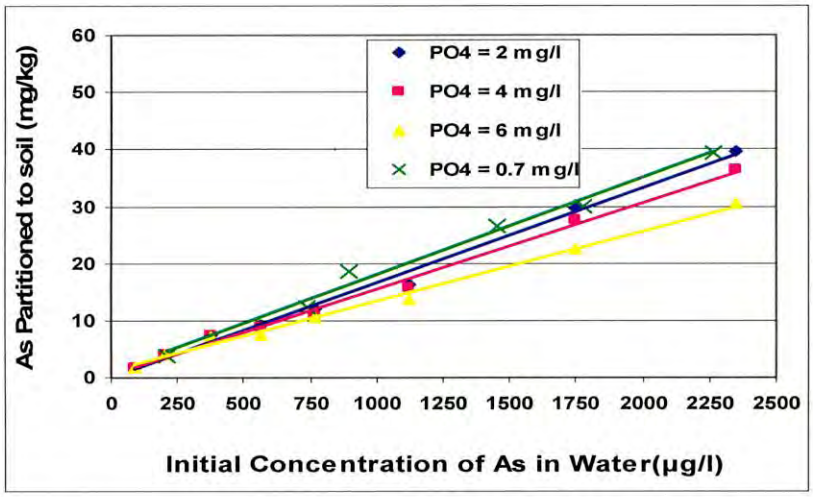

Fig. 3.7a: Adsorption of As on paddy field soil from Munshiganj in the presence of phosphate

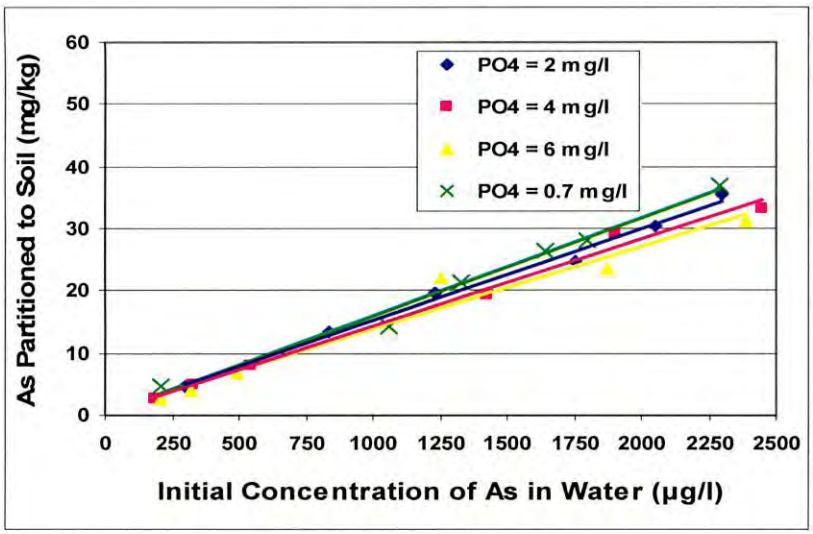

Fig. 3.7b: Adsorption of As on paddy field soil from Brahmanbaria in the presence of phosphate

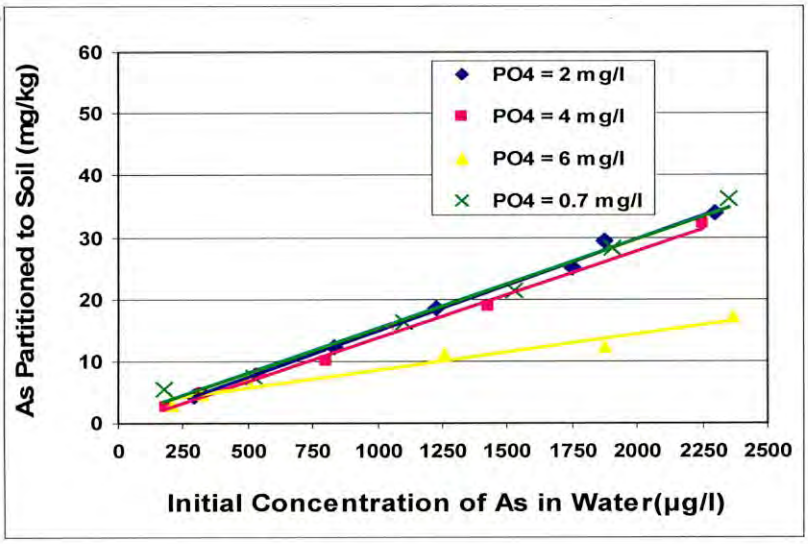

Fig. 3.7c: Adsorption of As on paddy field soil from Faridpur in the presence of phosphate

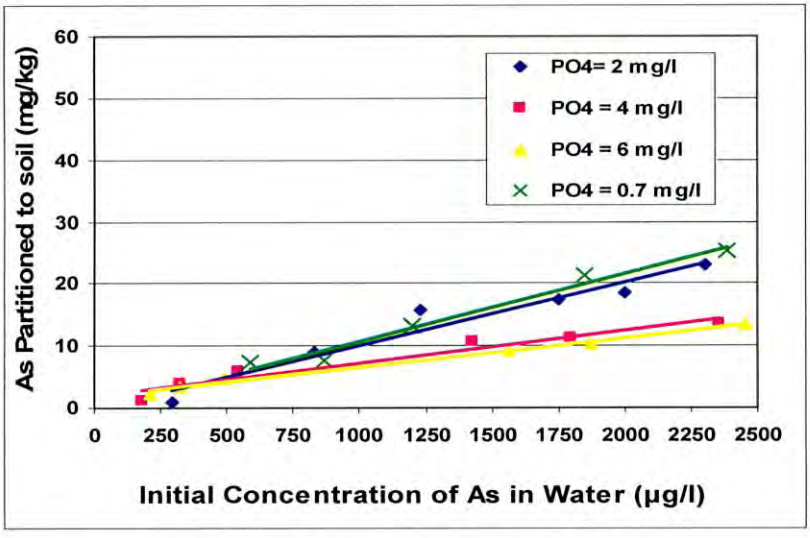

Fig. 3.7d: Adsorption of As on paddy field soil from Naogaon in the presence of phosphate

In order to induce stronger effect of phosphate on As adsorption, additional batch adsorption experiments were carried out with Faridpur and Naogaon soils (having relatively less Fe contents) where phosphate concentration was varied from 2 to 42 mg/l, and As (arsenite) concentration was fixed at 1000 µg/l. Figure 3.8 shows adsorption of arsenic on soil as a function of phosphate concentrations in water. Figure 3.8 shows that high concentration of phosphate could significantly reduce adsorption of As on soil. For example, for Naogaon soil, As adsorption came down from about 8 mg/kg to around 3 mg/kg as phosphate concentration in water increased from 2 to 42 mg/l.

