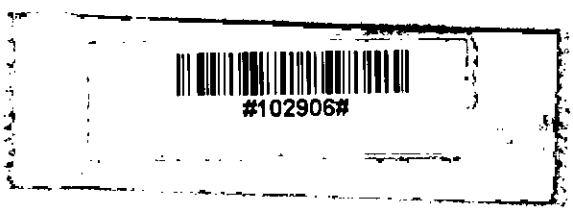
ACCUMULATION OF ARSENIC IN AGRICULTURAL SOIL AND SELECTED CROPS

BY
GANESH CHANDRA SAHA



DEPARTMENT OF CIVIL ENGINEERING
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ACCUMULATION OF ARSENIC IN AGRICULTURAL SOIL AND SELECTED CROPS

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GANESH CHANDRA SAHA

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

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The thesis titled "**Accumulation of Arsenic in Agricultural Soil and Selected Crops**" submitted by **Ganesh Chandra Saha, Student No. P10010401F**, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **Doctor of Philosophy** on February 05, 2006.

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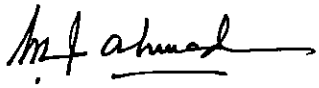
Dr. M. Feroze Ahmed Professor Dept. of Civil Engineering BUET, Dhaka-1000	**Member**	
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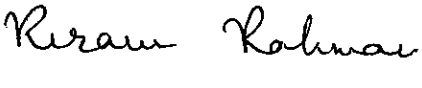
Dr. Md. Rezaur Rahman Professor Institute of Water and Flood Management, BUET, Dhaka-1000	**Member**	
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Signature of Candidate

DEDICATED

TO

MY MOTHER

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ABSTRACT

Groundwater from arsenic contaminated shallow aquifers is widely used for irrigation in Bangladesh. 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.

In this study, twelve *boro* (dry season paddy) fields in four arsenic affected and two unaffected areas have been monitored during 2003 for assessing As status in irrigation water, soil and paddy plant. Irrigation with arsenic-bearing groundwater is definitely causing an increase of arsenic content of paddy field soils. Arsenic contents of paddy field soils, irrigated with high arsenic-bearing irrigation water, have been found to vary significantly over a paddy field, with depth and with time. In general, arsenic concentrations in the top soil layers (up to 150 mm) increased significantly at the end of the irrigation season. In general, higher increase in soil arsenic content was observed for sampling points located close to the entry points of water into different sub-areas of the paddy fields. For example, for a paddy field in Munshiganj, average arsenic concentration in the top 0-75 mm of soil increased from about 8.4 mg/kg in March 2003 to 14.8 mg/kg right at the end of the irrigation season in May 2003. During the same period, it increased from about 4.7 to 8.0 mg/kg for a field in Comilla, 6.7 to 10.3 mg/kg in Brahmanbaria, and 5.7 to 7.2 mg/kg in Faridpur. Arsenic contents in the top soil layers at the end of the irrigation season have been found to be strongly correlated to the arsenic content of irrigation water. In the unaffected areas of Bogra and Naogaon, where arsenic concentration in the irrigation water was below 1 μg/l, arsenic levels in irrigated soils have been found to be comparatively low (varying from about 1.5 to 3.1 mg/kg) and did not vary significantly either with depth or sampling time.

Arsenic concentrations in the paddy field soils have been found to be quite dynamic. After the rainy season (which immediately follow the *boro* season), arsenic concentration in the top soil layer (0-150 mm) of paddy fields in the arsenic affected areas decreased significantly and came down to levels comparable to those found at the beginning of the *boro* season. Since the majority of the As in the top 0-75 mm segment of soil layer is associated with iron oxyhydroxides, this is most likely due to partitioning of As from soil into the aqueous phase during inundation by reductive dissolution of iron oxyhydroxides and desorption. Thus, long-term As accumulation in agricultural soil appears to be counteracted by biogeochemical pathways leading to arsenic removal from soil.

In both arsenic affected and unaffected study areas, the roots of paddy plants accumulated the maximum level of arsenic, followed by leaf and stem. Paddy grain and husk accumulated the least amount of arsenic. The arsenic content in top soil was found to be strongly correlated with arsenic concentration in root, moderately correlated with arsenic concentration in leaf and stem, and poorly correlated with husk and grain. Arsenic concentrations in grain and husk of samples from affected and unaffected areas did not differ significantly, although arsenic concentrations in both grain and husk have been found to be statistically higher in samples from the affected areas. Irrigation with arsenic-bearing groundwater appears to be causing a minor increase in human exposure to arsenic. Considering average arsenic contents of rice grains from affected and unaffected areas and average rice consumption of 450 gm/person/day, daily As intake in affected areas is estimated to be slightly higher (233 μg) compared to that in unaffected areas (176 μg). Since As toxicity is strongly dependent on its chemical form and reported values for

organic and inorganic fractions of arsenic in rice grains vary widely, speciation of As in rice grains of Bangladeshi rice varieties should be determined more carefully for making an assessment of arsenic exposure through rice and its possible health impacts.

From intensive monitoring of a paddy field in Munshiganj in 2004 that was irrigated with groundwater containing 366 μg/l arsenic, it was estimated that about 90% arsenic added to the paddy field with irrigation water is accumulated in the top 0-450 mm of soil; the top 0-75 mm soil accumulated about 71% of added arsenic. The arsenic taken up by paddy plants accounted for about 4.5% of total arsenic that is added to the paddy field with irrigation water. Of the total uptake by paddy plants, the root accumulated 47.3 %, stem 29.4 %, leaf 16.7%, husk 2.7% and grain 3.9%.

Arsenic concentrations in the edible parts of vegetables have been found to be strongly correlated with arsenic contents in irrigation water and root-soil. Accumulation of arsenic in the edible parts of all six vegetables studied have been found to be much lower for samples collected from Bogra, where irrigation water contained little arsenic. Whereas, accumulation was much higher for the same vegetables collected from the arsenic affected areas of Chandpur and Narayangonj, especially where irrigation was carried out with groundwater having high arsenic; among the six vegetables, relatively higher concentrations of arsenic (approaching or exceeding 1 mg/kg, the Australian food standard) were found in the edible parts of potato, tomato, data *shak*, and lal *shak*. Considering vegetable consumption of 130 g/person/day and average arsenic concentration of all six vegetables, this corresponds to an estimated daily intake of about 150 μg of arsenic for vegetables grown with arsenic bearing groundwater in Narayangonj; the estimated arsenic intake is about one-half (86 μg) for vegetables grown with surface water irrigation in Narayangonj and about one-fourth (36 μg) for vegetables grown with arsenic-free (< 1 μg/l) water in Bogra. Since groundwater irrigation is not widely used for growing vegetables and reported inorganic fractions of As in vegetables is relatively low (~ 5%), vegetables appear to account for a very small fraction of overall inorganic arsenic exposure through food chain.

Arsenite adsorption onto paddy field soil has been found to be a strong function of oxalate-extractable iron content of soil, and very high adsorption densities, approaching 200 mg/kg, have been recorded under the laboratory experimental conditions. The iron contents of paddy field soil appear to increase with increasing iron contents in irrigation water. Hence, arsenic adsorption to paddy field soil appears to be dependent on iron contents of both irrigation water and soil. Significant mobilization of arsenic from arsenic-rich paddy field soils has been recorded in batch experiments, where a reducing environment was created by adding a carbon source (glucose) to water in equilibrium with soil. Desorption and reductive dissolution of iron oxyhydroxides appear to be responsible for the mobilization of arsenic. Such mobilization appears 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, although paddy field soils have the capacity to accumulate significant amount of arsenic 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. Results of laboratory experiments, designed to simulate field conditions during inundation by flood water, showed a maximum arsenic loss of about 1.6% (of initial amount present in soil column), which could be attributed to microbial methylation of arsenic into volatile forms.

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Chapter 1

Introduction

1.1 GENERAL

The widespread presence of arsenic in groundwater at levels above the drinking water standard is a major concern in Bangladesh (BGS/ DPHE, 2001). 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 upazilas; 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.

In Bangladesh, groundwater extracted from shallow aquifers using hand-tubewells is the primary source of drinking and cooking water for most of its population of over 140 million. An estimated 10 to 12 million domestic hand tubewells constitute the backbone of rural water supply of the country. 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 tubewells and 24,718 deep tubewells were used for irrigation during the 2004 dry season (BADC, 2005) and groundwater irrigation covered about 75% of the total irrigated area. The contribution of groundwater to total irrigated area has increased from 41% in 1982-83 to 71% in 1996-97 and to about 75% 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% of total irrigated area.

Boro cultivation and irrigation increased together since 1970, and from 1980 up to present time, the area under groundwater irrigation increased by almost an order of magnitude (Harvey et al., 2005). The rapid increase in food grain production in recent years is

mainly attributed to the increase in the area under irrigation (and also use of high yielding varieties of rice). In the year 2003, *boro* accounted for over 48.5% of total rice production in Bangladesh (GoB, 2004). Thus, the food security of the country is heavily dependent on groundwater irrigation.

Although considerable work has been done on its presence in and exposure through drinking/cooking water and its removal from contaminated groundwater, the presence of arsenic in irrigation water received relatively less attention. However, 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.

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 and DMA in agricultural soil. Adsorption-desorption, volatilization as well as plant uptake of arsenic depend to a large extent on chemical forms/transformations of arsenic. 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. 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., 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. However, limited data from one Munshiganj paddy field site (Ali et al., 2003b) show that arsenic concentration in paddy soil may vary significantly with time. This issue is very important in the assessment of long-term accumulation of arsenic in agricultural soil and needs to be studied in more details. Most available data on arsenic concentration in agricultural soil are based on random sampling and data/information on spatial and temporal variability of arsenic concentration in agricultural soil are almost non-existent.

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.

The increased concentrations of arsenic in irrigation water and in topsoil are likely to result in increased concentration in plant and food grains. In a study (Duxbury et al., 2002), concentrations of total arsenic in 150 samples of paddy grains collected from Barisal, Comilla, Dinajpur, Rajshahi and Rangpur districts in Bangladesh were found to range from 10 to 415µg/kg (dry weight basis). Arsenic concentrations in grains were found to be higher for *boro* paddy (mean value 183µg/kg) compared to *aman* paddy (mean value 117µg/kg). In another study (Abedin et al., 2002) where a Bangladesh paddy variety was irrigated with water containing up to 0.8 mg/L of arsenate, the arsenic concentration in root, straw and paddy husk also increased significantly. Masud (2003) and Ali et al. (2003b) also reported higher accumulation of arsenic in root of paddy plant samples irrigated with arsenic bearing water in Munshiganj and Sonargaon. These studies

showed arsenic accumulation to be relatively less in paddy grains and husk. However, limited data are available showing possible linkages among arsenic concentrations in irrigation water, soil and paddy plants. It is also not clear whether arsenic levels in rice, the staple food of our population, are significantly different between arsenic-affected and unaffected areas; some data (e.g., Ali et al., 2003b) suggest that the differences may not be significant. Data on uptake of arsenic by different paddy varieties are also very limited.

Available data suggest that arsenic concentrations in different parts of certain common vegetables grown with arsenic bearing irrigation water are relatively high (Alam et al., 2003; Farid et al., 2003; Ali *et al.*, 2003b; Huq *et al.*, 2001b; Das et al., 2004). However, it is not clear whether these levels are significantly different from the background arsenic levels for these vegetables (i.e., arsenic levels of these vegetables grown in arsenic-unaffected areas). Most available data on arsenic concentration in vegetable samples are based on random sampling and hence it is difficult to correlate arsenic concentrations in water, soil and plant samples.

1.2 OBJECTIVES OF THE PRESENT RESEARCH

The overall objective of the study was to evaluate the processes and parameters governing fate of arsenic introduced with irrigation water in the plant-soil environment. Specific objectives include:

(1) Estimation of the mass of arsenic abstracted with groundwater each year through irrigation wells.

(2) Evaluation of the arsenic concentrations in paddy field soils irrigated with groundwater, both in selected arsenic-affected and unaffected areas, at different times (e.g., before, during and after the irrigation season).

(3) Assessment of arsenic contents in various parts of *boro* paddy plants grown with arsenic-bearing and arsenic-free irrigation water, and assessment of effects of arsenic concentration in water and soil on arsenic accumulation in different parts of paddy plants.

(4) Estimate of the total amount of arsenic added to a paddy field, the amount retained by top soil and the amount taken up by paddy plants; and assessment of possible bio-methylation of arsenic in regulating arsenic concentration in soil.

(5) Evaluation of arsenic contents in various parts of selected vegetables, grown in arsenic-affected and unaffected areas, and assessments of the effects of arsenic content of irrigation water and soil on arsenic accumulation in these vegetables.

(6) Assessment of the effects of different processes (e.g., adsorption/ desorption, reductive dissolution of iron oxyhydroxides), soil parameters (e.g., grain size, clay content, iron-oxyhydroxides) and water quality parameters (e.g., phosphate content) on accumulation of arsenic in paddy field soil.

1.3 SCOPE AND METHODOLOGY

In this study, an estimation of mass of arsenic extracted with ground water was made from secondary information on distribution (thana-wise) of irrigation wells (BADC, 2001-2005) and arsenic concentration database developed by DPHE/BGS (2000).

The arsenic level in irrigation water, top soil layers and paddy plant samples were measured for twelve *boro* paddy fields located in six different areas of Bangladesh during the 2003 dry season. These included four arsenic affected areas in the central region and two unaffected areas in the north-western region of the country. Due to time and resource constrains, possible variation in arsenic uptake by different paddy varieties could not be assessed in this study.

In this study, the effect of irrigation water on arsenic contents of six different types of vegetables (Tomato, *lal shak*, *data shak*, cabbage, cauliflower and potato), commonly grown during dry season with the help of irrigation water, have been evaluated. These vegetable samples were collected from two arsenic affected areas and one unaffected area.

In this study, an attempt was made to estimate the total amount of arsenic that is added to a paddy field with irrigation water and the amount that is retained by the top soil and the amount that is taken up by the paddy plants. This was done through intensive monitoring of irrigation water, soil and plant samples of a piece of paddy field in Munshiganj district. The possible loss of arsenic from arsenic-rich agricultural soil due to biomethylation was assessed in laboratory experiments, where the inundated condition of paddy field soil during flood/rainy season was simulated.

Adsorption-desorption characteristics of arsenic on agricultural soil were assessed with paddy field soils collected from four different areas of the country. The effect of soil composition, initial iron and arsenic contents of soil, and phosphate content of water on arsenic adsorption was assessed in batch experiments. Mobilization of arsenic from paddy field soils due to desorption and reductive dissolution of iron oxyhydroxides was also assessed in batch experiments.

Detailed methodologies for each item of works have been described in the respective Chapters of the thesis, and hence are not elaborated here. The following section briefly describes the analytical methods used for analysis of water and soil samples.

Analytical Methods

In this study, arsenic concentration in water samples was measured with an AAS (Shimadzu, AA6800) attached with a graphite furnace. Iron concentrations in the water samples were measured with flame emission atomic absorption spectrophotometry (Flame-AAS) using an AAS (Shimadzu, AA6800). pH was measured using a pH meter (Hach), and conductivity with a conductivity meter. Chloride was measured using $AgNO_3$ titration method. Ammonia, nitrate, and phosphate concentrations were determined 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.

1.4 ORGANIZATION OF THE THESIS

This thesis consists of seven chapters. Apart from this chapter, the remainder of the thesis has been divided into six chapters.

Chapter 2 provides an overview of the arsenic contamination of groundwater and the importance of groundwater in the agriculture of Bangladesh. This chapter also presents an estimate of the mass of arsenic abstracted with groundwater each year with irrigation water.

The third chapter presents results of the assessment of arsenic in irrigation water, paddy field soil and paddy plants. It summarizes results on the presence of arsenic in irrigation water and enrichment and depletion of arsenic in paddy field soils throughout a year in four arsenic-affected and two unaffected areas of the country. Comparison of arsenic levels in paddy plants from affected and unaffected areas have been made.

Chapter 4 presents results of intensive monitoring of a paddy field in Munshiganj, based on which estimates of arsenic partitioned to soil and paddy plants were developed. Results of laboratory experiments for assessing the importance of biomethylation process in regulating arsenic concentration in soil are also presented in this Chapter.

The fifth chapter presents an assessment of the effects of arsenic bearing irrigation water on some selected vegetables. It summarizes results on the presence of arsenic in water, soil and in different parts of the vegetable plants and their correlations both from arsenic affected and unaffected areas in Bangladesh.

Results of laboratory experiments to better understand the adsorption-desorption characteristics of arsenic on paddy field soil, including effects of dissolved phosphate and soil parameters on arsenic adsorption, and mobilization of arsenic due to desorption and reductive dissolution of iron oxyhydroxides are presented in Chapter 6.

Finally Chapter 7 presents the major conclusions from this study and the recommendations for future research works.

Chapter 2

Groundwater Arsenic Contamination and Groundwater Irrigation in Bangladesh

2.1 INTRODUCTION

Bangladesh is the largest delta in the world. It has fertile agricultural land and abundant water in the wet season, but limited water in the dry season. Agricultural productivity holds the key to the country's overall economic growth and welfare of its people. The economic development largely depends on the agricultural development, which is possible only by production of more crops. In Bangladesh irrigation plays a significant role in agricultural production.

Groundwater is the major source of water in Bangladesh for irrigation of crops both in Rabi (October to April) and Kharif (May to September) seasons. Groundwater of shallow aquifer in many regions of the country is contaminated with arsenic. Water from this aquifer is widely used for irrigation. The arsenic extracted from groundwater for irrigation accumulates at the top soil and may enter into different parts of crops grown on the irrigated soil. The knowledge about the distribution of arsenic in groundwater in shallow aquifer, the status of arsenic in soil and the ingestion pathways is important in the study of arsenic in food chain. This Chapter provides an overview of the presence of arsenic in groundwater and importance of groundwater in irrigation. This Chapter also provides an estimate of the amount of arsenic abstracted with irrigation water each year.

2.2 IRRIGATION IN BANGLADESH

2.2.1 Sources of Irrigation Water

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. Figures 2.1 and 2.2 and Table

2.1 show the increase of groundwater irrigation and at the same time decrease of surface water irrigation during 1970-2004 (Source of data: GoB, 1998, Harvy et al., 2005, and BADC, 2005). As shown in Fig. 2.2, 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. 2.1). 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% was irrigated by groundwater and 1011910.24 ha or about 25% was irrigated by surface water. The contribution of groundwater to total irrigated area has increased from 41% in 1982-83 to 71% in 1996-97 and to about 75% 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% to less than 25% during this period.

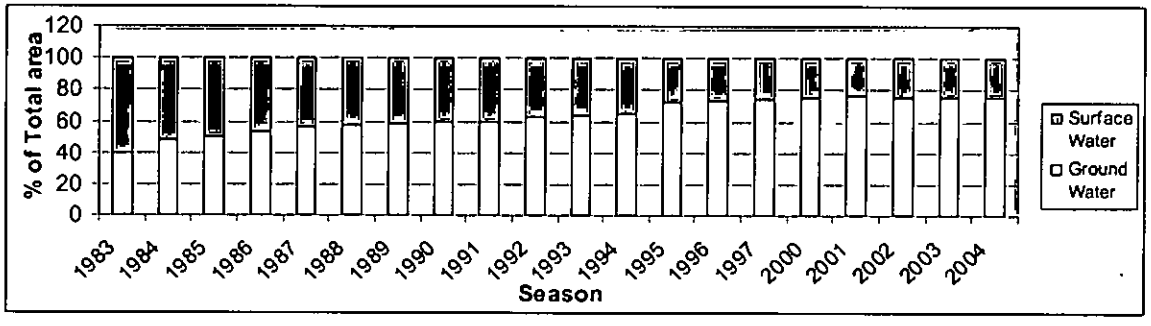


Figure 2.1: Percent of area irrigated by surface and groundwater sources
(Data Source: WARPO 1999, GoB, 1998, Harvy et al., 2005, and BADC, 2005)

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.

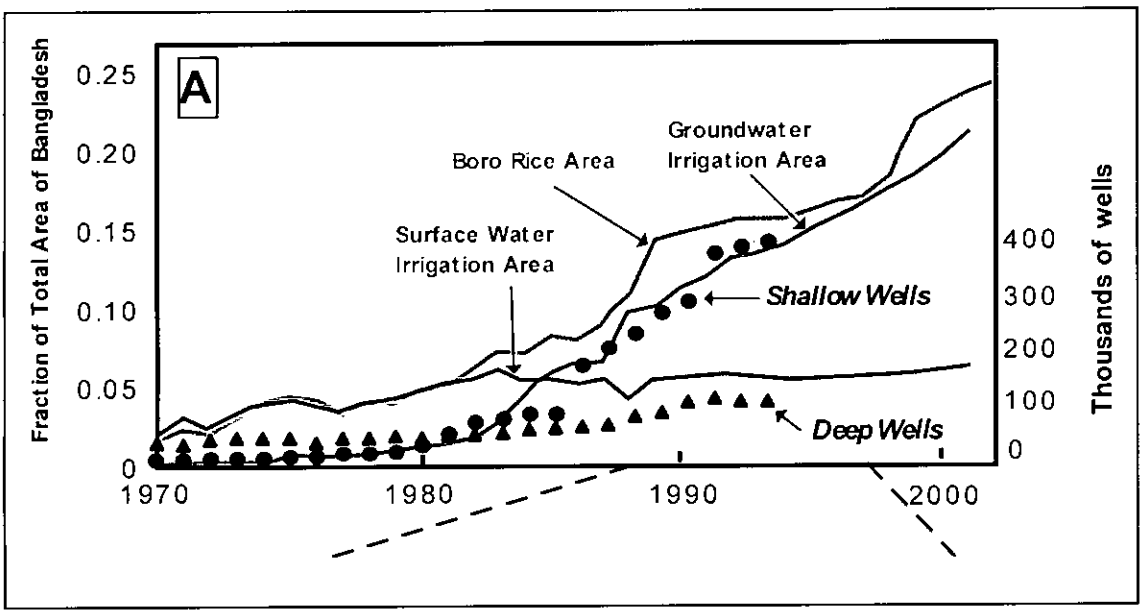


Figure 2.2: Source of water, irrigation equipment and irrigated area in Bangladesh. (Source: Harvey et al., 2005)

2.2.2 Irrigation Equipment

In the dry season, irrigation in Bangladesh is heavily dependent on groundwater. This water is mainly abstracted by shallow tubewell (STW), deep tubewell (DTW), artesian well, dug well, and non-mechanized pumps. Among them STW with motor pumps are very popular irrigation equipment. Mainly shallow tubewells having a discharge capacity of about 14 l/s are used in irrigation. Special emphasis was given on the use of STW in irrigation in view of the availability of water at shallow depth, comparatively lower unit cost and relatively easy drilling, operation and maintenance technology. All shallow tubewells including deep set shallow tubewell (DSSTW) and very deep set shallow tubewell (VDSSTW) abstract water from shallow aquifer, which is contaminated with arsenic in many areas of the country.

Figures 2.2 and 2.3 show irrigated area by different technologies during 1970-2004 (Source of data: Harvey et al., 2005, WARPO, 1999 and BADC, 2005). From these figures it is clear that during 1970-1980 contribution of shallow tubewell was lass than that of deep tube well and surface source equipment. The area under irrigation by surface water has remained more or less static during 1982-1997; while the area under irrigation by shallow tubewells has increased by a factor of about five. Much of this increase has

been accomplished through installation of shallow tubewells. According to BADC (2005), in boro season of 2004, a total of 925152 shallow tubewells, 24718 deep tubewells, 77784 low lift and floating pumps, and 64235 other equipments were used for irrigation all over Bangladesh (BADC, 2005). Table 2.2 shows the number of STW used countrywide from 2000 to 2004. It shows that contribution of STW is increasing day by day and the number of STW has increased by 30 % during the five-year period. The contribution of surface and groundwater sources to total irrigated area has changed considerably over time. During each irrigation season, an estimated 27209 Mm^3 of water (considering average discharge of 10 l/s and 1200 hours of irrigation per season) is extracted through shallow tubewells (Masud, 2003). This quantity is an order of magnitude higher than the amount of groundwater extracted for domestic purpose throughout the year.

Table 2.2: Irrigation equipment and irrigated area in different years
(Data Source: BADC, 2001; BADC, 2002; BADC, 2003; BADC, 2004 and BADC, 2005)

Season	Equipment/ Area	Type of irrigation			
		DTW	STW	LLP&FP	Other
Year 2000	No. of Equipment	23536	707574	58058	135263
	Irrigated Area(ha)	529640	2122511	581801	322578.34
	% of area	14.89	59.68	16.35	9.08
Year 2001	No. of Equipment	23182	865213	71309	130719
	Irrigated Area(ha)	538264	2295067	603787	321090.17
	% of area	14.29	60.94	16.24	8.52
Year 2002	No. of Equipment	23001	893359	77007	88242
	Irrigated Area(ha)	530291	2355033	628748	335695.37
	% of area	13.77	61.17	16.33	8.73
Year 2003	No. of Equipment	23434	924023	79872	72562
	Irrigated Area(ha)	587937	2409407	664018	356876.52
	% of area	14.63	59.96	16.53	8.88
Year 2004	No. of Equipment	24718	925152	77784	64235
	Irrigated Area(ha)	589482	2429127	630668	38912.41
	% of area	14.58	60.07	15.80	9.55

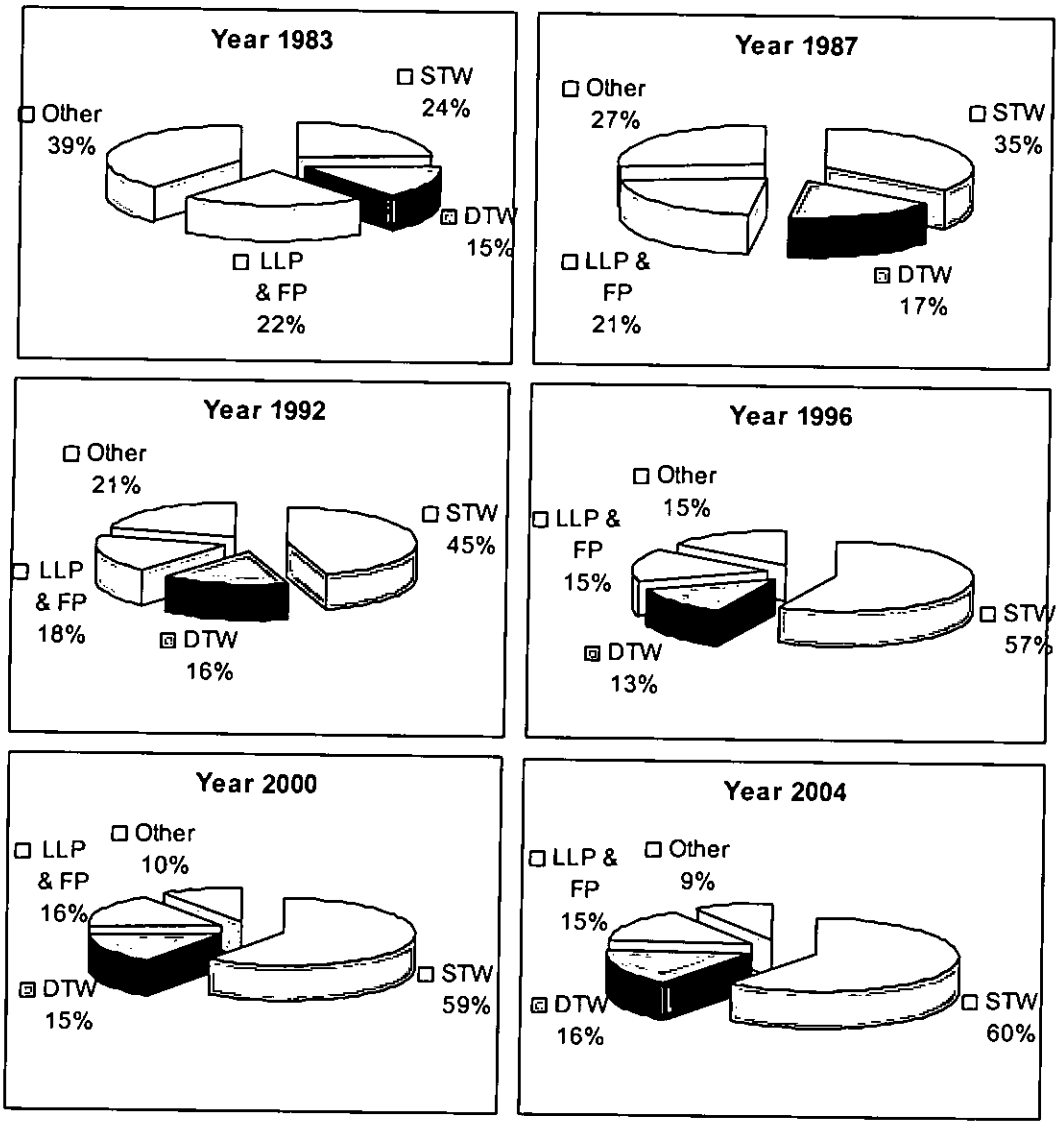


Figure 2.3: Area irrigated in Bangladesh by different technologies during 1983- 2004

2.2.3 Irrigation Coverage by Crop

Irrigation is very much essential for cultivation of major crops in the Rabi season, especially for *boro* rice and wheat cultivation. Besides, some parts of the country grow other crops like potato, oil, pulses, vegetables, etc., which require much less irrigation water compared to *boro* and wheat. Table 2.3 shows division-wise irrigated area for the year 2004. Of the total irrigated area, *boro* accounts for about 88.2 %, wheat 5.20 % and other crop about 6.57 %. Rajshahi and Dhaka division covers maximum land under *boro* cultivation.

Thus, boro rice (dry season rice) is the major recipient of irrigation water. It should be noted that in Bangladesh, total irrigation coverage accounts for over 75 percent of the net cultivable area. The rapid increase in boro production is mainly attributed to the increase in the area under irrigation (and also use of high yielding varieties of rice). In fact, growth in boro production and growth in area covered under irrigation are strongly correlated with a correlation coefficient of 0.98 (Chowdhury et al., 1997). Total production of paddy in the year of 2003 was 251.88 Lac metric tons, of which production of *aman*, *aus*, and *boro* varieties were 18.51, 111.15 and 122.22 Lac metric ton, respectively (GoB, 2004). Figure 2.4 shows the percentage of different variety of paddy grown in the year of 2003. It shows that *boro* accounted for over 48.53 % of rice production in the year 2003.

Table 2.3 Division-wise irrigated area for the year 2004.

	Name of Crop							
Name of Division	Boro (hectares)	%	Wheat (hectares)	%	Others crops (hectares)	%	Total (hectares)	%
Dhaka	1069651.5	29.98	41846.86	19.87	30894.27	11.624	1142392.7	28.25
Chittagong	470360.69	13.18	2855.22	1.356	12641.1	4.75	485857.01	12.01
Rajshahi	1278327.1	35.83	120837.47	57.39	152697.19	57.47	1551861.7	38.37
Khulna	374480.18	10.49	43053.98	20.45	68169.87	25.66	485704.03	12.01
Barishal	92672.18	2.59	1566	0.74	738	0.27	94976.18	2.348
Sylhet	282179.49	7.90	363	0.17	525	0.19	283067.49	6.99
Total	3567671.1	100	210522.53	100	265665.43	100	4043859.1	100

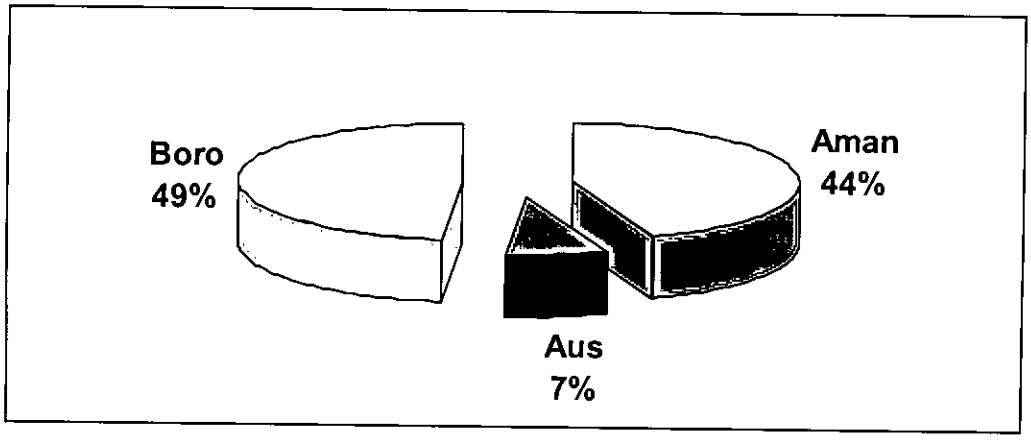


Figure 2.4 Percentage of different varieties of paddy grown in the year of 2003

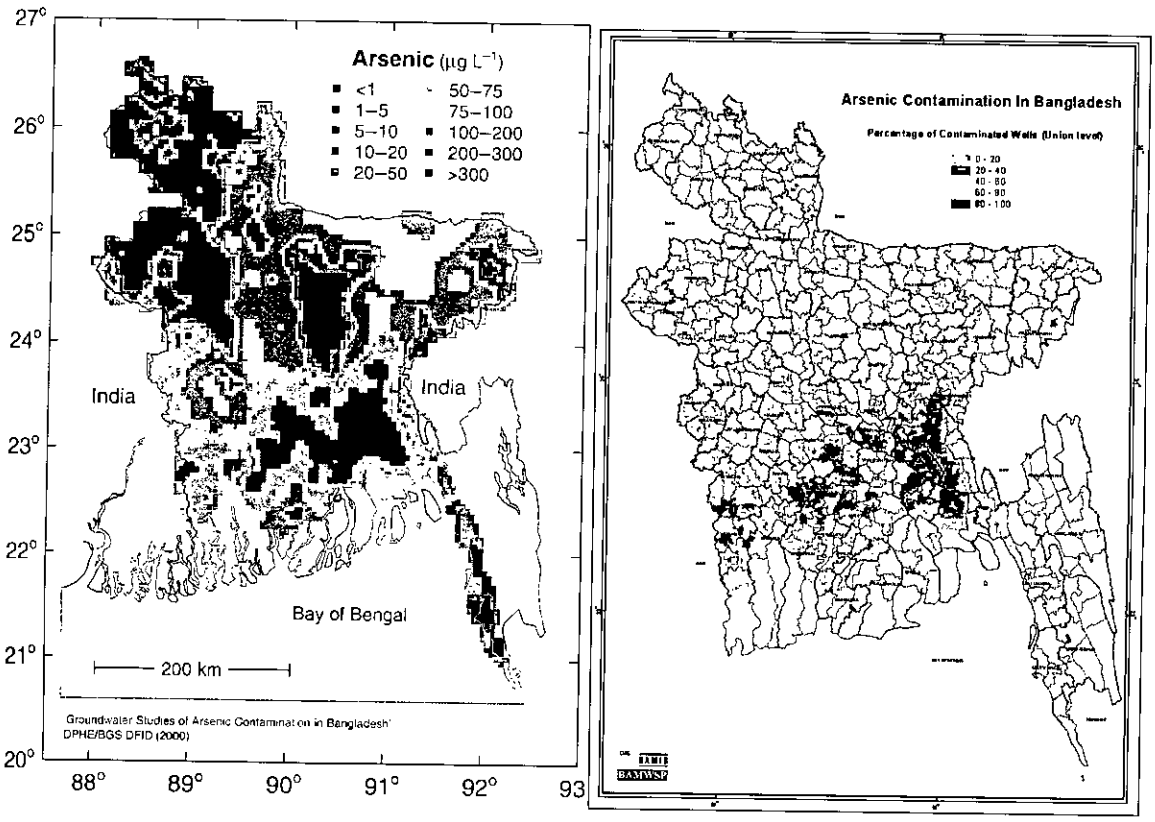
2.3 ARSENIC CONTAMINATION OF GROUNDWATER IN BANGLADESH

2.3.1 Distribution of Arsenic in Groundwater

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 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. Different organizations and research groups have carried out groundwater surveys to characterize distribution of arsenic in groundwater of Bangladesh. Many of these were small-scale studies focusing on a particular area or region (e.g., Nickson, 1997; Badruzzaman et al., 1998; Safiullah, 1998; Yokota et al., 2001; Vangeen et al., 2003; Swartz et al., 2004). NRECA (1997) surveyed around 570 tubewells spread around the country, and DPHE-UNICEF carried out a comprehensive nationwide survey (using field kits with 'detection limit' of 50 μg/l) which included 51,000 analyses up to October 1999 (BGS/DPHE, 2001). The first most comprehensive study on distribution of arsenic in groundwater of Bangladesh was carried out by the British Geological Survey (BGS) along with the Department of Public Health Engineering (DPHE) of Bangladesh Government (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. More recently, the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) carried out a very 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.

