Journal of Civil Engineering (IEB), 34(1), 2006, 25-41

Journal of
Civil Engineering
IEB

Mobilization of arsenic from paddy field soil through adsorption-desorption and reductive dissolution processes

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Received on 4 January 2006

Abstract

Batch adsorption experiments carried out with paddy field soils from three arsenic affected and one unaffected areas revealed that adsorption of both arsenite and arsenate to paddy field soil increases with increasing oxalate-extractable iron content (as well as total iron content) of soil. Iron content has been found to be high for soils of paddy fields irrigated with groundwater containing high concentration of iron. Arsenic adsorption to paddy field soil thus depends not only on the characteristics of soil, but also on the iron content of irrigation water. 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. Adsorption of both arsenite and arsenate on paddy field soil as a function of pH followed a concave downward profile with the maximum adsorption occurring at pH between 4 and 6. Desorption of As from As-rich paddy field soils in contact with water has been found to be significant at longer equilibration periods of about one month. Significant mobilization of As, beyond the level that could be explained by desorption alone, was recorded for soil samples equilibrated with water containing organic carbon (glucose). This is most likely due to reductive dissolution of iron oxyhydroxides and consequent partitioning of adsorbed As to water. Thus, although paddy field soils have the capacity to accumulate significant amount of As from irrigation water, natural geochemical processes, e.g., desorption and reductive dissolution of iron oxyhydroxides, appear to be preventing arsenic concentrations in soil to reach toxic levels.

Keywords: Arsenic, groundwater, irrigation, soil, paddy

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1. Introduction

In Bangladesh, groundwater extracted from shallow aquifers with hand-tubewells is the primary source of drinking and cooking water for most of its population of over 140 million (World Development Report, 2006); over 10 million domestic wells constitute the backbone of rural water supply of the country. Besides domestic use, groundwater all over the country including the arsenic (As) affected areas, is widely used for irrigation during the dry season (December to April), particularly for growing of the dry-season rice called *boro* which requires about 1 m of irrigation water each year. In 2004, groundwater irrigation through shallow tubewells covered about 60% of the total irrigated area. Considering 1 m of irrigation for *boro* rice, the amount of As cycled each year through irrigation water is estimated to be about 1000 metric tons (Saha, 2006). Due to its affinity for metal oxides/hydroxides in soil, higher accumulation of As in irrigated surface soils is expected and a number of studies (e.g., Huq et al., 2001; Meharg and Rahman, 2003; Ali et al., 2003; Ahmed, 2005; Jahiruddin et al., 2005, Dittmar et al., 2005; Saha, 2006, Roberts et al., 2006) have reported relatively higher concentrations of As in paddy field soils irrigated with As contaminated groundwater. Saha and Ali (2006) however reported that As concentration in paddy field soils irrigated with As contaminated groundwater varies significantly with both depth of soil and time; after the rainy season (which immediately follow the *boro* season), As concentration in the top soil layer of paddy fields decreased significantly and came down to concentrations comparable to those found at the beginning of the *boro* season. Accumulation of As in paddy field soils is a major concern because of its possible impact on bioaccumulation of As in rice grains and plants and on crop yield.

Adsorption-desorption of As onto soil are key to the understanding its fate in the irrigated agricultural soil. Adsorption is thought to be the principal mechanism by which As in irrigation water accumulates in the topsoil; whereas desorption and reductive dissolution of iron oxyhydroxides are thought to be the mechanisms through which As in arsenic-rich topsoil partitions back into the aqueous phase. Adsorption of As onto soil would reduce its bioavailability to plants. While desorption and reductive dissolution processes occurring during the irrigation season could increase bioavailability As to plants, the same processes occurring after the irrigation season would help reduce As concentration in paddy field soils. However, virtually no information is available in the literature on adsorption characteristics of As on agricultural soils of Bangladesh, and only limited information is available on adsorption of arsenite, As(III) (the principal chemical form of As in groundwater) on agricultural soil. Available information on adsorption of As are mostly concentrated on adsorption of arsenate [As(V)] and effect of phosphate on arsenate adsorption. Also, soil characteristics (e.g., clay content, iron oxyhydroxides) and water quality parameters (e.g., phosphate concentration) affecting adsorption-desorption of As (particularly of arsenite) are also not clearly understood.

Arsenate sorption on soils increases with pH until maximum sorption is reached and then decreases with further increase of pH (Goldberg and Glaubig, 1988; Xu et al., 1988). 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; Sun and Doner, 1996). Phosphate has been found to compete with arsenate for goethite surface sites since phosphate, like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism (Parfitt, 1978; Persson et al., 1996; Tejedor-Tejedor and Anderson, 1990). Barrow (1992) concluded that phosphate becomes more competitive over time since it is capable of slow sorption. Roy et al. (1986) found that the adsorption of arsenate was significantly reduced by competitive interactions with phosphate in three different soil types.

Adsorption of As on soil colloids depends on the adsorption capacity and behaviors of these colloids (e.g., clay, oxides/hydroxides of Al, Fe, Mn, calcium carbonates). In general, iron oxides/hydroxides are most commonly involved in the 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.

In this study, adsorption characteristics of arsenic (both arsenate and arsenite) on agricultural soils from three arsenic-contaminated and one uncontaminated areas has been assessed in batch experiments. Effect of soil composition and phosphate content and pH of water on As adsorption has also been assessed. Desorption of As from arsenic-rich paddy field soils have also been assessed under a wide range of conditions. Possible mobilization of As by reductive dissolution of iron oxyhydroxides has also been assessed in laboratory batch experiments. Results from this study provided useful insights into the mechanisms governing fate of As in paddy field soils.

2. Methodology

2.1 Site selection

Soil samples were collected from irrigated paddy fields of three As affected and one unaffected areas. The As affected areas were: (i) Sreenagar in the Munshiganj district, (ii) Nabinagar in the Brahmanbaria district, and (iii) Vanga in the Faridpur district. The unaffected area was Nazipur in the Noagaon district.

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 samples were collected by inserting into the soil, a 37.5 mm diameter PVC pipe sampler, about 750 mm 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.