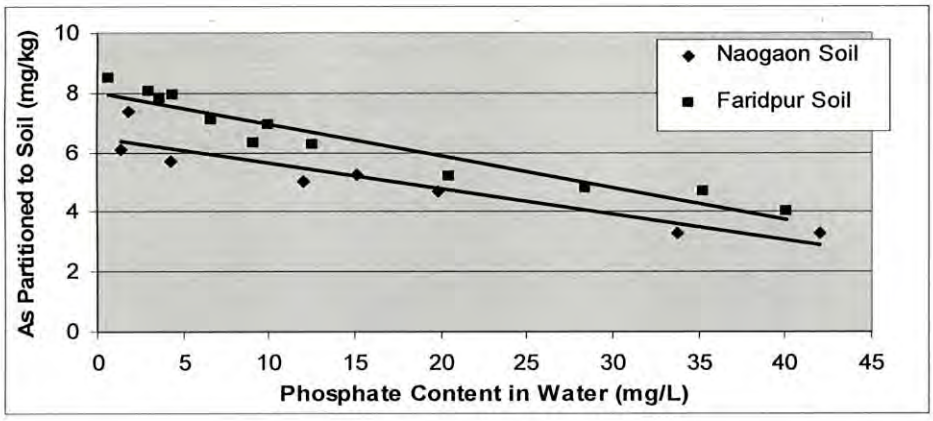

Fig. 3.8: Adsorption of As on paddy field soil from Faridpur and Naogaon in the presence of phosphate

In the batch adsorption experiments, arsenite was used since this is the principal form of arsenic in groundwater. But in actual field condition, some of the As(III) is oxidized within the irrigation channel and in the paddy field. As(V) has much stronger affinity for soil (iron oxyhydroxides) compared to As(III) and this fraction of total arsenic could compete with phosphate for available adsorption sites on soil. Roberts et al. (2006) reported that for a paddy field site in Munshiganj, 25% of total As (400 μg/l) in well water was initially present as As(V), and that 24% of arsenic, initially present as As(III), was oxidized to As(V) within the irrigation channels.

Many researchers have shown that phosphate reduces arsenate adsorption (Barrow, 1974; Hingston et al., 1971; Livesey and Huang, 1981; Melamed et al., 1995), but the extent of the suppression varied among soils. Woolson et al. (1973) found that when the P and As concentrations were similar, P was sorbed in preference to arsenic. Arsenic and phosphorus are members of the nitrogen group of elements (N, P, As, Sb, Bi). There is an apparent similarity between the chemistry of arsenic and P because they both commonly form oxyanions (arsenate and phosphate) in the 5 + oxidation state in soils. However, phosphate is stable over a much wider range of Eh and pH conditions than arsenate. The consensus of most investigators is that arsenate and phosphate are sorbed in soils by the same mechanism (Roy et al., 1986). Similarly charged arsenic and P species compete for sorption sites on the soil components. Phosphate anions are smaller than arsenate anions and have a higher charge and therefore, phosphate binds more strongly than arsenate. However, if the arsenic: phosphorus concentration ratio was increased then P could be desorbed and the solution concentration of P increased. Research has demonstrated that

As adsorption to mineral surfaces may be reduced in the presence of oxy-anions such as PO_4^{3-} and SO_4^{2-} (Manning and Goldberg, 1996).

3.4 SUMMARY

Results from this study shows that adsorption of both arsenite and arsenate on paddy field soils increases with increasing oxalate-extractable iron content (as well as total iron content) of soil. Iron content of paddy field soil, in turn, has been found to be related to the dissolved iron content in irrigation water. Thus, arsenic adsorption to paddy field soil depends not only on the characteristics of soil, but also on the characteristics of (e.g., iron content) of irrigation water.

In the presence of high arsenic concentration in water, very high adsorption density, approaching 200 mg/kg was observed for paddy field soil from Munshiganj. This indicates that paddy field soil is capable of accumulating very high concentration of As. It may be noted that some recent field measurements showed As concentration in top 10 mm of soil to be about 150 mg/kg at the end of the irrigation season (Dittmar et al., 2005). This is a cause of concern because adverse effects on growth of plants and yield of crops have been recorded at similar and lower soil arsenic concentrations.

Phosphate was found to adsorb strongly on paddy field soils and its adsorption also increases with increasing iron content of soil. Arsenite adsorption was found to decrease with increasing phosphate concentrations; but since the batch experiments were carried out with low sorbate to sorbent ratios, the effects were apparent only when concentrations of both As and phosphate were high.

Effect of pH on adsorption of both arsenate and arsenite appear to follow the same trend. Adsorption of arsenate was only slightly higher than that of arsenite. Adsorption of both arsenite and arsenate was significantly higher on the Munshiganj soil compared to that in the Naogaon soil and there is a sharp fall of adsorption curve with increasing pH at Munshiganj soil than that of Naogaon. This is probably due to very high concentrations of adsorption sites (i.e., soil) compared to the concentration of arsenic in water and most likely related to the much higher oxalate extractable iron concentration (22.05 mg/kg) in the Munshiganj soil (which is the principal adsorbent of arsenic) compared to that in the

Naogaon (9.86 mg/kg). Adsorption as a function of pH followed a concave down ward profile with the maximum adsorption occurring at pH between 4 and 6.

Arsenic adsorption by soil may play an important role in reducing arsenic availability to plant and its introduction into the food chain. The greater adsorption capacity of soils could decrease the availability of arsenic to the plant and retard transport of the element through the subsurface.

CHAPTER 4

ARSENIC MOBILIZATION FROM PADDY FIELD SOIL

4.1 INTRODUCTION

Arsenic is highly toxic and therefore represents a potential threat to the environment and human health. The mobility and bioavailability of arsenic in soil is mostly controlled by adsorption and desorption reactions. A number of studies (e.g., Huq et al., 2001; Meharg and Rahman, 2003; Ali et al., 2003b; Masud, 2003; Ahmed, 2005; Jahiruddin et al., 2005; Saha, 2006) have found that significant amount of As is accumulated in top soils of paddy fields irrigated with As contaminated groundwater. However, it has been found that after the rainy season, As concentration in the top soil decreases significantly (Saha, 2006). Thus a large fraction of As associated with the top soil is mobilized during inundation with flood/rain water. Desorption from soil and reductive dissolution of iron oxyhydroxides, the principal adsorbent is soil, are most probably responsible for significant reduction of soil As content at the end of the irrigation season. Under reducing conditions, the most stable soluble form of inorganic arsenic is as arsenious acid [H_3AsO_3]; under oxidizing conditions, most of the arsenic will be in the As(V) form [$H_2AsO_4^-$, $HAsO_4^{2-}$]. Again, the mobility of arsenic may depend on its charge, so at neutral pH, arsenious acid is more mobile than the dissociated forms of As(V). That means arsenic will probably be more mobile under reducing conditions because more of the arsenic will be present as arsenious acid. Just as the pH of the system affects binding sites on soil particles, the redox potential also affects the binding sites. Many of the binding sites for arsenic are made of oxidized iron, aluminum or manganese species that form a coating on the soil particles or on the rock surface. Sometimes, the metals on the soil surface can also be reduced, releasing them into solution. That means the binding sites are no longer available on the surface and the arsenic that used to be bound is released into solution.