Much of our understanding about the distribution of arsenic across Bangladesh comes from the comprehensive study of BGS/DPHE (2001) and BAMWSP (2005). The regional pattern of arsenic distribution obtained from these two 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 2.5a and 2.5b show the distribution of arsenic concentration in Bangladesh based on the nationwide survey carried out by BAMWSP and BGS/DPHE,

respectively. BGS/DPHE (2001) provides a detailed assessment of different aspects of groundwater arsenic contamination in Bangladesh. 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 analyzed in the BGS/DPHE study, only 9% were from deep (>150 m) tubewells and the rest were from shallow wells. Of 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). It should be noted that since the deep tubewells are mainly from the coastal region and Sylhet in the north-east, they are not necessarily representative of deep wells elsewhere in the country. The survey results revealed some 'hot spots' with high arsenic concentration in some least contaminated regions (e.g., Chapai Nawabgonj 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'.



(a) (b)

Figure 2.5: Distribution of As in groundwater of Bangladesh: Map based on (a) BGS/DHPE survey (Source: BGS/DPHE, 2001), and (b) BAMWSP survey (Source: BAMWSP, 2005)

An important observation from this and other arsenic surveys is the significant variation of arsenic concentration in well waters within short distances. Arsenic concentrations have been found to be extremely patchy over small scales. Neighbouring 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.

2.3.2 Population Affected by Arsenic Contamination

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 10 μg/l, the standard of the World Health Organization (WHO).

The most commonly reported symptoms (often referred to as arsenicosis) of chronic arsenic exposure are *hyperpigmentation* (dark spots on the skin), *hypopigmentation* (white spots on the skin) and *keratosis* (skin hardens and develops raised wart-like nodules). Sometimes *hyperpigmentation* and *hypopigmentation* are commonly referred to as *melanosis*. Arsenic also causes skin cancer, internal cancers, and a wide range of other health problems e.g., abdominal pain, nausea, vomiting, diarrhea, anemia. The most commonly manifested disease in Bangladesh so far is a skin lesion (*melanosis* and *keratosis*).

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 a survey conducted in 270 villages of Bangladesh, more than 7000 arsenicosis patients have been identified (Rahman et. al., 2000). In the nationwide screening program carried out by the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP, 2005), over 66 million people of every household of 270 arsenic-affected upazilas were surveyed for arsenicosis

patients. Figure 2.6 shows the distribution of arsenicosis patients in the survey area. A total of 38,430 arsenicosis patients were identified in this survey. While the results from this survey are currently being analyzed, results from 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.

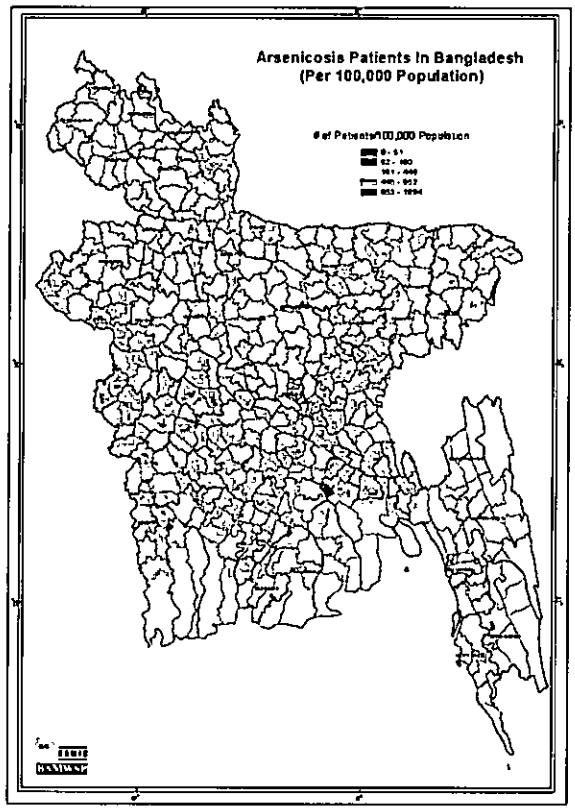
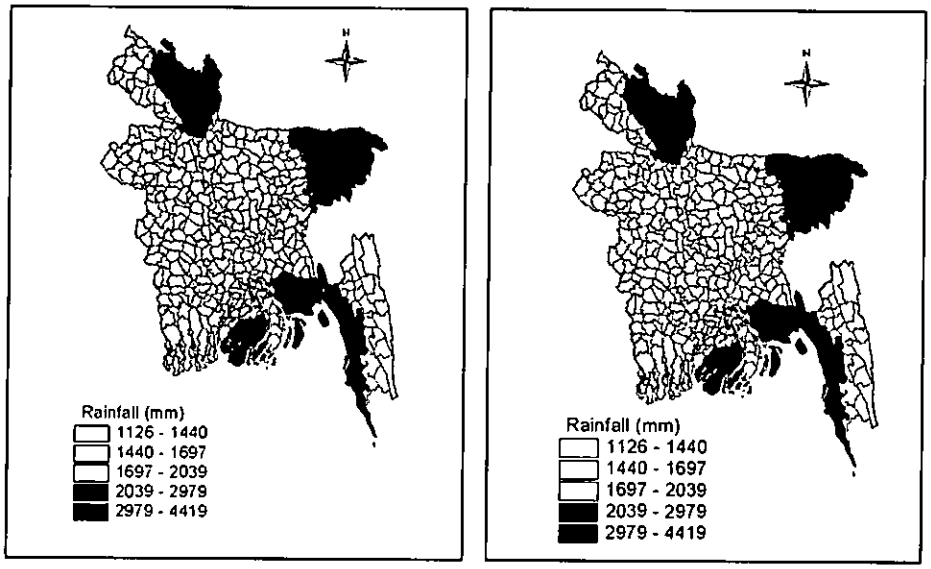


Figure 2.6: Distribution of arsenicosis patients in Bangladesh (BAMWSP, 2005)

2.4 WATER CYCLING AT LOCAL SCALE: RAINWATER VS. GROUNDWATER IRRIGATION

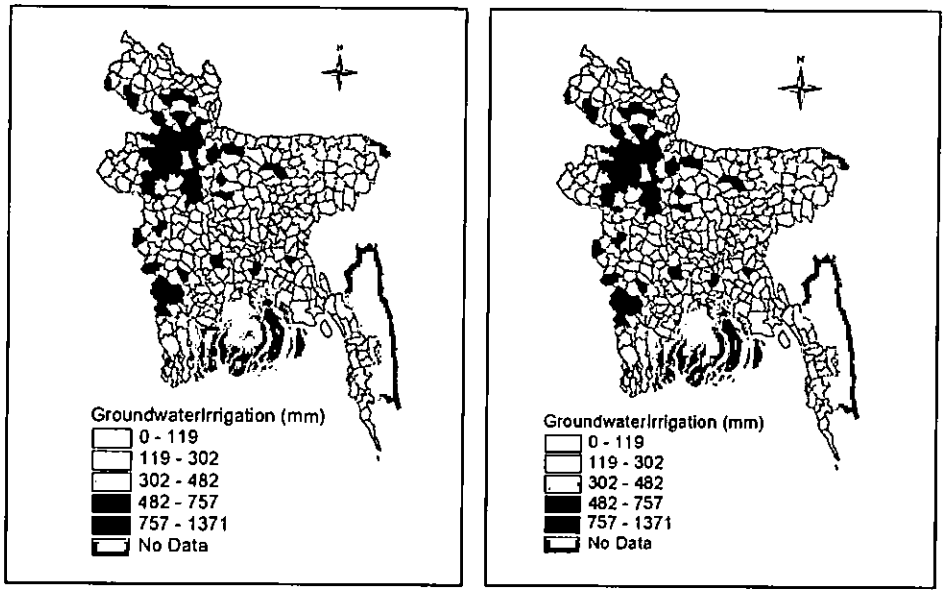
Figures 2.7a and 2.7b show thana wise annual rainfall distribution in mm throughout the country for year 2003 and 2004. In order to compare the quantity of groundwater that is cycled each year through irrigation with the quantity of annual rainfall (expressed in mm), the amount of water abstracted for each thana was expressed as mm of water over the entire thana area. For this purpose, only *boro* irrigation of 1000 mm per thana was

considered. For each thana, total area and area under boro cultivation were taken from BADC (2004) and BADC (2005), respectively. Figures 2.8a and 2.8b show the distribution of groundwater (expressed as mm over the entire thana) abstracted by deep and shallow tubewells.



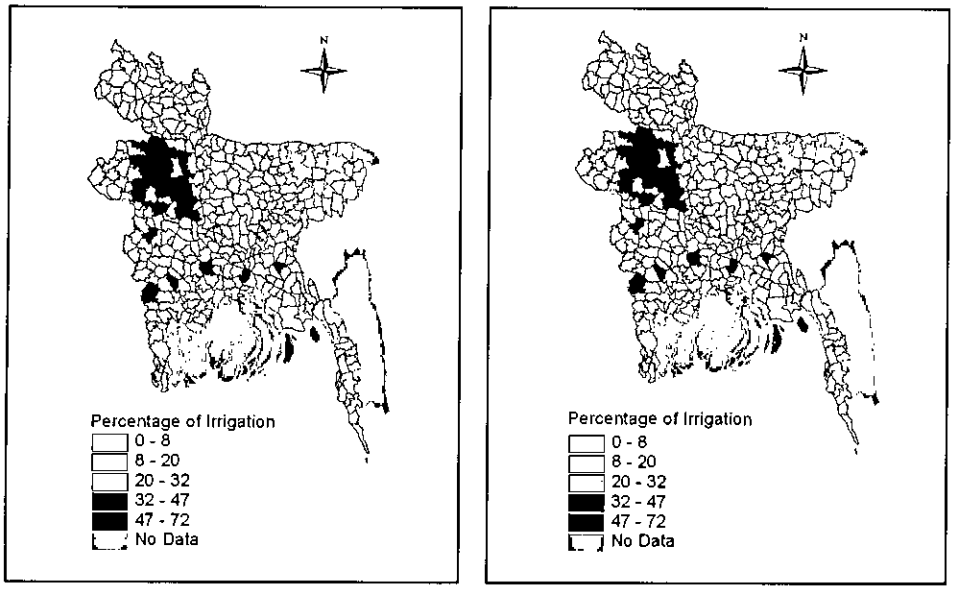
(a) (b)

Figure 2.7: Distribution of annual rainfall (thana-wise) for the years: (a) 2003 and (b) 2004 (Data source: BBS, 2005)



(a) (b)

Figure 2.8: Distribution of groundwater (expressed as mm over the entire thana) abstracted by deep and shallow tubewells for the years: (a) 2003, and (b) 2004 (Data source: BADC, 2005)



(a) (b)

Figure 2.9: Percentage of groundwater (abstracted for irrigation) to rainwater for each thana for the years: (a) 2003, and (b) 2004 (Data source: BBS, 2005 and BADC, 2005)

Available data show that average annual rainfall for the year 2003 and 2004 are 1964 mm and 2484 mm, respectively. On the other hand, the calculated amount of irrigation water expressed as mm over the entire country are 234 mm and 237 mm for the year of 2003 and 2004, respectively. Overall (i.e., for the entire country) groundwater abstracted for irrigation accounted for 11.91% and 9.54% of annual rainfall for the year 2003 and 2004, respectively. Figure 2.9 show the percentage of groundwater (abstracted for irrigation) to rainwater for each thana of the country. It shows that for many thanas, groundwater accounts for a significant amount of total water that is cycled through the hydrosphere. Thus irrigation water plays a major role in the local hydrology of many areas of the country.

2.5 ESTIMATION OF ARSENIC ABSTRACTED WITH GROUNDWATER

Figures 2.10a and 2.10b show the distribution (thana-wise) of shallow irrigation wells in Bangladesh for the *boro* season of 2000 to 2004. These figures show that the distribution of shallow wells has not changed significantly during this period. As shown in Fig. 2.10a and 2.10b, high concentrations of shallow irrigation wells could be found in northern and north-western Bangladesh. A comparison between Fig. 2.5a and Fig. 2.10a show that the

regions with heavy concentrations of irrigation wells (north and north-western region) are, in general, different from those with highest concentrations of arsenic in tubewell water (e.g., southern, central and north-eastern region).

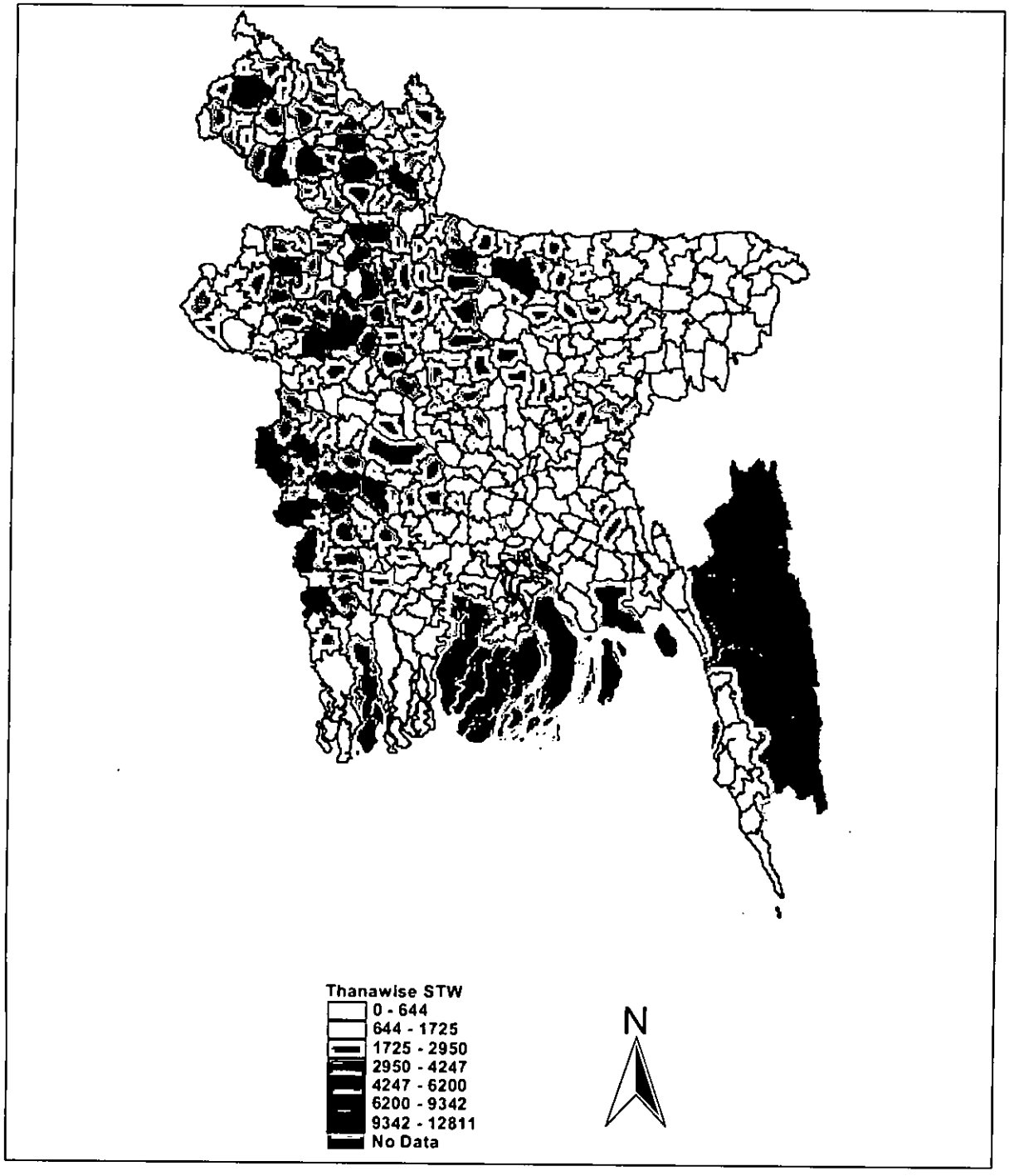


Figure 2.10a: Distribution of shallow irrigation wells in Bangladesh in *boro* season of 2004

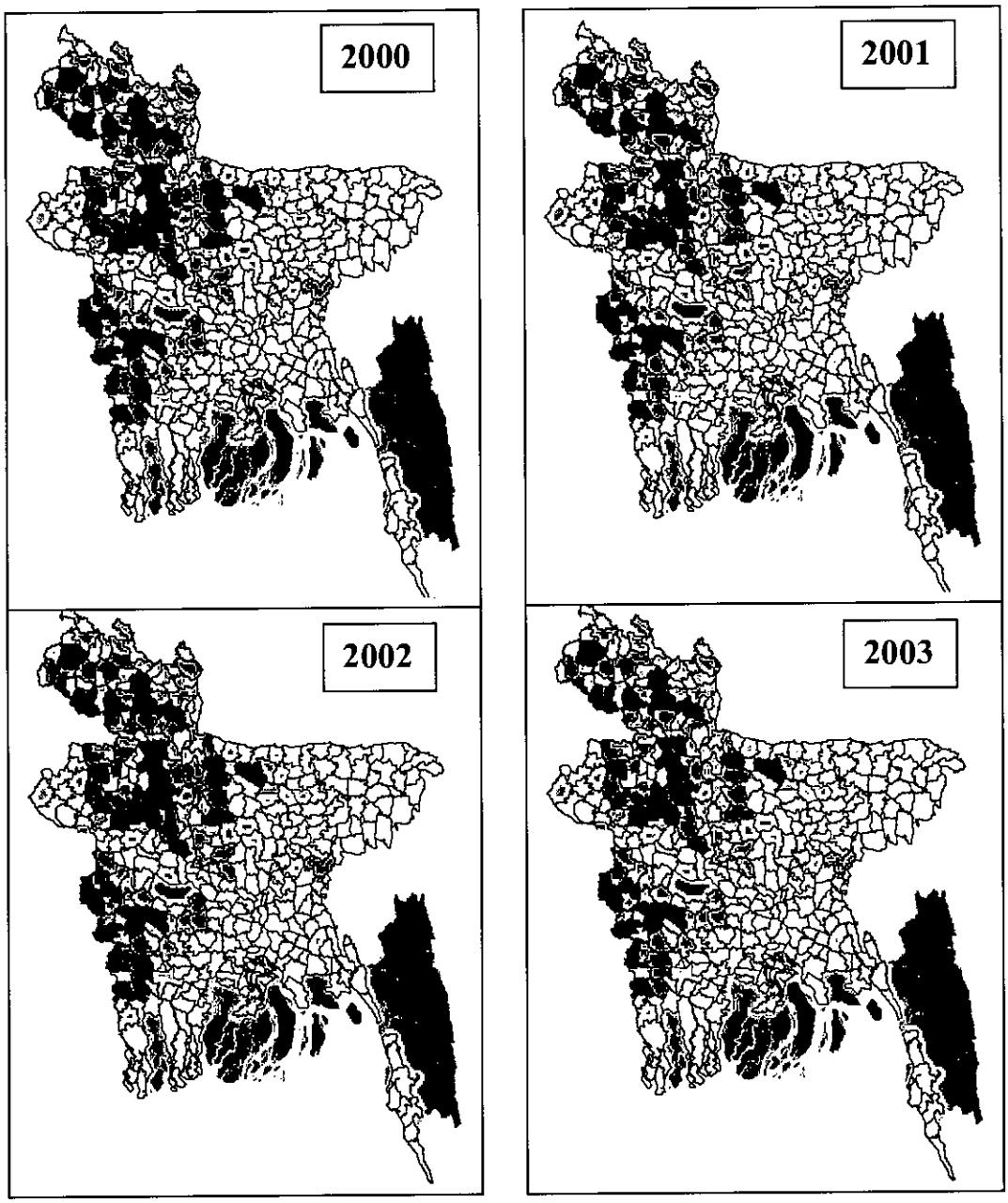


Figure 2.10b: Distribution of shallow irrigation wells in Bangladesh in *boro* seasons from 2000-2003

A preliminary estimate of the quantity of arsenic extracted through irrigation water was made for each *thana* by assuming an irrigation requirement of 1000 mm for *boro* rice and taking arsenic concentration in the irrigation water as the average of the values reported for that *thana* in the arsenic-database developed by DPHE/BGS (2000). It should be noted that information on arsenic concentration, number of shallow irrigation wells and irrigated area were available for 372 *thanas* and only these information were used in this

estimation process. Figure 2.11a shows the amount of arsenic extracted through irrigation wells in 2004 *boro* season for all the *thanas* in Bangladesh. Thus, if all irrigable lands are irrigated, an estimated 971 metric tons of arsenic would be extracted through irrigation water. The estimates are particularly high for south-western and south-central (excepting the hill districts) regions of Bangladesh, where both irrigation intensity and arsenic concentration in shallow wells are very high. Figure 2.11b and Table 2.4 show estimated amount of arsenic extracted through shallow irrigation wells for the dry seasons of 2000 to 2004. It shows that the quantity of arsenic cycled through irrigation water is increasing gradually as the area under *boro* cultivation is increasing.

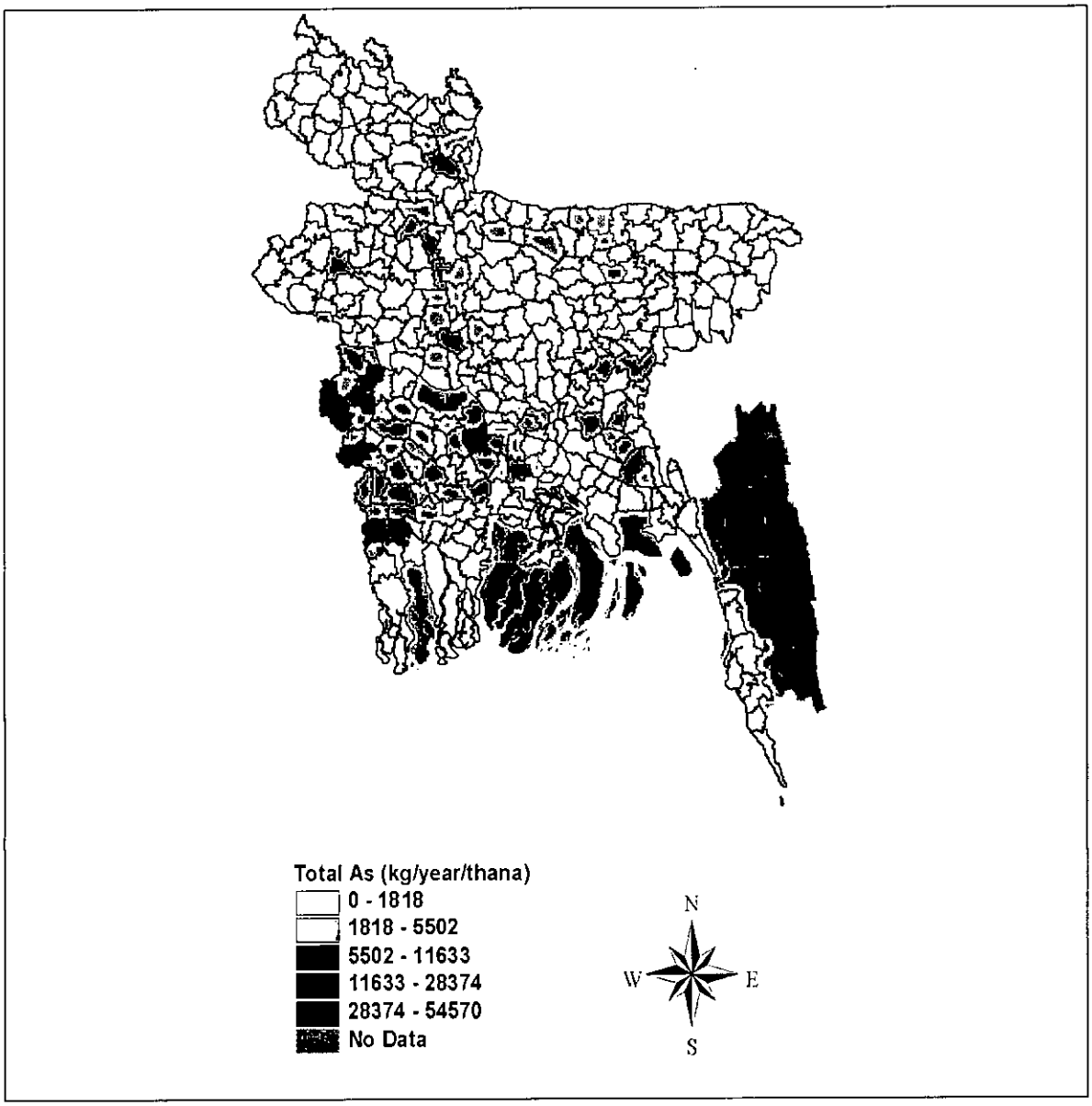


Figure 2.11a: Estimates of arsenic extracted through shallow irrigation wells in Bangladesh for the year 2004

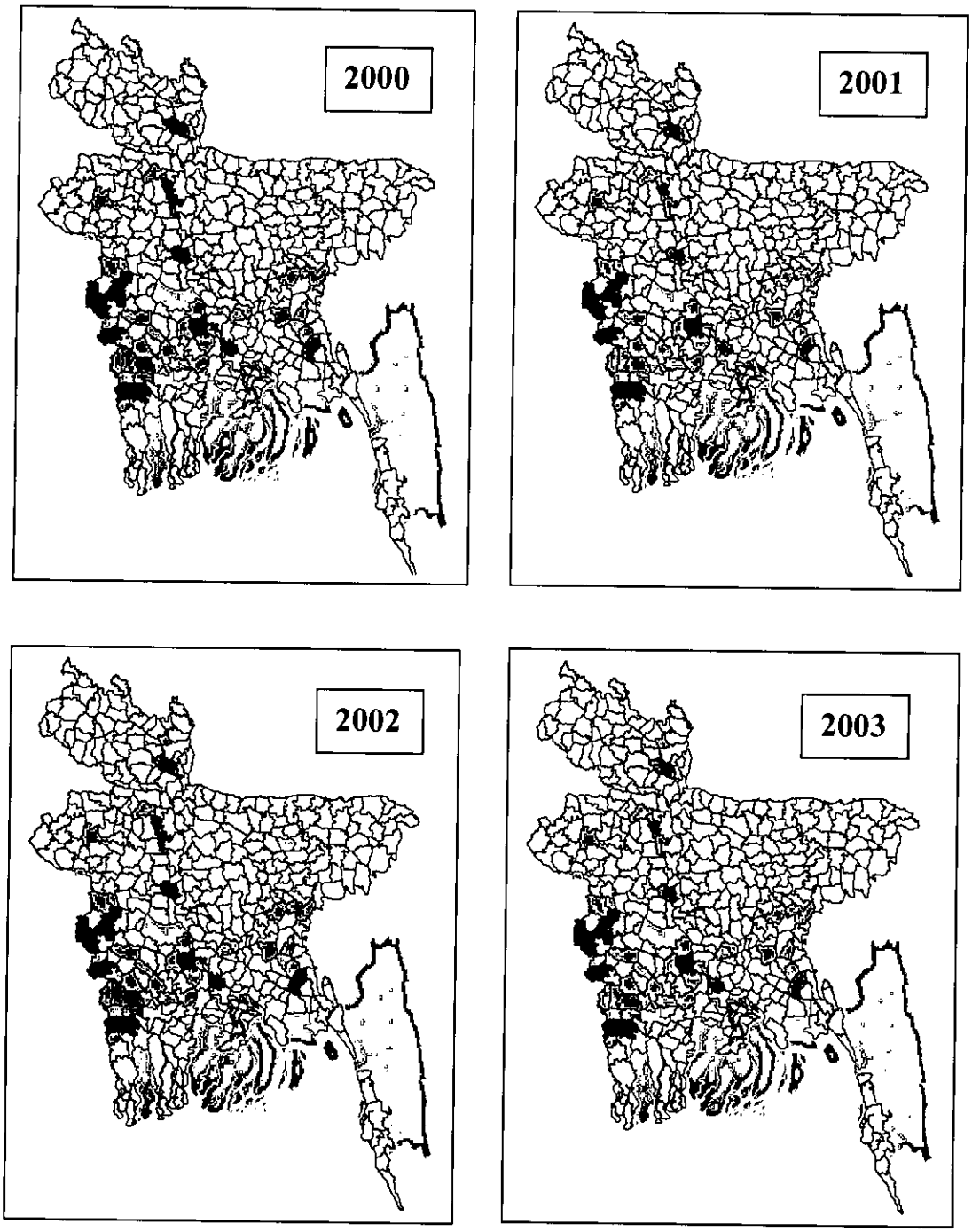


Figure 2.11b: Estimates of arsenic extracted each year through shallow irrigation wells in Bangladesh during 2000-2003

Table 2.4: Estimates of arsenic extracted through shallow irrigation wells

Parameter	Year				
	2000	2001	2002	2003	2004
Area under *boro* cultivation using STW (ha)	2,122,511	2,295,067	2,355,033	2,409,407	2,429,127
As abstracted (ton)	837	911	945	965	971

Figure 2.11a and 2.11b show that although the north-eastern region of Bangladesh is heavily affected by arsenic contamination, relatively lower quantity of arsenic is cycled through irrigation water in this region because of lower irrigation intensity (using groundwater). In fact, compared to the arsenic affected north-eastern region, more arsenic appears to be cycled through irrigation water in the relatively arsenic-free northern regions of Bangladesh where irrigation intensity is very high.

Figure 2.12a shows thana-wise estimates of average arsenic loading on agricultural land (i.e., amount of arsenic deposited in agricultural land per hectare of irrigated area) for 2004 *boro* season. This estimate was made by dividing the estimated total arsenic for each thana (presented in Fig. 2.11a) by the irrigated area for that thana (BADC, 2005). The highest arsenic loading of 4.21 kg/ha was calculated for Chandpur Sadar thana of Chandpur district. According to this estimate, the districts with high deposition of arsenic include Chandpur, Munshigonj, Comilla, Gopalgonj, Faridpur, Madaripur, Jessore, Jhenaidah, Bagerhat, and Kushtia. Figure 2.12b shows average arsenic loading in agricultural land from 2000 to 2004.

This preliminary estimate, which shows that a huge quantity of arsenic is cycled each year through irrigation water, further emphasizes the importance of understanding the fate of arsenic extracted through irrigation water and delivered to the agricultural lands. The districts and regions where arsenic deposition on agricultural lands appears to be higher may be targeted for additional studies.

2.6 SUMMARY

For Bangladesh, attainment of self-sufficiency in food production is strongly related to its ability to produce food during the dry season with the help of irrigation. In Bangladesh the major portion of irrigation water comes from groundwater especially from shallow aquifer and this is increasing rapidly because of scarcity of surface water sources.

Shallow tubewells are widely used for irrigation in Bangladesh. According to a recent BADC survey (BADC, 2005), a total of 925152 shallow tubewells and 24718 deep tubewells were used for irrigation during the 2004 boro season. The contribution of groundwater to total irrigated area was over 75% in 2004, and shallow tubewells

accounted for over 60% of irrigated area. 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.