2.3 Laboratory analysis

Arsenic and iron contents of soil: Total (aqua-regia extractable) and oxalate-extractable As and iron (Fe) contents of the soil samples were determined following the procedures 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) As and Fe, each segment of soil sample was dried in an oven at 110 ^{o}C for 24 h. After drying, the sample was ground and sieved before digestion. For digestion, 5 g of soil sample was weighed into a 500 mL flask to which 2.5 mL concentrated nitric acid and 7.5 mL concentrated hydrochloric acid were added. The suspension was kept overnight in the flask and then it was refluxed for 2 h, followed by dilution with deionized water to 500 ml, stirring for 5 minutes and filtering (0.80 μm) after cooling. The filtrate was stored in a plastic bottle for analysis of As using an AAS attached with a graphite furnace (Shimadzu, Japan, AA6800).

Determination of oxalate extractable arsenic and iron: Oxalate-extractable Fe provides an estimate of the amount of iron present as amorphous iron oxy-hydroxides, and oxalate extractable As provides an estimate of the quantity of As associated with the amorphous iron oxyhydroxides. 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 in a centrifuge tube and mixed for 2 hours in an end-over-end rotator. Then the tubes were then centrifuged for 20 to 25 minutes for solid-liquid separation. 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 As and iron using an AAS (Shimadzu, AA6800).

Analysis of water samples: Water used in laboratory batch experiments was analyzed for total As and Fe, pH, conductivity, ammonium, nitrate and phosphate. Arsenic concentration was determined with an AAS (Shimadzu, Japan, AA6800) attached with a graphite furnace. Iron concentrations were determined with flame emission atomic absorption spectrophotometry, using an AAS (Shimadzu, Japan, AA6800). Detection limits of arsenic and iron were 1 μg/L and 0.02 mg/L, respectively. pH was measured using a pH meter (HACH Co., USA), and conductivity with a conductivity meter. Ammonia, nitrate, and phosphate concentrations were determined with a spectrophotometer (HACH Co. USA, DR4000U). Ammonia was measured using the Nessler method, nitrate by the Cadmium Reduction method and phosphate by the Molybdenum Blue method. The detection limits of ammonia, nitrate and phosphate were 0.06 mg/L, 0.001 mg/L, and 0.01 mg/L, respectively.

Standard QA/QC protocol was followed throughout, including replicate analysis (1 in every 5 samples), checking of method blanks (1 in every 10 analysis) and standards (1 in every 10 analysis), and spike recovery (1 in every 20 analysis).

2.4 Batch adsorption experiments

Adsorption of arsenic and phosphate: Adsorption characteristics of As and phosphate on soil 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 concentrations of As (250 to 17000 μg/l).

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 As (arsenate or arsenite) or phosphate to each tube; e aqueous solutions were prepared by adding required quantities of arsenic stock solution to groundwater samples collected from Shahid Sarwardi Uddan pump station (adjacent to the Mazar of National Poet Kazi Nazrul Islam). The resulting soil concentration in tubes was 80 g/l, (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 solid-liquid separation, (v) measure As/phosphate concentration in the supernatant liquid collected from the tubes, (vi) estimate the amount of adsorbed As/phosphate by using the initial and final concentrations of As/phosphate in the aqueous solution in contact with the soil.

Effect of phosphate on adsorption of As: Effect of phosphate concentration on adsorption of As (arsenite) on paddy field soils from the four field sites was assessed in similar batch experiments (described above) by varying phosphate and arsenite concentration of the aqueous solution in contact with the soil (80 g/l). In these experiments, arsenite concentration was varied from 150 to 2500 μg/l; and for each arsenite concentration, phosphate concentration was fixed at 0.7, 2, 4, and 6 mg/l.

Effect of pH on adsorption of As: Effect of pH on adsorption of As (both arsenite and arsenate) 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, As concentration was fixed at 950 μg/l.

2.5 Desorption of As from soil

Desorption of As 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 above. After completion of the batch adsorption experiments (where As concentration was varied from 150 to 2,500 μg/l, and phosphate from 0.7 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 rotator. 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 As desorbed from the soil samples were calculated.

Desorption of As from As-rich paddy field soil: Desorption of As from paddy field soils over longer time periods was evaluated using soil from top 0-75 mm layer of soil cores collected from the paddy field sites in Munshiganj and Noagaon at the end of the irrigation season. The Munshiganj soil had a high As concentration (27.0 mg/kg), while the Naogaon soil had a low As concentration (1.7 mg/kg). One gram of soil sample was taken in a 15 ml centrifuge tube, to which 12.5 ml of As free (As < 1μg/l) groundwater was added. Then the centrifuge tubes were equilibrated in an end-over-end rotator for different equilibration periods varying 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 As desorbed from the soil samples was calculated.

2.6 Mobilization of As from As-rich paddy soil under reducing condition

Arsenic mobilization from paddy field soils was assessed in batch experiments using soil samples collected from the paddy fields in Munshiganj, Brahmanbaria, Faridpur and Naogaon districts at the end of the irrigation season. One gram of soil sample was taken in each of a series of 15 ml centrifuge tubes to which 12.5 ml aqueous solutions containing different concentrations of glucose (organic matter) were added. Glucose was used as a carbon source to create reducing condition in the centrifuge tubes. The tubes were then equilibrated for two different time periods (24 hours and 7 days) in an end-over-end rotator. The tubes were then centrifuged and the supernatant liquid was decanted. For one set of experiment with Munshiganj soil, glucose content was fixed at 0, 10, 15, 20 and 25 mg/l as carbon. These carbon concentration ranges (10 to 25 mg/l) are similar to those reported for river, eutrophic lake and marsh (Thurman, 1985). In other experiments, higher concentration of glucose (0, 3200, 6400 and 9600 mg/l as carbon) was used.

3. Results and discussion

3.1 General characteristics of water and soil samples

Characteristics of paddy field soil samples: Table 1 shows composition of soil samples collected from the four sampling sites, estimated from hydrometer analysis. It also shows the total (aqua-regia extractable) and oxalate-extractable As and Fe contents of the soil samples. The As and Fe concentrations of irrigation water used in the respective paddy fields are also shown in Table 1. Table 1 shows that silt comprises the major fraction of the soil samples from all four areas. Silt content varies from 70.5% for Naogaon soil to 84.6% for Munshiganj soil. Sand content was less than 10% for all samples, except for 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%) soils. These data do not show any significant correlation between soil composition and As content of soil.

Data presented in Table 1 suggest that As and Fe contents of irrigation water strongly influences the As and Fe contents of top soil of paddy field. The high As (366 μg/l) and Fe (7.64 mg/l) contents of irrigation water in Munshiganj appear to have contributed to the high As and Fe contents of Munshiganj top soil. In Naogaon, where irrigation water contains low As (<1 μg/l) and Fe (0.46 mg/l), the top soil was also found to have relatively low As and Fe.