That makes two independent factors that are likely to increase the mobility of arsenic under reducing conditions:

- reduction of As(V) to As(III), which is more mobile
- reduction of binding sites, releasing bound arsenic

In this study, laboratory batch experiments have been performed to assess desorption of arsenic from As-rich paddy field soils in contact with water as a function of time. This Chapter presents the results of laboratory experiments carried out for assessing mobilization of arsenic from As-rich paddy field soils.

4.2 METHODOLOGY

4.2.1 Desorption of Arsenic from Soil

4.2.1.1 Desorption of Arsenic from Soil used in Adsorption Experiments

Desorption of As was evaluated in batch experiments using the soil samples remaining in the centrifuge tubes after completion of the batch adsorption experiments described in Chapter 3 (in Section 3.3.4.1). After completion of the batch adsorption experiments (where As concentration was varied from 150 to 2,500 μg/l, and phosphate from 2 to 6 mg/l), the supernatant liquid in each centrifuge tube was decanted. Then As-free (As < 1μg/l) groundwater was added to each centrifuge tube and equilibrated for 24 hours in an end-over-end rotators. The tubes were then centrifuged for solid-liquid separation. Arsenic concentration in the supernatant liquid of each centrifuge tube was then determined, and the amount of arsenic desorbed from the soil samples were calculated for different equilibration periods.

4.2.1.2 Desorption of As from As-rich Paddy Field Soil

Desorption of arsenic from paddy field soils over longer time periods was evaluated using the top soil samples (0~15mm) collected from the paddy field sites in Munshiganj and Noagaon. The samples were collected at the end of the irrigation season. The Munshiganj soil had a high As concentration (26.98 mg/kg), while the Naogaon soil had a low As concentration (1.68 mg/kg). Desorption of arsenic was evaluated in batch experiments carried out in 15 ml centrifuge tubes as described above. One gram of soil sample was

taken in each centrifuge tube, to which 12.5 ml of arsenic free (As < 1μg/l) groundwater was added. Then the centrifuge tubes were equilibrated in end-over-end rotators for different equilibration periods from 24 hrs to 33 days. The tubes were then centrifuged for solid-liquid separation. Arsenic concentration in the supernatant liquid was then determined and the amount of arsenic desorbed from the soil samples was calculated.

4.2.2 Mobilization of As from As-rich Paddy Soil under Reducing Condition

Arsenic mobilization from paddy field soils was assessed using the soil samples collected from the paddy field in Munshiganj, Brahmanbaria, Faridpur and Naogaon districts at the end of the irrigation season. Three different types of soils from Munshiganj were used in these batch experiments: natural paddy field soil collected at the end of the irrigation season and paddy field soil undergoing adsorption experiments in the presence of 400 μg/l and 1200 μg/l of As. Mobilization of As from soil was assessed in batch experiments carried out in 15 ml centrifuge tubes. One gram of soil sample was taken in each centrifuge tube and 12.5 ml of aqueous solutions containing different concentrations of glucose (organic matter). Glucose was used as an organic matter to create reducing condition in the centrifuge tubes. The tubes were equilibrated for different time periods (24 hours and 7 days) in end-over-end rotators. The tubes were then centrifuged and As of the supernatant liquid was determined. For one set of experiment with Munshiganj soil, glucose content was fixed at 0, 10, 15, 20 and 25 mg/l of carbon. In subsequent experiments using paddy filed soil from four districts (Munshiganj, Brahmanbaria, Faridpur and Naogaon) higher concentration of organic matter (0, 3200, 6400 and 9600 mg/l of carbon in the form of glucose) was used.

All reagents used in the laboratory experiments were of reagent grade. As(III) stock solution was prepared using Waco As(III) standard solution (containing 1005 mg/l As) and phosphate stock solution was prepared using reagent grade $NaH_2PO_4.2H_2O$.

4.3 RESULTS AND DISCUSSION

4.3.1 Desorption of Arsenic from Soil Used in Adsorption Experiments

Desorption of As from soil which were earlier used in adsorption experiments was assessed. In the adsorption experiments conducted earlier, As concentration was varied from 150 to 2500 μg/l, and for each initial As concentration phosphate concentration was

fixed at 2 mg/l, 4 mg/l, and 6 mg/l. The initial total As concentration of the soils used in the desorption experiments was calculated as the sum of initial As content of original soils (shown in Table 3.1) and the amount of As adsorbed on it in adsorption experiment.

Figures 4.1a-d shows the quantity of desorbed As (expressed as mg/kg of soil, dry wt. basis) plotted against initial total As content of soil from the 4 districts. They show that the quantity of As desorbed from soil is relatively small compared to the total initial concentration of As in soil. The highest desorption (within 24-hour equilibration time) of As (~2-6 mg/kg) was obtained for the Munshiganj soil, which had initial total As concentration of about 70 mg/kg (Fig. 4.1a). Maximum desorption from the Naogaon and Faridpur soils was about 1 mg/kg; these soils had maximum initial As contents of about 42 and 25 mg/kg, respectively. From these figures, it appears that the quantity of As desorbed is more or less proportional to the initial As concentration in soil.

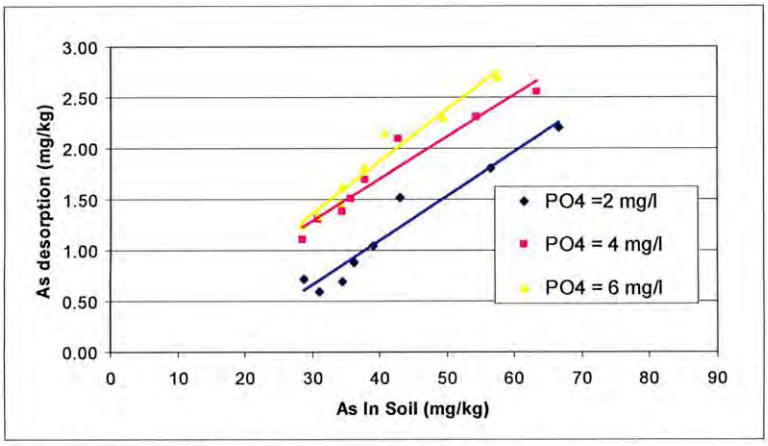

Fig. 4.1a: Arsenic desorption in 24 hrs from Munshiganj soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