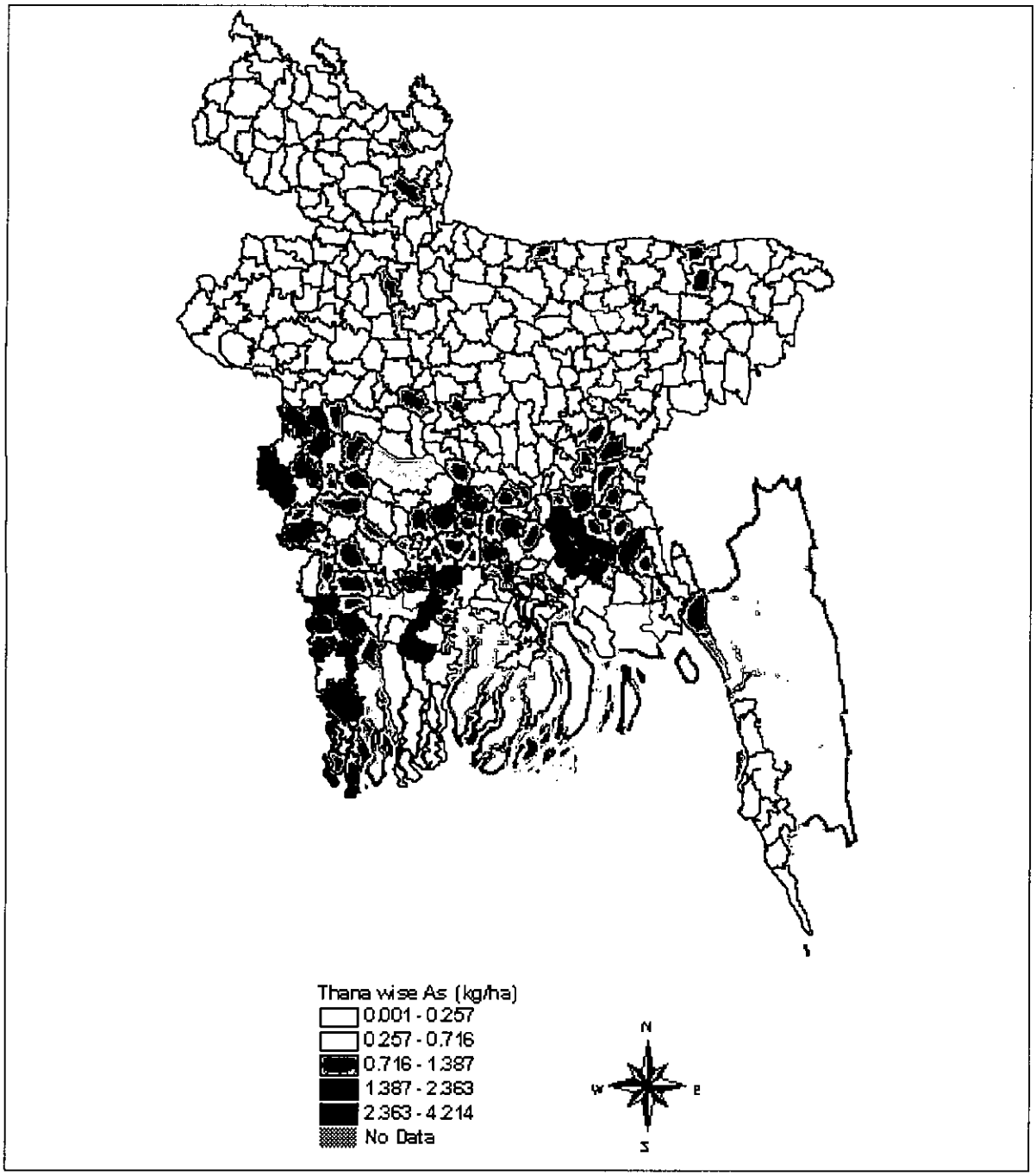


Figure 2.12a: Estimates of thana-wise average arsenic loading (kg/ha) on agricultural land for year 2004

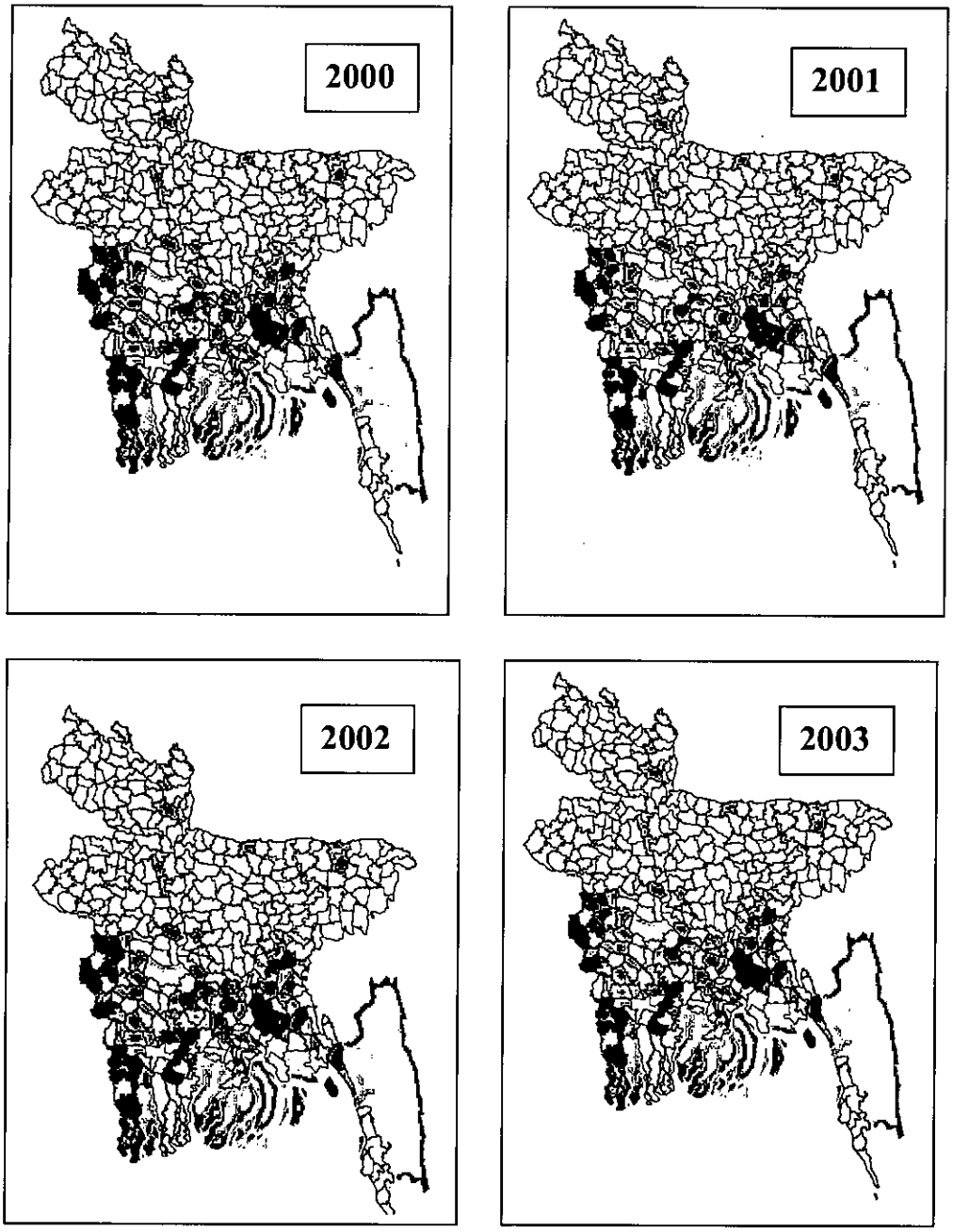


Figure 2.12b: Estimates of thana-wise average arsenic loading (kg/ha) on agricultural land during 2000-2003

High concentrations of shallow irrigation wells could be found in northern and north-western Bangladesh. Areas with heavy concentrations of irrigation wells are, in general, different from those with highest concentrations of arsenic in tubewell water (e.g., southern, central and north-eastern region). If arsenic concentration in irrigation water is

100 ppb and if a total of 1000 mm of irrigation water is provided to the field over the dry season (e.g., for *boro* rice), then this adds 1 kg of arsenic per hectare of irrigated land each year. According to the present study, close to 1000 metric tons of arsenic could be cycled each year through irrigation water. The estimates are particularly high for south-western and south-central (excepting the hill districts) regions of Bangladesh, where both irrigation intensity and arsenic concentration in shallow wells are very high. According to this study, the districts with highest cycling of arsenic per unit of irrigated area include Chandpur, Munshigonj, Comilla, Gopalgonj, Faridpur, Madaripur, Jessore, Jhenaidah, Bagerhat, and Kushtia.

The *boro* rice is the main crop, which receives large amount of irrigation. The *aman* rice, wheat and some other crops are also receiving irrigation water. Arsenic in irrigation water poses a potential challenge to the agriculture sector. Ingestion of food items irrigated with arsenic contaminated groundwater may be a major route of human exposure to arsenic. More studies are needed to develop a better understanding of arsenic accumulation in soil and food chain and its possible long-term impacts.

Chapter 3

Accumulation of Arsenic in Irrigated Soil and Paddy

3.1 INTRODUCTION

In Bangladesh, the presence of dissolved arsenic in shallow groundwater above acceptable level is a major public health concern. An estimated 270 *upazilas* (administrative unit) out of 465 have been affected with significantly high concentrations of arsenic, with the greatest contamination in the south and south-east region of the country and least in the north-west and the uplifted areas in north central region (BGS/ DPHE, 2001). In Bangladesh, groundwater extracted from shallow aquifers using hand-tubewells is the primary source of drinking and cooking water for most of its population of over 140 million. An estimated 10 million domestic wells constitute the backbone of rural water supply of the country. 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 924,023 shallow tubewells and 23,434 deep tubewells were used for irrigation during the 2003 dry season (BADC, 2003), and groundwater irrigation covered about 75% of the total irrigated area. *Boro* cultivation and irrigation increased together since 1970, and from 1980 up to present time, area under groundwater irrigation increased by almost an order of magnitude (Harvey et al., 2005). During 2003 dry season, about 87% of the total irrigated area of about 4 million hectare (about 28% of the total area of the country) was under *boro* cultivation and *boro* accounted for about 48.5% of the total rice production (GoB, 2004). Thus, groundwater irrigation greatly increased agricultural production in Bangladesh and the country's food security is heavily dependent on groundwater irrigation during the dry season. Estimates presented in Chapter 2 show that close to 1000 metric tons of arsenic is cycled each year with irrigation water. Thus, accumulation of arsenic in paddy field soil and its introduction into the food chain through uptake by paddy plants are major concerns.

Two major objectives of this research work were: (a) to develop better understanding of the dynamics of arsenic concentration in paddy field soils, and (b) to assess the effect of arsenic bearing irrigation water on accumulation of arsenic in different parts of paddy plants, including grains. In this study, arsenic concentrations in irrigation water and in top soil layers of 12 rice fields located in both arsenic affected and unaffected areas have been monitored during 2003. Paddy plant samples were also collected from these field sites at harvest time. This chapter presents the results of laboratory analysis of water, soil and paddy plant samples, collected from six different areas of Bangladesh, and make an assessment of the dynamics of arsenic concentration in irrigated paddy field soil and effect of arsenic bearing irrigation water on bioaccumulation of arsenic in paddy plants.

3.2 PREVIOUS STUDIES

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., Ullah, 1998; Alam and Sattar, 2000; Jahiruddin et al., 2000; Huq et al., 2001; Meharg and Rahman, 2003; Huq et al., 2003; Ali et al., 2003b; Panaullah et al., 2003; Ahmed, 2005; Farid et al., 2005; Islam et al., 2005; Jahiruddin et al., 2005) have reported relatively higher levels of arsenic in paddy field soils irrigated with arsenic bearing groundwater. In a study conducted in five *upazilas* (Senbagh, Brahmanbaria, Paba, Tala and Faridpur) of the country, Islam et al. (2005) found wide variation in total As concentrations in soil samples. The arsenic level 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 (Paba, Tala and Faridpur upazilas) had higher soil As levels compared to those of Meghna river floodplain (Brahmanbaria and Senbagh upazilas). Mean total As levels in Senbagh, Brahmanbaria, Paba, Tala and Faridpur *upazilas* were 4.6, 6.5, 7.2, 19.4 and 19.6 μg/g, respectively. Of the 456 samples, 53% had total As from 0-10.0 μg/g, 26% between 10.1-20.0 μg/g, 17% between 30.1-40.0 μg/g, and the remaining 1% of the soils had arsenic exceeding 40.0 μg/g. Jahiruddin et al. (2005) also analyzed arsenic concentration in irrigation water (from shall tubewells) and in the receiving agricultural soil in Chapai Nawabganj Sadar *upazila*. Arsenic concentration in irrigation water varied from 0.015 to 0.352 mg/l and the soil As content varied from 5.8 to 17.7 μg/g, and a good correlation was observed between water As and soil As.

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. A 2002 USAID study, covering 456 sites, reported 48% of the soil samples having arsenic concentration exceeding the 10 mg/kg. On the other hand, 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. (2003b) showed that in a paddy field in Munshiganj (irrigated with arsenic bearing irrigation water), soil arsenic level at the beginning and at the end of the irrigation season could vary by a factor of over two. Thus, some or much of the variation of soil arsenic concentrations reported in the literature may be attributed to the variation in sampling time. More studies are needed to better understand the dynamics of arsenic concentration in agricultural soils irrigated with arsenic bearing irrigation water.

It has been reported that increasing concentration of arsenate significantly decreases plant height, grain yield, the number of grains, grain weight and root biomass. Rice production is reported to decrease by 10% at 25 mg/kg arsenic concentration in soil (Xiong et al., 1987). Pot studies (Jahiruddin et al., 2004) showed that higher arsenic in irrigation water and soil resulted in lower yield of a local rice variety (BR-29). Pot studies (Jahiruddin et al, 2004) have also shown that As (arsenate) in irrigation water above 1 ppm and soil As content above 5 ppm reduce the yield of BR-29 rice, the most productive *boro* rice variety. These treatments also showed residual effects on BR-33 rice in the following *aman* season. Talukder (2005) found that concentration of arsenic in soil has a marked effect on plant growth and yield. With increasing arsenic dose (from 0 to 40 mg/kg of soil), grain yield significantly decreased from 30 to 20 g/pot in *t-aman* and from 49 to 25 g/pot in *boro* rice. The treatment without arsenic yielded the most straw production (32 g/pot in *t-aman* and 106 g/pot in *boro* rice), while the lowest straw production (22 and 69 g/ pot in *t-aman* and *boro* rice, respectively) was found in the highest arsenic treatment (40 mg/kg of soil). These results are also consistent with the findings of Abedin *et al* (2002), who reported, based on a greenhouse study, that increasing the concentration of arsenic in irrigation water significantly decreased plant height, grain yield, the number of filled grains, grain weight, and root biomass of BR-11 rice variety. The possible impact of arsenic bearing irrigation water on crop yield is another area of concern. In this context, it

is important to have a better understanding about the present level as well as possible future level of arsenic in agricultural soil irrigated with arsenic bearing irrigation water.

The increased concentration of arsenic in irrigation water and in root-zone soil is likely to result in increased concentration of arsenic in plants. Recently several surveys of arsenic in paddy grain have been undertaken (Shah et al., 2004; USAID, 2003; Duxbury et al., 2003; Hironaka and Ahmad, 2003, Meharg and Rahman, 2003). Utilizing the distribution of these grain arsenic concentrations and per capita daily consumption of rice (450 gm), Lauren and Duxbury (2005) estimates that daily arsenic intakes from 24% of the paddy samples would be in excess of daily water intakes at the current Bangladeshi standard of 50 ppb. Alternatively, daily arsenic intakes from 84% of the Bangladeshi paddy samples would exceed daily arsenic intakes from water at the US and European drinking water standard of 10 ppb. These simplified estimates of arsenic consumption from only paddy and water indicate that arsenic from paddy is an important source of exposure in the Bangladeshi food system.

In a study (Duxbury et al., 2002), concentrations of total arsenic in 150 samples of paddy grains collected from Barisal, Comilla, Dinajpur, Rajshahi and Rangpur districts in Bangladesh were found to range from 10 to 415 μg/kg (dry weight basis). Arsenic concentrations in grains were higher for Boro (dry season) paddy (mean value 183 μg/kg) compared to Aman (wet season) paddy (mean value 117 μg/kg). In a study conducted in five upazilas - Senbagh, Brahmanbaria, Paba, Tala and Faridpur - of the country, Islam et al. (2005) reported mean arsenic level in *boro* rice grain to be 0.42, 0.48, 0.07, 0.44 and 0.33 mg/kg, respectively. Islam et al. (2005) also reported average As concentrations in *boro* rice grain and straw for the five upazilas to be 0.34 and 3.44 mg/g, respectively; whereas As concentrations of *aman* rice grain and straw were about 0.25 and 2.0 mg/g, respectively (Islam et al., 2004 b; Jahiruddin et al., 2004). Masud (2003) reported that arsenic in *boro* rice grain collected from Sreenagar, Munshiganj varied from 0.05 to 1.52 mg/kg (with a mean of 0.48 mg/kg) and that from Sonargaon varied from 0.05 to 1.23 mg/kg (with a mean of 0.46 mg/kg). In another study (Abedin et al., 2002), where a Bangladesh paddy variety was irrigated with water containing up to 0.8 mg/L of arsenate, significant increase in arsenic concentration of root, straw and husk was observed. Masud (2003) also reported higher accumulation of arsenic (mean value 8.9 mg/kg for Sreenagar

site and 11.9 for Sonargaon site) in root of paddy plant samples irrigated with arsenic bearing water.

Paul et al. (2005) reported that arsenic concentration in grains of the wet season rice of Bangladesh varies from 0.03 to 0.30 μg/g, with a mean of 0.13 μg/g (n = 15). This is similar to the results of the *aman* rice survey reported by Duxbury et al. (2003), with a mean grain arsenic level of 0.12 μg/g (0.07 to 0.17 μg/g). However, there is large variability in the mean arsenic concentrations of rice grains (0.10-0.95 μg/g) reported in other Bangladeshi rice surveys. This is mirrored by the large variability in soil arsenic level of individual paddy fields in Bangladesh (3.1- 42.5) μg/g (Meharg and Rahman, 2003). Simultaneous sampling and analysis of irrigation water, agricultural soil and paddy plants is needed to better understand the effect of arsenic bearing irrigation water on soil and in different parts of paddy plants, including grains.

The forms of arsenic present in rice grains need to be better characterized, as inorganic species are believed to be more toxic than methylated species (Cullen and Reimer, 1989). The studies to date are relatively limited (Heitkemper et al, 2001; Scoof et al, 1999; Kohlmeyer et al 2003; D'Amato et al, 2004). It appears that arsenite [As(III], arsenate [As(V)] and dimethylarsinic acid [DMA(V)] are the predominant species present.

Paul et al (2005) found highly significant differences in the percentage of recovered inorganic arsenic between Bangladeshi, USA, Indian and European market rice. In European, Bangladeshi and Indian rice 64 ± 1 % (n=7), 80 ± 3 % (n = 11) and 81 ± 4 % (n = 15) of the recovered arsenic was found to be present in inorganic form, mostly as As(III). Scoof et al (1998) report similar values of 61%, 58% and 67% of inorganic arsenic for Taiwanese rice. In contrast DMA(V) was the predominant species in rice from the USA, with only 42 ± 5 % (n = 12) of the arsenic being inorganic. This data is in agreement with Scoof et al (1999), who report that DMA accounts for 54% (n = 4) of the arsenic in the grain of US rice. An EPA study found the percentage of inorganic arsenic in rice to be 35% (EPA 1988). A study conducted in West Bengal found the percentage of inorganic arsenic in rice to be 95%; another study conducted in West Bengal found the percentage of inorganic arsenic in rice to be 43.8% (Roychowdhury et al., 2003).

3.3 METHODOLOGY

3.3.1 Site Selection

In this study, arsenic level in irrigation water, the top soil layers and paddy plant samples were measured for twelve *boro* paddy fields located in six different areas of Bangladesh during the 2003 dry season. These included four arsenic affected areas in the central region and two unaffected areas in the north-western region of Bangladesh (Figure 3.1). The arsenic affected areas were: (i) Sreenagar, Munshiganj; (ii) Barura, Comilla; (iii) Nabinagar, Brahmanbaria; and (iv) Vanga, Faridpur. The unaffected areas were: (i) Bogra Sadar, Bogra and (ii) Nazipur, Noagaon.

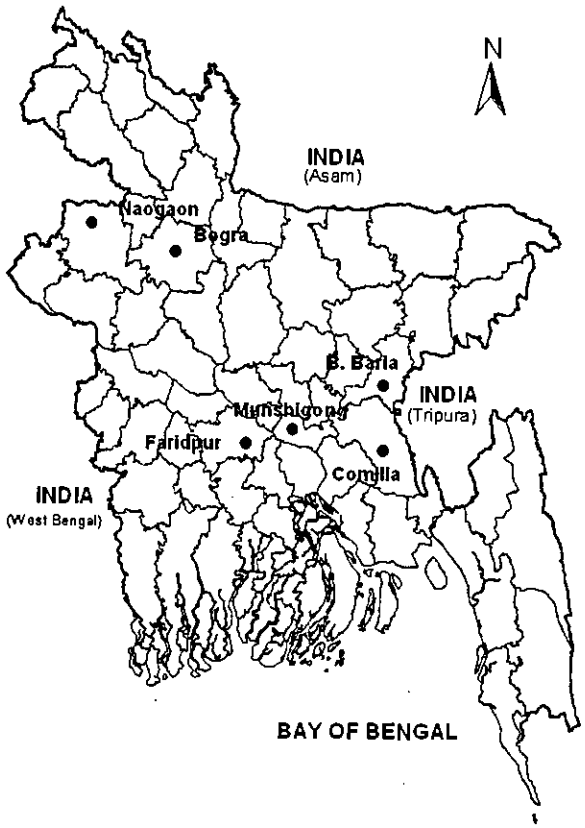


Figure 3.1: Bangladesh map showing sampling areas

In each sampling area, arsenic concentrations of irrigation water of six to eight different paddy fields were measured using a field kit (Hach) at the beginning of the irrigation season (February 2003). At each of the four arsenic affected areas, two fields with higher measured arsenic levels in irrigation water were selected for monitoring. In the two unaffected areas, arsenic concentration of irrigation water for all the fields was below the

detection level of the Hach field kit. In each of the two unaffected areas, two fields were selected for monitoring. Thus, at each of the six sampling areas, two *boro* paddy fields, irrigated by groundwater, were selected for monitoring of arsenic levels in irrigation water, top (~ 450 mm) soil layers, and paddy plants.

3.3.2 Sample Collection

3.3.2.1 Collection of Water Samples

Well water used for irrigating each of the 12 *boro* paddy fields at the six sampling areas were collected at two different times – at the beginning of the irrigation season (February 2003) and mid-way into the irrigation season (March 2003). At each paddy field, well water sample was collected in two pre-washed 500 ml plastic bottles, after running the well for at least 15 minutes. Water sample in one bottle was acidified with 1 ml concentrated hydrochloric acid, which was later analyzed for dissolved arsenic and iron.

3.3.2.2 Collection of Soil Samples

In a typical paddy field, the area under the influence of a particular irrigation well is usually divided into a number of sub-areas (usually belonging to different owners). Groundwater from the irrigation well is carried to the different sub-areas through shallow irrigation canals. In order to estimate average arsenic level in the top soil layer of a paddy field irrigated by a particular irrigation well, soil core samples were collected from 6 to 8 sub-areas within the paddy field. Location of paddy field, approximate area of field, number of sub areas in the paddy field and number of soil core sample collected from each field in the six sampling areas are shown in Table 3.1. Figure 3.2 through Figure 3.7 show schematic representation of the twelve paddy field sites along with approximate sampling locations and sample identification number. It should be noted that since farmers did not allow sampling to be carried out from the middle of their planted paddy fields, most of the sampling points are located close to the berms dividing the paddy fields into sub-areas; in most cases the sampling points are also located close to the entry point of water into the sub-area within which the sampling point is located.

Table 3.1 Approximate total area and number of sub-areas of paddy fields, and number of core samples collected from paddy fields in the six sampling areas.

Location of Field		Approximate Area of Paddy Field (ha)	Number of Sub-areas	No. of Soil Core Sample Collected
Sreenagar	Field 1	4.75	27	8
Munshiganj	Field 2	3.75	20	8
Barura	Field 1	1.75	8	6
Comilla	Field 2	2.50	9	6
Vanga	Field 1	2.00	8	6
Faridpur	Field 2	3.00	15	6
Nabinagar	Field 1	4.75	22	8
Brahmanbaria	Field 2	5.00	21	8
Bogra Sadar	Field 1	5.00	28	8
Bogra	Field 2	5.25	26	8
Nazipur	Field 1	4.50	24	8
Noagaon	Field 2	3.50	17	8

In Bangladesh, depending on location, dry season irrigation for paddy commences sometime between the last week of December and the first week of February and continues for a period of about three to three and a half months. In this study, soil core samples from the paddy fields were collected at four different times – beginning to mid-way into the irrigation season (March 2003, 1st Sampling), at the end of irrigation season (May-June 2003, 2nd Sampling), during the flood/ rainy season (June-July 2003, 3rd Sampling), and after the rainy season (i.e., before the beginning of the next irrigation season) (November 2003 to January 2004, 4th Sampling). It should be noted that during the rainy season, all the paddy fields monitored in this study were inundated with water for a period of about 3 months.

Besides paddy fields, six soil core samples were collected from raised grounds of village areas at each of the six sampling locations during November 2003 to January 2004. These soil core samples from village areas, which do not usually come in contact with irrigation water, are expected to provide estimates of background level of arsenic in soil for the respective areas.

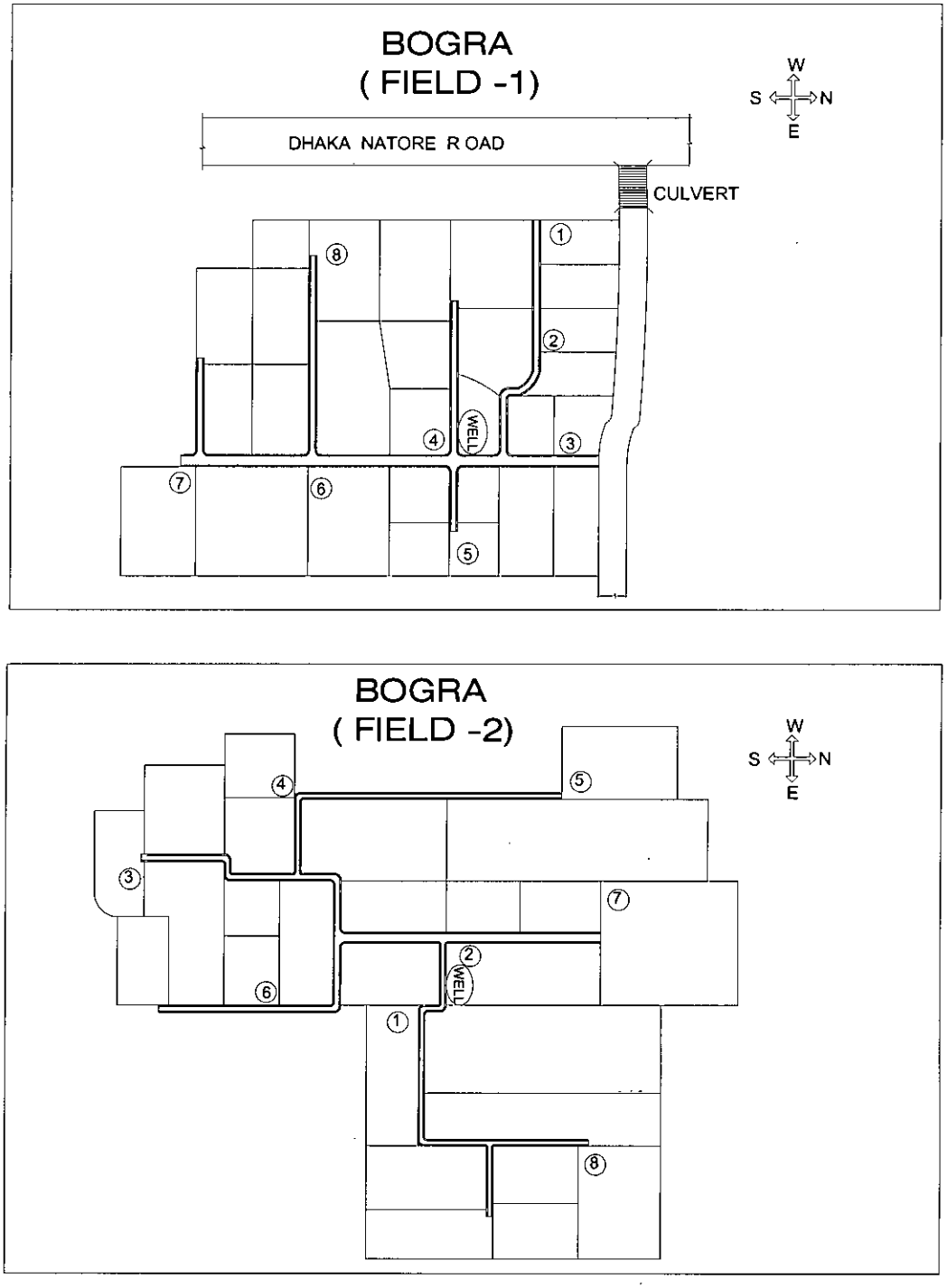
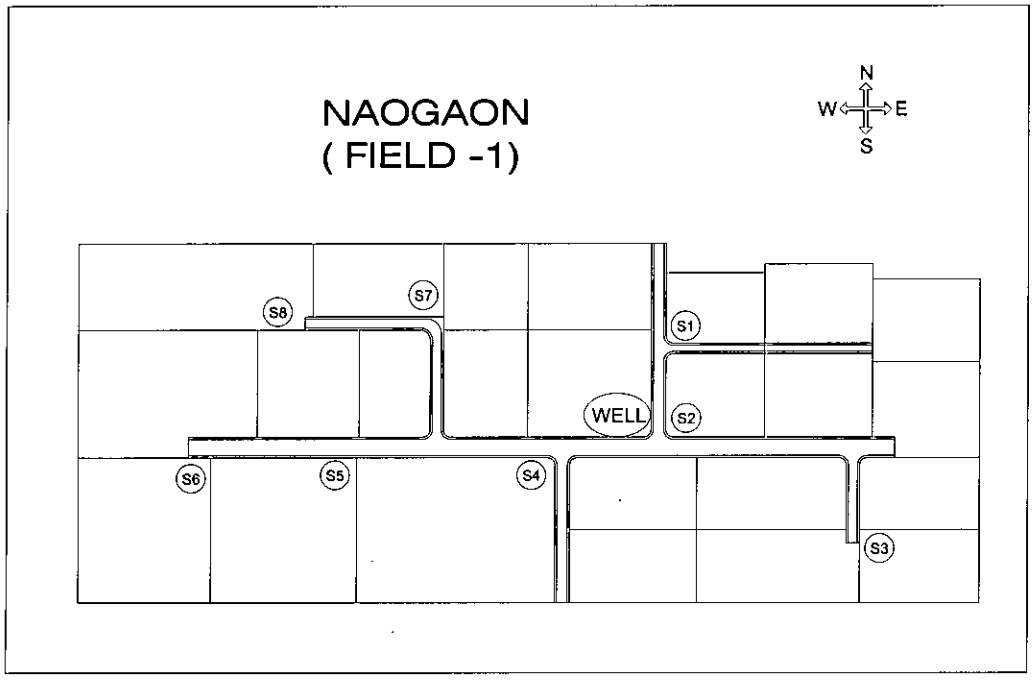


Figure 3.2: Schematic representation of the paddy fields at Bogra Sadar, Bogra along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)



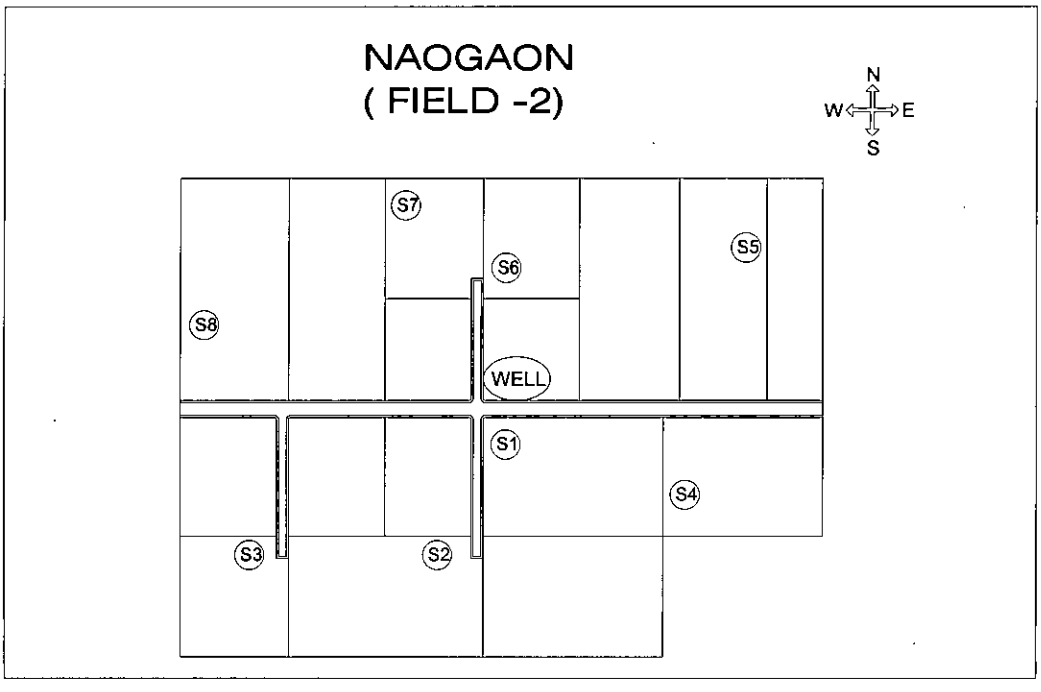


Figure 3.3: Schematic representation of the paddy fields at Nazipur, Noagaon along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)

