

## DESORPTION OF ARSENIC IN SOILS AS AFFECTED BY RESIDENCE TIME, SOLUTE CONCENTRATION AND SOIL PROPERTIES

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### ABSTRACT

A laboratory batch experiment was conducted using calcareous (Ishurdi series) and non-calcareous soils (Amjhupi and Dhamrai series) to evaluate the desorption pattern of arsenic under three *viz.*, 5, 10 and 20  $\mu\text{g ml}^{-1}$  imposed treatments of arsenic. The desorption was observed at 2, 4, 6, 8 and 24 hour residence time with arsenic solution followed by 2, 4, 6 and 24 hour of extraction to release the sorbed arsenic with 0.1 N EDTA solution. Average percent desorption of arsenic decreased with increasing residence time from 2 hour to 8 hour of arsenic sorption irrespective of the calcareousness of the soil. 87.21 % of the sorbed arsenic desorbed back into the solution for the 2 hour sorbed one and the minimum of 3.88 % desorbed for the 8 hour sorption. Quantity wise, a maximum of 9.49  $\mu\text{g g}^{-1}$  As was found to have desorbed from soils having 24 hour of sorption that amounted to 11.4 % of the amount sorbed. Desorption of As was more in the non-calcareous Dhamrai soil. Although the highest imposed treatment of arsenic (20  $\mu\text{g ml}^{-1}$ ) caused the highest desorption, the desorptivity of the element however, did not vary widely with solute concentration.

**Keywords:** Calcareous, non-calcareous, sorption, desorption, desorptivity, residence time.

### INTRODUCTION

It is now well recognized that ingestion of arsenic contaminated groundwater is the major cause of arsenic poisoning in the country (Imamul Huq *et al.*, 2001a). A few studies have revealed that the average background concentration of As in Bangladesh is much below 10 mg/kg soil (Imamul Huq *et al.*, 2001 b; Ali *et al.*, 2003). However, in some areas the concentration has been found to be as high as 80 mg/kg soil. The soil As varies both spatially and vertically. The soil formation and the aquifer characters control the spatial variation, while the vertical distribution is controlled by the clay contents (Imamul Huq and Naidu, 2005). The load of As in soil has been calculated to be as high as 5.5 kg/ha/yr through irrigation for certain crops (Imamul Huq and Naidu, 2003). Irrigating with As contaminated water raises the concentration of its buildup in soil and subsequent entry into the cultivated crops (Correll *et al.*, 2006). Adsorption-desorption of arsenic onto iron oxide surfaces are important controlling reactions in the subsurface because iron oxides are widespread in the hydro-geologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron oxide surfaces in acidic and near neutral pH conditions. Desorption of arsenate is favored at higher (i.e. alkaline) pH values (Ali and Ahmed, 2003). In Bangladesh arsenic-rich iron oxyhydroxides present in aquifer materials appear to be the primary source of arsenic in groundwater. In the subsurface environment, adsorption-desorption of arsenic onto iron oxyhydroxides is an important mechanism controlling its mobility. Presence of ligands, which may compete with arsenic for adsorption sites on iron

oxyhydroxides, e.g., phosphate, silicate and sulfate can also influence the desorption or mobility of arsenic in the subsurface, if present in large enough concentrations (Ali and Ahmed, 2003). In the long term, it is the ability of sorbed arsenic to desorb back into solution that will control arsenic bioavailability and mobility. In Bangladesh, the soils developed on Gangetic alluvium have been found to contain relatively higher amount of arsenic (Imamul Huq and Naidu, 2003). Moreover, the soils of Gangetic alluvium are in general have pH values above 7.0 with many soils being calcareous in nature (having free  $\text{CaCO}_3$ ). There is relatively little information on the desorption of arsenic from soils. Therefore, this study was undertaken to find out the kinetics of arsenic desorption along with time and soil variables; the time variable being the residence time and the soil variable being calcareousness of the soils.