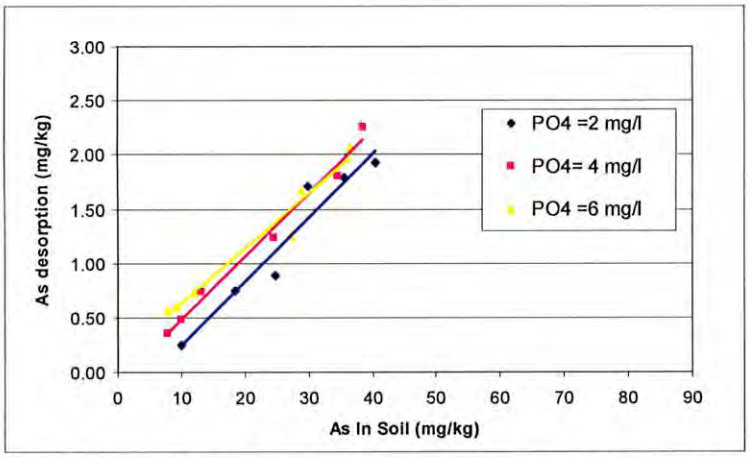

Fig. 4.1b: Arsenic desorption in 24 hrs from Brahmanbaria soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

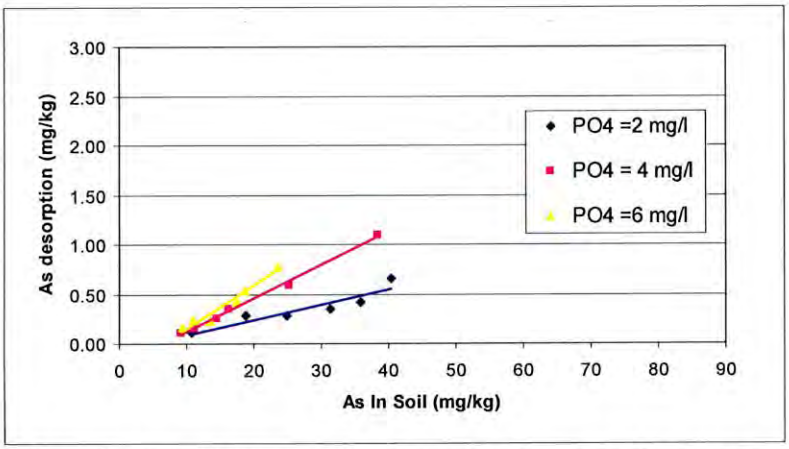

Fig. 4.1c: Arsenic desorption in 24 hrs from Faridpur soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

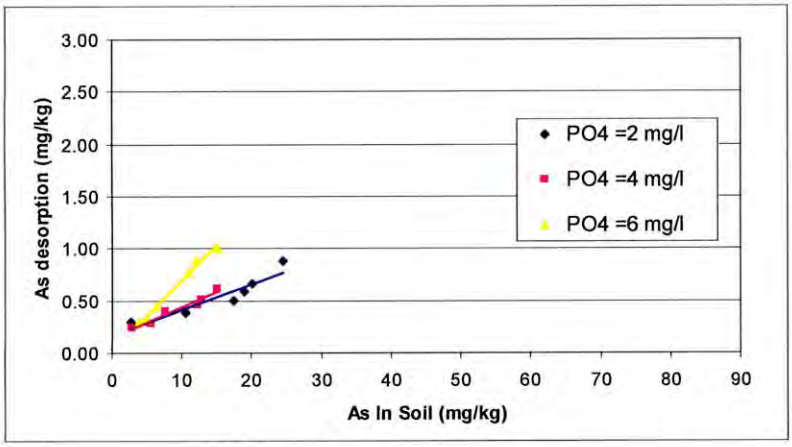

Fig. 4.1d: Arsenic desorption in 24 hrs from Naogaon soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

Figures 4.2a-d shows the quantity of desorbed As (expressed as mg/kg of soil, dry wt. basis) and plotted against the amount of As adsorbed on these soils during the adsorption experiments. These figures shows that the amount of As desorbed from soil within 24 hours is small even compared to the amount of As adsorbed onto these soils during the adsorption experiments. Therefore, it appears that significant amount of As adsorbed onto paddy field soils from irrigation water does not desorb readily (i.e., within 24 hours) to water. However, since desorption kinetics are usually slow, more arsenic is likely to come off from soils under longer equilibration times (as demonstrated in Section 4.4.2).

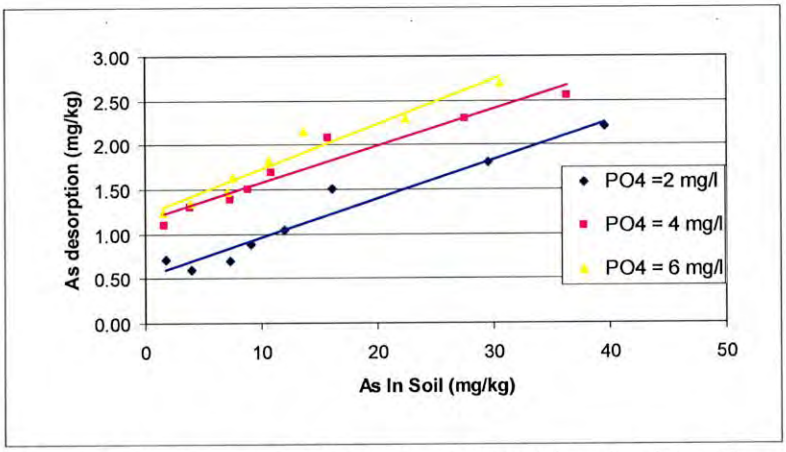

Fig. 4.2a: Arsenic desorption in 24 hrs from Munshiganj soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of the adsorbed concentration of Arsenic

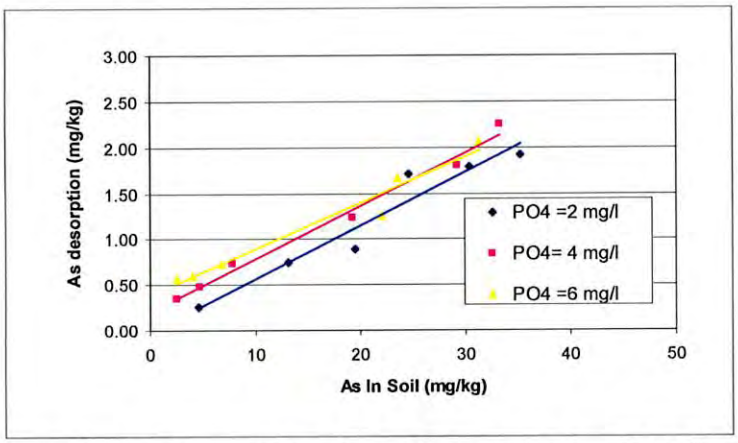

Fig. 4.2b: Arsenic desorption in 24 hrs from Brahmanbaria soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of the adsorbed concentration of Arsenic