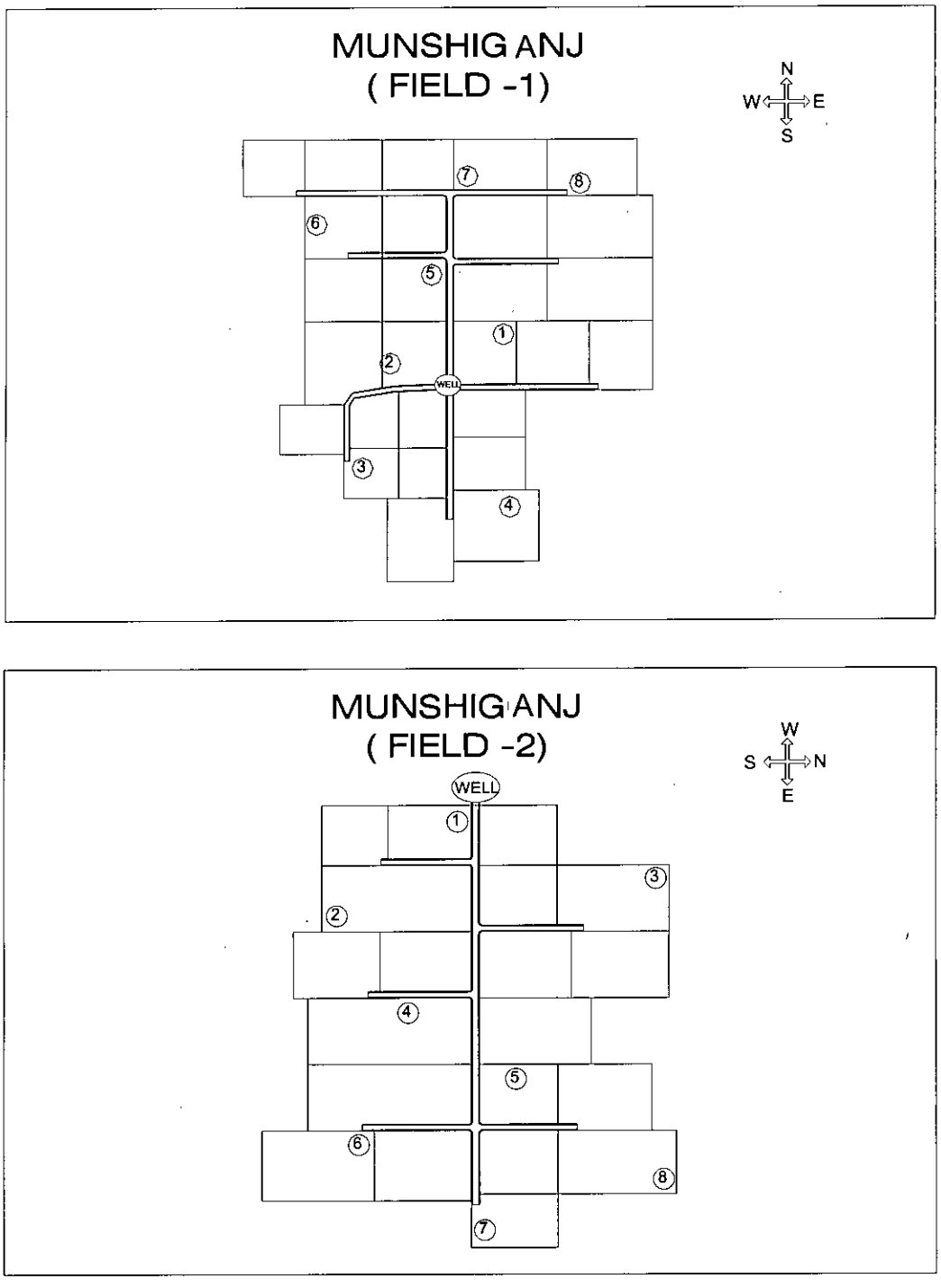


Figure 3.4: Schematic representation of the paddy fields at Sreenagar, Munshiganj along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)

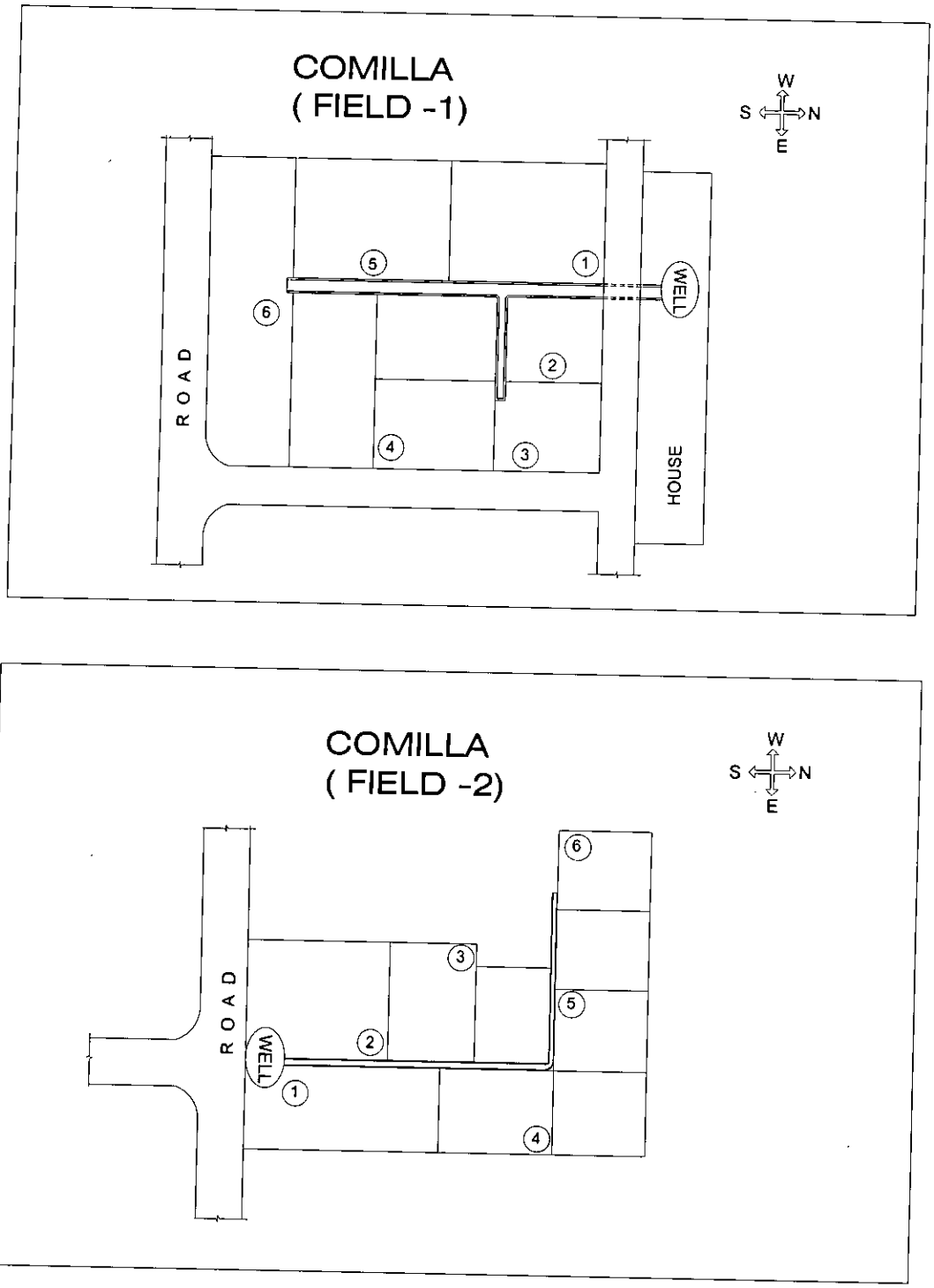
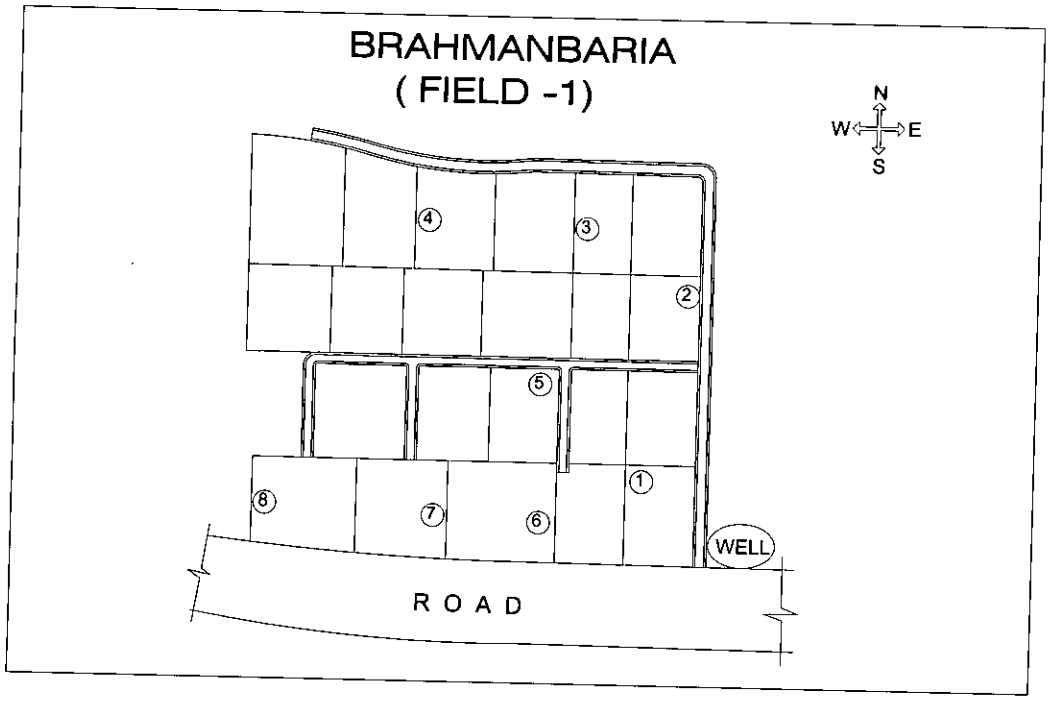


Figure 3.5: Schematic representation of the paddy fields at Barura, Comilla along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)



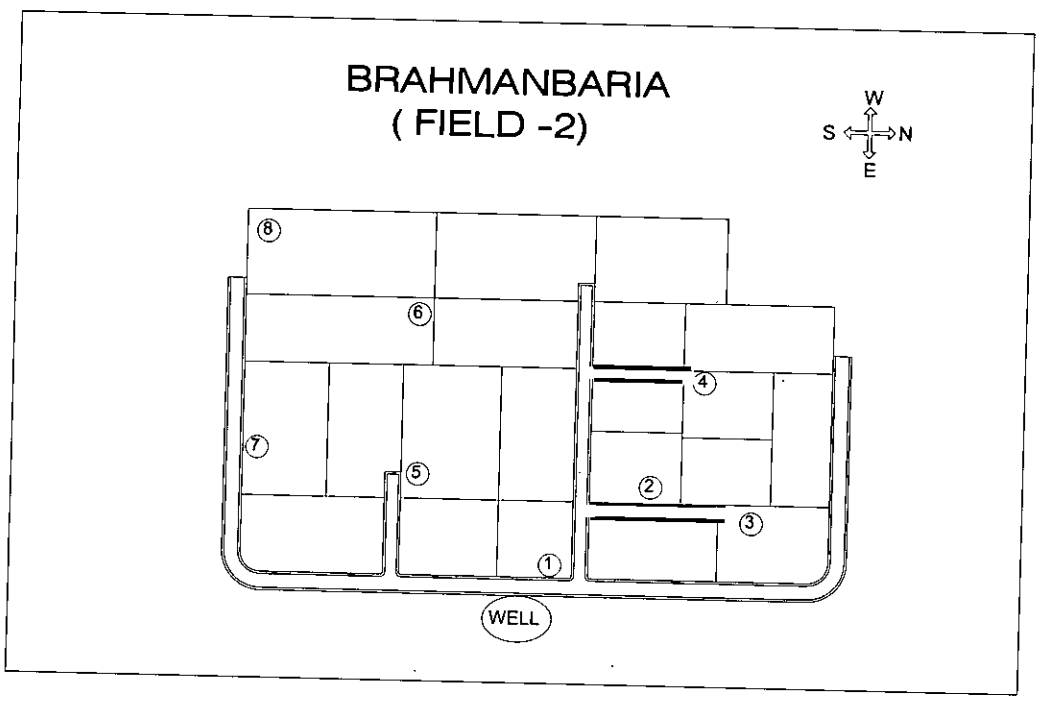


Figure 3.6: Schematic representation of the paddy fields at Nabinagar, Brahmanbaria along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)

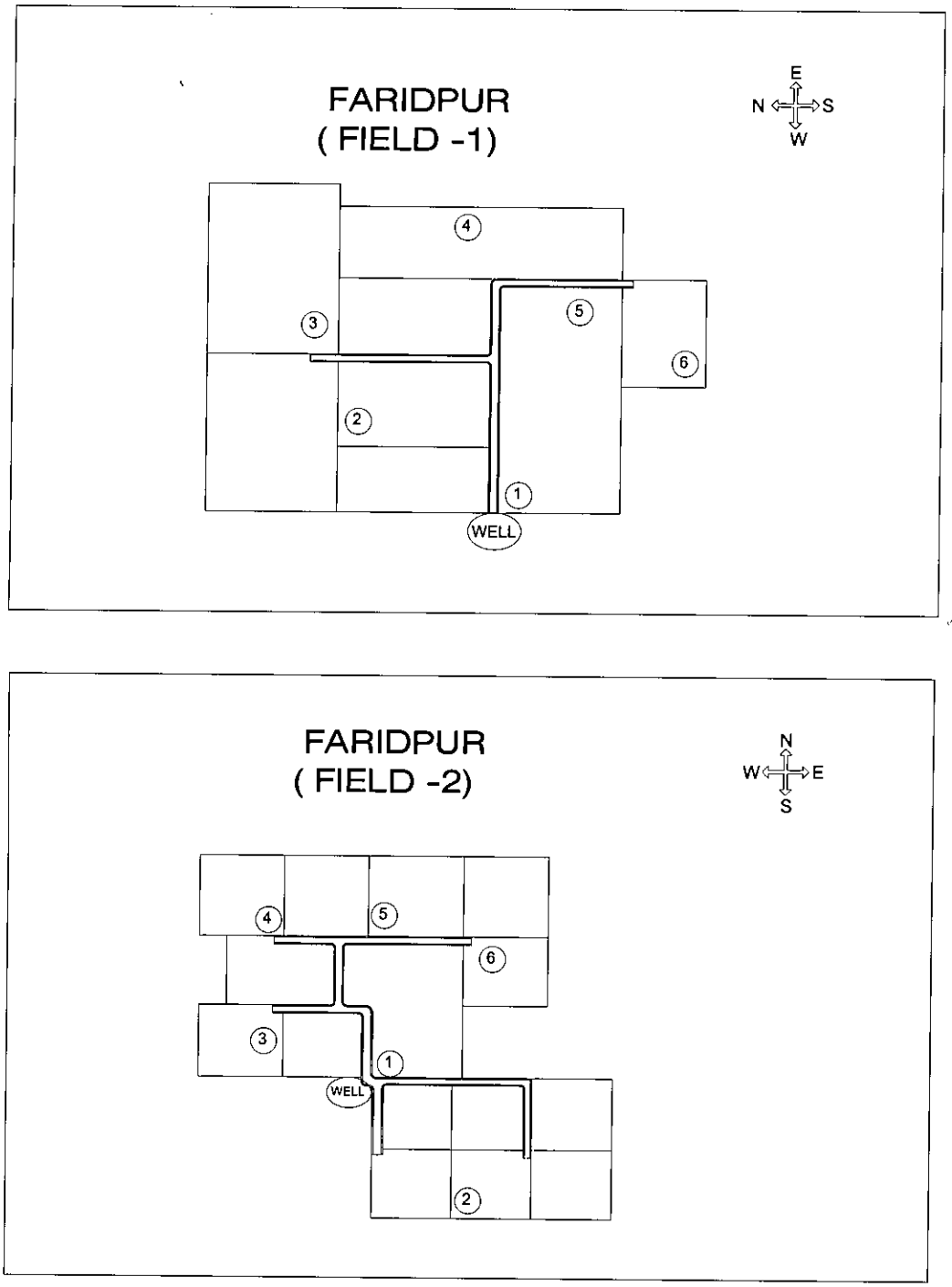


Figure 3.7: Schematic representation of the paddy fields at Vanga, Faridpur along with approximate sampling locations and sample identification numbers (indicated by numbers within circles)

While collecting soil samples, efforts were made to collect core samples with a depth covering the root zone depth for paddy, which is reported to be within 400 mm to 600mm (average 500 mm) (Rashid, 1997). In this study, a core sampler 750mm in height was used for collecting soil samples. During sampling, each sampling point in a paddy field was identified by measuring distances from one edge and one side of the sub-area within which the sampling point was located. Soil core 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 a depth of about 500 mm. After withdrawing the sampler along with the soil core, both the ends were sealed with tapes to reduce contact with air and transported to the laboratory.

3.3.2.3 Collection of Paddy Plant Samples

Paddy plant samples were collected just before harvest time. Entire paddy plants (including roots) were collected. Paddy plant samples were collected from the different sub-areas of each paddy field. A total of 88 paddy plant samples were collected from the 12 paddy fields of the six sampling areas. Table 3.2 shows the paddy variety and number of plant samples collected from different field sites. It shows that BR-28 and BR-29 are the predominant paddy varieties grown at the selected field sites.

Table 3.2 Paddy variety and no of plant sample collected from different field sites.

Location of Field		Sample ID							
		S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Sreenagar	Field 1	BR-29	BR-29	BR-16	BR-29	BR-29	BR-29	BR-29	BR-29
Munshiganj	Field 2	BR-29	BR-29	BR-29	BR-29	BR-16	BR-29	BR-29	BR-16
Barura	Field 1	MI	BR-28	BR-28	MI	BR-28	BR-20	-----	-----
Comilla	Field 2	BR-28	CI	BR-28	BR-28	BR-28	CI	-----	-----
Vanga	Field 1	BR-29	BR-29	BR-29	BR-27	BR-29	BR-29	-----	-----
Faridpur	Field 2	BR-29	BR-27	BR-29	BR-29	BR-29	BR-29	-----	-----
Nabinagar	Field 1	SB	BR-29	PI	MI	BR-29	BR-29	BR-29	BR-29
B.Baria	Field 2	SB	PI	BR-29	BR-29	BR-29	SB	BR-29	BR-29
Bogra Sadar	Field 1	BR-29	BR-29	CI	BR-29	BR-29	CI	BR-29	BR-29
Bogra	Field 2	BR-29	BR-29	BR-29	BR-29	BR-29	CI	CI	BR-29
Nazipur	Field 1	BR-28	BR-28	BR-28	BR-28	BR-28	MI	BR-28	BR-28
Noagaon	Field 2	BR-28	MI	BR-28	BR-28	MI	BR-28	BR-28	BR-28

(MI = Mala IRRI, SB= Shahi Balam, PI= Pakistani IRRI, CI=China IRRI)

3.3.3 Laboratory Analysis of Water, Soil and Paddy Plant Samples

3.3.3.1 Analysis of Water Samples

Water from acidified sampling bottles was used in the laboratory for analysis of arsenic and iron. Water from the non-acidified bottles collected in March 2003 was used for analysis of a wide range of water quality parameters, including pH, conductivity, chloride, sulfate, ammonia, nitrate and phosphate. Analysis of water samples was carried out following methods described in section 1.3

3.3.3.2 Analysis of Soil Samples

Division of Core Sample:

Before analysis, each soil core sample was divided into four segments; the first segment consisting of the top 75 mm of soil, the second segment consisting of the next 75 mm, the third segment consisting of the next 150 mm, and the fourth segment consisting of the rest of the core. Each segment of soil was analyzed for total (aqua-regia extractable) arsenic. Besides, selected segments of core samples were analyzed for aqua-regia extractable iron, and oxalate extractable arsenic and iron; this extractant (i.e., oxalate) primarily targets amorphous iron oxyhydroxides and arsenic co-precipitated with amorphous iron oxy-hydroxides. Besides, soil associated with the roots of each paddy plant sample, referred to here as "root-soil", was collected by washing the roots with deionized water. The root-soil and each segment of the soil core samples were analyzed for total (aqua-regia extractable) arsenic.

Digestion of Soil Sample:

For determination of aqua-regia extractable arsenic, 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).

Oxalate Extraction:

Oxalate extractable arsenic and iron were measured for 24 soil cores colleted during the 1st sampling (January 2003) and 24 soil cores collected during the 2nd sampling (May 2003); in each case two cores from each of the 12 paddy fields were selected for analysis. For each soil core, the top three segments were analyzed for oxalate extractable arsenic and iron. The 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).

3.3.3.3 Analysis of Paddy Plant Samples

Division of Plant Sample:

Before analysis, the paddy plant samples were divided into five parts: (i) root, (ii) stem, (iii) leaf, (iv) grain, and (v) husk.

Digestion of Plant Sample:

For analysis of total arsenic, the different parts/segments of the paddy plant samples were digested. A number of similar but different digestion procedures are available in the literature (e.g., Bennett et al., 2000; Chen and Folt, 2000; Shimadzu AAS Cookbook, 1999). At first three different digestion procedures were tested and compared (in terms of extraction efficiency and reproducibility). The procedure reported in Shimadzu AAS Cookbook was found to be more satisfactory than the others and was selected for use in this study.

Briefly the digestion procedure consists of the following steps: (i) wash plant samples with distilled water, (ii) divide the plant sample into parts (as described above), (iii) take weight of each part of the sample, (iv) oven-dry the sample at 65°C for 24 hours and take weight of the oven-dried sample, (v) take approximately 2 grams of oven-dried sample in a volumetric flask and make it moist by adding a few milliliters of deionized water, then

add 25 ml nitric acid to the flask and keep it overnight, (vi) heat the flask for two hours to boiling, then after cooling add 10 ml of perchloric acid to the flask and heat again (to boiling) for one hour, (vii) if color of the sample turns yellow, digestion is assumed to be complete, (viii) if color of the sample turns dark, add 2 to 3 ml of nitric acid to the flask and apply heat; repeat the process until the color turns yellow. Arsenic analysis of plant samples were carried out with hydride generation atomic absorption spectrophotometry (HVG-AAS) using an AAS (Shimadzu, AA6800).

3.4 RESULTS AND DISCUSSION

3.4.1 Irrigation Water Quality

Concentration of selected chemical constituents of water samples collected from the irrigation wells of the twelve paddy fields monitored in this study are shown in Table 3.3. It shows that, in general, well waters from the arsenic affected areas contain much higher arsenic, iron, ammonia and phosphate, compared to those collected from the unaffected areas (Bogra and Naogaon). Highest arsenic, iron and ammonia concentrations were recorded for well water samples collected from the two paddy fields in Munshiganj. It may be noted that high arsenic concentrations in groundwater have often been found to be associated with high iron, phosphate and ammonia concentrations (e.g., BGS/DPHE, 2001; Harvey *et al.*, 2002).

Table 3.3 Concentration of selected chemical constituents of irrigation well water samples

Location of Well	pH	Conductivity (μS/cm)	As (μg/l)	Fe (mg/l)	NH_3-N (mg/l)	PO_4^{3-} (mg/l)	NO_3-N (mg/l)
Munshiganj, Field 1	6.51	631	320	6.74	9.98	2.50	0.95
Munshiganj, Field 2	6.85	698	436	5.83	7.30	4.45	< 0.01
Comilla, Field 1	6.60	964	199	4.17	2.35	6.70	1.4
Comilla, Field 2	7.12	416	154	3.79	3.05	4.60	1.7
Brahmanbaria, Field 1	6.75	540	138	3.05	5.40	3.52	2.2
Brahmanbaria, Field 2	6.55	445	149	3.38	7.15	4.42	2.9
Faridpur, Field 1	6.69	915	79	2.96	0.40	7.50	1.9
Faridpur, Field 2	6.59	683	96	3.62	< 0.06	4.60	0.5
Bogra, Field 1	6.52	216	< 1	0.04	0.06	0.85	4.7
Bogra, Field 2	6.86	271	< 1	0.05	0.10	1.25	3.2
Noagoan, Field 1	6.82	267	< 1	0.31	0.08	1.82	3.75
Noagaon, Field 2	6.72	282	< 1	0.46	0.15	1.36	4.22

3.4.2 Enrichment and Depletion of Arsenic in Paddy Field Soil

Spatial Variation of Arsenic in Paddy Field Soil

Arsenic concentrations in different layers of soil core samples collected from the different sampling locations in each of the 12 paddy fields show that arsenic concentration varies significantly over a paddy field. Figures 3.8 through 3.13 show As concentrations of the top 0-75 mm segment of soil for core samples collected in March 2003 (first sampling) and May-June 2003 (second samplings) from field-1 of all six sampling areas. Arsenic concentrations of cores collected from field-2 of the six sampling areas are presented in Appendix A. These figures show that As concentration in soil varies significantly over the paddy fields, both at the beginning and at the end of the irrigation season. Similar variation was also observed for the other soil layers and also for samples collected during the rainy/flood season (third sampling) and after the rainy season (fourth sampling). Table 3.4 shows range, mean and standard deviation of arsenic contents in the top 0-75 mm segment of the soil cores collected from the field sites at different sampling times.

For soil cores collected during the first sampling (i.e., March 2003), As contents of soil from the unaffected areas of Bogra and Naogaon were found to be much lower compared to those found for samples collected from the paddy fields in the four arsenic affected areas. For example, for field-1 in Bogra, arsenic concentration in the top 0-75 mm soil varied from 0.56 to 2.54 mg/kg; for field-1 of Naogaon it varied from 1.16 to 4.58 mg/kg. Arsenic concentration of soil core samples collected from the four arsenic affected areas also showed significant spatial variability, but the arsenic concentrations were much higher compared to those found for Bogra and Naogaon. For example, for field-1 in Munshiganj, arsenic concentrations in the top 0-75 mm soil varied from 4.18 to 12.04 mg/kg; for field-1 in Brahmanbaria, it varied from 4.33 to 8.59 mg/kg.

In order to assess the effect of irrigation on As content of paddy field soil, As concentrations of the top 0-75 mm segment of soil cores collected during first sampling (March 2003) were compared with those collected during the second sampling (May-June 2003). Figures 3.8 and 3.9 show As concentrations of the top 0-75 mm soil layer for core samples collected from Bogra and Naogaon, respectively. These two sampling areas, located in the north-western region of Bangladesh, have not been affected by As contamination of groundwater. Average As concentration of all four irrigation wells at

these two sites was below 1 ppb. These figures show that for both Bogra and Naogaon, As concentrations in the top soil layer (0-75 mm) did not vary significantly at the end of the irrigation season in May-June 2003. For example, for field-1 in Bogra, average As concentration in the top 0-75 mm soil layer was 1.40 mg/kg in March 2003, which increased to about 2.12 mg/kg at the end of the irrigation season in May 2003.

However, the situation was different for the top layer (0-75 mm) of paddy field soil collected from the four arsenic affected areas (see Figs. 3.10 to 3.13). For example, for field-1 in Munshiganj, arsenic concentrations in the top 0-75 mm soil varied from 8.65 to 22.35 mg/kg at the end of the irrigation season (May-June 2003), compared to 4.18 to 12.04 mg/kg in March 2003. A closer look at these figures (Figs. 3.8 to 3.13) reveals that the increase in arsenic concentration at the end of the irrigation season differed significantly among the sampling points of a particular paddy field. With few exceptions, higher increase in arsenic concentration has been found for sampling points that are located close to the entry points of water in the sub-area within which the sampling point is located. In fact, such variation in increase of arsenic concentration is expected because arsenic present in irrigation water is quickly adsorbed or co-precipitated (with iron) onto soil as arsenic bearing irrigation water travels through the paddy field. Some recent studies (Dittmar et al., 2006; Roberts et al., 2006; Dittmar et al., 2005) suggest that input of arsenic into paddy field soils decreases significantly with increasing distance from the irrigation water inlet. Roberts et al. (2006) estimated that over the irrigation season, the total arsenic input to paddy field soil was three to five times higher near the water inlet than that at the opposite side of the field. In fact, Dittmar et al. (2005) found that in a paddy field in Munshiganj, soil arsenic concentrations near the water inlet were about twice as high as that at the opposite side of the field.

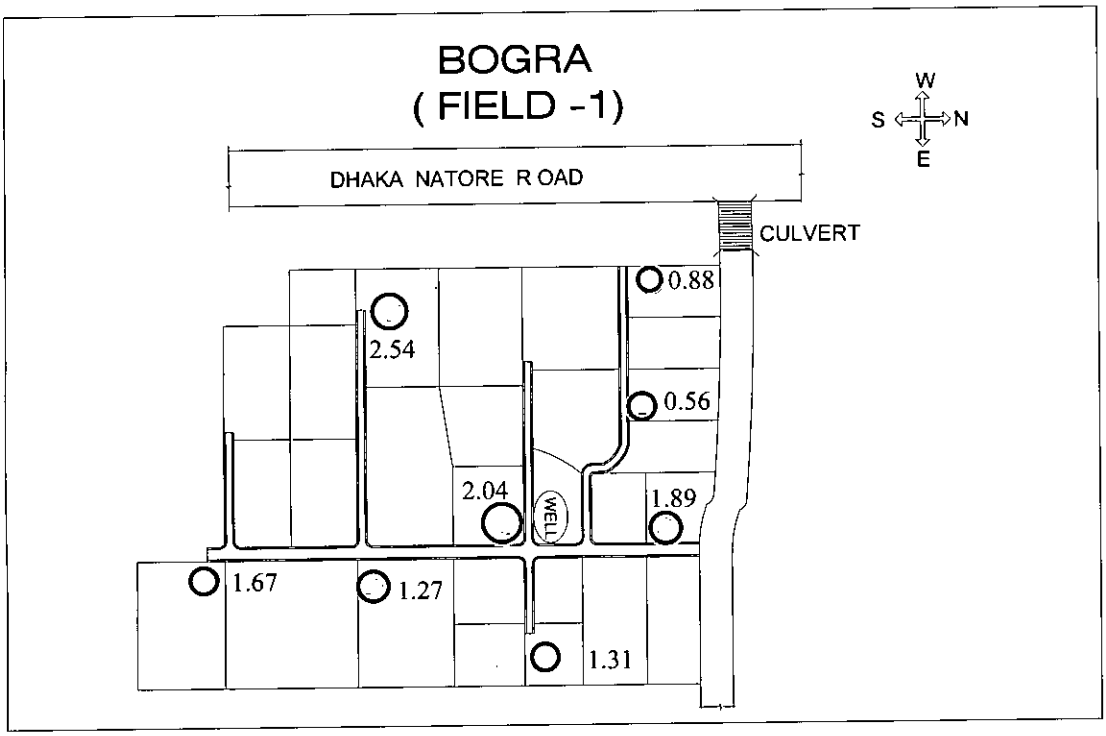
In general, highest accumulation of As in the top soil layer (0-75 mm) at the end of the irrigation season was observed for Munshiganj paddy fields, where As concentration in irrigation water was also the highest among the sampling areas. For field-1 in Mushiganj, average arsenic concentration in the top 0-75 mm soil layer increased from about 8.4 mg/kg in March 2003 to about 14.8 mg/kg in May-June 2003; for field-1 in Brahmanbaria, it increased from 6.7 mg/kg to 10.3 mg/kg. However, it should be kept in mind that since most of the sampling points were located close to the water entry points in

the paddy fields (see section 3.3.2.2) where higher accumulation of arsenic is expected, the calculated average value for a particular paddy field is likely to overestimate the accumulation of arsenic in soil.

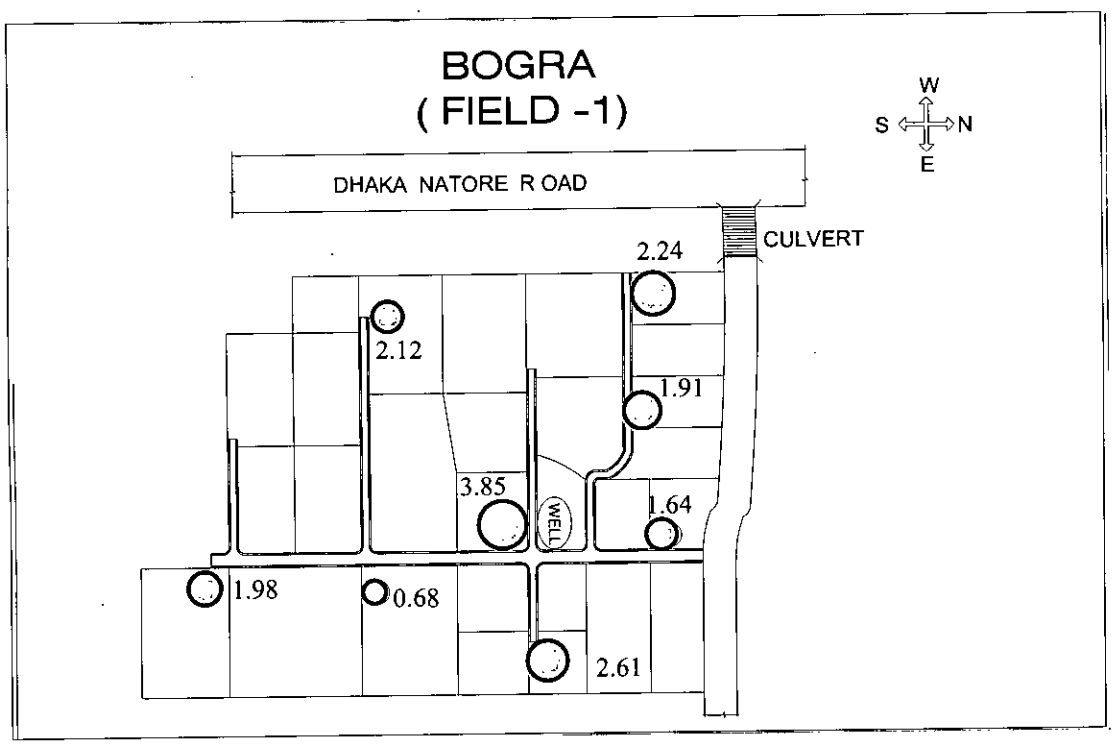
Since there were significant variations of arsenic concentrations in the top soil layers at the end of the irrigation season among soil cores collected from each paddy field (primarily depending on the location of the sampling points with respect to entry point of water in the field; see Table 3.4), mean arsenic levels are probably not ideal for comparison of arsenic levels among different sampling times. Hence, for each paddy field, arsenic in the different segments of the soil cores collected at different times were compared using Student's t distribution; the results are presented in Table 3.5.