Characteristics of water used in batch adsorption experiments: The groundwater used in batch adsorption-desorption experiments contained relatively low concentrations of As (<1 μg/l) and Fe (0.05 mg/l). The water also contained relatively low concentrations of ammonia (0.06 mg/l), chloride (5.6 mg/l), nitrate (0.30 mg/l) and phosphate (0.70 mg/l). The pH of the water was 6.88.

Table 1
Some selected soil parameters of different paddy field soil (top 0-75 mm) 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 (mg/kg)	27.0	9.5	5.3	1.7
Oxalate-extractable As (mg/kg)	18.6	6.5	3.9	0.8
Total Fe (g/kg)	42.4	22.2	24.3	15.5
Oxalate- extractable Fe (g/kg)	22.1	14.4	16.7	9.9
As in irrigation water (μg/l)	366	96	149	<1
Fe in irrigation water (mg/l)	7.64	3.62	3.38	0.46

3.2 Adsorption of As on paddy field soil

Figure 1 shows adsorption isotherms of arsenite on paddy field soils from four different field sites and Fig. 2 shows adsorption isotherms of arsenate on paddy field soils from Munshiganj and Naogaon. These figures show quantity of As partitioned to soil (expressed as mg/kg of soil) as a function of initial concentration of As (µg/l) in water. Figures 1 and 2 show that in all cases As partitioning to soil increases with increasing concentration of As in water. These figures show that arsenate adsorbs much more strongly onto soil than arsenite. For the same initial concentration of As, arsenate adsorption is almost 3 times greater than that of arsenite.

Figure 1 shows that for any initial concentration (up to 17000 µg/l), partitioning of arsenite to soil is highest for the Munshiganj soil and least for the Naogaon soil. Brahmanbaria and Faridpur paddy field soils lie in between. Figure 2 shows the same trend; arsenate adsorption on to Munshiganj soil is much higher compared to Naogaon soil. This trend is consistent with total and oxalate-extractable iron concentrations in the paddy field soil (see Table 1). Arsenic adsorption was higher on soil with higher total and oxalate extractable iron contents.

Figure 3 shows the correlation between calculated distribution coefficient (K_d) for arsenite adsorption (i.e., slope of adsorption curves in Fig. 1) 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 Fe contents of soils. Initial concentration of As of soil does not appear to have any influence on limiting adsorption of As onto soil. Also, other soil parameters including composition of soil do not appear to have any major influence on As partitioning to soil.

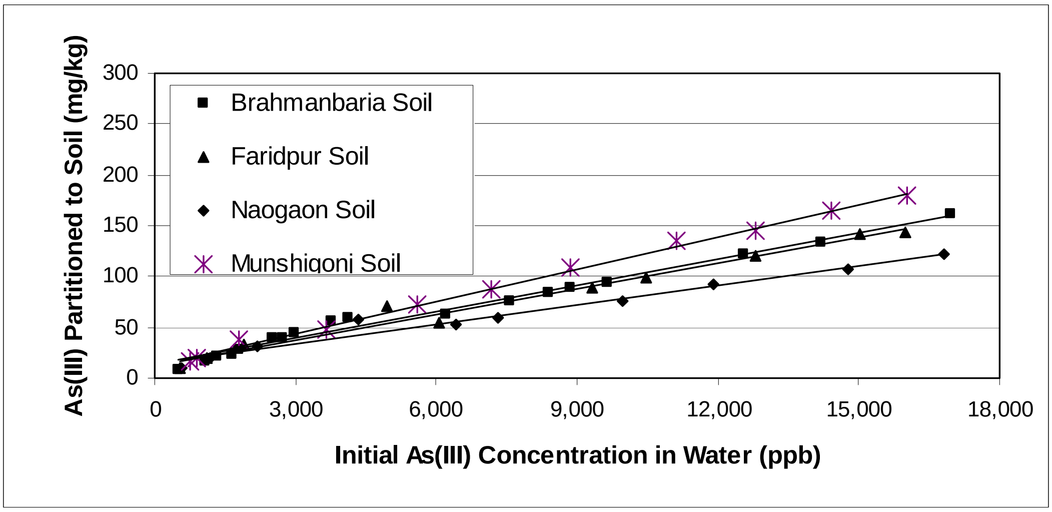

Fig. 1. Arsenic partitioning to paddy field soil in batch adsorption experiments as a function of initial As concentration in water (soil concentration: 80 g/l; pH of water: 6.8-7.0)

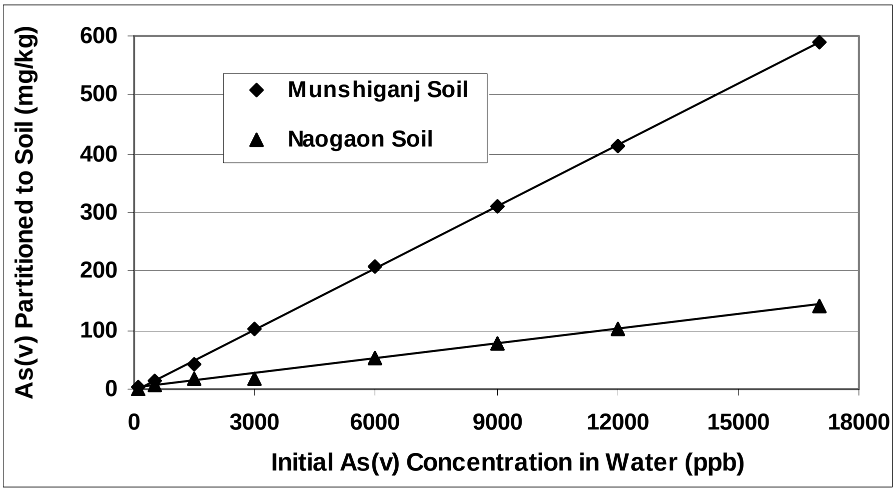

Fig. 2. Arsenic partitioning to paddy field soil (80 g/l) in batch adsorption experiments as a function of initial As concentration in water (soil concentration: 80 g/l; pH of water: 6.8-7.0)

Iron and aluminum oxyhydroxides are the principal adsorbents in natural soil. The increasing adsorption of As to soil with increasing soil Fe content suggests that iron oxyhydroxides are probably the principal adsorbent in soil. The relatively high adsorption densities of arsenite (approaching adsorption density of ~180 mg/kg for Munshiganj soil) observed in this study are not surprising considering the very low sorbate/sorbent ratios used in the batch experiments. If oxalate extractable iron (i.e., amorphous iron oxyhydroxide) is considered the principal adsorbent, then concentration of adsorbent varies from 0.176 mol Fe/kg of soil for Naogaon to 0.395 mol 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 (sorbent) concentration of $1.4\text{x}10^{-2}$ mol/l for Naogaon soil and $3.16\text{x}10^{-2}$ mol/l for Munshiganj soil (for batch experiments where concentration of soil was 80 g/l). Thus, available surface sites of iron alone are about two orders of magnitude higher than the highest concentration of As (sorbate) used in the batch experiments (17000 μg/l or $2.27\text{x}10^{-4}$ mol/l). It should be noted that Dittmar et al. (2005) found As concentration in the top soil of a paddy field in Munshiganj to be approaching 100 mg/kg.