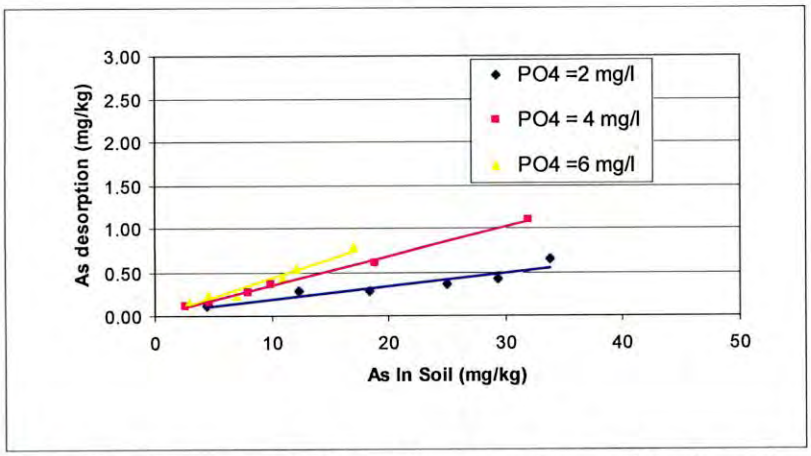

Fig. 4.2c: Arsenic desorption in 24 hrs from Faridpur soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of the adsorbed concentration of Arsenic

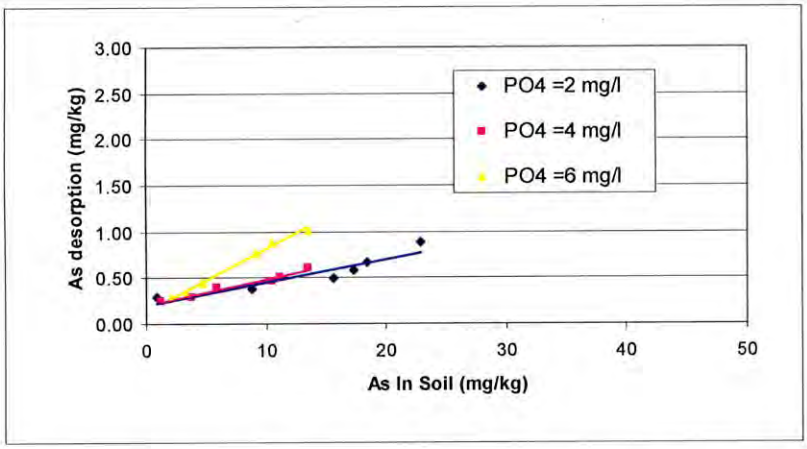

Fig. 4.2d: Arsenic desorption in 24 hrs from Naogaon soil [soils undergoing As adsorption with 2 mg/l (♦), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of the adsorbed concentration of Arsenic

From Figs. 4.1 and 4.2, it can be seen that for any particular initial soil As-concentration, desorption of As is higher from soils with higher phosphate content. The soils that went through adsorption experiments with higher phosphate concentrations (e.g., 6 mg/l) (and subsequently used for desorption experiments) had higher phosphate contents. This phenomenon is probably due to possible re-adsorption of some of the phosphates that are initially desorbed from soil. Since phosphate has significantly higher affinity for soil compared to arsenite, some of the phosphate initially desorbed from soil probably gets re-adsorbed displacing a portion of adsorbed arsenite.

4.3.2 Arsenic Desorption from Soil over Longer Time Periods

Desorption of arsenic from paddy field soils over longer time periods was evaluated using the soil samples collected from paddy fields of Munshiganj and Naogaon, with initial As concentrations of about 27 and 1.7 mg/kg, respectively. Figure 4.3a shows results of desorption experiments for Munshiganj and Naogaon soils, where amount of desobed As [expressed as mg As/kg of soil (dry wt. basis)] has been plotted against time; in Fig. 4.3b the amount of desorbed As has been expressed as percentage of initial concentration of As in soil. Fig 4.3 shows that significant amount of As is desorbed from the Munshiganj paddy field soil, which had a high As concentration of about 27 mg/kg. Desorption of As from this soil increased with time and it appears that more As would desorb from this soil under longer equilibration periods. Thus, it appears that significant amount of As could be

mobilized from As-rich paddy field soils during inundation by water during the wet season.

On the other hand, desorption of As from the Naogaon paddy field soil which had a low As concentration of about 1.7 mg/kg was insignificant and did not change significantly with equilibration time. Thus, it appears that As concentration of such soils are not likely to change significantly during inundation in the wet season.

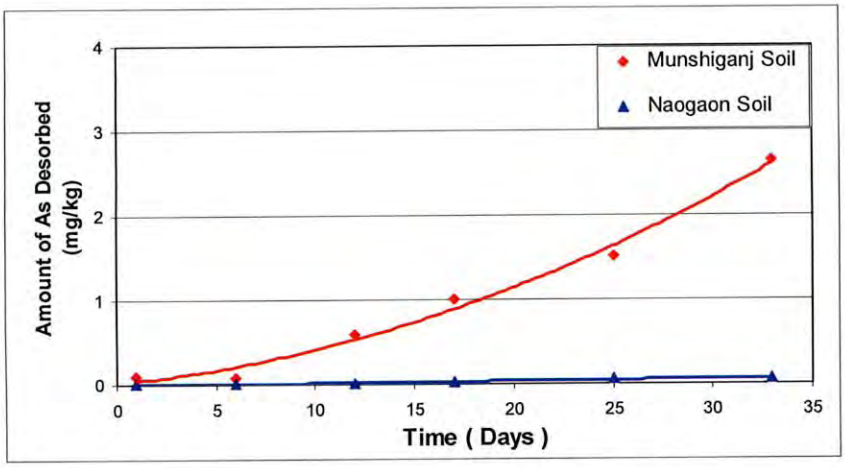

Fig. 4.3a: Desorption of As (expressed as mg/kg of soil) from natural soils collected from paddy fields of Munshiganj and Naogaon districts as a function of time

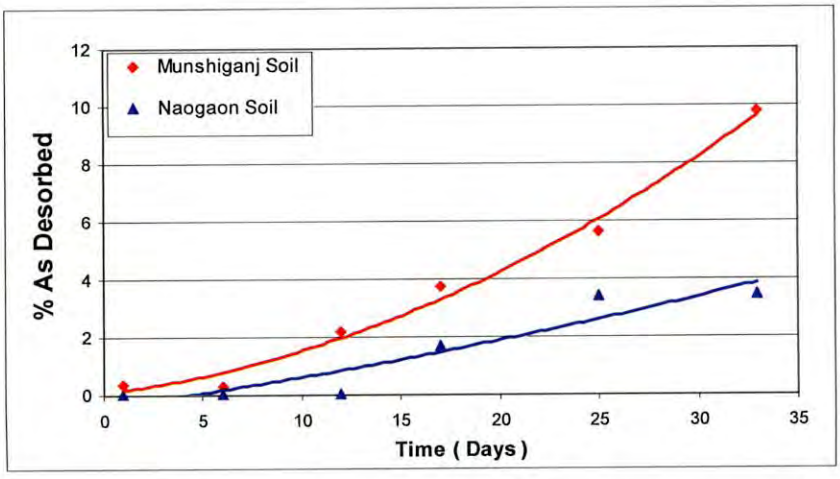

Fig. 4.3b: Desorption of As (expressed as % of initial concentration of As in soil) from natural soils collected from paddy fields of Munshiganj and Naogaon districts as a function of time