### MATERIALS AND METHODS

Three soils were selected for the study. Two of the soils represented the Gangetic alluvium- one calcareous and the other one non-calcareous, while the third soil, also a non-calcareous, represented the Brahmaputra alluvium. The three soils represented the Amjhupi (89°19.764' E and 23°20.247' N), Ishurdi (89°13.235' E and 23°11.118' N) and Dhamrai (90°11.250' E and 23°54.116' N) series respectively. The soil samples were collected and prepared and the common physical, chemical and physicochemical properties of the three soil series were analyzed following the standard methods as described by Imamul Huq and Alam (2005).

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Table 1: Moisture content, Particle size distribution and textural class of the soils studied

Soil Series	Moisture Content %	% Sand	% Silt	% Clay	Textural Class
Amjhupi	5.6	37.4	34.5	28.1	Clay loam
Ishurdi	9.0	35.1	33.0	31.9	Clay loam
Dhamrai	1.6	34.9	61.1	4.7	Silt loam

Table 2 Various chemical and physicochemical properties of the soils

Soil Series	pH	Organic Carbon %	Organic Matter %	Total N %	Total As, mg/kg <sup>-1</sup>	EDTA As, mg/kg <sup>-1</sup>	Water soluble As, mg/kg <sup>-1</sup>	Free CO <sub>3</sub> <sup>-2</sup> %	CEC meq %	Exchangeable Cations meq %			
										Ca	Mg	Na	K
Amjhupi	6.89	0.47	0.81	1.08	4.2	0.64	0.01	N.D.	35.4	22.5	7	0.6	0.4
Ishwardi	7.73	0.62	1.1	0.57	5.75	0.85	0.03	9.3	41.6	31.3	4.5	0.5	0.4
Dhamrai	7.08	0.22	0.38	0.3	3.62	0.32	N.D.	N.D.	15.4	8.3	2.5	0.2	0.2

N.D. = not detected

The desorption studies were carried out in batch mode. There were three treatment rates (1:5 soil: solution ratio) for arsenic solution- 5, 10 and 20  $\mu\text{g ml}^{-1}$  along with a control (0  $\mu\text{g ml}^{-1}$ ) which was made from NaAsO<sub>2</sub>. All treatments were replicated three times. The tubes were shaken on a reciprocating shaker (50 turns/min) for two hours and were allowed to equilibrate at a constant temperature (room temperature) for 2, 4, 6, 8 and 24 hours respectively. Following the equilibration period, the suspensions were immediately centrifuged at 2000 rpm (2000 g) over 5-50 minutes, filtered and the residues were collected (Garcia-Sanchez *et al.*, 1999; Joardar *et al.*, 2005). Desorption was done for each time period of sorption. The treated residue of the soils in the centrifuge tubes were shaken with 0.1N EDTA (in 1: 5 ratio) (Page *et al.*, 1982), allowed to equilibrate at a constant room temperature for 2, 4, 6 and 24 hours, centrifuged, filtered and were analysed for As with a Varian Spectraa-220 Atomic Absorption Spectrophotometer. All assays were carried out in triplicate and only the mean values are presented in the text.

Desorption of arsenic by the soils (Y) was calculated using the following formula:

$$Y = (\text{Eq. Conc.} \times V) / W$$

Where,

Y = Amount of desorbed material in the solution ( $\mu\text{g ml}^{-1}$ )  
 Eq. Conc. ( $\mu\text{g ml}^{-1}$ ) = (Machine reading  $\times$  Dilution factor) / 1000

V = Volume of extraction for the soils (ml).

W = Mass of the soil taken (g).

All data were subjected to statistical analysis by MINITAB package; regression analyses were performed and the values of regression coefficients are discussed in the text.

## RESULTS AND DISCUSSION

The common physical, chemical and physicochemical properties of the three soil series were analyzed and the results of the analyses are presented in the tables- 1 and 2. Desorption of arsenic from the three soils were conducted individually for each time period of sorption *i.e.*, for 2, 4, 6, 8 and 24 hours. The desorption included the 2, 4, 6 & 24 hour of extraction to desorb As from the soils. Desorption of As from the three soils with increasing As treatment for each of the residence times are presented in Fig. 1, 2, 3, 4 and 5. The percent desorption of each soils are also presented in Fig. 6. Desorption of As has been found to differ significantly from one soil to another, with respect to 'Residence time', 'Concentration of arsenic in solution' and 'Variation in the calcareousness of the soils'.