Table 3.4 Range, mean and standard deviation (SD) of arsenic content in the top 0-75 mm segment of soil core samples collected from different sampling areas

Sampling Location	Parameter	1st Sampling, March 2003 (mg/kg)	2nd Sampling, May-June 2003 (mg/kg)	3rd Sampling June-July 2003 (mg/kg)	4th Sampling, November-03-January 04 (mg/kg)
Bogra Field-1	Range	0.88-2.54	0.68-3.85	1.90-3.25	0.82-2.36
	Mean ± SD	1.40 ± 0.62	2.12 ± 0.84	2.37±0.52	1.29 ± 0.55
Bogra Field-2	Range	0.69-2.05	0.98-3.84	1.36-3.01	2.04-3.90
	Mean ± SD	1.49 ± 0.50	2.68 ± 1.09	2.39 ± 0.50	2.90 ± 0.58
Naogaon Field-1	Range	1.16-4.58	1.70-4.99	1.18-3.27	1.31-3.07
	Mean ± SD	2.45 ± 1.02	3.36 ± 1.08	2.61 ± 0.75	2.39 ± 0.71
Naogaon Field-2	Range	1.26-3.35	2.17-3.65	0.79-3.03	1.36-3.89
	Mean ± SD	2.25 ± 0.64	2.80 ± 0.53	2.18 ± 0.63	2.58 ± 0.80
Munshiganj Field-1	Range	4.18-12.04	8.65-22.35	5.15-14.18	5.58-11.04
	Mean ± SD	8.38 ± 2.31	14.75± 3.88	9.96 ± 2.82	6.87 ± 1.86
Munshiganj Field-2	Range	4.22-10.36	7.26-24.65	4.26-16.03	4.57-15.36
	Mean ± SD	7.62 ± 1.70	12.39± 5.42	8.58 ± 3.51	8.22 ± 3.17
Comilla Field-1	Range	3.27-7.69	4.26-9.67	4.83-8.62	3.65-9.92
	Mean ± SD	4.67± 1.41	7.97 ±1.87	6.74 ± 1.39	5.90 ± 2.23
Comilla Field-2	Range	3.20-5.68	4.06-8.61	3.03-7.37	1.87-7.00
	Mean ± SD	4.36 ± 0.89	6.20 ± 1.35	4.85 ± 1.31	4.51 ± 1.56
Faridpur Field-1	Range	2.07-7.62	4.68-10.44	3.52-7.66	2.03-6.35
	Mean ± SD	5.74 ± 1.74	7.22 ± 2.22	6.03 ± 1.44	4.84 ± 1.42
Faridpur Field-2	Range	4.23-7.19	4.71-12.33	5.04-11.36	4.76-8.69
	Mean ± SD	5.66 ± 0.98	9.86 ± 2.45	9.13 ± 2.08	6.51 ± 1.63
Brahmanbaria Field-1	Range	4.33-8.59	5.85-17.62	4.98-14.68	4.62-7.42
	Mean ± SD	6.675 ± 1.34	10.29 ± 3.58	8.96 ± 2.94	5.95 ± 0.81
Brahmanbaria Field-2	Range	2.60-6.36	3.41-16.65	2.24-7.35	2.65-5.40
	Mean ± SD	4.15 ± 1.21	9.22 ± 3.64	4.45 ± 1.55	3.95 ± 0.94

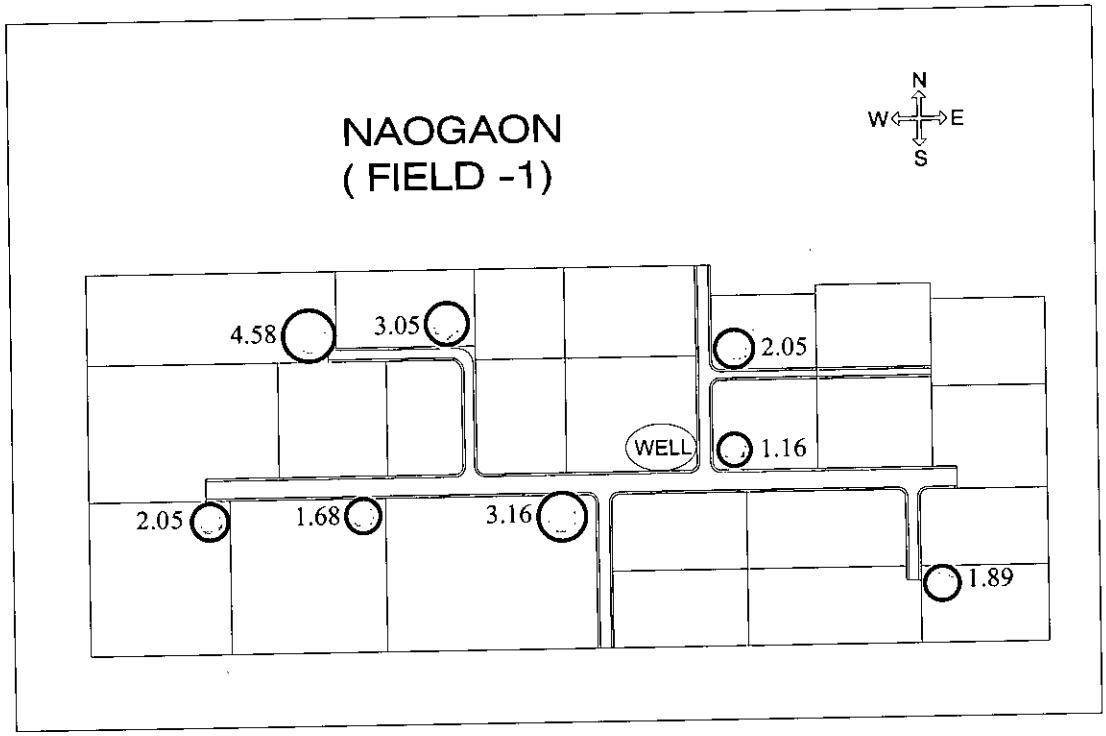


(i)

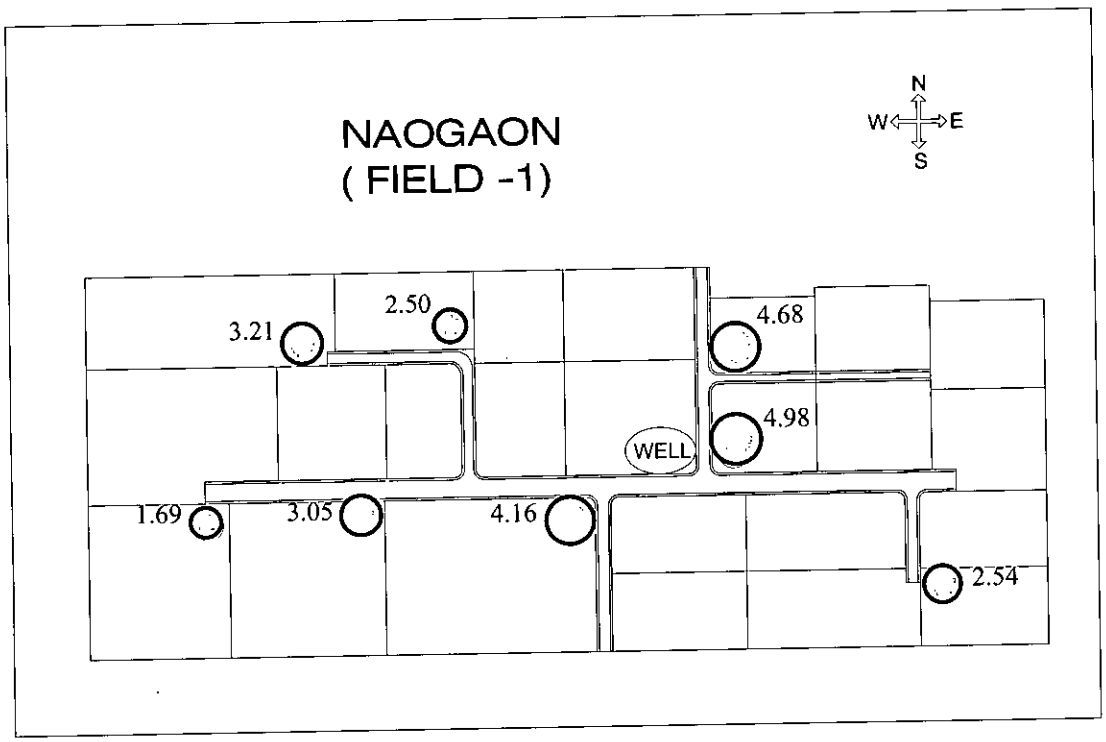


(ii)

Figure 3.8: Schematic representation of the paddy field-1 in Bogra along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

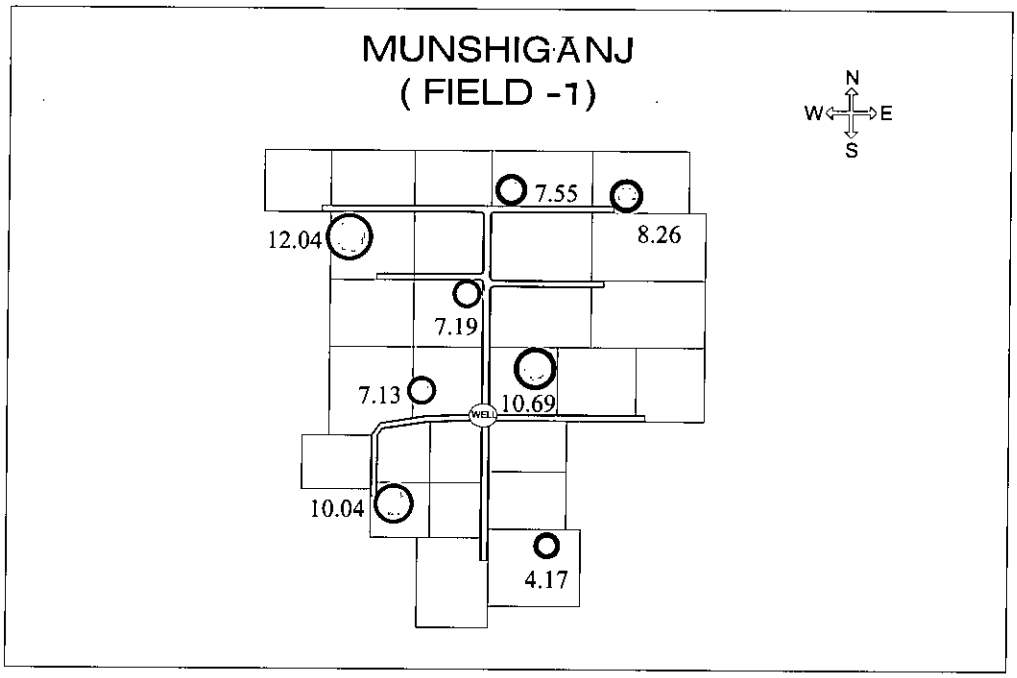


(i)

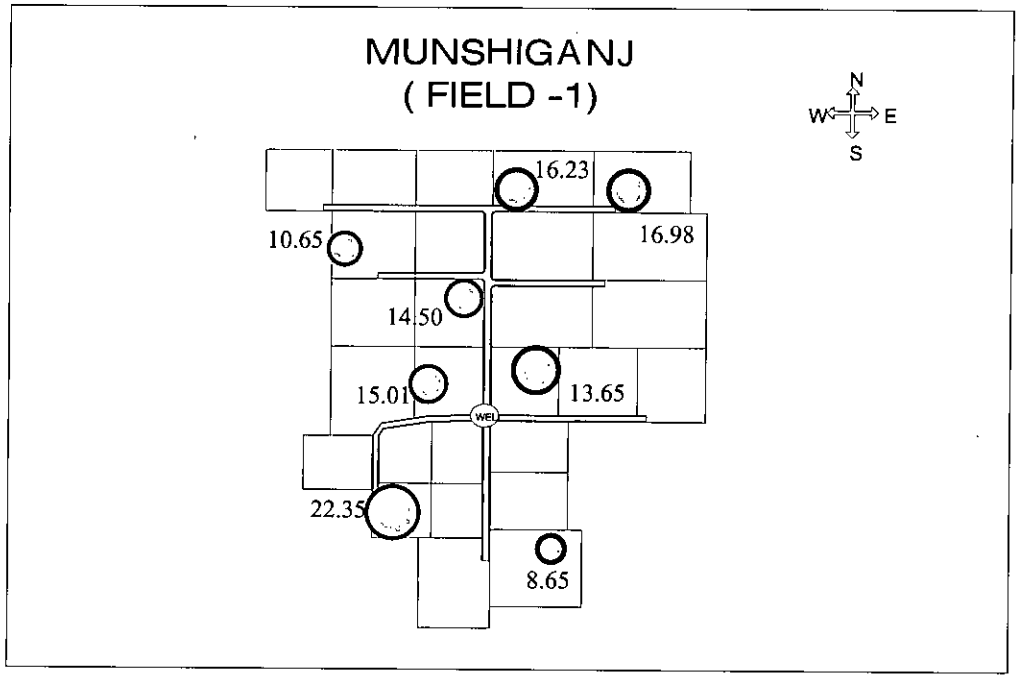


(ii)

Figure 3.9: Schematic representation of the paddy field-1 in Naogaon along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

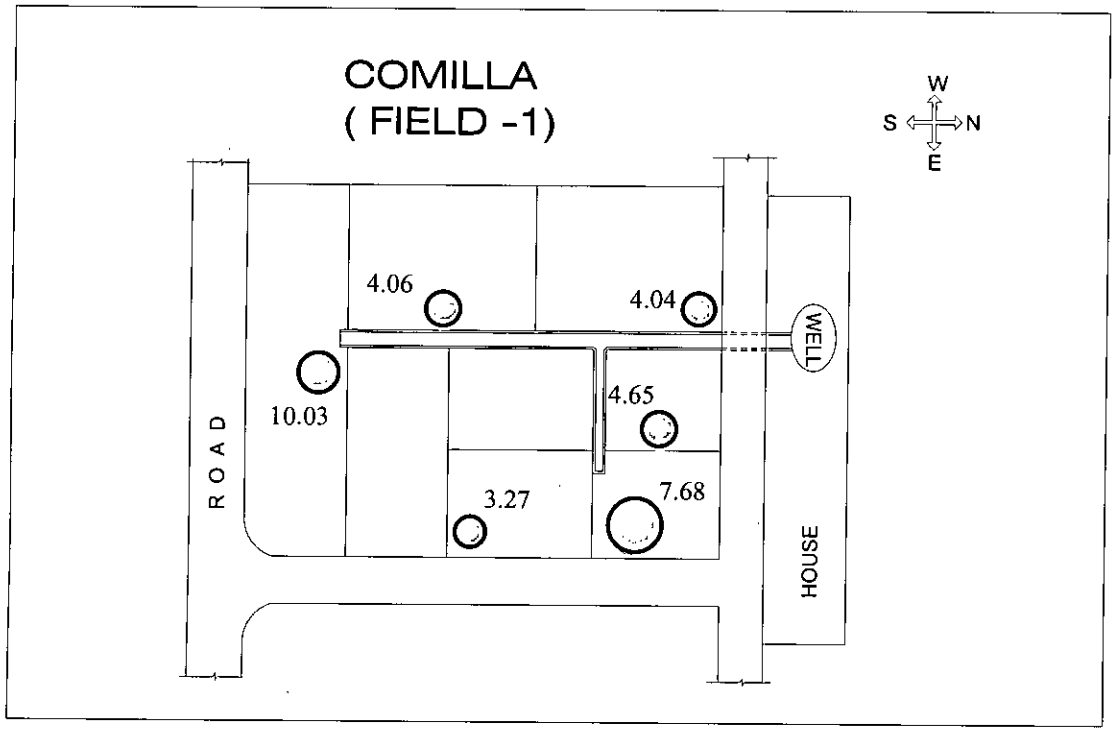


(i)

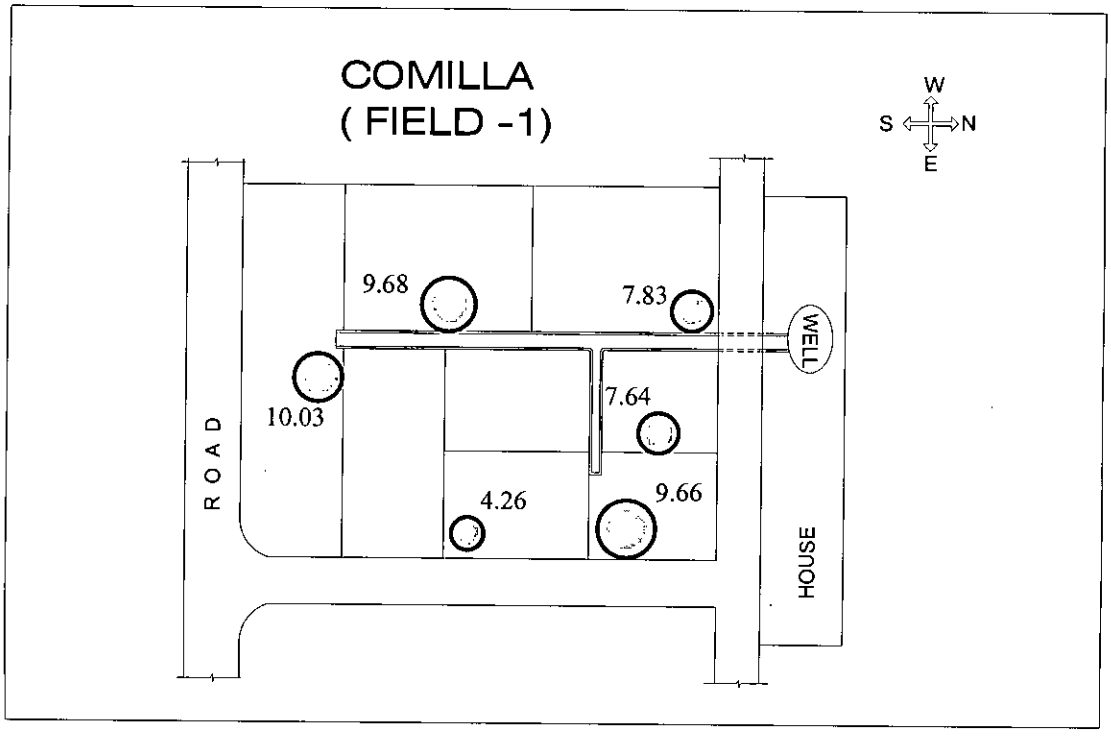


(ii)

Figure 3.10: Schematic representation of the paddy field-1 in Munshiganj along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

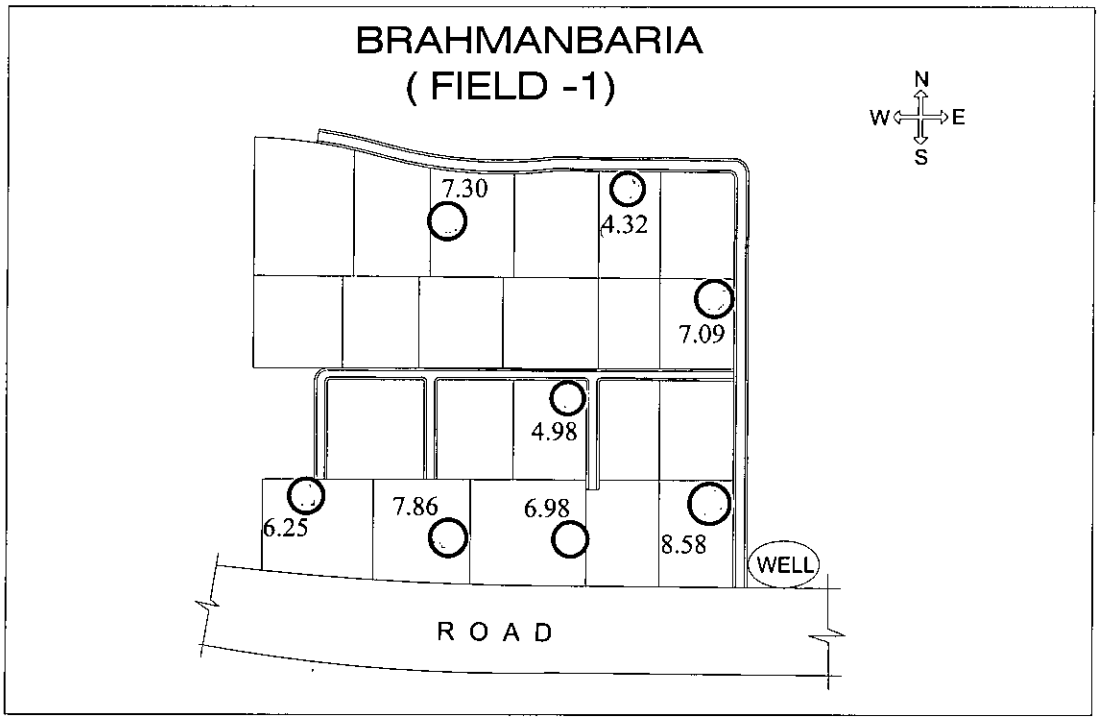


(i)

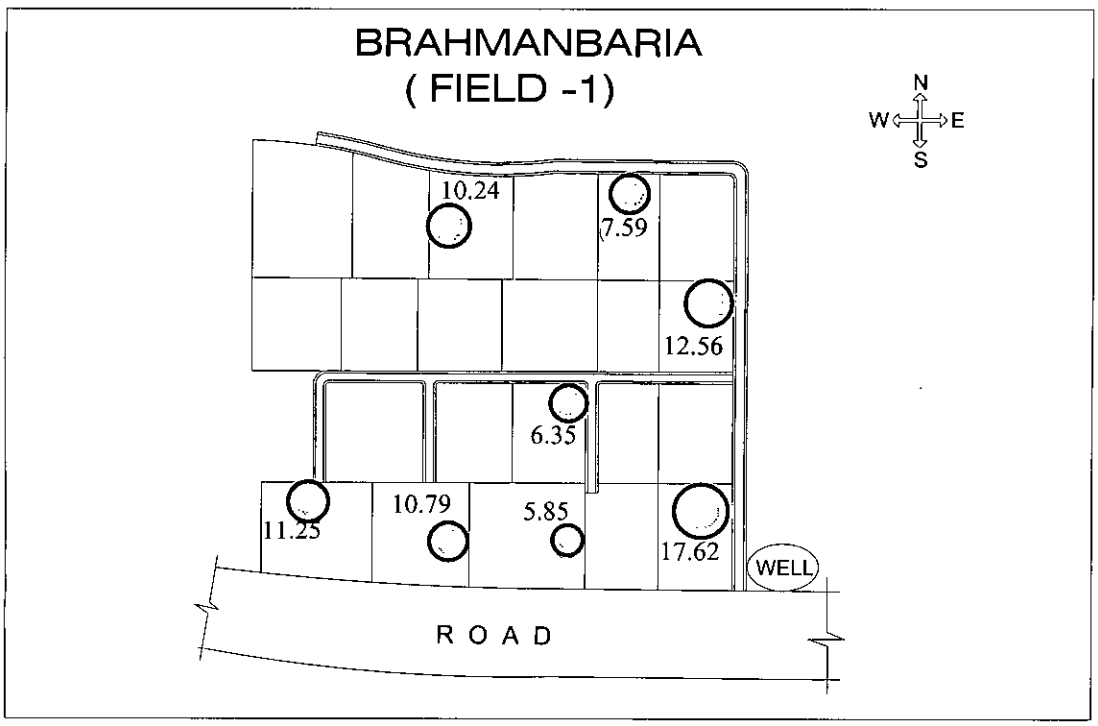


(ii)

Figure 3.11: Schematic representation of the paddy field-1 in Comilla along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

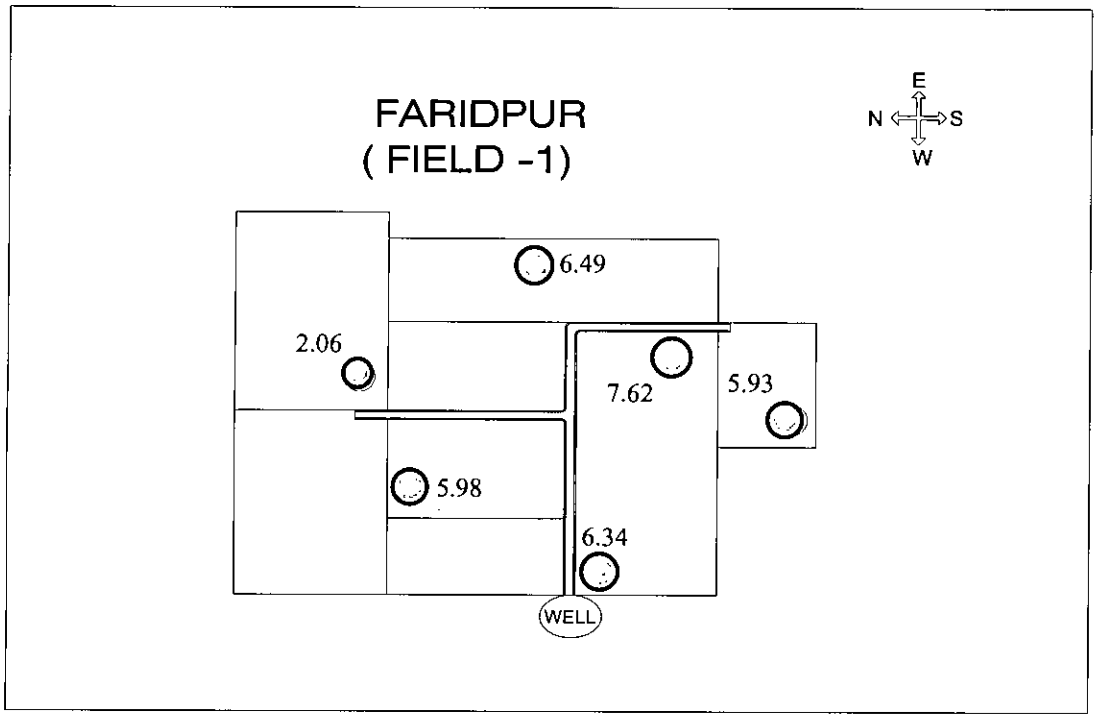


(i)

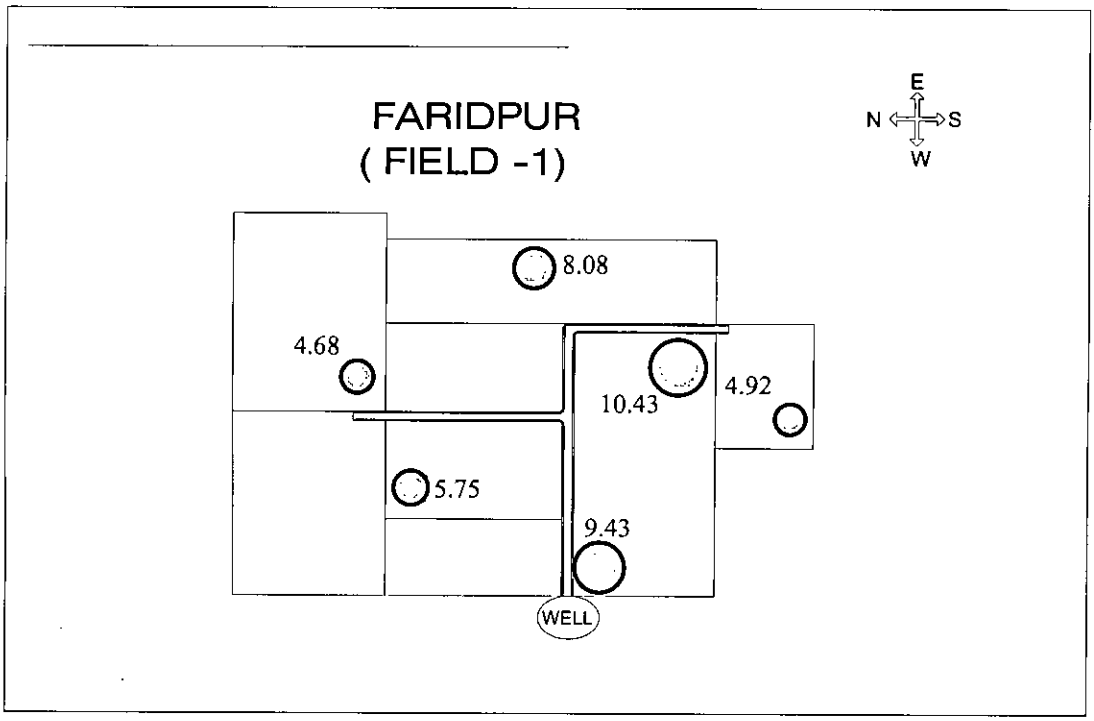


(ii)

Figure 3.12: Schematic representation of the paddy field-1 in Brahmanbaria along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)



(i)



(ii)

Figure 3.13: Schematic representation of the paddy field-1 in Faridpur along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

Table 3.5 shows comparison of As levels in the top 0-75 mm segment of soil cores collected during the first (March 2003) and the second (May-June 2003) rounds of sampling. It shows that for the four paddy fields in the unaffected areas (Bogra and Naogaon), As levels in the top 0-75 mm segment of soil are equal/identical for the first- and second-round soil core samples. Among the paddy fields in the four As-affected areas, As levels in the second-round core samples are statistically higher than those of the first-round samples for all the paddy fields, except for one (Field 1 of Faridpur). Thus, despite significant spatial variation within different sub-areas of a particular paddy field, As levels at the end of the irrigation season have been shown to be statistically higher than those at the beginning of the irrigation season.

Table 3.5 Comparison of arsenic levels in the top 0-75 mm segment of soil core samples collected during the first (March 2003) and the second (May 2003) rounds of sampling

Location	Comparison	t	$t_{critical}$	Comment
Munshiganj Field 1	1st sampling vs. 2nd sampling	3.449	2.365	Concentration in 2nd sampling is higher
Munshiganj Field 2	1st sampling vs. 2nd sampling	5.164	2.365	Concentration in 2nd sampling is higher
Comilla Field 1	1st sampling vs. 2nd sampling	3.536	2.571	Concentration in 2nd sampling is higher
Comilla Field 2	1st sampling vs. 2nd sampling	2.970	2.571	Concentration in 2nd sampling is higher
Faridpur Field 1	1st sampling vs. 2nd sampling	2.109	2.571	Concentrations of two sites are equal/identical
Faridpur Field 2	1st sampling vs. 2nd sampling	3.966	2.571	Concentration in 2nd sampling is higher
Brahmanbaria Field 1	1st sampling vs. 2nd sampling	4.201	2.365	Concentration in 2nd sampling is higher
Brahmanbaria Field 2	1st sampling vs. 2nd sampling	4.543	2.365	Concentration in 2nd sampling is higher
Bogra Field 1	1st sampling vs. 2nd sampling	2.349	2.365	Concentrations of two sampling are equal/identical
Bogra Field 2	1st sampling vs. 2nd sampling	2.149	2.365	Concentrations of two sampling are equal/identical
Noagaon Field 1	1st sampling vs. 2nd sampling	1.505	2.365	Concentrations of two sampling are equal/identical
Noagaon Field 2	1st sampling vs. 2nd sampling	1.473	2.365	Concentrations of two sampling are equal/identical

Variation of Arsenic Concentration of Paddy Field Soil with Depth:

Figures 3.14 through 3.19 show arsenic profiles of soil core samples collected from 12 paddy fields, two from each of the six sampling locations. Each data point in the figures represents the average concentration of arsenic for a particular segment of the soil core and has been plotted at a depth representing the mid-depth of the segment. It should be noted that each data point showing arsenic concentration at a particular depth represents average of 6 to 8 samples taken from the particular field, and thus gives the average condition of arsenic content of soil over the entire paddy field for that particular depth. As explained earlier, because of the way the sampling points were selected, these average values most likely overestimate the accumulation of arsenic in soil at the end of the irrigation season. Nevertheless, these average values are useful for assessing the trend of variation of arsenic concentration in different layers of soil as a function of depth.

Figures 3.14 and 3.15 show arsenic profiles of soil core samples collected from Bogra and Naogaon, respectively. Average arsenic concentration of all four irrigation wells at these two sites was below the detection limit of 1 ppb. These figures show that in both Bogra and Naogaon, arsenic levels in the irrigated soils do not vary significantly with depth and that variation of arsenic concentration over the sampling time (from March to November 2003) is not very significant. However, it appears that arsenic level in the top soil layers increased slightly at the end of the irrigation season and then came down after the rainy season. For example, for Field 1 of Bogra, average arsenic concentration in the top 0-75 mm segment of soil in March 2003 was about 1.40 mg/kg, which increased to about 2.12 mg/kg at the end of the irrigation season in May 2003, and then came down to about 1.29 mg/kg after the rainy season.