4.3.3 Mobilization of As From As-Rich Paddy Soil under Reducing Condition

Mobilization of As from paddy field soil under reducing condition was evaluated using soil samples collected from the paddy fields of the four study areas at the end of the

irrigation season. The first set of experiments was carried out with soils collected from the Munshiganj paddy field. Three different types of soils were used in these batch experiments: (i) natural paddy field soil collected at the end of the irrigation season, (ii) paddy field soil undergoing adsorption experiments in the presence of 400 μg/l of As, and (iii) paddy field soil undergoing adsorption experiments in the presence of 1200 μg/l of As. In these batch experiments, 1 gm of soil was equilibrated with water having different concentration of carbon (0, 10, 15, 20 and 25 mg/l of carbon) added in the form of glucose; the carbon source (glucose) was added to create reducing condition. These carbon concentration ranges (10 to 25 mg/l) are similar to those reported for river, eutrophic lake and marsh (Thurman, 1985).

Figure 4.4a-c show partitioning of As to water from Munshiganj paddy field soils at the end of 24 hours and 7 days. These figures show relatively low mobilization of As from natural soil within 24-hour equilibration period. This could be due to the fact that significant reductive dissolution of iron oxyhydroxides (and concomitant As mobilization to water) is not likely to take place within the 24-hour equilibration period. However, at the end of 7-day equilibration period, appreciable mobilization (varying from about 2.5 to 4.0 mg/kg) occurred in the presence of 25 mg/l carbon. In the absence of the carbon, amount of As mobilized at the end of 7 day period varied from about 1.5 to 2.5 mg/kg, which could be attributed to direct desorption of As from soil (assuming the natural soil had little or no organic matter content). The additional mobilization in each case may be attributed to mobilization due to reductive dissolution of iron oxyhydroxides, which appears to increase with increasing concentration of carbon. Slightly higher As was mobilized from the soils undergoing adsorption experiments (Fig. 4.4b, c) compared to that from the natural soil (Fig. 4.4a). This may be due to the weak bondage of adsorbed As. Thus, it appears that the arsenic that is accumulated (by adsorption) in soil during the irrigation season from arsenic contaminated irrigation water can relatively easily desorbed and washed out during inundation.

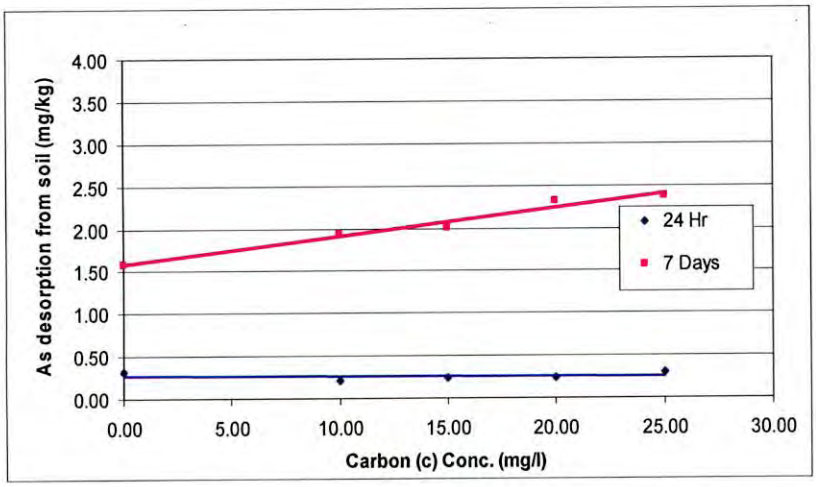

Fig. 4.4a: Mobilization of As from natural Munshiganj paddy field soil in presence of organic carbon (glucose)

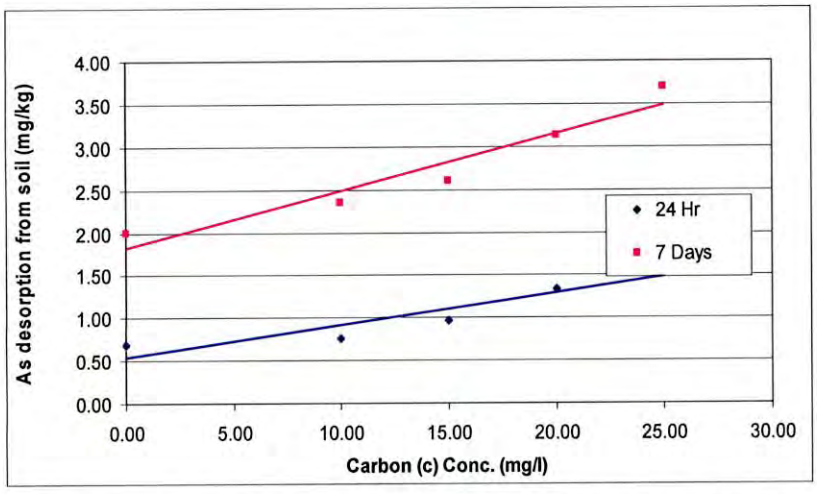

Fig. 4.4b: Mobilization of As from Munshiganj paddy field soil [soil undergoing adsorption with 400µg/l As] in presence of organic carbon (glucose)

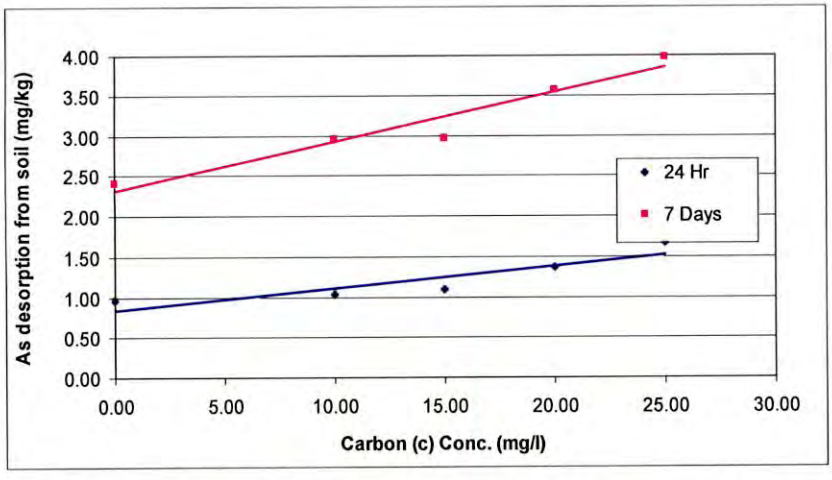

Fig. 4.4c: Mobilization of As from Munshiganj paddy field soil [soil undergoing adsorption with 1200 µg/l As] in presence of organic carbon (glucose)

In order to assess mobilization of As from soil to water, additional experiments were carried out with natural soils from paddy fields of all four areas in the presence of high concentrations of organic matter (3200 to 9600 mg/l carbon, added in the form of glucose). Figures 4.5 to 4.8 show mobilization of As from paddy field soils from Munshiganj, Brahmanbaria, Faridpur and Naogaon, respectively. As before (Fig. 4.4), relatively low mobilization was observed at the end of 24-hour, but relatively higher mobilization was observed at the end of 7 days. As mobilization of about 4 mg/kg was observed for the Munshiganj soil, which accounts for about 20% of oxalate-extractable As (18.6 mg/kg) initially present in the soil. Fig. 4.5 shows that about 2 mg/kg of this has been mobilized in the absence of the carbon source, which could be attributed to direct desorption of As from soil.