*Effect of residence time:* Desorption of arsenic in general, was high initially and it decreased gradually with increasing extraction time. On the other hand, with residence time from 2 to 24 hours, desorption decreased. The results showed that desorption values were higher from soils subjected to shorter periods of sorption than those subjected to longer period of sorption. This could perhaps happen because of lesser chemisorption.

After 2 hour sorption maximum desorption of  $7.88 \mu\text{g g}^{-1}$  As has occurred within 2 hour of extraction and then with increasing extraction time it decreased. For all treatments the highest values of desorption were 4.81, 6.99 and  $7.88 \mu\text{g g}^{-1}$  at 5, 10 and  $20 \mu\text{g ml}^{-1}$  which were obtained for 2 hour desorption period for Ishurdi soil. When the sorption period was increased from 2 hour to 4 hour a significant amount of As remained sorbed on the soil solids preferably by ion exchange or by complexation. This could be the reason for decreased desorption of As from the previous 2 hour desorption results. After four hours of incubation with arsenic maximum desorption of 1.08, 5.03 and  $9.36 \mu\text{g g}^{-1}$  were obtained at 5, 10 and  $20 \mu\text{g ml}^{-1}$  respectively. Arsenic sorbed after 6 hour showed a lower amounts of desorption compared to the desorption after 2 hour sorption and there is a slight variation with the desorption of 4 hour residence time. The highest desorption value of  $4.35 \mu\text{g g}^{-1}$  was observed for Ishurdi soil at  $20 \mu\text{g ml}^{-1}$  and at 6 hour sorption and 24 hour desorption period. After 8 hour of sorption, desorption decreased markedly than the 2 hour sorption results where the maximum desorption observed was  $4.34 \mu\text{g g}^{-1}$  at  $10 \mu\text{g ml}^{-1}$  and 24 hour desorption time. The arsenic in solution increased when the residence time with arsenic as well as the desorption time was increased to 24 hours. The maximum value of desorption was  $9.49 \mu\text{g g}^{-1}$  for 24 hour time lag and at  $20 \mu\text{g ml}^{-1}$  for Ishurdi series. On the other hand, the average percent desorption of arsenic was the highest after allowing 2 hour contact whereas the desorption decreased to a minimum after 24 hour residence time. Maximum desorption of 87.21 % occurred at the highest dose of arsenic and at the least residence time. Although the minimum desorption of arsenic was 3.88 % at 8 hour residence yet, desorption decreased markedly after 24 hour in all the soils. The regression analysis showed that after 2 hour sorption the most significant desorption has occurred for the Dhamrai soil ( $R^2 = 0.9937^{**}$ ) followed by the Amjhupi soil ( $R^2 = 0.9816^{**}$ ) both of which are non-calcareous. This indicates that, the desorptivity of non-calcareous soil is higher than the calcareous soil. On the other hand, after 4 hour ( $R^2 = 0.98^{**}$ ), 6 hour ( $R^2 = 0.9899^*$ ) or 8 hour ( $R^2 = 0.9595^*$ ) residence time with arsenic, the most significant desorption values were obtained for Ishurdi series which is a calcareous soil. After 24 hour of sorption the temporal variation of desorption was not so significant except in one case for Dhamrai soil ( $R^2 = 0.947^*$ ). This indicates that, after certain period of residence time some arsenic might become chemically fixed with the soil colloids and they would not revert back to the solution.

Some previous studies showed that, arsenic is not easily desorbed or removed. Johnston and Barnard (1979) tested many soil extractants, but none of them removed more than 80% of the As after 18 hours of shaking; similar observations have also been made by Waychunas *et al.* (1993) and Woolson *et al.* (1973). In the present study

similar phenomenon has also been observed which indicated that some arsenic might become bound as sorbed arsenic. Manning and Goldberg (1997) observed that – desorption of As from As treated layer silicates with  $1\text{mM PO}_4$  indicated that a portion of bound As was not extractable. Study by O'Reilly *et al.* (2001) described that, initially desorption of As was quite rapid with > 35% of the total adsorbed. As being desorbed within 24 hour at pH 6.0 and after the initial rapid desorption, only a small amount of additional desorption occurred at longer times. A significant amount of As remained bound to the goethite after 5 month of desorption.