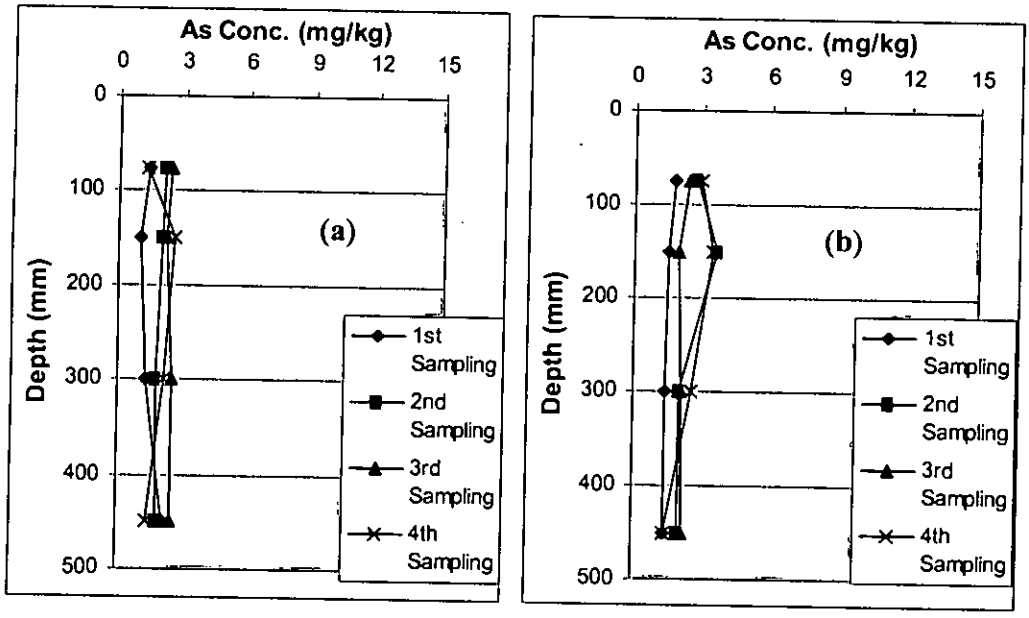


Figure 3.14: Arsenic profile of soil cores from irrigated agricultural land in Bogra (a) Field 1, As: < 1 μg/l; (b) Field 2, As: < 1 μg/l

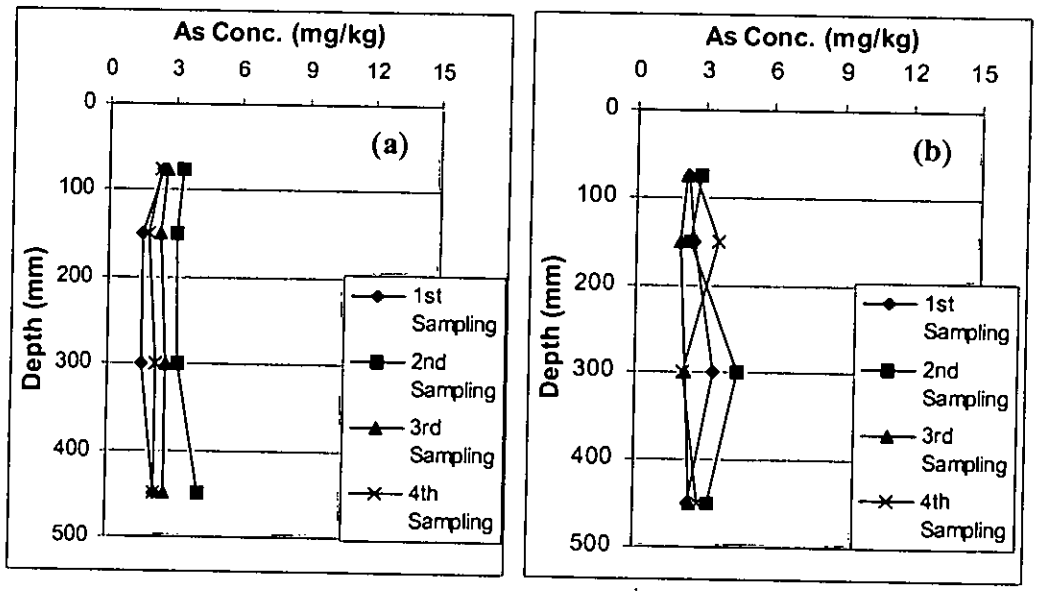


Figure 3.15: Arsenic profile of soil cores from irrigated agricultural land in Naogaon (a) Field 1, As: < 1 μg/l; (b) Field 2, As: < 1 μg/l

Figures 3.16 through 3.19 show arsenic profiles of soil core samples collected from Munshiganj, Comilla, Brahmanbaria and Faridpur, respectively. As noted earlier, each data point in the figures showing arsenic concentration at a particular depth represents average of 6 to 8 samples taken from the respective fields. Figures 3.16-3.19 show that, unlike the trend observed for the unaffected sampling areas (Bogra and Naogaon), arsenic levels of irrigated soils in the arsenic affected areas vary significantly with depth as well as with time of sampling. In general, arsenic concentration in the top soil layers (up to 150 mm) increased significantly at the end of the irrigation season. For example, for Field 1 of Munshiganj, average arsenic concentration in the top 0-75 mm segment of soil increased from about 8.4 mg/kg in March 2003 to 14.8 mg/kg right at the end of the irrigation season in May 2003. During the same period, it increased from about 4.7 to 8.0 mg/kg for Field 1 in Comilla, 6.7 to 10.3 mg/kg for Field 1 in Brahmanbaria, and 5.7 to 7.2 mg/kg for Field 1 in Faridpur. The increase was the highest for the two fields in Munshiganj, where arsenic concentration in the irrigation water was also the highest among the four arsenic-affected areas studied.

Figures 3.16 through 3.19 show that after the rainy season and before the beginning of the next irrigation season, arsenic level in the top two segments of soil layers (i.e., up to top 150 mm) decreased significantly and came down to levels comparable to those found in March 2003. For example, for the soil core samples collected after the rainy season (during November 2003 to January 2004), average arsenic concentration in the top 0-75 mm segment of soil of Field 1 of the four arsenic affected areas - Munshiganj, Comilla, Brahmanbaria and Faridpur - were 6.8, 5.9, 4.0 and 4.8 mg/kg, respectively. In fact, for Munshiganj, Brahmanbaria and Faridpur these values are slightly less than those for the samples collected in March 2003.

From the average arsenic profiles shown in Figs. 3.16-3.19, it appears that in many cases while the levels of arsenic in the top 150 mm soil layer (i.e., the top two segments) decreased after the rainy season, those in the bottom layers (150 to 450 mm) increased. This trend was most pronounced for Munshiganj (Figure 3.16) and Brahmanbaria (Field 1, Fig 3.18a). In fact, except for two cases (Field 2 of Brahmanbaria and Faridpur; Figs. 3.18b, 3.19b), arsenic levels in the bottom two segments of soil core samples after the rainy season were higher than those at the beginning of the irrigation season.

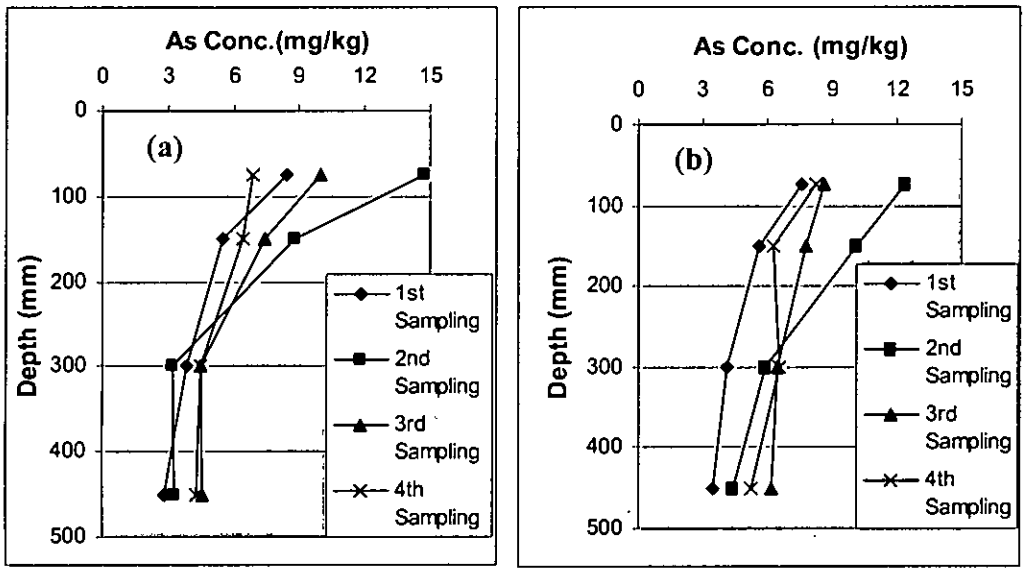


Figure 3.16: Arsenic profile of soil cores from irrigated agricultural land in Munshiganj (a) Field 1, As: 320 μg/l; (b) Field 2, As: 436μg/l

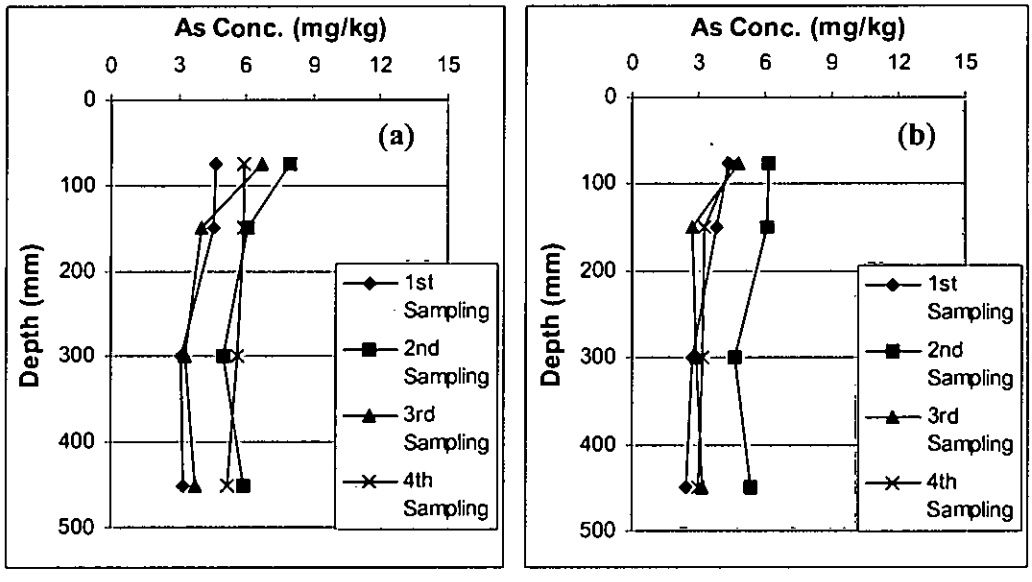


Figure 3.17: Arsenic profile of soil cores from irrigated agricultural land in Comilla (a) Field 1, As: 199 μg/l; (b) Field 2, As: 154μg/l

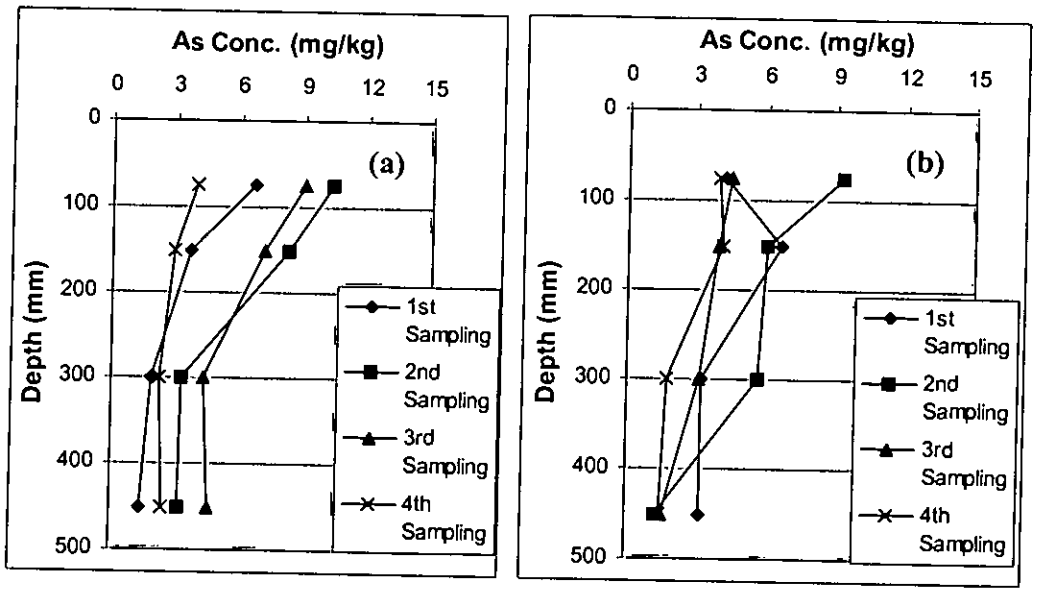


Figure 3.18: Arsenic profile of soil cores from irrigated agricultural land in Brahmanbaria (a) Field 1, As: 138 μg/l; (b) Field 2, As: 149μg/l

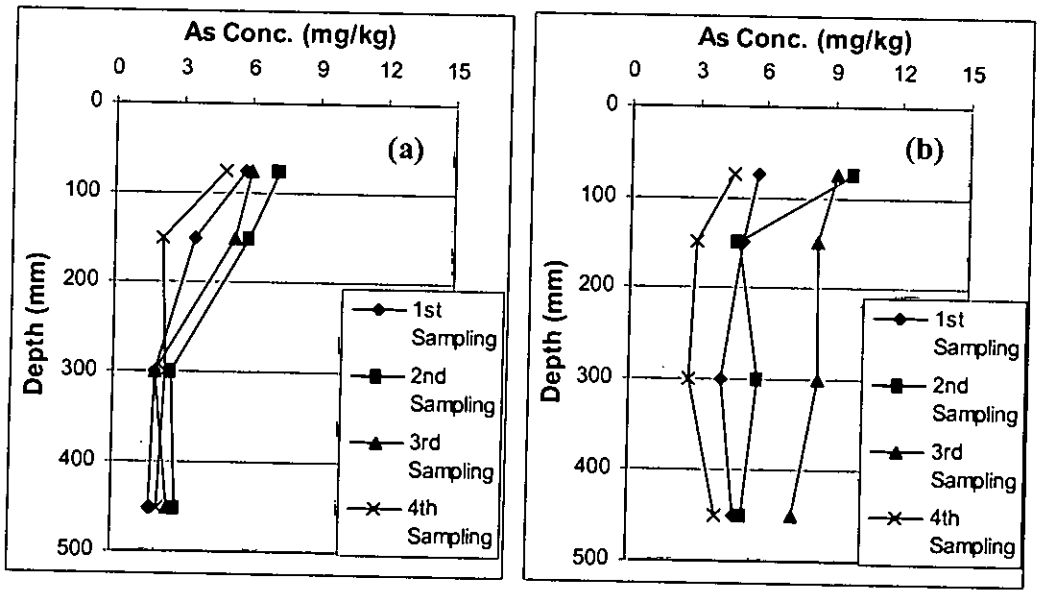


Figure 3.19: Arsenic profile of soil cores from irrigated agricultural land in Faridpur: (a) Field 1, As: 79 μg/l; (b) Field 2, As: 96 μg/l

Results from this study showed that a significant fraction of arsenic associated with the top soil layers is oxalate extractable and therefore primarily associated with iron oxyhydroxides. If average of all the samples analyzed for a particular area is considered, oxalate extractable arsenic in the top 0-75 mm segment accounted for 67.4% of total (aqua-regia extractable) arsenic in Munshiganj, 63.3% in Comilla, 66.1% in Brahmanbaria, and 61.4% in Faridpur. It should be noted that Dittmar et al. (2005) reported oxalate extractable arsenic to account for 66% of total arsenic content for a Munshiganj paddy field site, a value very close to those found in this study. As noted by Dittmar et al. (2005), it means that over 60% of total soil arsenic probably exists as adsorbed arsenic onto amorphous Fe- (or Al-) oxyhydroxides.

Since reducing condition prevails in the top soil layers during inundation by flood/rain water, arsenic associated with the top soil is likely to partition to the aqueous phase during this period due to reductive dissolution of iron oxyhyroxides and desorption. In fact, Islam et al (2004) showed that arsenic is liberated from sediments collected from West Bengal, India by the addition of organic carbon. Laboratory studies carried out in this study (results reported in Chapter 4) also showed that arsenic is liberated from top soil to aqueous phase in the presence of organic matter. The arsenic liberated from the top soil layers could be transported back into the subsurface with percolating water or be carried away from the site with receding flood water, causing a decrease of arsenic in the top soil layers during inundation. These processes are most likely responsible for the observed decrease of arsenic after the rainy season in the top 0-150 mm soil segments of the core samples. Downward movement (percolation) of water may in turn be responsible for the apparent increase in arsenic levels in the bottom segments (150-450 mm) of soil cores due to re-partitioning of arsenic to soil at these layers. It should be noted that loss of arsenic from soil into the atmosphere by the microbial methylation process during inundation has also been suggested (McLaren et al., 2001; Turpeinen et al., 2002) as an important process-governing fate of arsenic in natural soils. This issue has been addressed in more detail in chapter 4 of this thesis.

Figure 3.20 shows average arsenic profiles of soil cores collected from non-irrigated village locations of each of the six sampling areas. Each data point in this figure, showing arsenic level at a particular segment of village soil, represents average of 6 samples collected from each area. For all 6 sampling areas, average arsenic level did not vary significantly with depth. Average arsenic level in the different layers of the soil cores collected from the village areas varied from 1.67 to 2.79 mg/kg for Bogra and from 2.38 to 2.93 mg/kg for Naogaon. Thus, for these two unaffected areas, arsenic levels in irrigated agricultural soil and non-irrigated village soil do not appear to vary significantly. For the village soil cores collected from the four arsenic affected areas, the average arsenic concentration in the top soil layer (0-75 mm) varied from a low of 3.10 mg/kg for Comilla to a high of 3.14 mg/kg for Faridpur. These values are slightly higher than those found for soil cores collected from the unaffected areas of Bogra and Naogaon (2.4 to 2.6 mg/kg). Possible overflow of arsenic-bearing irrigation water to non-irrigated lands could be partly responsible for the relatively higher levels of arsenic in village soils of arsenic affected areas. These could also represent the naturally high background arsenic levels for these arsenic affected areas.

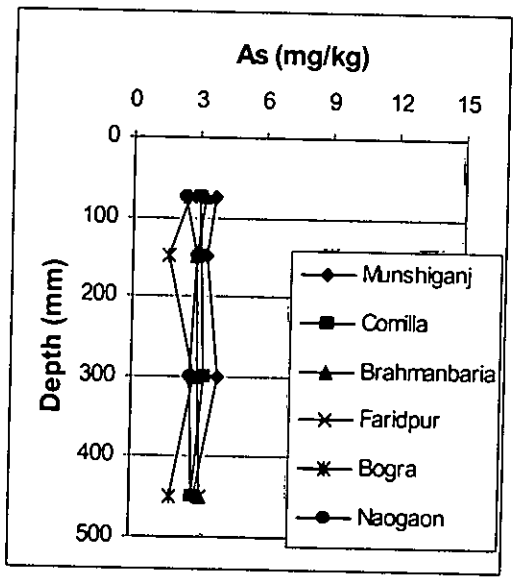


Figure 3.20: Arsenic profiles of soil cores collected from non-irrigated village areas

In the arsenic affected areas, the average arsenic levels in the top layers of irrigated agricultural soils are clearly higher than those found for soils from the non-irrigated

village areas. For example, average arsenic concentration in top 0-75 mm segment of soil of Field 1 of Munshiganj, Comilla, Brahmanbaria and Faridpur in March 2003 were about 8.4, 4.7, 6.7 and 5.7 mg/kg, respectively; while the corresponding values for non-irrigated village areas are 3.7, 3.1, 3.2 and 4.1 mg/kg, respectively.

Correlation Between As in Water and As in Soil:

Figures 3.21a and 3.21b show the relationships between arsenic in irrigation water and average arsenic in root-soil and top 75 mm segment of soil, respectively, for all the paddy fields. The figures show that, in general, arsenic contents of root-soil and top 0-75 mm segment of soil increase with increasing concentration of arsenic in the irrigation water. Arsenic in root-soil and top 75 mm segment of soil are both strongly correlated with arsenic in irrigation water, with correlation coefficients of R^2=0.77 and R^2=0.7397, respectively. In a study conducted in Hajiganj upazilla of Chandpur district and Sharishabari upazilla of Jamalpur district, Das et al. (2004) also observed a positive correlation (R^2 = 0.74) between arsenic in tubewell water and arsenic in soil; samples were collected randomly in this study.

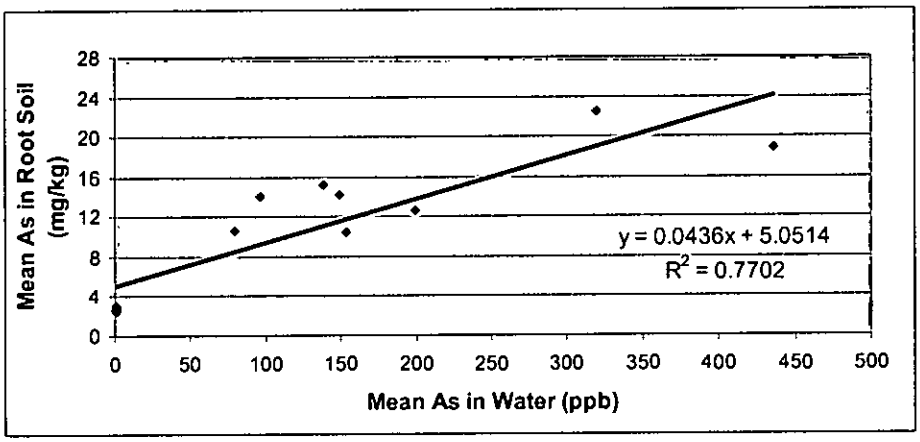


Figure 3.21a: Relationship between arsenic in irrigation water and arsenic in root-soil of paddy fields

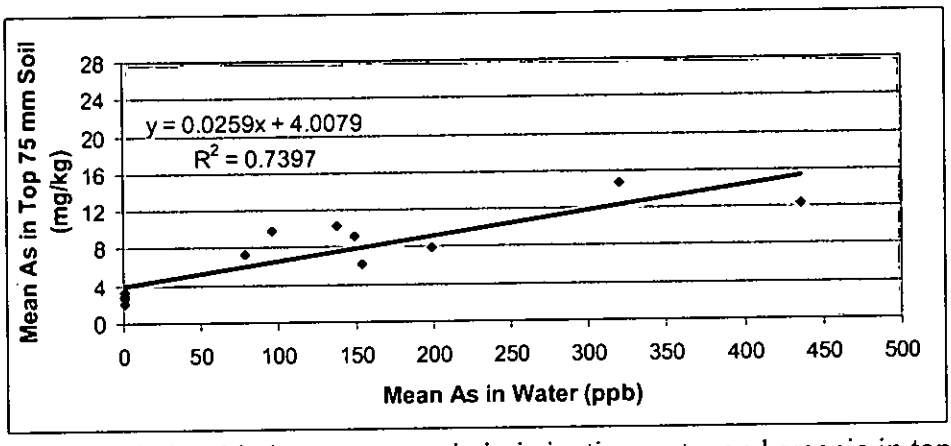


Figure 3.21b: Relationship between arsenic in irrigation water and arsenic in top 75 mm segment of soil layer of paddy fields

3.4.3 Arsenic in Paddy Plant Samples

Figures 3.22 through 3.27 show arsenic concentrations in paddy grains and different parts of paddy plants collected from Field-1 of each of the six sampling areas of Bogra, Naogaon, Munshiganj, Comilla, Brahmanbaria, and Faridpur. Additional data have been presented in Appendix A. Figure 3.28 shows the average arsenic concentrations in water, soil, paddy grains and different parts of paddy plants collected from the arsenic unaffected areas of Bogra and Naogaon, and affected areas of Munshiganj, Comilla, Brahmanbaria and Faridpur. These figures show that in both affected and unaffected areas, the roots of paddy plants accumulated the maximum level of arsenic, followed by leaf and stem. Paddy grain and husk accumulated the least amount of arsenic. For example, for Field-1 in Munshiganj, average arsenic concentration in root, leaf, stem, grain and husk are 15.79, 4.89, 4.01, 0.74 and 0.45 mg/kg, respectively. For field-1 in Bogra these values are 6.44, 2.01, 1.78, 0.70 and 0.39 mg/kg, respectively. This trend of arsenic accumulation in different parts of paddy plant in agreement with those reported by Abedin et al. (2002) based on a greenhouse study, and Ali et al. (2003b) based on a study carried out in Munshiganj, Sonargaon, and Dinajpur.

Higher concentration of arsenic in root may be due to "iron plaque" accumulation on root. A study by Liu et al. (2004) has added greatly to our understanding of arsenic dynamics in the rhizosphere of paddy plants. Their findings suggest that arsenic is sequestered in iron plaque on root surfaces, regulated by phosphorus status, and that there is considerable varietal variation in arsenic sequestration and subsequent plant uptake. The results suggest that iron plaque may act as a 'buffer' for As in the rhizosphere.

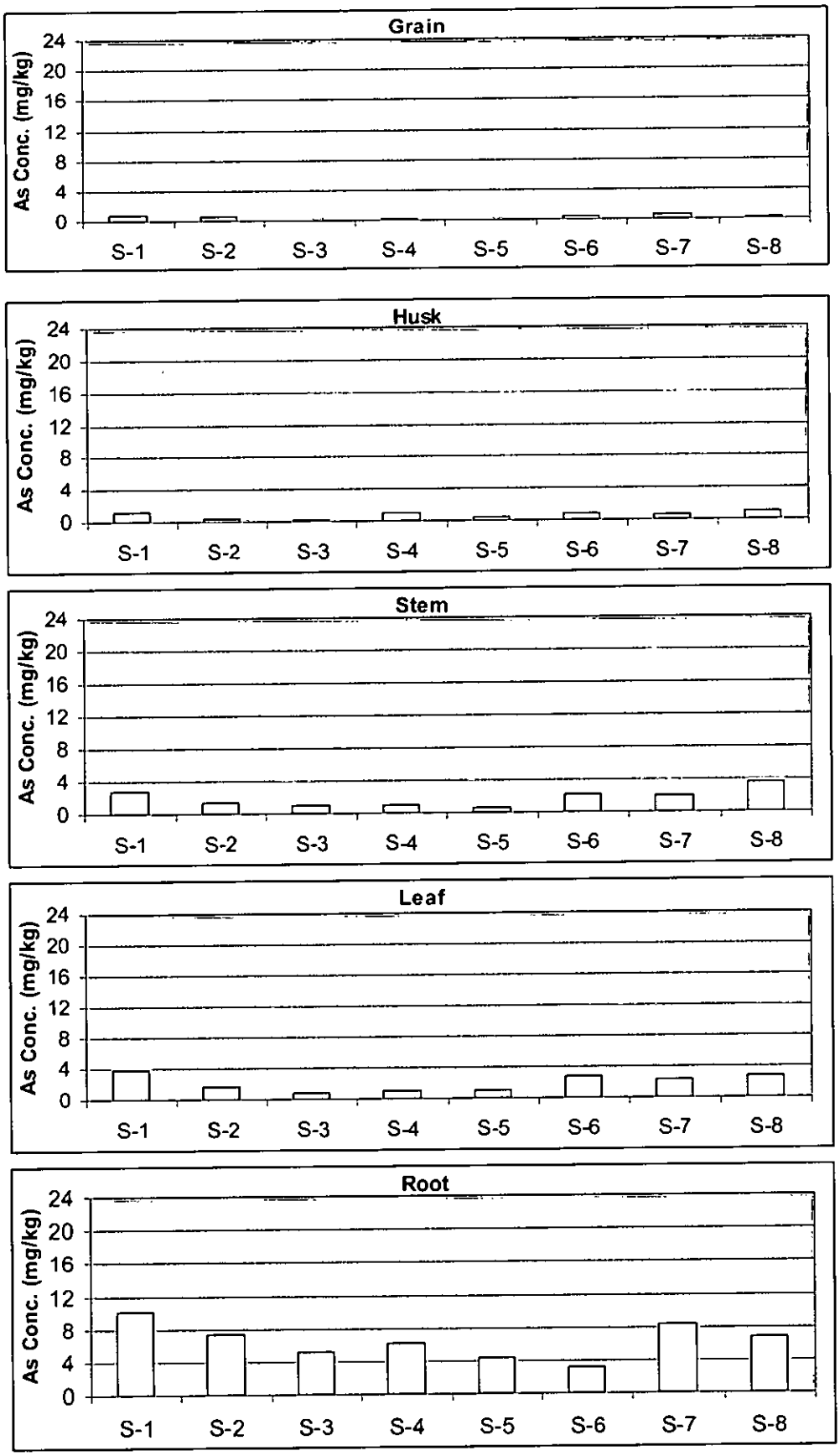


Figure 3.22: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Bogra (S = sample number)

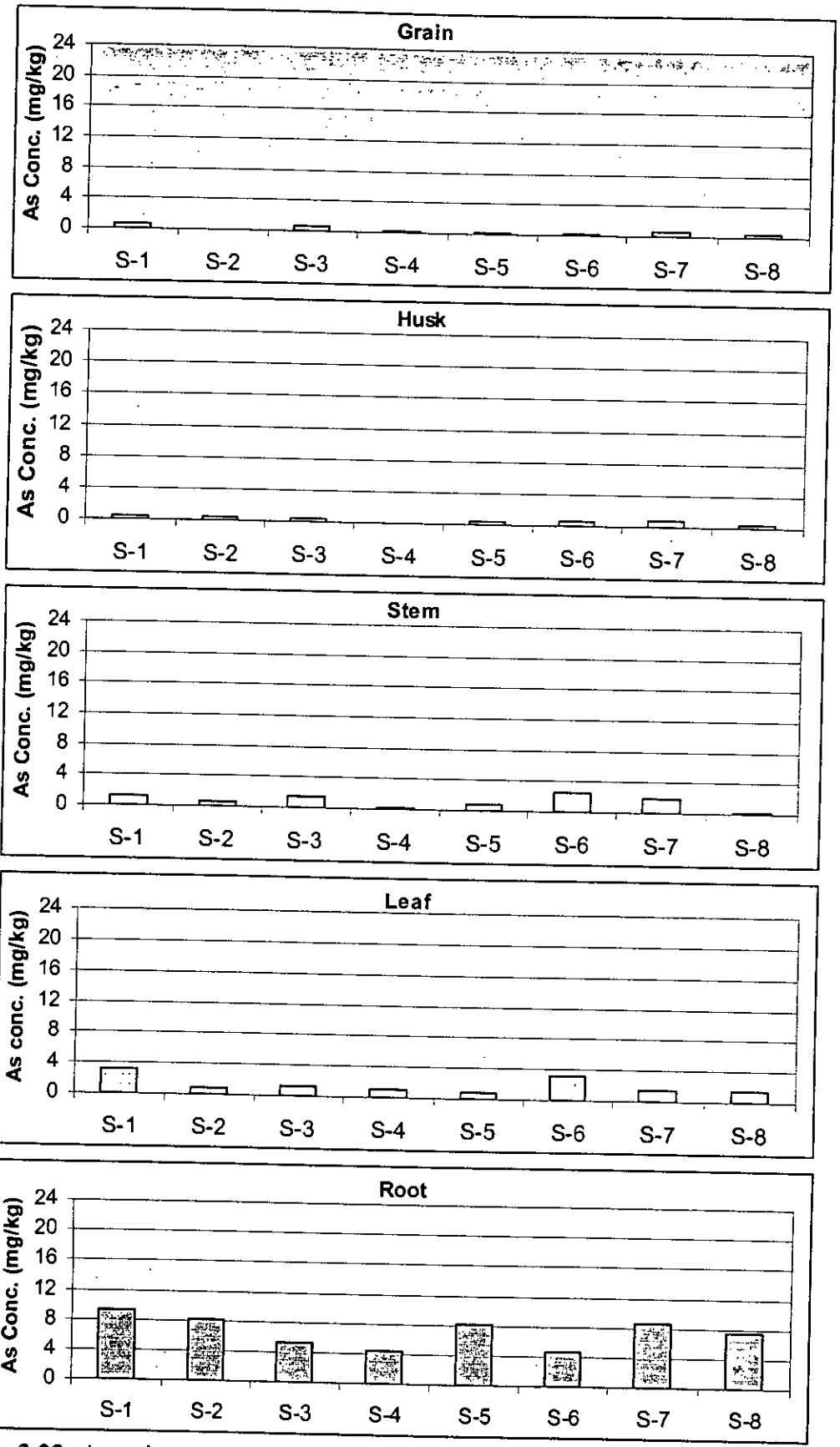


Figure 3.23: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Naogaon (S = sample number)

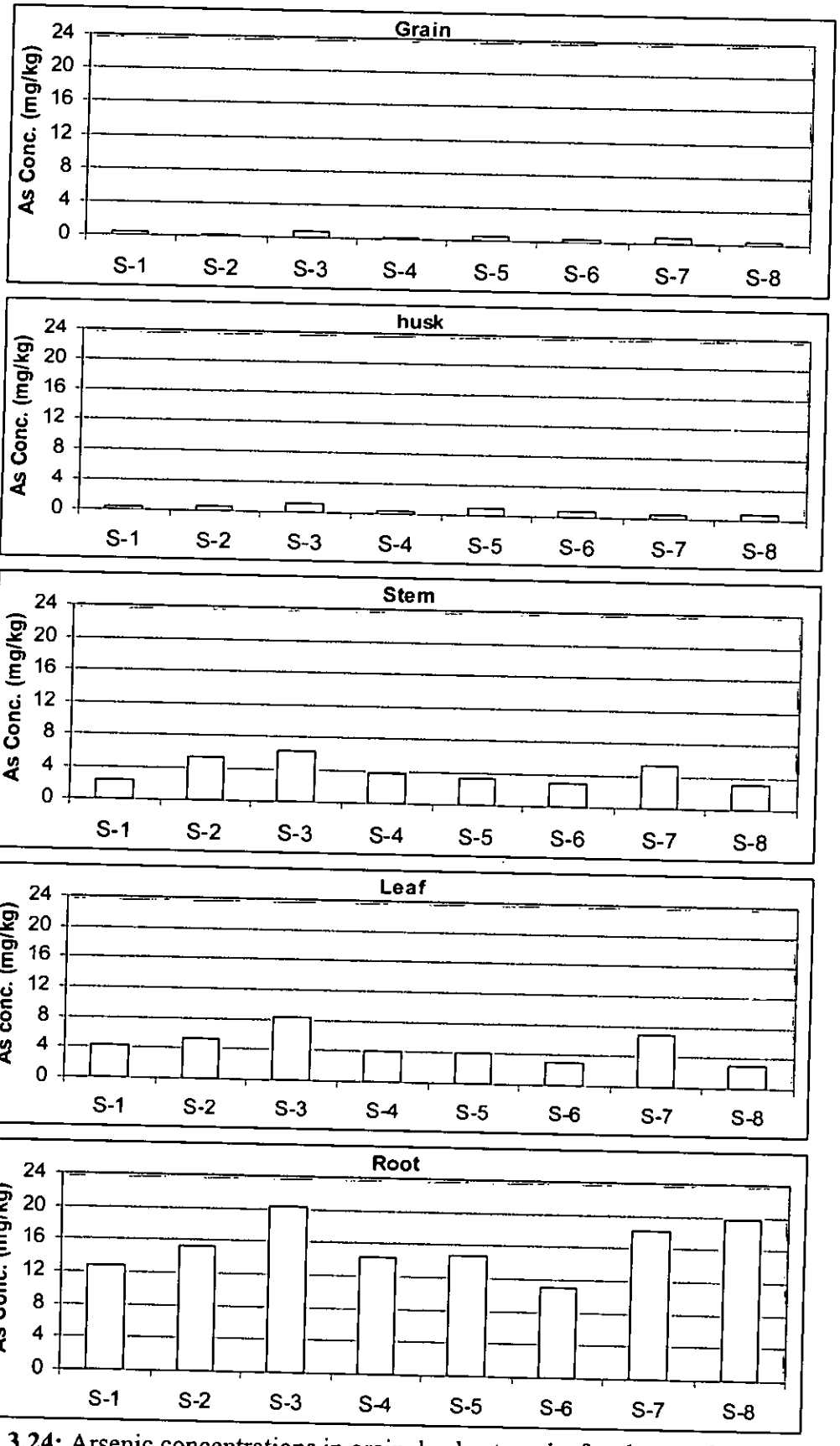


Figure 3.24: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Munshiganj (S = sample nmber)