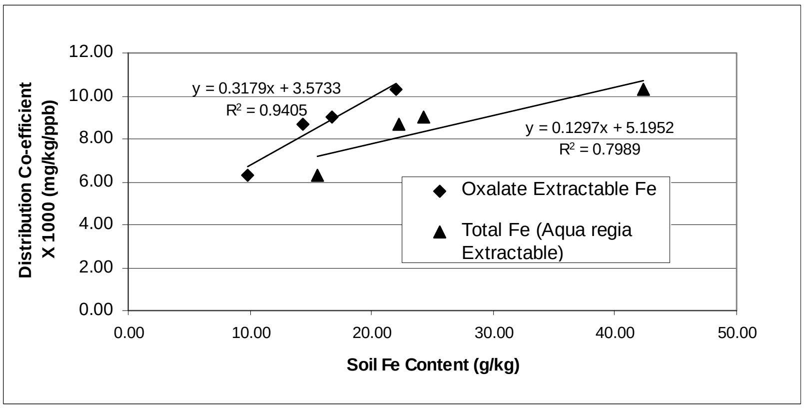

Fig. 3. Correlation between calculated distribution coefficient for As(III) adsorption and oxalate and aqua-regia extractable Fe concentrations in paddy field soil

3.3 *Effect of phosphate on arsenic adsorption*

Figures 4 and 5 show the As adsorption on Munshiganj and Faridpur paddy field soils, respectively in the presence of phosphate. These figures show that 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 As 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, the effect of phosphate on arsenite 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 (Saha, 2006), which have relatively less oxalate-extractable Fe contents (and hence have relatively less adsorption sites).

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 higher phosphate concentration varying from 2 to 42 mg/l was used; As (arsenite) concentration was fixed at 1000 μg/l. Figure 6 shows adsorption of arsenite on soil as a function of phosphate concentrations in water. Figure 6 shows that high concentration of phosphate could significantly reduce adsorption of arsenite 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.

In the batch adsorption experiments, arsenite was used since this is the principal form of As 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 As could compete more strongly 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.

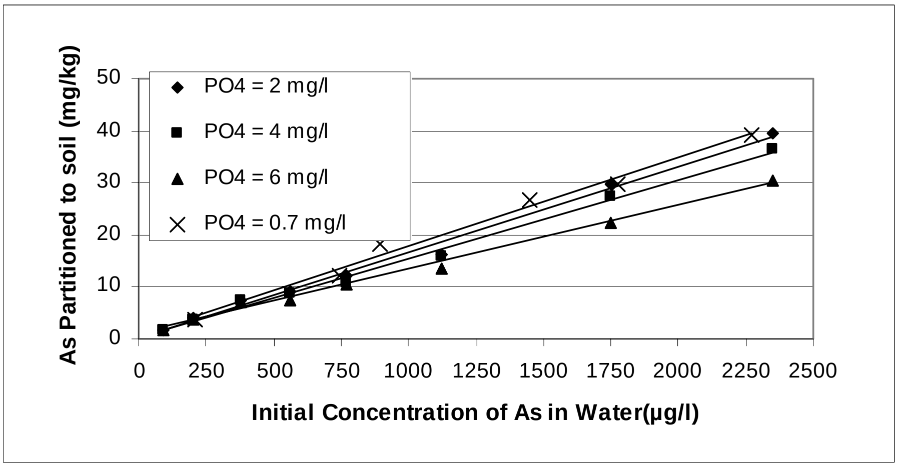

Fig. 4. Adsorption of As on paddy field soil from Munshiganj in the presence of phosphate (soil concentration: 80 g/l; pH of water: 6.8-7.0)

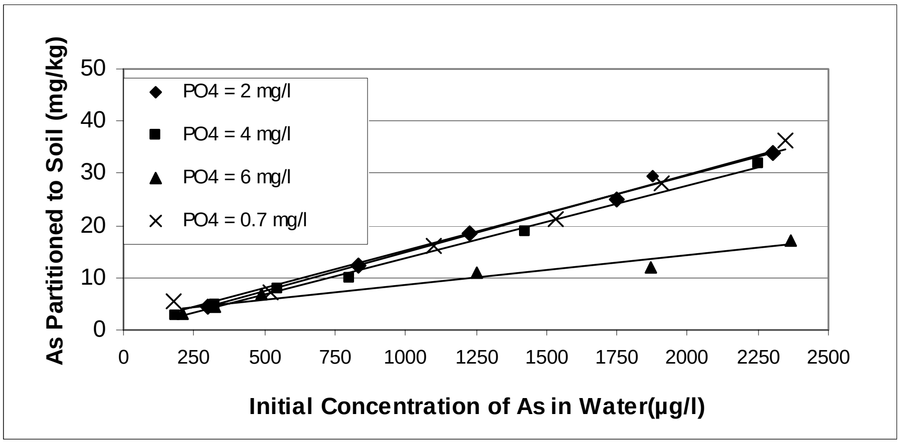

Fig. 5. Adsorption of As on paddy field soil from Faridpur in the presence of phosphate (soil concentration: 80 g/l; pH of water: 6.8-7.0)