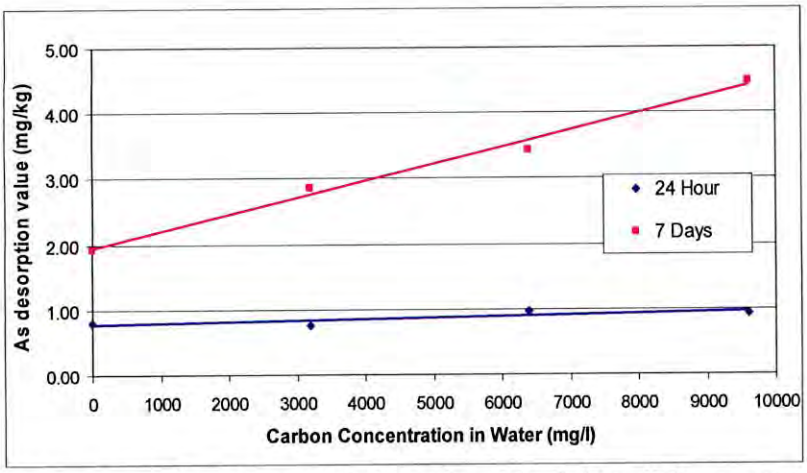

Fig. 4.5: Mobilization of As from Munshiganj paddy field soil in presence of organic carbon (glucose)

For Brahmanbaria and Faridpur soils, maximum mobilization observed was about 3 mg/kg (Figs. 4.6 and 4.7), a significant part of which (about 1 mg/kg) may be attributed to direct desorption from soil. Oxalate-extractable As in soils from these two areas were 3.9 mg/kg and 6.5 mg/kg, respectively. Thus, it appears that a significant fraction of the oxalate-extractable As was mobilized from these soils within the 7days. Despite significant variation in initial oxalate-extractable As contents (18.5 mg/kg for Munshiganj and 3.9 mg/kg for Brahmanbaria) of soils from the three As-affected areas, quantity of mobilized As at the end of 7-day period was comparable (varying from about 3 mg/kg for Brahmanbaria to 4 mg/kg for Munshiganj).

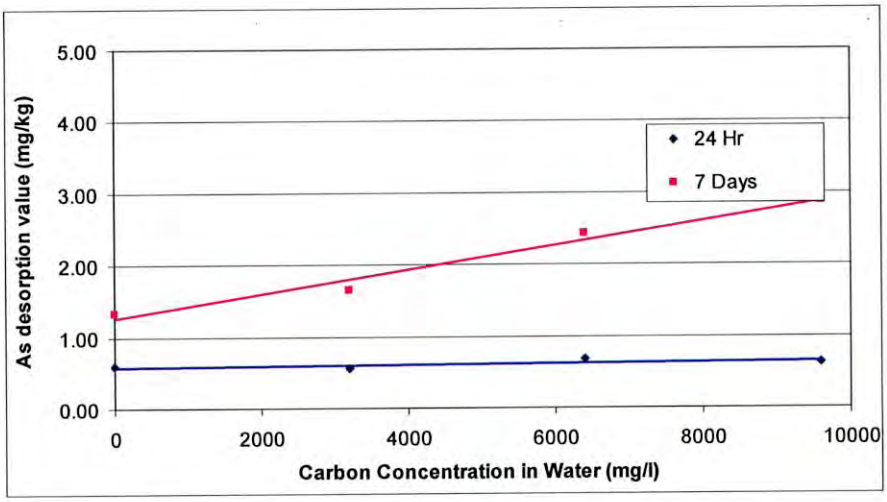

Fig. 4.6: Mobilization of As from Brahmanbaria paddy field soil in presence of organic carbon (glucose)

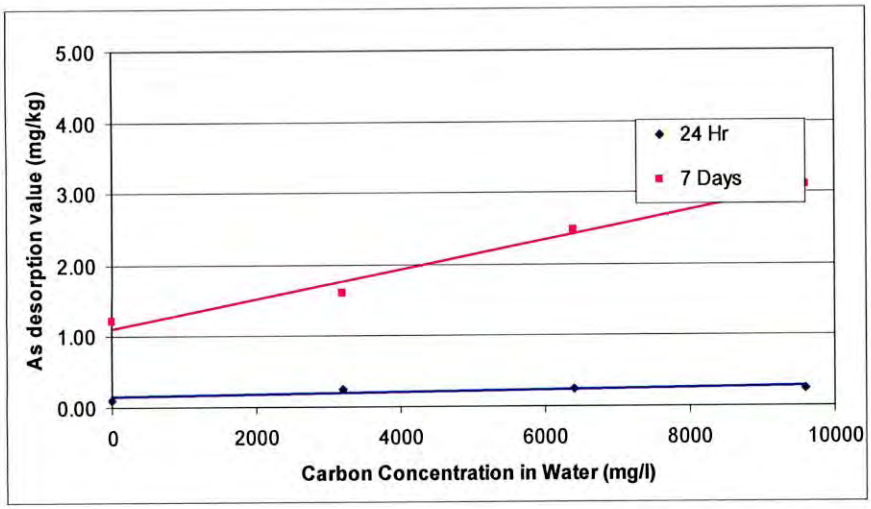

Fig. 4.7: Mobilization of As from Faridpur paddy field soil in presence of organic carbon (glucose)

Very small amount of As was mobilized from the paddy field soil from Naogaon (Fig. 4.8), which is an area not affected by As contamination. This is probably due to the fact that Naogaon soil had the least oxalate-extractable As (1.7 mg/kg), and it is this fraction of As that is likely to be mobilized due to desorption and reductive dissolution. As shown in Fig. 4.3, desorption of As from the Naogaon paddy field soil was also insignificant even for long (33-day) equilibration period.