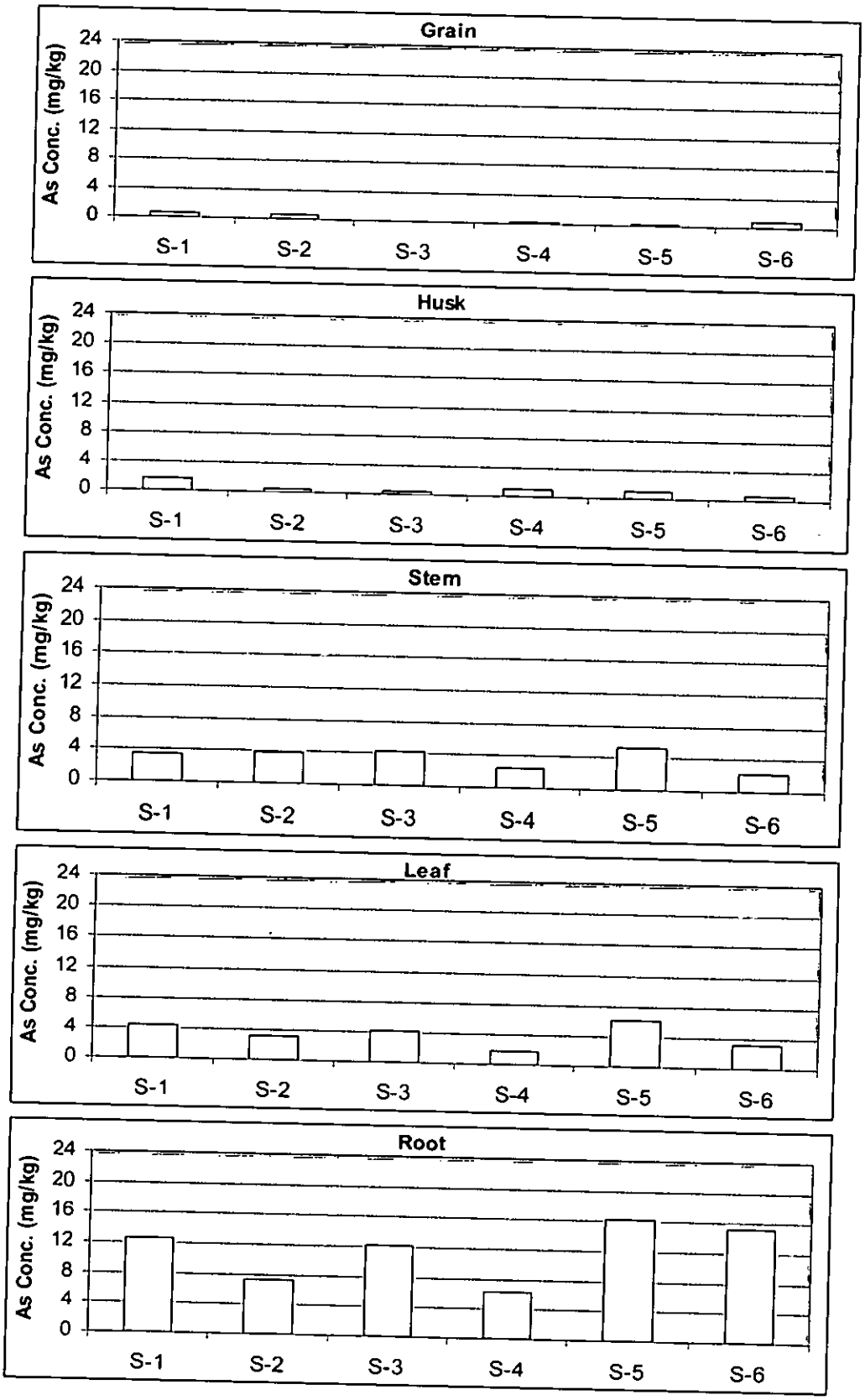


Figure 3.25: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Comilla (S = sample number)

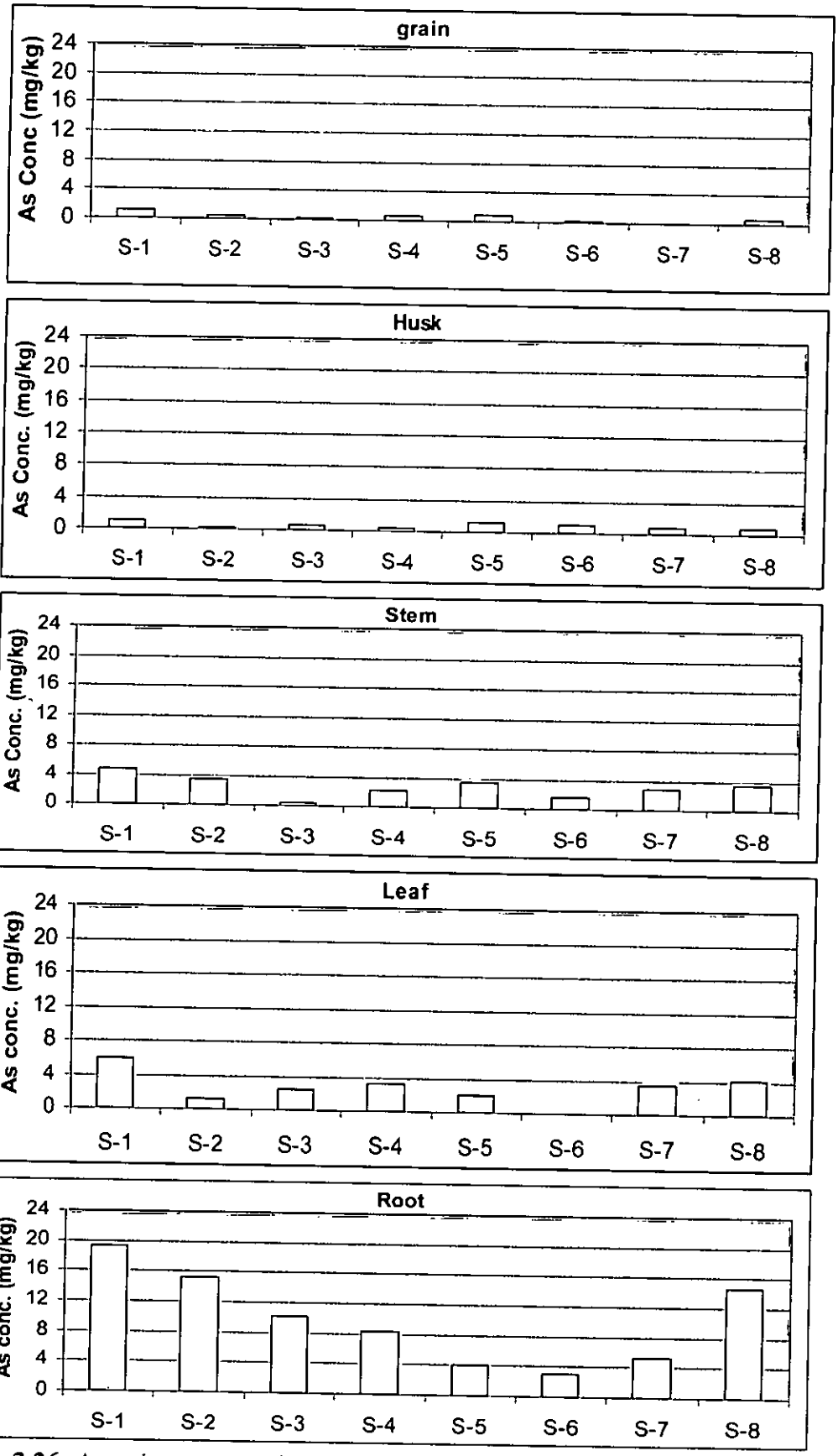


Figure 3.26: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Brahmanbaria (S = sample number)

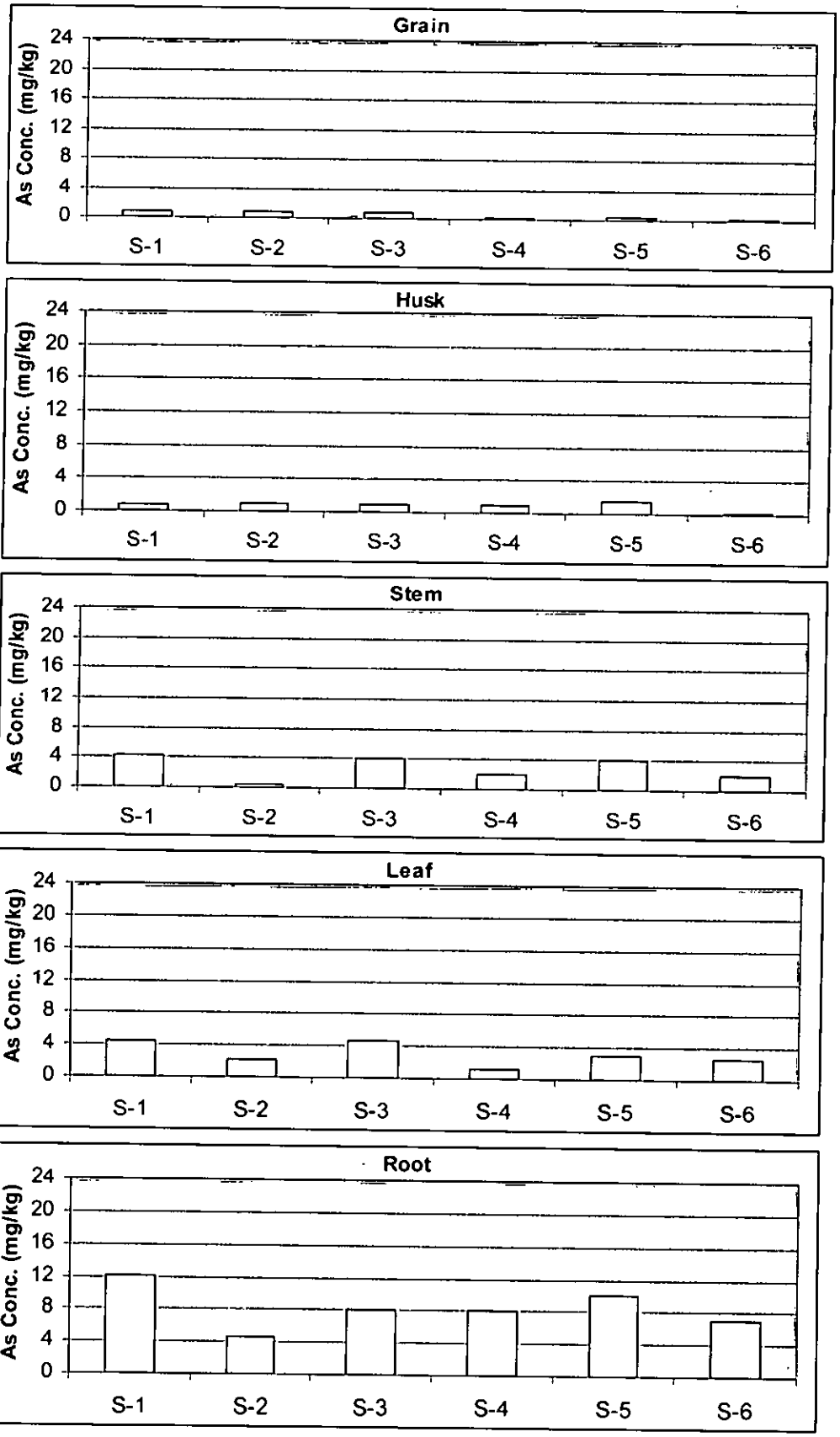


Figure 3.27: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-1 in Faridpur (S = sample number)

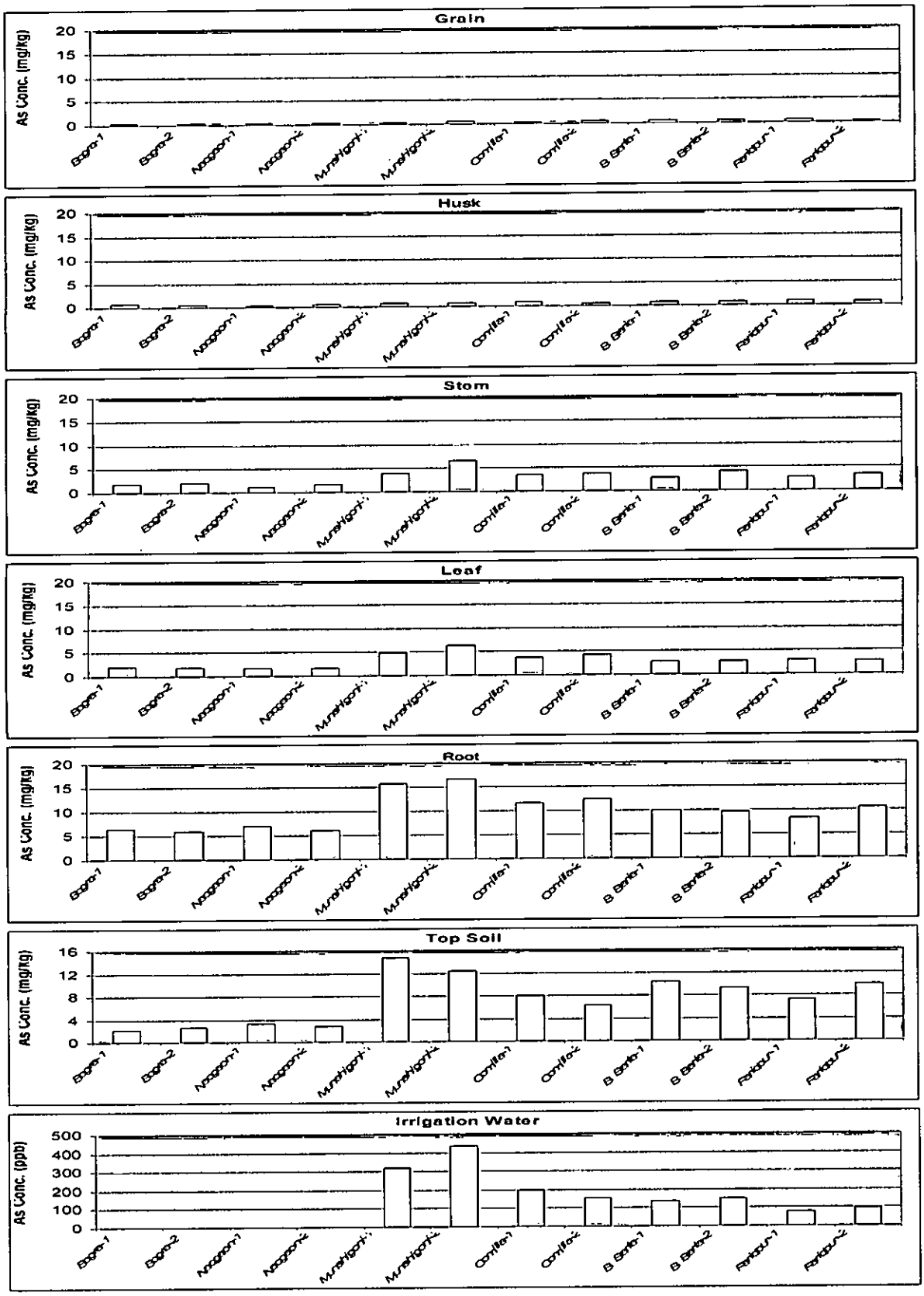


Figure 3.28: Average arsenic concentrations in water, soil, paddy grains and different parts of paddy plants collected from the arsenic affected and unaffected areas

Range, mean and standard deviation (SD) of arsenic content in different parts of paddy plant samples collected from the different sampling areas are shown in Table 3.6. The level of arsenic in root, leaf and stem of plant samples collected from the unaffected areas were found to be significantly lower compared to those found in the samples collected from the arsenic affected areas. Average arsenic concentration in root, leaf and stem of paddy plant samples collected from the four fields of two unaffected areas are 6.38, 1.83 and 1.65 mg/kg, respectively. Whereas for the paddy plant samples collected from affected areas, the corresponding average values are 11.88, 3.83 and 3.87 mg/kg, respectively. Thus, higher arsenic concentration in irrigation water and topsoil is clearly causing an increase of arsenic content in root, leaf and stem of paddy plants. For root, leaf and stem, mean arsenic concentration in affected and unaffected areas differ by a factor of around two.

As shown in Table 3.6, the mean arsenic concentrations in paddy grains from the unaffected areas vary from 0.33 to 0.44 mg/kg, and those from the affected areas vary from 0.43 to 0.60 mg/kg. Three-grain samples (out of eight) from Munshiganj-2, one (out of six) from Comilla-2 and one (out of eight) from B.Baria-1 and B.Baria-2 exceeded the Australian food hygiene limit of 1.0 mg/kg. None of the grain samples from the unaffected areas exceeded this limit. Table 3.6 also shows that mean arsenic concentrations in paddy husks from the unaffected areas vary from 0.42 to 0.70 mg/kg and for those from the affected areas vary from 0.56 to 0.91 mg/kg. Thus, it appears that unlike root, stem and leaf, arsenic concentrations in grain and husk do not differ significantly among the samples collected from the arsenic affected and unaffected areas. A statistical analysis (Student-t distribution) was therefore performed to compare arsenic levels in grain and husk samples collected from affected and unaffected areas and the results are presented in Table 3.7. It shows that concentration of arsenic in both grain and husk are statistically higher for samples collected from the affected areas compared to those from the unaffected areas.

Table 3.6 Range, mean and standard deviation (SD) of arsenic content in different parts of paddy plants samples collected from different sampling areas

Sampling Location	Parameter	Avg. Arsenic				
		Root (mg/kg)	Leaf (mg/kg)	Stem (mg/kg)	Husk (mg/kg)	Grain (mg/kg)
Bogra Field-1	Range (n=8)	3.25-10.11	0.86-3.73	0.92-3.55	0.21-1.21	0.05-0.86
	Mean ± SD	6.44 ± 2.05	2.01 ± 0.93	1.78 ± 0.95	0.70 ± 0.35	0.39 ± 0.29
Bogra Field -2	Range (n=8)	4.15-9.35	0.98-3.14	0.32-3.35	0.05-1.03	0.04-0.92
	Mean ± SD	5.92 ± 1.99	1.89 ± 0.88	1.99 ± 0.86	0.62 ± 0.40	0.44 ± 0.25
Noagaon Field -1	Range (n=8)	4.35-9.35	0.79-3.24	0.26-2.65	0.04-0.75	0.09-0.68
	Mean ± SD	7.02 ± 1.82	1.68 ± 0.94	1.21± 0.77	0.42 ± 0.20	0.40 ± 0.19
Noagaon Field -2	Range (n=8)	3.25-8.32	0.25-3.68	0.89-3.25	0.09-1.05	0.04-0.65
	Mean ± SD	6.17 ± 1.63	1.74 ± 1.21	1.64 ± 0.74	0.57 ± 0.32	0.33 ± 0.18
Munshiganj Field-1	Range (n=8)	11.21-20.31	3.11-8.32	2.29-6.15	0.36-1.25	0.24-0.81
	Mean ± SD	15.79 ± 3.09	4.89 ± 1.75	4.01 ± 1.26	0.74 ± 0.29	0.45 ± 0.19
Munshiganj Field -2	Range (n=8)	10.25-22.35	2.23-9.25	3.33-10.36	0.16-1.89	0.05-1.12
	Mean ± SD	16.70 ± 3.80	6.34 ± 2.41	6.56 ± 2.08	0.82 ± 0.61	0.60 ± 0.45
Comilla Field -1	Range (n=6)	6.32-16.25	1.81-6.24	2.14-5.23	0.43-1.77	0.20-0.89
	Mean ± SD	11.63 ± 3.72	3.81 ± 1.36	3.54 ± 1.07	0.88 ± 0.46	0.43 ± 0.27
Comilla Field -2	Range (n=6)	6.24-18.24	2.25- 6.80	1.25-7.74	0.04-1.25	0.28-1.12
	Mean ± SD	12.41 ± 4.40	4.27 ± 1.44	3.83 ± 2.05	0.56 ± 0.40	0.55 ± 0.28
Brahmanbaria Field-1	Range (n=8)	2.95-19.35	0.02-5.87	0.49-4.70	0.12-1.23	0.05-1.24
	Mean ± SD	10.03 ± 5.56	2.81 ± 1.68	2.79 ± 1.22	0.76 ± 0.35	0.52 ± 0.39
Brahmanbaria Field -2	Range (n=8)	3.52-15.03	0.97-5.32	1.25-6.23	0.26-1.72	0.09-1.06
	Mean ± SD	9.63 ± 4.19	2.78 ± 1.46	4.04 ± 1.64	0.81 ± 0.39	0.59 ± 0.28
Faridpur Field-1	Range (n=6)	4.65-12.17	1.13-4.57	0.44-4.37	0.23-1.52	0.16-0.83
	Mean ± SD	8.38 ± 2.34	2.99 ± 1.22	2.85 ± 1.46	0.91 ± 0.38	0.54 ± 0.28
Faridpur Field-2	Range (n=6)	5.82-12.35	0.95-4.02	0.52-4.27	0.04-1.98	0.32-0.95
	Mean ± SD	10.47 ± 2.91	2.82 ± 0.99	3.36 ± 1.70	0.83 ± 0.67	0.46 ± 0.22

Table 3.7 Comparison of arsenic concentrations of grain and husk of samples collected from affected and unaffected areas

Samples	Comparison	t	$t_{critical}$	Comment
Grain	Affected vs. Unaffected Areas	2.07	1.98	Concentration in affected area is higher
Husk	Affected vs. Unaffected Areas	2.79	1.98	Concentration in affected area is higher

Farid et al. (2005) showed that in Brahmanbaria, As contents of paddy field soil varied from 3.21 to 24.4 mg/kg (mean 9.42 mg/kg), in straw (i.e., stem and leaf) it varied from 0.33 to 4.02 mg/kg (mean 2.00 mg/kg), and in grain it varied from 0.16 to 1.20 mg/kg (mean 0.43 mg/kg). Based on a study carried out in Chapai Nawabganj Sadar *upazila*, Jahiruddin et al. (2005) reported that paddy-grain As concentration in the study area ranged from 0.24 to 1.30 mg/kg; 11% of the samples had As levels <0.5 mg/kg, and the remaining 89% were in the range of 0.50 to 1.0 mg/kg. Arsenic concentrations in paddy straw ranged from 1.48 to 17.6 mg/kg. Arsenic concentration in paddy grain and straw reported by Farid et al. (2005) and Jahiruddin et al. (2005) agrees well with results obtained in this study.

Figure 3.29 shows correlation between As in irrigation water and As in paddy grains. It shows that As in paddy grains is not strongly correlated with As in irrigation water. In fact, As in irrigation water was not found to be strongly correlated with As in any part of paddy plant. Figure 3.30 shows correlation between As present in top soil (75 mm) and As concentrations in different parts of paddy plants. It shows that As content in top soil is strongly correlated with As concentration in root (R^2=0.61) and moderately correlated with As concentration in leaf (R^2=0.50) and stem (R^2=0.52). As shown in Figure 3.30, poor correlation exists between the As concentration in top soil and in paddy grains (R^2=0.14) and husk (R^2=0.10). Jahiruddin et al. (2005) also reported poor correlation between grain-As concentration and As concentration in soil and in irrigation water. These observations are similar to those found in this study. Farid et al. (2005), however, found good correlation between As content of soil and As content of grain (correlation coefficient 0.62) and straw (correlation coefficient 0.84) in Brahmanbaria area.

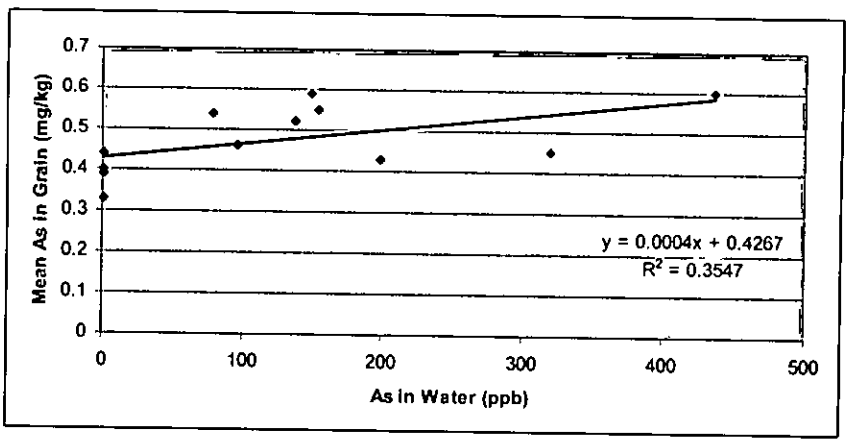
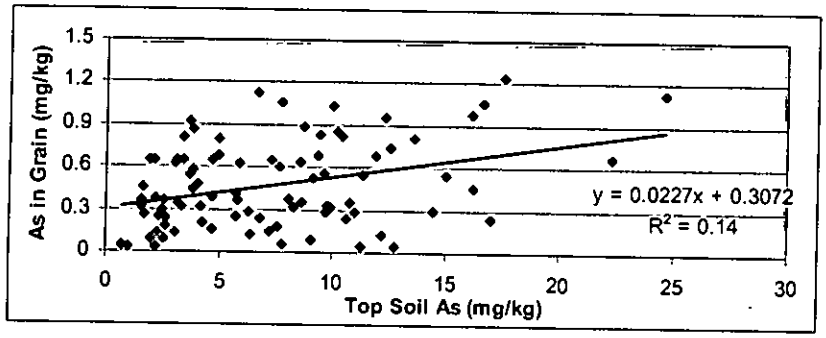
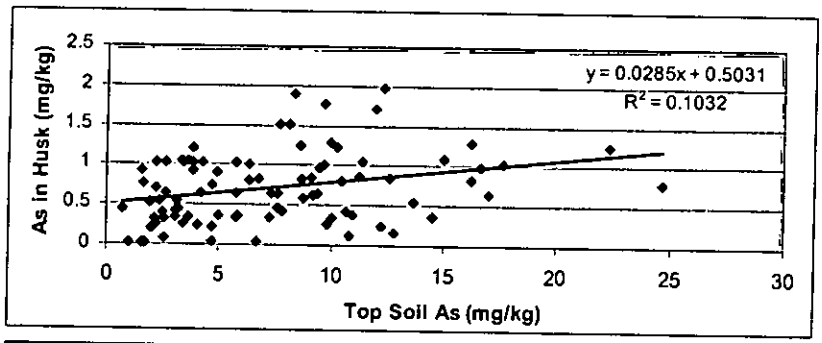
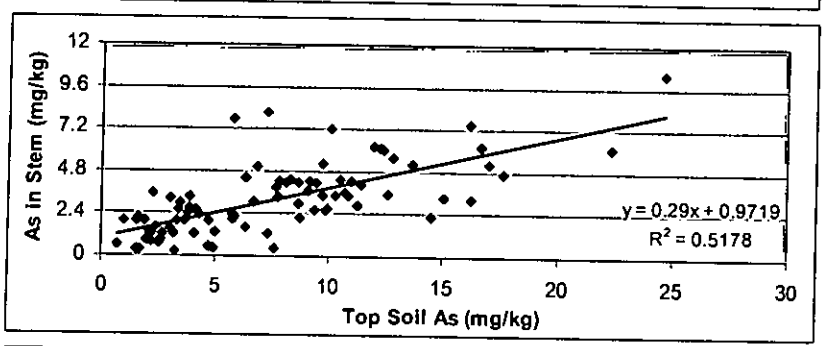
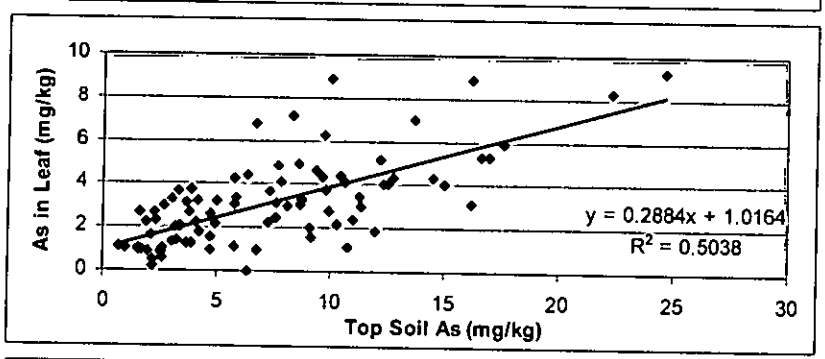


Figure 3.29: Correlations between the As in irrigation water and As in paddy grains









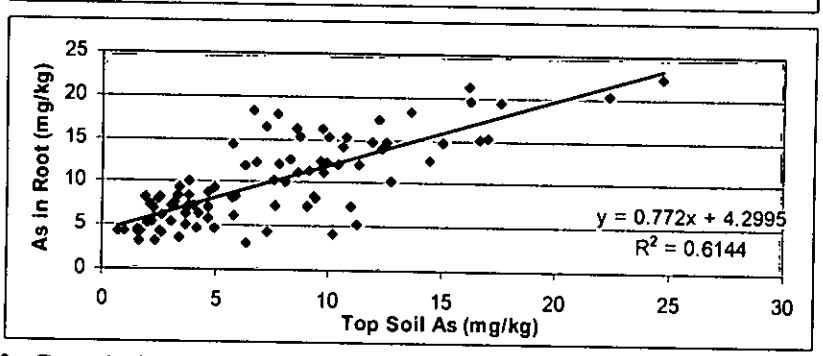


Figure 3.30: Correlations between the arsenic present in top (75 mm) soil and arsenic concentration in different parts of paddy plants

Figure 3.31 shows correlations between the As present in grains and other parts of paddy plants. Relatively poor correlation was observed between arsenic in grains and As in root and leaf with correlation co-efficient 0.17 and 0.25, respectively; correlations between As in grains and As in stem (R^2=0.09) and husk (R^2=0.07) were very poor.

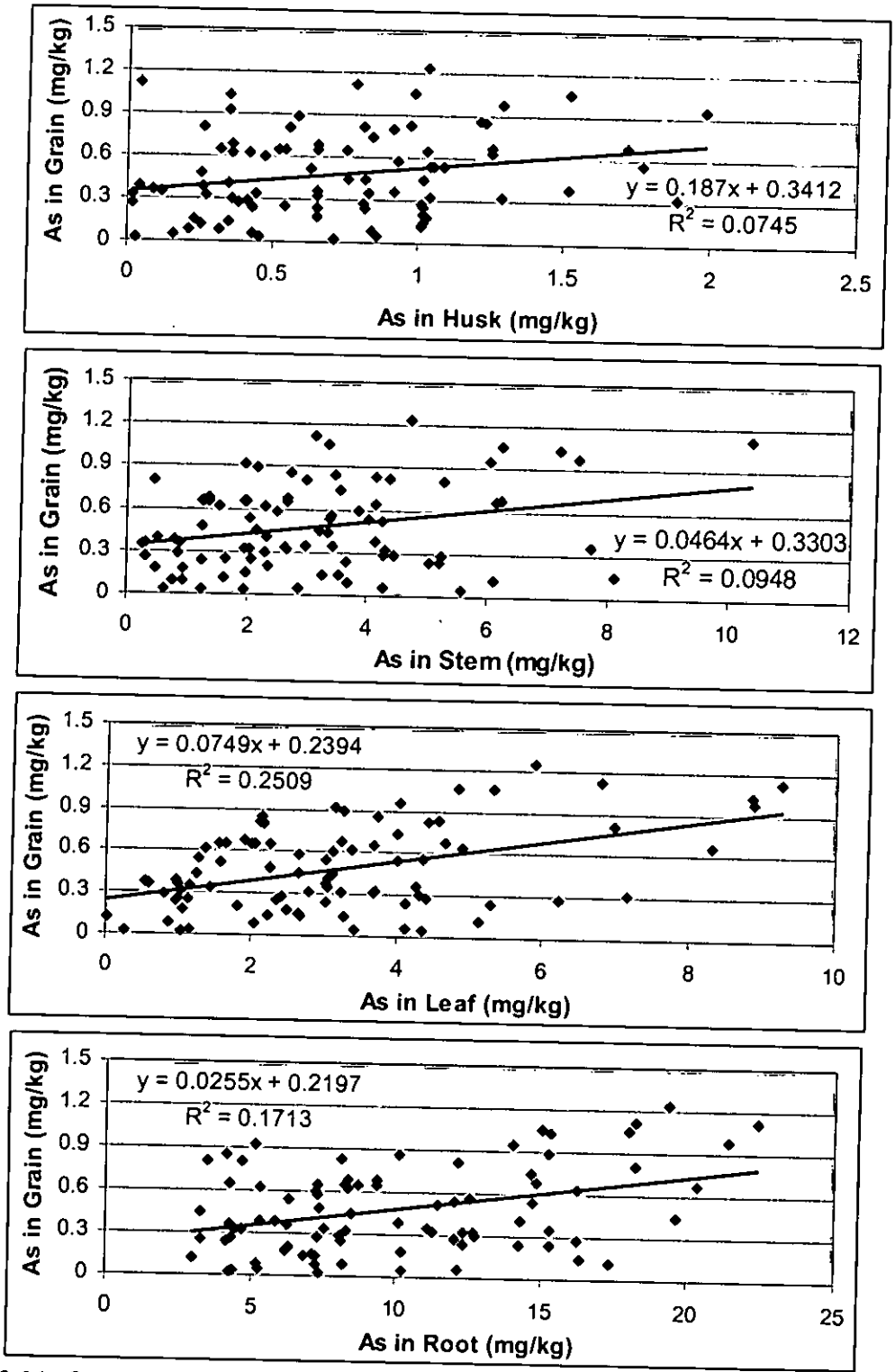


Figure 3.31: Correlations between the arsenic in grains and other parts of paddy plants

3.5 SUMMARY

In this study, twelve paddy fields in four arsenic affected and two unaffected areas of Bangladesh have been monitored for assessing the As status in irrigation water, soil and paddy plant. Soil core samples from *boro* (i.e., dry season) paddy fields were collected at four different times over the *boro* season of 2003. In the unaffected areas of Bogra and Naogaon, where arsenic concentration in the irrigation water was below 1 μg/l, average arsenic levels in irrigated soils have been found to be comparatively low (varying from about 1.5 to 3.1 mg/kg) and did not vary significantly either with depth or sampling time. Within a particular paddy field, arsenic concentration in the soil was found to vary significantly among the sampling points, located in different sub-areas of the paddy fields. For these two areas, arsenic concentrations in top layers of irrigated paddy field soil and non-irrigated village soil were comparable.