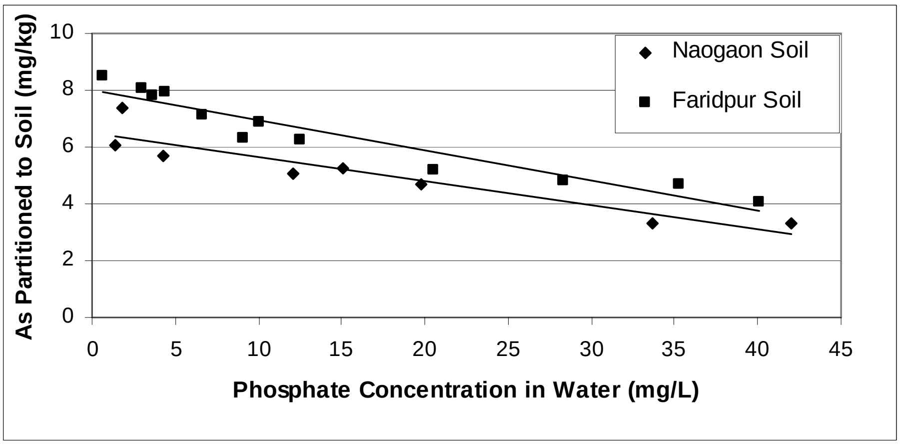

Fig. 6. Adsorption of As on paddy field soil from Faridpur and Naogaon in the presence of phosphate (soil concentration: 80 g/l; As(III) concentration: 1000 µg/l; pH of water: 6.8-7.0)

3.4 *Effect of pH on arsenic adsorption*

Effect of pH on adsorption of arsenate and arsenite on soil was assessed using top layer (0-75 mm) of paddy field soils from Munshiganj and Noagaon. Figure 7 shows adsorption of arsenic (expressed as mg/kg, dry weight basis) as a function of pH (final pH of water in contact with soil) for the Munshiganj 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 downward profile with the maximum adsorption occurring at pH between 4 and 6. For Naogaon paddy field soil, there was no significant variation of As adsorption in the neutral pH range; however, at higher pH (pH > 8), adsorption decreased.

Although arsenate adsorbs more strongly onto soil compared to arsenite, Fig. 7 shows that adsorption of arsenate is only slightly higher than that of arsenite for the Munshiganj soil. This is probably due to the very high concentrations of adsorption sites (i.e., soil) compared to the concentration of As in water in the batch experiments. Also, adsorption of both arsenite and arsenate was found to be significantly higher on the Munshiganj soil compared to that in the Noagaon soil. This is most likely related to the much higher oxalate extractable Fe concentration (22.1 mg/kg) in the Munshiganj soil compared to that for the Naogaon soil (9.9 mg/kg). The variation of As 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).

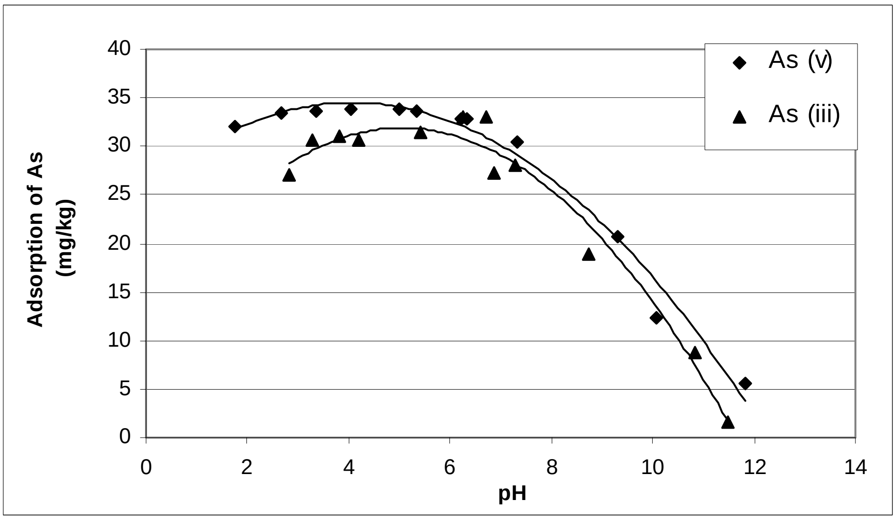

Fig. 7. Effect of pH on adsorption of As on Munshiganj paddy field soil (soil concentration: 80 g/l)

3.5 Desorption of As from soil used in adsorption experiments

Figures 8 and 9 show the quantity of desorbed As (expressed as mg/kg of soil, dry wt. basis) plotted against initial total As content of Munshiganj and Faridpur soils, respectively. These figures show that As desorption is more or less proportional to the initial As concentration in soil and the quantity of As desorbed in 24 hours is relatively small compared to the initial concentration of As in soil. In fact, the amount of As desorbed in 24 hours is small even compared to the amount of As that was adsorbed onto these soils during the adsorption experiments. Therefore, it appears that significant amount of As adsorbed onto paddy field soils from irrigation water may not desorb readily (i.e., within 24 hours) to water during inundation of the paddy fields in the rainy/flood season. However, since desorption kinetics are usually slow, more As is likely to desorb from soil under longer equilibration times. The highest desorption of As (~2.6 mg/kg) was obtained for the Munshiganj soil; maximum desorption from the Naogaon and Faridpur soils was found to be about 1 mg/kg (Saha, 2006).

Figures 8 and 9 show that for any particular initial soil As concentration, As desorption is higher from soils which were earlier subjected to batch experiments in the presence of higher phosphate concentrations. These soils subjected to adsorption experiments with higher phosphate concentrations (e.g., 6 mg/l) had higher soil-phosphate contents. Therefore, the observed 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.

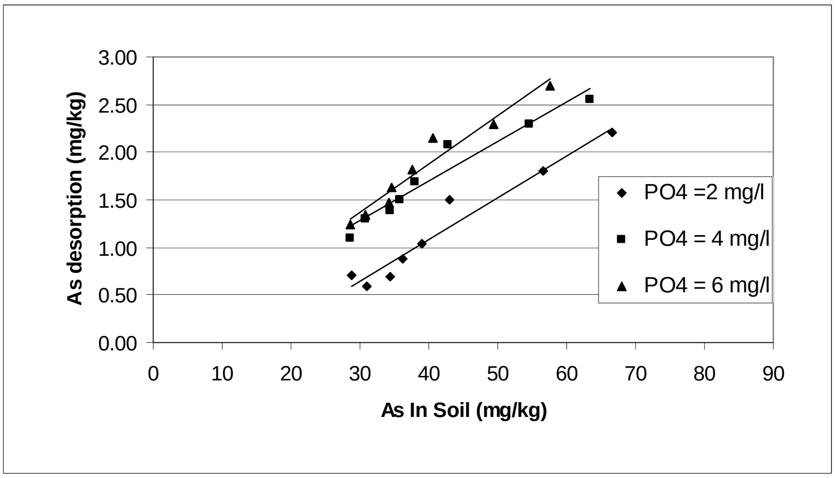

Figure 8: Arsenic desorption in 24 hrs from Munshiganj soil [soils undergoing As adsorption with 2 mg/l (◆), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