*Concentration of arsenic in solution:* Desorption of arsenic increased with increasing As concentration in solution irrespective of the soil or of the residence time for sorption. In most cases the maximum desorption occurred for  $20 \mu\text{g ml}^{-1}$  As treatment although the increases in desorption were not large enough with the increase in As concentration. At  $5 \mu\text{g ml}^{-1}$  treatment, the maximum desorption was  $4.81 \mu\text{g g}^{-1}$  from the calcareous soil (Ishurdi series) whereas the maximum desorption was  $6.99 \mu\text{g g}^{-1}$  at  $10 \mu\text{g ml}^{-1}$  and  $9.49 \mu\text{g g}^{-1}$  at  $20 \mu\text{g ml}^{-1}$  from the same soil. On the contrary, the maximum averages percent desorption were higher for the Dhamrai soil which is a non-calcareous soil. Maximum of 87.21 %, 83.7 % and 82.5 % desorption was observed at 20, 10 and  $5 \mu\text{g ml}^{-1}$  for the Dhamrai, Ishurdi and Amjhupi soils respectively.

*Variation in the soil properties:* Arsenic desorption varied in calcareous and non-calcareous soils. In general, total desorption was at its highest for the calcareous soil i.e. the Ishurdi soil when the sorption time was 2, 4, 6, 8 or 24 hours (Fig. 1 to 5) whereas the most significant desorption with time has occurred from the Dhamrai soil ( $R^2 = 0.9937^{**}$ ). It needs to be mentioned here that the Ishurdi soil contains free carbonate (9.3 %) which was absent for the non-calcareous soils, and this free carbonate might have an effect on the desorption of arsenic. Previous findings showed that, desorption of arsenate is favored at higher (i.e. alkaline) pH values (Ali and Ahmed, 2003). As Ishurdi series has the highest pH (7.73) value among the three soils it desorbed the maximum amounts of arsenic. The total desorption of As followed the trend: Ishurdi > Amjhupi > Dhamrai. On the other hand, percent desorption of the total sorbed arsenic was different from the total desorption results. The maximum desorptivity was observed in the Dhamrai (87.21 %) followed by the Ishurdi (83.7 %) and Amjhupi series (82.51 %) soils after 2 hour of residence time (Fig. 6) and the trend of desorption was: Dhamrai > Ishurdi > Amjhupi.

The physicochemical properties of the three soil series showed that Dhamrai soil has the lowest amount of clay content (4.7 %) which might have a great influence on desorption. In the present work it was observed that, the

greater the clay content the lesser was the percent desorption. On the contrary, organic matter content might also have an influence on arsenic desorption. Dhamrai soil has the least amount of organic matter (0.38%) than either the Ishurdi (1.1%) or the Amjhupi (0.81%) soils.

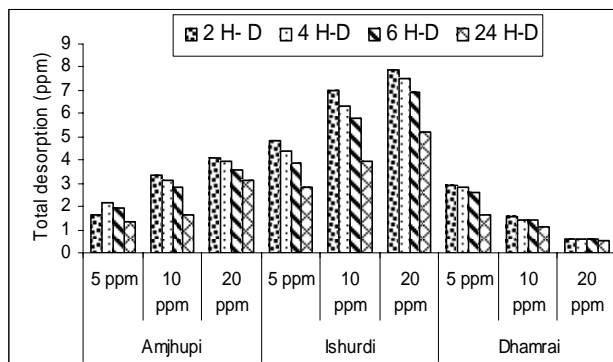


Fig. 1 Desorption of As after 2 hour sorption (2H -D= desorption after 2 hour; 4 H-D = desorption after 4 hour; 6H-D= desorption after 6 hour & 24 H-D = desorption after 24 hour).