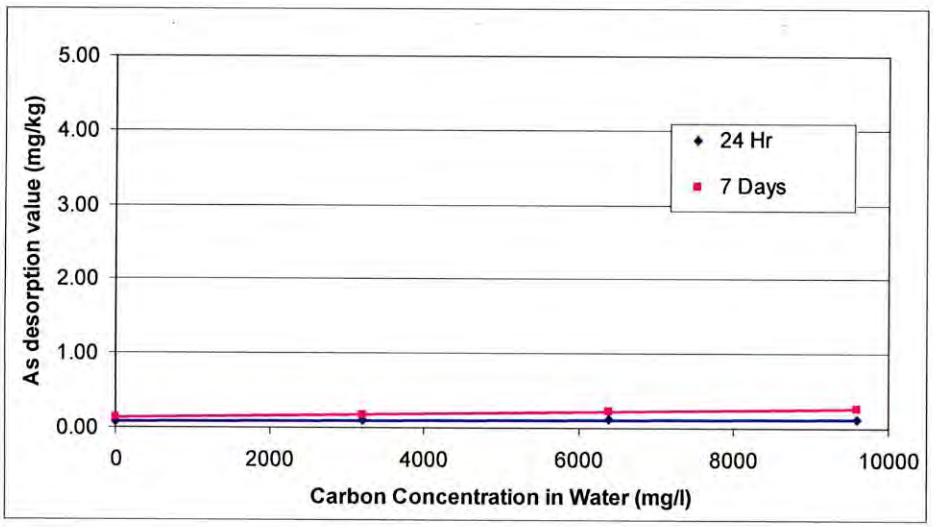

Fig. 4.8: Mobilization of As from Naogaon paddy field soil in presence of organic carbon (glucose)

Figures 4.4 and 4.5 demonstrate the effect of organic carbon concentration on the mobilization of As from soil. Figure 4.4a shows that As mobilization (from natural Munshiganj paddy field soil) due to reductive dissolution increases from about 0.5 mg/kg to 1.0 mg/kg, as carbon content of water increases from about 15 mg/l to 25 mg/l. Figure 4.5 shows that As mobilization increases from about 1 mg/kg to 2.5 mg/kg, as carbon content increases from 3200 mg/l to 9600 mg/l. Thus, concentration of organic carbon did not appear to have a dramatic influence on mobilization of As from soil within the 7-day inundation period. It appears that significant mobilization could take place due to reductive dissolution in the presence of relatively low concentration of organic matter, which is likely to be the case in actual field condition. Mobilization appears to be a stronger function of time than concentration of organic carbon.

4.4 SUMMARY

Some recent studies (e.g., Saha, 2006; Roberts et al., 2006) suggest that significant amount of As is mobilized from paddy field soil during inundation with flood/rain water. Desorption from soil and reductive dissolution of iron oxyhydroxides, the principal adsorbent is soil matrix, are thought to be responsible for significant decrease of soil As content at the end of the irrigation season. Results obtained from this study confirm that significant amount of As could be mobilized from paddy field soils by desorption,

especially over longer time periods, and through reductive dissolution. Arsenic mobilization through reductive dissolution also appears to be a strong function of time. Since paddy fields are inundated in flood/rain water for periods of about three months, significant amount of soil As could be mobilized during this time. Both desorption and reductive dissolution of iron oxyhydroxides appears to be important processes in governing fate of arsenic in irrigated paddy fields. These natural processes appear to play a major role in preventing As concentration in soil to reach toxic levels.

CHAPTER 5

CONCLUSIONSAND RECOMMENDATIONS

5.1 CONCLUSIONS

The primary objectives of this study were: (1) to assess adsorption characteristics of As on paddy field soils, including effect of different water quality (e.g., pH, phosphate concentration) and soil parameter (e.g., grain size, iron content) on adsorption; (2) to assess mobilization (i.e., release) of As from As-rich paddy field soils by desorption and reductive dissolution.

The conclusions from this study are summarized below:

- Arsenic adsorption on paddy field soils has been found to increase with increasing oxalate extractable iron content of soil. The iron content of paddy field soil on the other hand has been found to increase with increasing iron contents in irrigation water. Hence, arsenic adsorption onto paddy field soil has been found to depend characteristics of soil as well as irrigation water.

- As adsorption by soil may play an important role in reducing As availability to plant and its introduction into the food chain. The greater adsorption capacity of soils could decrease the availability of As to plants and retard its transport through the subsurface.

- Phosphate adsorption onto paddy field soils also increases with increasing iron content of soil. Presence of phosphate at high concentrations could reduce As adsorption on paddy field soil. Effect of pH on adsorption of both arsenate and arsenite appear to follow the same trend. Adsorption as a function of pH followed a concave down ward profile with the maximum adsorption occurring at pH between 4 and 6. Significant reduction of As adsorption on soil was observed only at very high pH (exceeding pH 8). Since pH of natural groundwater usually is

slightly acidic to neutral, pH is not likely to have any significant effect on As adsorption on paddy field soil.

- Arsenic adsorption by soil may play an important role in reducing arsenic availability to plant and its introduction into the food chain. The greater adsorption capacity of soils could decrease the availability of arsenic to the plant and retard transport of the element through the subsurface.

- Results from this study suggest that significant As associated with paddy field soil could be mobilized by desorption and reductive dissolution during inundation by flood/rain water. Arsenic mobilization by desorption and reductive dissolution has been found to be a strong function of time. Since paddy fields are inundated in flood/rain water for periods of up to three months, significant amounts of soil arsenic could be mobilized during this time. Thus, natural geochemical processes, e.g., desorption and reductive dissolution of iron oxy hydroxides, appear to play a major role in preventing arsenic concentrations in soil to reach toxic levels.

- Possible desorption of arsenic from As-rich soil during the irrigation may in fact increase bio-availability of As to plants.

5.2 RECOMMENDATIONS

5.2.1 Recommendations for Future Studies

The following issues should be addressed in future studies:

(1) There are twelve agro-ecological regions of Bangladesh having different soil types. As arsenic adsorption kinetics is highly correlated with soil composition, so detailed field studies should be carried out to assess accumulation of As in paddy field soils in different agro-ecological regions of Bangladesh.

(2) Mobilization of As associated with soil by desorption and reductive dissolution over longer time periods (e.g., 3 months) should be assessed to better understand the implications of these processes during inundation of paddy fields in rain/flood water.

(3) Studies should be carried out to assess the possible role of bio-methylation (i.e., microbial conversion of As associated with soil into volatile forms) in regulating As concentration in soil.

(4) Studies should be carried out to assess the effect of phosphate fertilizer on arsenic adsorption-desorption as phosphate fertilizer is widely used for agricultural production in Bangladesh.

(5) Studies should be carried out to better understand the fate of As in agricultural soil.

5.2.2 Policy Recommendations

The following policy recommendations are suggested based on the results of this study:

(1) Since paddy field soils have been found to be capable of accumulating very high concentrations of As that could potentially affect crop yield, the Government should take steps to monitor As concentration of paddy field soils in As affected areas.

(2) Government should sponsor studies to assess the effect of As in irrigation water on agriculture in the arsenic affected areas, especially its long-term effect on soil quality, crop yield, bio-accumulation of As and its health impacts.

(3) Where feasible, farmers may be encouraged to use As-free groundwater from deeper aquifer (if available) in agriculture instead of As-contaminated groundwater from shallow aquifer. Necessary support should be provided by the Government in this regard.

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