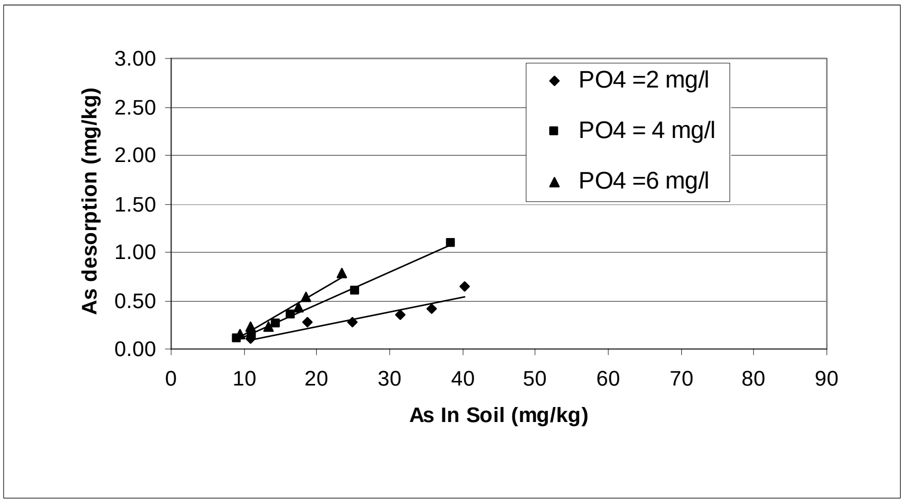

Figure 9: Arsenic desorption in 24 hrs from Faridpur soil [soils undergoing As adsorption with 2 mg/l (◆), 4 mg/l (■), and 6 mg/l (▲) phosphate] as a function of total initial concentration of Arsenic

3.6 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. Figure 10 shows desorption of As [expressed as mg As/kg of soil (dry wt. basis)] from Munshiganj and Naogaon soils as a function of time. It shows that desorption of As from Munshiganj soil (which had an initial As concentration of 27.0 mg/kg) increased with time and it appears that even more As would desorb from soil under longer equilibration periods. Thus, significant amount of As could be released from As-rich paddy field soils by desorption during the long inundation (up to about 3 months) by rain/floodwater during the wet season. On the other hand, desorption of As from the Naogaon paddy field soil, which had relatively low initial As concentration (1.7 mg/kg), was insignificant and did not change significantly with time.

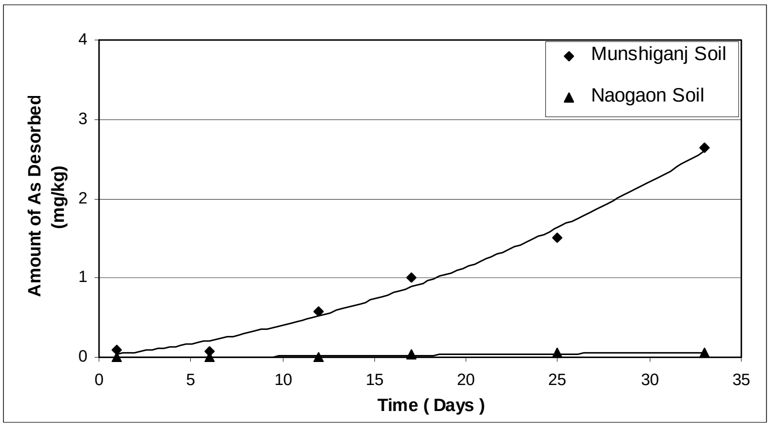

Fig. 10. Desorption of As (expressed as mg/kg of soil) from paddy field soils collected from Munshiganj and Naogaon as a function of time (soil concentration: 80 g/l; pH of water: 6.8-7.0)

3.7 Mobilization of As from As-rich paddy soil under reducing condition

Mobilization of As from paddy field soils under reducing condition was evaluated in batch experiments where a carbon source (glucose) was added to create reducing condition. Figure 11 shows partitioning of As to water from Munshiganj paddy field soils at the end of 24 hours and 7 days in batch experiments where glucose concentration was varied from 0 to 25 mg/l (as carbon). It shows relatively low mobilization of As from natural soil within the 24-hour equilibration period. This could be due to the fact that significant reductive dissolution of iron oxyhydroxides does 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 glucose (as C). In the absence of glucose (carbon source), 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.

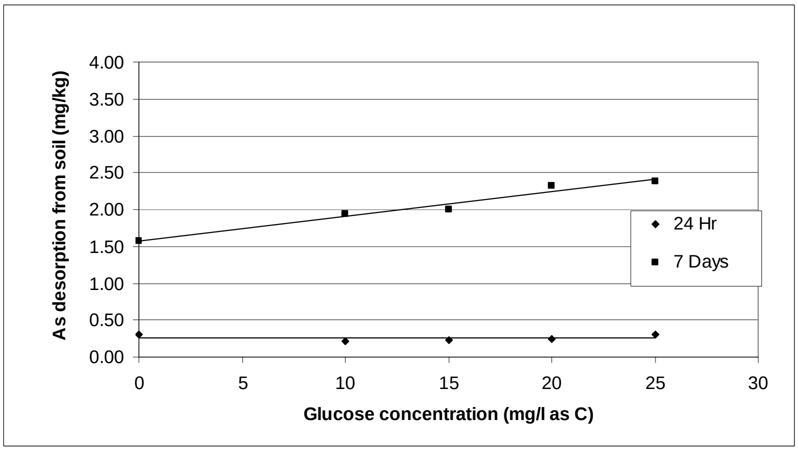

Fig. 11. Mobilization of As from natural Munshiganj paddy field soil in presence of a carbon source (soil concentration: 80 g/l; pH of water: 6.8-7.0)

Figures 12 to 14 show mobilization of As from paddy field soils from Munshiganj, Faridpur and Naogaon, respectively in batch experiments where glucose concentration was varied from 0 to 9600 mg/l (as C). As before (Fig. 11), relatively low mobilization was observed at the end of 24 hours, but relatively higher mobilization was observed at the end of 7 days. Arsenic mobilization of about 4 mg/kg was observed for the Munshiganj soil, which accounts for about 20% of the oxalate-extractable As initially present in the soil. Figure 12 shows that about 2 mg/kg of this As has been mobilized in the absence of the carbon source, which could be attributed to desorption of As from soil.