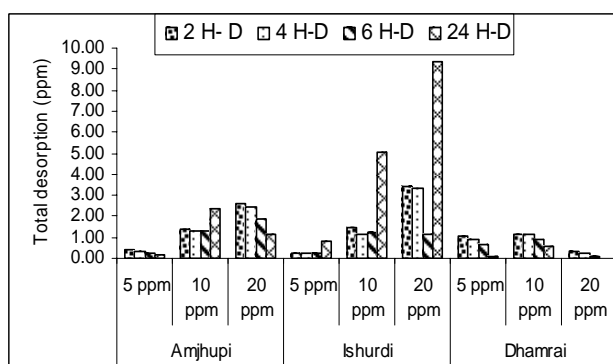


Fig. 2 Desorption of As after 4 hour sorption.

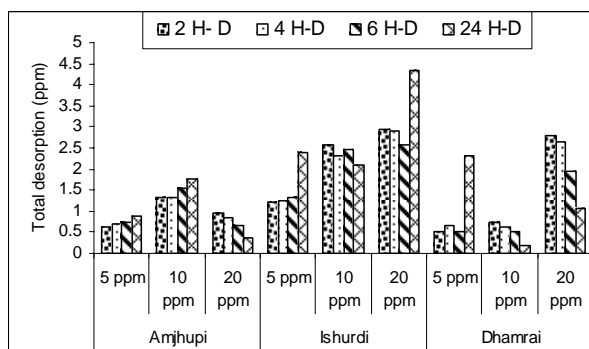


Fig. 3. Desorption of As after 6 hour sorption.

The findings showed that at longer residence time for arsenic sorption the desorption is reduced. At higher solute concentration desorption increased. Soil properties

especially the calcareousness of the soil might have a bearing on the release of the portion of sorbed arsenic. The phytoavailability of arsenic in soils could be related to the desorptivity of soils and needs further study.

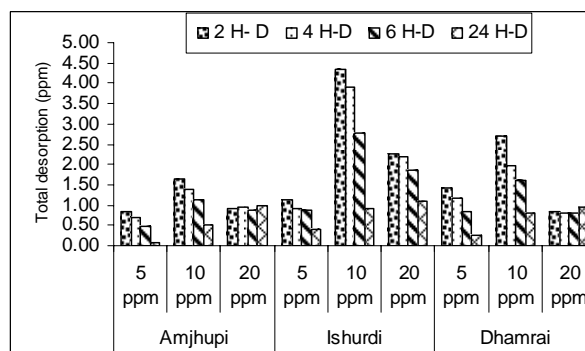


Fig. 4 Desorption of As after 8 hour sorption.

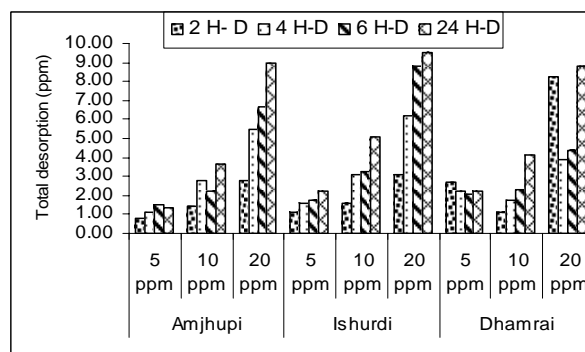


Fig. 5 Desorption of As after 24 hour sorption.

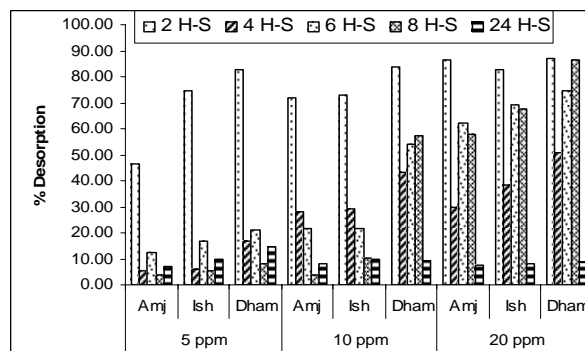


Fig. 6. Percent Desorption of As by the three soils with increasing treatment for different residence time (2H -S= sorption after 2 hour; 4 H-S = sorption after 4 hour; 6H-S= sorption after 6 hour, 8H-S= sorption after 8 hour & 24 H-S = sorption after 24 hour)

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