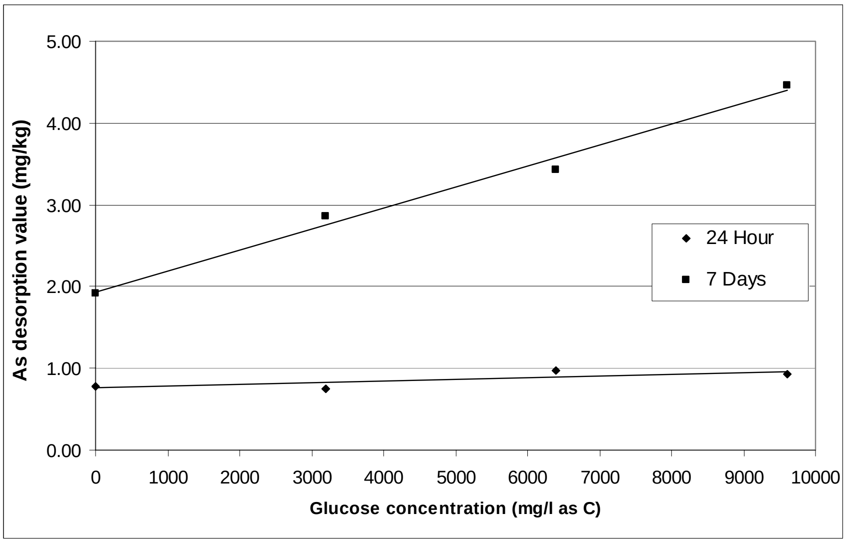

Fig. 12. Mobilization of As from Munshiganj paddy field soil in presence of relatively higher concentration of organic carbon (soil concentration: 80 g/l; pH of water: 6.8-7.0)

For Faridpur (and also Brahmanbaria) soil, maximum mobilization observed was about 3 mg/kg (Figs. 13; Saha, 2006), a significant part of which (about 1 mg/kg) could be attributed to direct desorption from soil. Oxalate-extractable As in soils of Faridpur and Brahmanbaria were 6.5 and 3.9 mg/kg, respectively (Table 1). Thus, a significant fraction of the oxalate-extractable As was mobilized from these soils within 7 days. Despite significant variation in 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). Very small amount of As was mobilized from the paddy field soil from Naogaon (Fig. 14), which had the least oxalate-extractable As (1.7 mg/kg). As shown in Fig. 10 desorption of As from the Naogaon paddy field soil was also insignificant even under long equilibration periods (up to 33 days).

Figures 11 and 12 demonstrate the effect of organic carbon concentration on the mobilization of As from soil. Figure 11 shows that As mobilization from 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 11 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 have a dramatic influence on mobilization of As from soil within the 7-day equilibration 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.

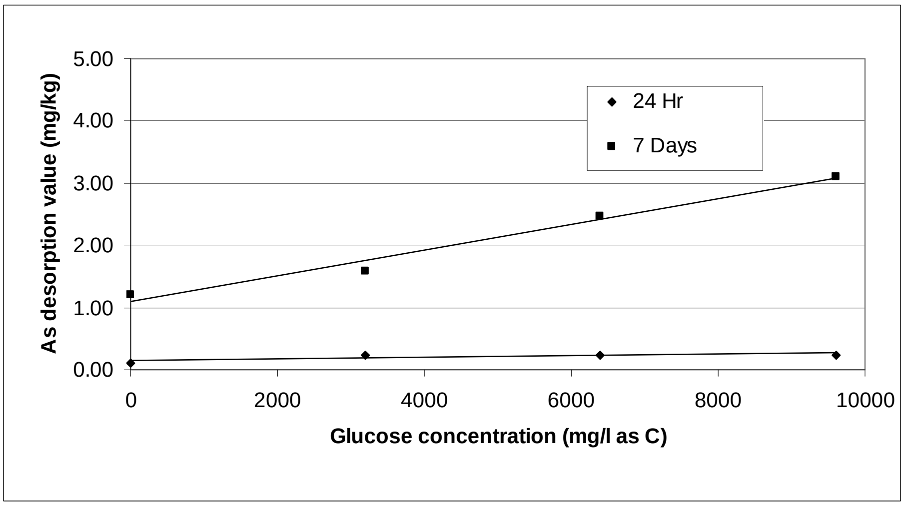

Figure 13. Mobilization of As from Faridpur paddy field soil in presence of organic carbon (soil concentration: 80 g/l; pH of water: 6.8-7.0)

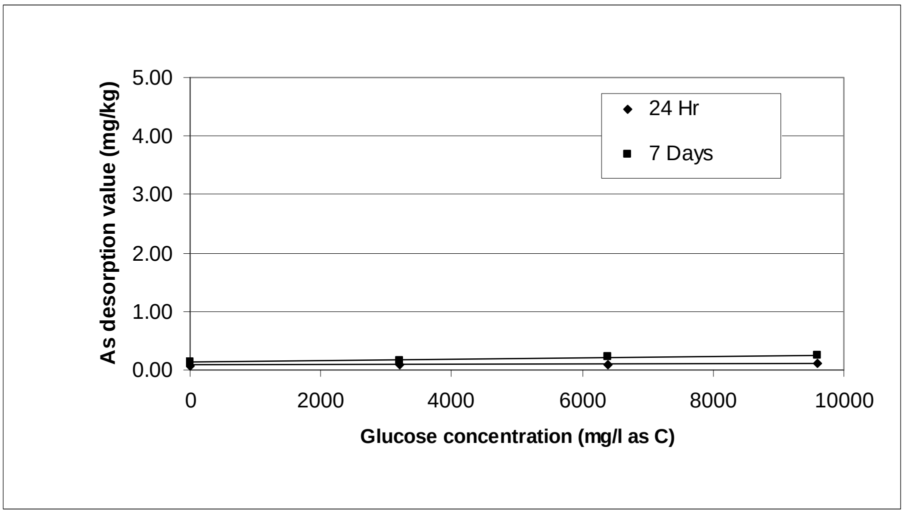

Figure 14. Mobilization of As from Naogaon paddy field soil in presence of organic carbon (soil concentration: 80 g/l; pH of water: 6.8-7.0)

4. Conclusions

Adsorption of both arsenite and arsenate on paddy field soils has been found to increase 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 increase with increasing iron concentration of irrigation water. Thus, As adsorption to paddy field soil depends not only on the characteristics of soil, but also on the characteristics (e.g., iron content) of irrigation water. 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. Since pH of natural groundwater in Bangladesh is usually slightly acidic to neutral, pH is not likely to have any significant effect on variation of As adsorption on paddy field soils in different regions of the country. Arsenic adsorption by soil may play an important role in reducing As availability to plant and its introduction into the food chain.

Results from this study suggest that significant As associated with paddy field soil at the end of the irrigation season 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 As concentrations in soil to reach toxic levels.

Since paddy field soils are capable of accsmulating very high concentrations of As from As contaminated irrigation water that could potentially affect crop yield, the Government should take steps to monitor As concentration of paddy field soils in the As affected areas. Where feasible, farmers may be encouraged to use As-free groundwater from the deeper aquifer in agriculture instead of As-contaminated groundwater from the shallow aquifer. Necessary supportS should be provided by the Government in this regard.

References

Ahmed, Z. U. (2005). Water-Soil-Crop Arsenic Interrelationships. In: Proceedings of Symposium on Behavior of Arsenic in Aquifers, Soil and Plants: Implication for Management, Organized by CIMMYT, CU, TAMU, USGS, and GSB, Dhaka, Bangladesh, January 2005.

Ali, M. A. (2006). Arsenic Contamination of Groundwater in Bangladesh, *International Reviews for Environmental Strategies*, 6(2), 329-360.

Ali, M. A., Badruzzaman, A. B. M., Jalil, M. A. Hossain, M. D., Ahmed, M. F., Kamruzzaman, M., Rahman, M. A. and Masud, A. A., (2003). Fate of Arsenic extracted with ground water, In: Proceedings of the BUET-UNU International Symposium on Fate of Arsenic in the Environment, Ahmed, M. F., Ali, M. A. and Adeel, Z. eds., 19, Dhaka, February 2003, 7-20.

Barrow, N.J. (1992). The effect of time on the competition between anions for sorption, J. Soil Sci. 43:421–428.

Dittmar, J., Voegelin , A., and Kretzschmar , R. (2005). Arsenic contamination of paddy soil through irrigation water in Bangladesh : Field evidence and investigation of relevant processes, 3rd Swiss Geoscience Meeting, Zurich, Switzerland.

Dzombak D.A., Morel F.M.M. (1990). Surface complexation modeling: Hydrous ferric oxide. NY: John Wiley.

Fendorf, S., Eick, P. Grossl M.J., and D.L. Sparks. (1997). Arsenate and chromate retention on goethite: I. Surface stru.cture. *Environ. Sci. Technol.* 31:315–320.

Saha, G. C. (2006), "Accumulation of Arsenic in Agricultural Soil and Selected Crops", Ph.D. Thesis, Department of Civil Engineering, Bangladesh Universith of Engineering and Technology (BUET), Dhaka 1000, Bangladesh, February 2006.

Goldberg, S. and Glaubig, R.A. (1988). Anion sorption on a calcareous, montmorillonitic soil-arsenic, *Soil Sci. Soc. Am. J.* 52:1297–1300.

Grossl, P.R., Eick, M. Sparks, D.L. Goldberg, S. and Ainsworth, C.C. (1997). Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique, *Environ. Sci. Technol.,* 31:321–326.

Huq S. M. I., Ahmed K. M., Suktana N. and Naido R.(2001). Extensive Arsenic Contamination of Groundwater and Soils of Bangladesh, In: Proceeding of Arsenic in The Asia Pacific Region Workshop, Adelaide, Managing Arsenic for the Future, 94-96.

Jahiruddin, M., Islam, M. R., Shah, M. A. L., Rashid, M. A., Rashid, M. H., and Ghani, M. A.(2005). Arsenic in the Water-Soil-Crop Systems: PETRRA-BRRI-BAU-AAS Study", In: Proceedings of Symposium on Behavior of Arsenic in Aquifers, Soil and Plants: Implication for Management, Organized by CIMMYT, CU, TAMU, USGS, and GSB, Dhaka, Bangladesh, January 2005.

Keon N. E., Swartz C. H., Brabander D. J., Harvey C., and Hemond H. F. (2001). Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ. Sci. Technol.* 35, 2778–2784.

Manning, B.A. and Goldberg, S. (1996). Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals, *Soil Sci. Soc. Am. J.*, 60:121–131.

Meharg, A. A. and Rahman, M. M. (2003). Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. Environ *Sci Technol.*, 37, 229 –34.

Parfitt, R.L. (1978). Anion adsorption by soils and soil materials, *Adv. Agron.*, 30:1–50.

Persson, P., Nilsson, N. and Sjoberg, S.(1996). Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface, *J. Colloid Interface Sci.*, 177:263–275

Roberts, L. C., Dittmar, J., Saha , G. C., Hug , S. J., Voegelin , A., Kretzschmar , R., Ali , M. A. and Badruzzaman , A. B. M. (2006). Spatial heterogeneity of Arsenic input to paddy soil through irrigation water in Bangladesh, Accepted for International Symposium on Environmental Sustainability (ISES), Dhaka, Bangladesh, February 2006.

Roy, W. R., Hassett, J. J. and Griffin, R. A. (1986). Competitive interactions of phosphate and molybdate on arsenate adsorption, *Soil Sci.*, 142, 203–210.

Sadiq, M. (1997). Arsenic Chemistry in Soils: An Overview of Thermodynamic Predictions and Field Observations, Water, Air, and Soil Pollution, 93: 117-136, 1997.

Saha, G. C. and Ali, M. A. (2006). Dynamics of Arsenic in Agricultural Soils Irrigated with Arsenic Contaminated Groundwater in Bangladesh, submitted for publication in the Special Issue of the *Science of the Total Environment: Arsenic in the Environment: Biology and Chemistry.*

Sun, X., and Doner. H.E. (1996). An investigation of arsenate and arsenite bonding structures on goethite by FTIR, *Soil Sci.* 161:865–872.

Tejedor-Tejedor, M.I., and Anderson. M.A. (1990). Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility, *Langmuir* 124:79–110.

Thurman, E. M. (1985). Organic Geochemistry of Natural Waters, Martinus Nijhoff/Dr W. Junk Publishers.

World Development Report. Equity and Development, A copublication of The World Bank and Oxford University Press, 2006.

Xu, H., Allard, B. and Grimvall. A. (1988). Influence of pH and organic substance on the adsorption of As(V) on geological materials, *Water Air Soil Pollut.*, 40:293–305.