In the four arsenic affected areas, arsenic levels in top soil layers of irrigated paddy fields have been found to be much higher than those found for soils collected from non-irrigated village areas and those collected from paddy fields in the unaffected areas. Arsenic concentrations in the top soil layers (~ 450 mm) have been found to vary significantly with both depth and time of sampling, and among sampling locations within a paddy field. In general, average arsenic levels in the top 0-150 mm soil layer of paddy fields increased significantly at the end of the irrigation season in May-June 2003 compared to levels found for samples collected in March 2003. For the top 0-75 mm segment of soil cores of the paddy fields, arsenic level increased by a factor varying from 1.26 to 2.2 during this period. Higher increase in soil arsenic content was observed for sampling points located close to the entry point of water in the sub-area within which the sampling point was located.

After the rainy season and before the beginning of the next irrigation season, the As level in the top soil layer decreased significantly and came down to levels comparable to those found in March 2003. Since majority of the As in the top 0-75 mm segment of soil layer is associated with iron oxyhydroxides that could be extracted with 0.2M solution of oxalic acid, this is most likely due to partitioning of As from soil into the aqueous phase during inundation by reductive dissolution of iron oxyhydroxides and desorption, and its subsequent transport away from the site, e.g., with percolating water or receding

flood/rain water. Thus, part of the As withdrawn from the subsurface with irrigation water may eventually be transported back into the aquifer with percolating water. Possible bio-methylation may also contribute to decreased level of As in the top soil layer after the rainy season. This issue has been addressed in Chapter 6. Thus, results from this study suggest that long-term As accumulation in agricultural soil is counteracted and limited by biogeochemical pathways leading to arsenic removal from soil.

In both arsenic affected and unaffected study areas the roots of paddy plants accumulated the maximum level of arsenic, followed by leaf and stem. Paddy grain and husk accumulated the least amount of arsenic. Arsenic content in top soil was found to be strongly correlated with arsenic concentration in root and moderately correlated with arsenic concentration in leaf and stem. The level of arsenic in root, leaf and stem of the paddy plant samples collected from arsenic-free sites were found to be significantly lower (by a factor of almost 2) compared to those found in the samples collected from the arsenic affected sites. Since paddy straw is used as cattle feed, this may pose a risk to cattle health in the arsenic-affected areas.

Average arsenic concentrations in husk and grain of samples from affected and unaffected areas did not differ significantly, though As concentration in both grain and husk have been found to be statistically higher in samples from the affected areas. Poor correlation was observed between As content of irrigation-water/paddy-soil and As content of paddy grain and husk. In some cases, As concentration in grain of samples collected from the affected areas exceeded the Australian food hygiene limit of 1.0 mg/kg; none of the samples from the unaffected areas exceeded this limit

From the results obtained from this study, it appears that population exposure to As from rice intake does not differ significantly in arsenic affected and unaffected areas. For example, average arsenic concentration in rice grains from the two unaffected areas (Bogra and Naogaon) is 0.39 mg/kg, and that for the four arsenic affected areas is 0.518 mg/kg. Considering average rice consumption of 450 gm/person/day (Duxbury and Zavala, 2005), this corresponds to an estimated daily intake of about 176 μg of As for people living in the unaffected areas, and 233 μg As for people in the As-affected areas. These estimated As intake values are comparable to the daily As intake (~ 200 μg) from water (@ 4 liter/ person/day) containing 50 μg/l arsenic, which is the drinking water

standard for Bangladesh. Thus, it appears that intake from rice could constitute an important part of overall arsenic intake for people living in the arsenic affected areas, though exposure through rice does not differ significantly among arsenic affected and unaffected areas.

It should be noted that the quantities of organic and inorganic arsenic in food should always be quantified, since the form of arsenic affects its bioavailability and thus its toxicity to humans. Unlike water, where arsenic exists in the more toxic inorganic form, food can contain either organic or inorganic arsenic. As noted earlier (section 3.2), reported values for organic and inorganic fractions of arsenic in rice grains vary widely. Hence speciation of As in rice grains of Bangladeshi rice varieties should be determined more carefully for making an assessment of arsenic exposure through rice and its possible health impacts.

Chapter 4

Fate of Arsenic in Agricultural Soil

4.1 INTRODUCTION

In Bangladesh, groundwater is the major source of irrigation water during the dry season. As discussed in Chapter 2, groundwater from shallow aquifer is widely used for irrigation. In 2003, groundwater accounted for 75 % of the irrigation coverage, of which shallow aquifer accounted for 80 % coverage. *Boro* rice is the main recipient of irrigation water, followed by wheat. Since groundwater of shallow aquifer in many areas of the country contains high concentration of arsenic, significant amount of arsenic is added to the agricultural soil through irrigation water. For example, if As concentration in water is 200 μg/l, then considering 1 m irrigation (typical for *boro* rice) over the season, As loading on agricultural soil will be 2 kg per hector per season. A preliminary estimate of the quantity of arsenic extracted through irrigation water was made in Chapter 2 for each thana by assuming an irrigation requirement of 1 m for boro rice and taking arsenic concentration in the irrigation water as the average of the values reported for that thana in the arsenic-database developed by BGS/DPHE (2001). According to this estimate, 971 metric tons of arsenic was cycled through irrigation water during the dry season of 2004. The estimates are particularly high for south-western and south-central (excepting the hill districts) regions of Bangladesh, where both irrigation intensity and arsenic concentration in shallow groundwater are also high.

Understanding the fate of arsenic extracted through tubewell water in soil-water-plant environment is vital for assessing its impacts on the food chain and the environment in general. Figure 4.1a schematically shows the probable fate of arsenic, extracted through groundwater, in the soil-water-plant environment and Figure 4.1b shows a mass balance equation of arsenic in agricultural soil-water-plant environment. The arsenic pumped with tubewell water can go through the following processes:

(i) Undergo adsorption and precipitation and thus become retained onto soil.

(ii) Volatilize into the atmosphere as a result of different biogeochemical transformations,

(iii) Be taken up by plants, and subsequently enter into the food chain, and

(iv) Arsenic retained on soils may undergo desorption/ dissolution and partition back into aqueous phase (i.e., flood water/ rainwater) and subsequently transported away from the site with runoff or percolating water.

The arsenic pumped with tubewell water primarily exists as As(III). In the irrigation field, it may undergo photo-oxidation in the presence of sunlight. Limited data suggest presence of both As(III) and As(V) as well as MMAA and DMAA in agricultural soil.

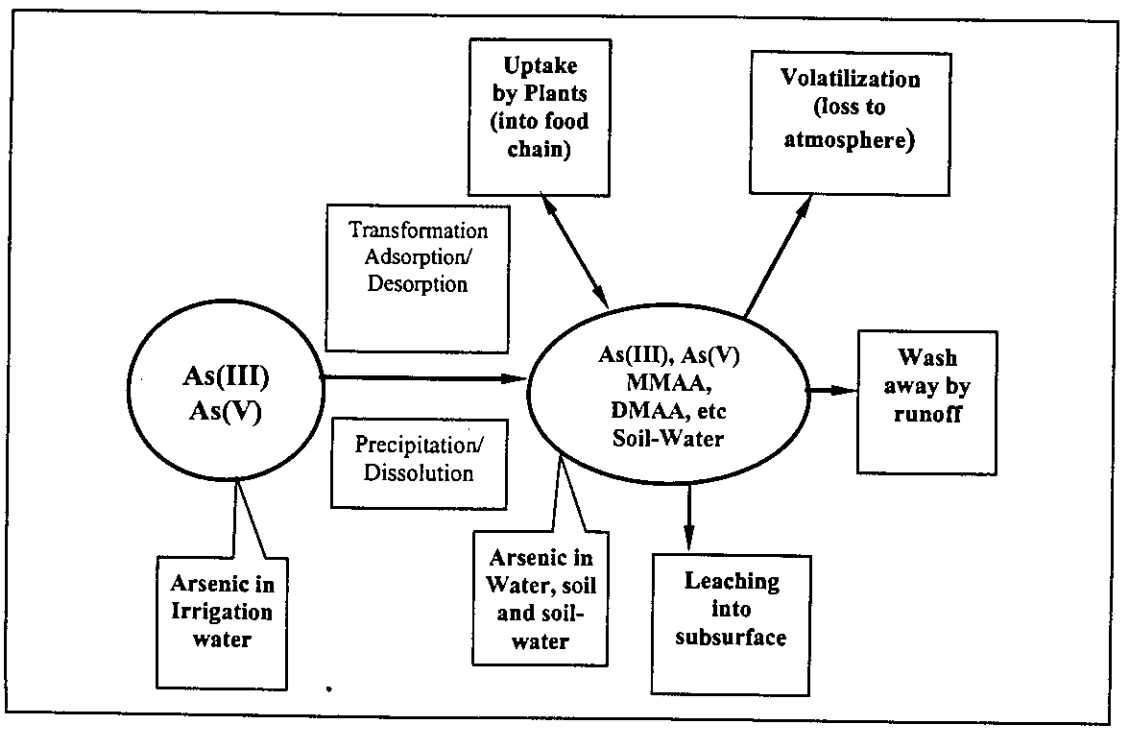


Figure 4.1a: Fate of arsenic in soil-water-plant environment

Adsorption-desorption, volatilization as well as plant uptake of arsenic depend, to a large extent, on chemical forms/transformations of arsenic. For example, among the different arsenic species, arsenate is most strongly adsorbed and retained onto soil. However, the processes of transformation/ bio-transformation of arsenic in the agricultural fields 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, importance of such processes in determining the fate of arsenic in agricultural fields is not clearly understood. Increased bio-methylation and volatilization of gases such as di- and tri-methylarsine from soil can reduce arsenic accumulation in agricultural fields. However, the importance of such processes in significantly reducing arsenic levels in non-manipulated soils (i.e., natural agricultural soils) has been questioned (McLaren et al., 2001).

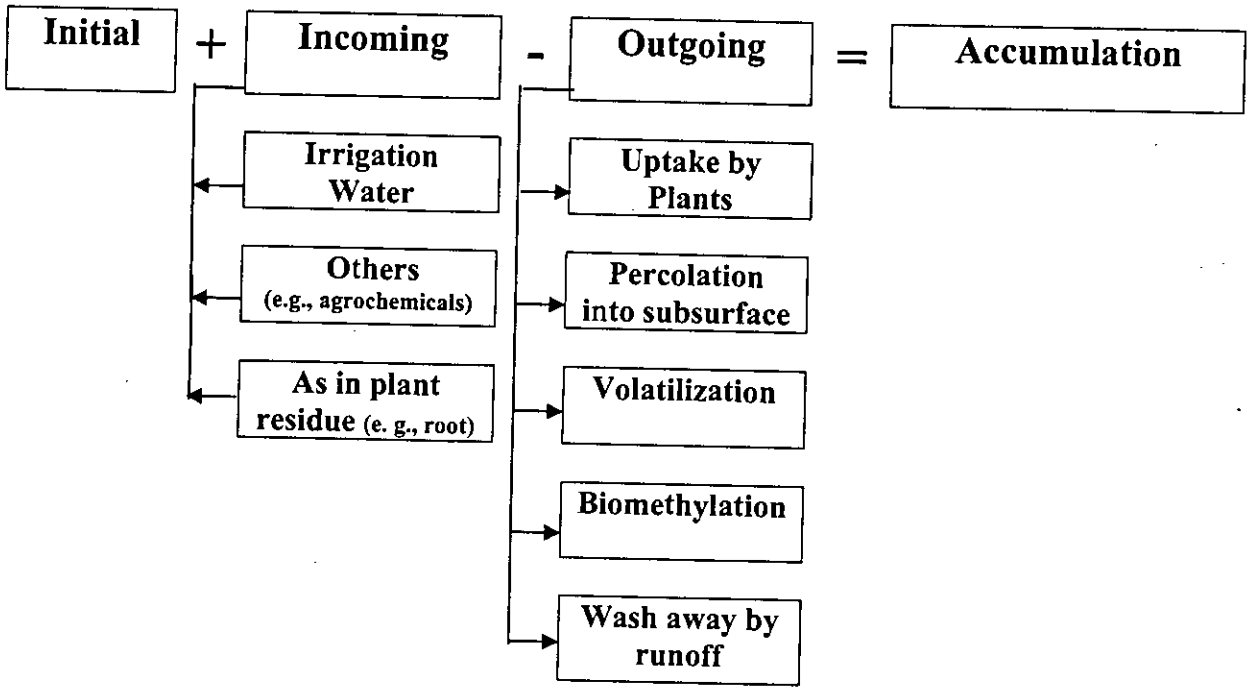


Figure 4.1b: Mass balance equation of arsenic in agricultural soil-water-plant environment

In Chapter 3, the results of monitoring of twelve paddy fields in four arsenic-affected and two unaffected areas of Bangladesh have been presented. In the four arsenic affected areas, average arsenic levels in the top (0-75 mm) soil layer of paddy fields increased significantly at the end of the irrigation season (harvest time) compared to levels measured 3 to 4 weeks into the irrigation season. These results show that significant amount of arsenic added to the soil with irrigation water is retained by the top soil during irrigation season. After the irrigation season most paddy fields get inundated with floodwater and/or rainwater. After the rainy season and before the beginning of the next irrigation season, the arsenic level in the top soil layer decreased significantly and came

down to levels comparable to those found at the beginning of the irrigation season. The decreased arsenic concentration may result from a number of factors including.

a) Partitioning of arsenic from soil to aqueous phase (flood/rain water) during inundation by reductive distribution of iron oxyhydroxides, and subsequent transport of arsenic away from the top soil, either with percolating groundwater or receding floodwater/rainwater.

b) Possible loss of arsenic from top soil to the atmosphere due to biometlylation of arsenic into volatile methylarsine.

However, the relative importance of these processes is not known. The amounts of arsenic accumulated in paddy plants appear to constitute a small portion of total arsenic that is applied to the paddy field with irrigation water.

One of the broader objectives of this study was to develop a mass balance for arsenic that is added to the paddy field with irrigation water. This could not be done from the data (presented in Chapter 3) obtained from monitoring of 12 rice fields, because these data showed that arsenic concentrations over a paddy field vary widely and that sampling points need to be chosen carefully to capture the average condition in a paddy field. It may be noted that for these 12 rice fields, most of the sampling points were located close to the berms dividing the sub-areas within the paddy fields (see discussion in section 3.3.2.2), and therefore the data obtained could not be used to assess average condition within the paddy fields.

Hence, only one sub-area (about 3255 sq.m. in size) of a *boro* paddy field in Sreenagar, Munshiganj was intensively monitored in 2004 in order to estimate the amount of arsenic that is added to a paddy field with irrigation water and the amount that is retained by the top soil at the end of the irrigation season. The amount of arsenic accumulated in paddy plants was also estimated for this paddy field. Irrigation water samples and soil core samples were collected at different time during the irrigation season and analyzed for arsenic. Paddy plant samples were collected at harvest time and arsenic concentration in different part of the paddy plants were analyzed. The data was then used to estimate the

fraction of total arsenic (added with irrigation water) that is accumulated in top soil and in paddy plants.

The possible role of microbial biomethylation in reducing As concentration in soil after the irrigation season was assessed through laboratory experiments using 250 mm diameter soil core samples collected from the paddy field. The laboratory experiment attempted to simulate the condition similar to those prevailing in the paddy fields during inundation by rainwater / floodwater. This chapter presents the result of these experiments.

4.2 PREVIOUS STUDIES

Microbes play an important role in many reactions that have an influence on the speciation of arsenic. The inorganic forms of arsenic, arsenite [As(III)] and arsenate [As(V)] , can be oxidized or reduced due to microbial activity (Woolson, 1977). Inorganic arsenic species can also be biomethylated to monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA) and trimethylarsine oxide (TMAO) (Woolson, 1977; Cullen and. Reimer, 1989; Gadd, 1993; Turpeinen et al., 1999), while other microbes can demethylate organic forms back to inorganic species (Sohrin et al., 1997). In soil, water-soluble arsenic species can also be volatilized by microbes to gaseous arsines (Bachofen et al., 1995; Gao and Burau, 1997), which are extremely toxic compounds to mammals (Buchet and Lauwerys, 1981). As(V) and As(III) can be volatilized to arsine [AsH_3], MMAA to monomethylarsine [MMA, $AsH_2(CH_3)$], DMAA to dimethylarsine (DMA, $AsH(CH_3)_2$] and TMAO to trimethylarsine [TMA, $As(CH_3)_3$] (Cullen and Reimer, 1989). The evolution of arsines is thus greatly dependent on the form of arsenic in soil and most often arsines are formed from methylated species (Woolson, 1977; Gao and Burau, 1997).

The speciation of arsenic in soil has become an important issue due to the different toxicity of the inorganic As(V) and As(III) species and gaseous species such as arsine, MMA, DMA and TMA. The most often detected arsenic species in soils is As(V) (Cullen and Reimer, 1989). Alexander (1977) and Woolson (1977) proposed that the major pathway by which arsenic is lost from soil is through a reduction of As(V) to As(III) and a series of methylation reactions of As(III) with trimethylarsine TMA as a final product. Arsines may travel in air for long distances or they are oxidized rapidly depending on

environmental conditions (Pongratz, 1998). Oxidation returns arsenic back to inorganic species and the arsenic cycle is completed because atmospheric inorganic arsenic is deposited back to soil by rain or by dry deposition (Pongratz, 1998) as illustrated in Fig. 4.2.

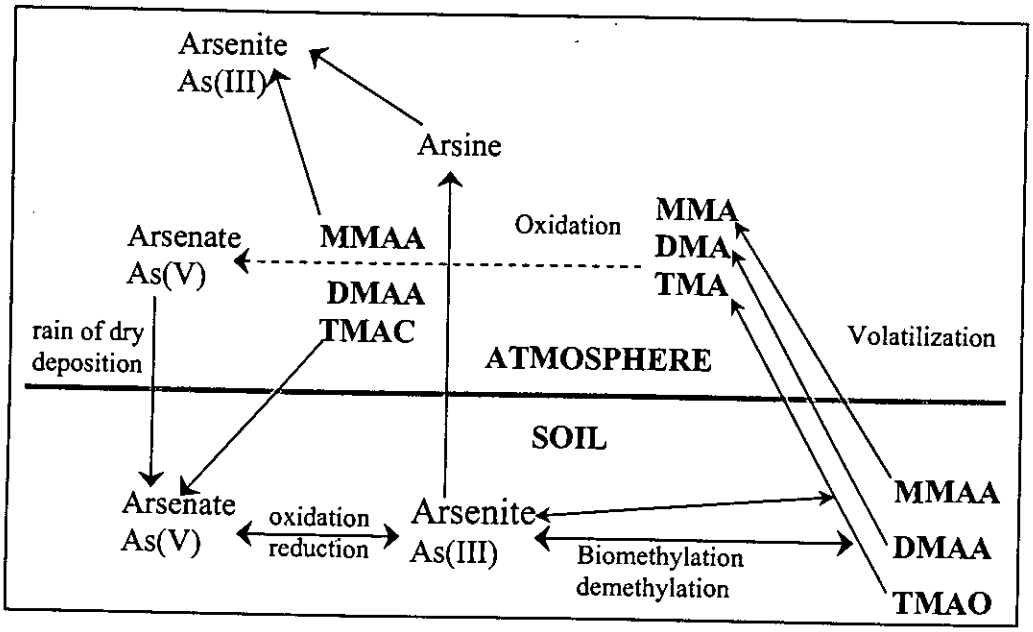


Figure 4.2. Microbial transformations of the dominant arsenic species, As(V), in soil. (MMAA: monomethylarsonic acid; DMAA: dimethylarsinic acid; MMA: methylarsine; DMA: dimethylarsine; TMA: trimethylarsine)
(Source: Turpein, 2002)

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% of the arsenic applied and present in a soil is lost through volatilization of alkylarsines each year. Woolson and Isensee (1981) report total losses of 14–15% per year from soil treated with sodium arsenite, DMA or MMA. Most of the loss was through volatilization, although some apparent loss was caused by movement to or mixing with subsoil. Sandberg and Allen (1975) estimated an arsenic loss of 17–35% per year through volatilization. Sanford and Klein (1988) report that arsenic volatilization showed a direct relationship with nutrient levels and microbial growth in soil.

Adsorption-desorption of arsenic onto soil is key to the understanding of its fate in the environment. 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. As a result, accumulation of arsenic in surface soils is expected and some recent data (Huq et al., 2001; Alam and Sattar, 2000; Ullah, 1998; Meharg and Rahman, 2003; Panuallah *et al.*, 2003; Ahmed, 2005; Farid et al., 2005; Islam et al., 2005; Jahiruddin et al., 2005) suggest higher arsenic concentration in agricultural soil (as high as 83 mg/kg) against a background concentration of about 3-9 mg/kg. In general, higher arsenic concentrations have been reported in the top layers of soil (Huq et al., 2001; Ali *et al.*, 2003b). From available data it appears that most of the arsenic accumulation in irrigated agricultural fields is restricted to the top 150 to 200 mm of soil. However, data on accumulation of arsenic on irrigated agricultural soil over time is very limited. Also there appears to be a lack of information on desorption kinetics of arsenic from soil, which is needed for better understanding of its long-term retention on soil or its transportation back into the subsurface. Microbial influences on adsorption-desorption are also unclear.

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. The percentage of recovery of applied arsenic averaged 67%, 57% and 39% 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 (Hiltbold et al., 1974). Elfving et al. (1994) 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. Peryea and Creger (1994) studied the vertical distribution of arsenic in six contaminated orchard soils. Most of the arsenic was restricted to the upper 40 cm, with maximum arsenic concentrations ranging from 57.8 to 363.8 mg/kg. Absolute soil enrichment with arsenic occurred to depths between 45 and > 120 cm, with arsenic concentrations of 5.3–47.3 mg/kg at 120 cm. The authors state that the deeper movement found in this study compared with many others is due to high loading rates of lead arsenate, coarse soil texture, low organic matter content and use of irrigation. The use of phosphate fertilizers significantly increases the amount

of arsenic leached from soil contaminated with lead arsenate pesticide residues (Davenport and Peryea, 1991).

Richardson et al. (1978) 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% of the amount applied would be 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.

The plant uptake is another important pathway governing the fate of arsenic extracted through tubewell water. Plant uptake of arsenic and translocation to plant top is highly variable among plant species and is also influenced by soil characteristics, soil fertility, and concentration and chemical forms of arsenic in soil. Uptake studies have showed significant variation in uptake of both As(III) and As(V) among varieties. In a recent study with paddy, active uptake of both As(III) and As(V), at about the same rate, was observed (Meharg et al., 2001). The organic species MMAA and DMAA were taken up to a lesser extent than the inorganic species. Since phosphate and arsenate are analogous in certain respects (e.g., adsorption characteristics), the effect of phosphate fertilizer on plant-uptake of arsenic is of particular interest. In a recent study, it has been shown that high rates of phosphate fertilizer did not significantly affect arsenic uptake by paddy (Meharg et al., 2001). It has been argued that conversion of soil As(V) to As(III) and subsequent uptake of As(III) by plant is the reason behind the lack of the effect of phosphate.

4.3 METHODOLOGY

4.3.1 Site Selection

For estimating the amount of arsenic added to a paddy field with irrigation water, the amount retained in the top soil layer and the amount accumulated in paddy plants, a *boro* paddy field, measuring about 3.17 hector located in Srinagar, Munshiganj was selected. A detailed survey of the paddy field was carried out; a map of the entire paddy field covered by one irrigation well (owned by Mr. Ripon) is shown in Fig. 4.3.

The entire paddy field was divided into 18 sub-areas. One sub-area of the paddy field, measuring about 3255 sq. m. (identified by 'R' in Fig. 4.3) was selected for intensive monitoring of arsenic in top soil from the beginning to the end of *boro* season of 2004. Paddy plant samples were collected from the piece of land at harvest time for assessing As concentration in different parts of paddy plants.

4.3.2 Collection of Water Samples

Irrigation water samples from the irrigation well were collected once in every two weeks, during the period from December 2003 to April 2004. Water samples were collected in two pre-washed 500 ml plastic bottles, after running the well for at least 15 minutes. Water sample in one bottle was acidified with 1 ml concentrated hydrochloric acid, which was later analyzed of dissolved arsenic and iron.

4.3.3 Estimation of Irrigation Water Quantity

In order to estimate the volume of water added to the paddy field, the owner of irrigation well (Mr. Ripon) was employed to record the schedule of pumping over the entire irrigation period (24 December 2003 to 22 April 2004). Rate of pumping from the irrigation well was estimated by recording the time required to fill an 80-L bucket.

4.3.4 Collection of Soil Samples

Figure 4.3 shows the map of the paddy field site used in this assessment, which is divided into 18 sub-areas. Groundwater from the irrigation well is carried to the different sub-areas through shallow irrigation canals (Figure 4.3). The sub area identified as 'R' in Fig. 4.3 was selected for collection of soil core samples. Soil core samples were collected from the sub area 'R' at four different times, just before the commencement of irrigation season (December 2003, 1st Sampling), at the end of irrigation season (May 2004, 2nd Sampling), during the rainy/flood season (June 2004, 3rd Sampling), and after the rainy season (November 2004, 4th Sampling). During each sampling, a total of 7 soil core samples were collected from the sub area 'R' of the field.

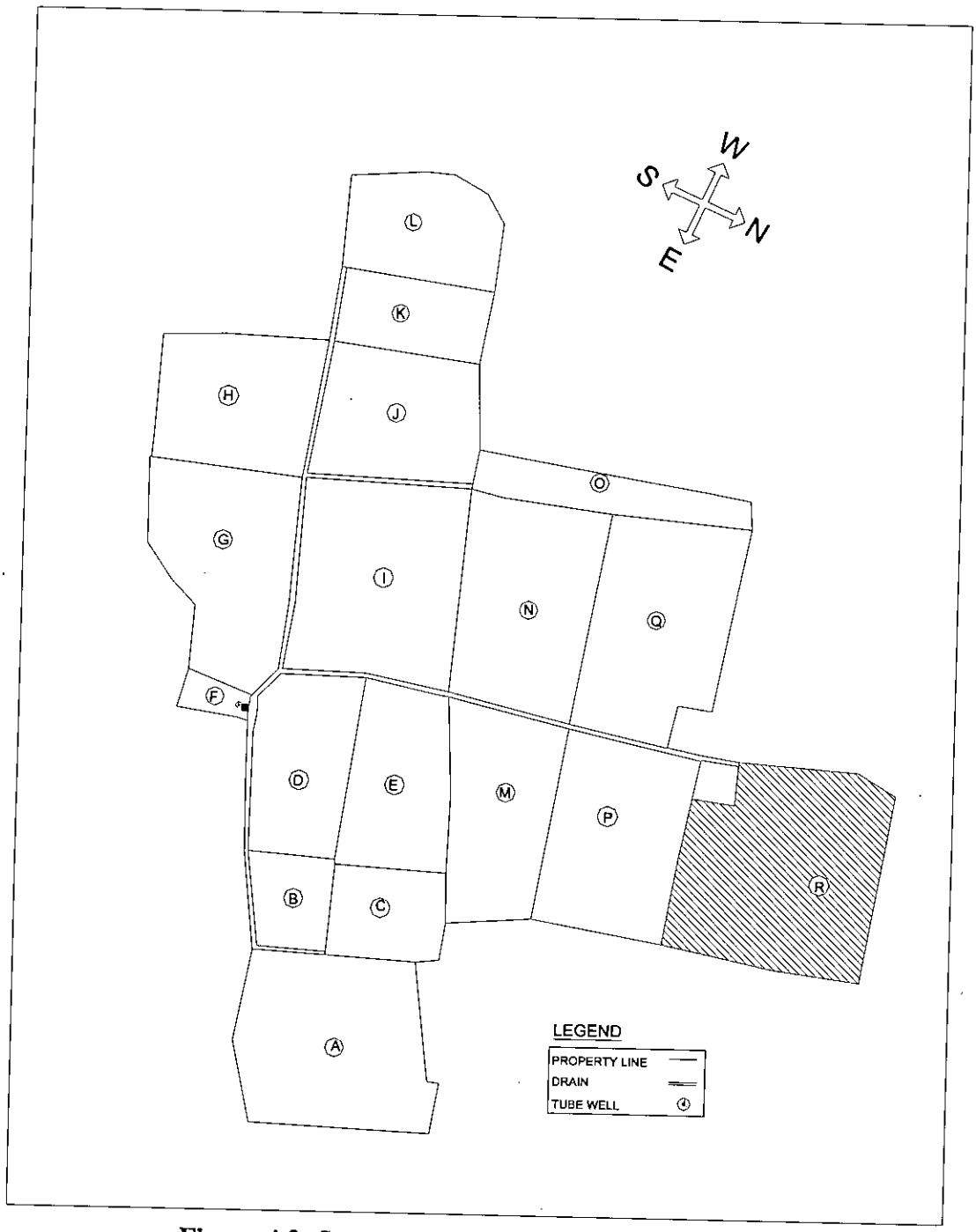


Figure 4.3: Survey map showing sampling areas

During sampling, each sampling point in the paddy field was identified by measuring distances from one edge and one side of the sub-area. As described in Chapter 3, soil core 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 a

depth of about 500 mm. After withdrawing the sampler along with the soil core, both its ends were sealed with tapes to reduce contact with air and transported to the laboratory.

4.3.5 Collection of Paddy Plant Samples

Paddy samples were collected just before harvest time. Entire paddy plants (including roots) were collected. Boro paddy of BR-29 variety was cultivated in the sub area 'R'. A total of 7 paddy plants were collected from the sub area 'R' of the paddy field.

4.3.6 Collection and Analysis of Fertilizer Samples

Samples of four different types of fertilizers used in paddy cultivation were collected from local vendors. These were TSP (Triple Super Phosphate), Urea, Zinc, and Potash. Chemical characterization (including determination of arsenic content) of the fertilizer samples were carried out at EAWAG (Swiss Federal Institute of Aquatic Science and Technology), Switzerland.

4.3.7 Laboratory Analysis of Water, Soil and Paddy Samples

4.3.7.1 Analysis of Water Samples

Water from acidified sampling bottles was analyzed in the laboratory for arsenic and iron. Water from the non-acidified bottles was analyzed for a wide range of water quality parameters, including pH, conductivity, ammonia, nitrate and phosphate. Analysis of water samples was carried out following methods described in section 1.3. Bio-rad resin was used to separate As(III) and As(V) in water samples. For separation of As(III) and As(V), 50 ml of freshly colleted water sample was taken in a centrifuge tube and its pH was adjusted between 2.7-3.0 using concentrated H_2SO_4. Then 1 gm of Bio-rad resin was added to the water and the tube was shaken by hand for one minute. The water sample was then kept in this condition for four minutes. During this time, As(V) gets adsorbed by the Bio-rad resin and settles to the bottom of the centrifuge tube. The supernatant liquid containing [As(III)] was then collected by decanting the tube. Arsenic concentration in the supernatant liquid i.e., As(III) was then determined by AAS. As(V) adsorbed on Bio-rad resin was then desorbed by using 1 M HCl solution and its concentration was

measured by an AAS. For checking the accuracy of separation, total arsenic concentration of the water sample was also measured and compared with the sum of As(III) and As(V) concentrations.

4.3.7.2 Analysis of Soil Samples

Before analysis, each soil core sample was divided into five segments; the first segment consisting of the top 37.5 mm of soil, the second segment consisting of the next 37.5 mm, the third segment consisting of the next 75 mm, the fourth segment consisting of the next 150 mm, and the fifth segment consisting of the rest of the core. Each segment of soil was analyzed for total (aqua-regia extractable) arsenic. Besides, selected segments of core samples were analyzed for oxalate extractable arsenic; this extractant (i.e., oxalate) primarily targets the arsenic co-precipitated with amorphous iron oxy-hydroxides. For determination of aqua-regia extractable arsenic, each segment of soil sample was digested following the procedure discussed in Chapter 3. Analysis of arsenic was carried out using an AAS attached with a graphite furnace (Shimadzu AA6800).

4.3.7.3 Analysis of Paddy Samples

As discussed in Chapter 3, before analysis, the paddy plant samples were divided into five parts: (i) root, (ii) stem, (iii) leaf, (iv) grain and (v) husk. For analysis of total arsenic, the different parts/segments of the paddy plant samples were digested following the procedure discussed in Chapter 3. Arsenic analyses of crop samples were carried out with hydride generation atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800).

4.3.8 Laboratory Experiments to Assess Possible Loss of Arsenic from Soil due to Biomethylation

For assessing possible loss of arsenic from agricultural soil due to microbial methylation during inundation of paddy field by flood water/rainwater, laboratory experiments were carried out using 250 mm diameter and 550 mm deep soil core samples collected from the paddy field (sub-area 'R'). A total of six such core samples were collected from the field right after harvest time in May 2004. Cylindrical samplers 250 mm in diameter and 750 mm in height made of galvanized steel sheet were used for collection of these soil cores.

Besides, 6 more soil core samples 37.5 mm in diameter and 550 m in height were collected from the same field (Sub-area 'R') using 37.5 mm dia PVC samples (following the procedure described in chapter 3). All the 12 soil core samples were collected from close proximity of each other.

4.3.8.1 Laboratory Experiment with Large Diameter (250 mm) Soil Core

After transporting to the laboratory, the bottom of the 250 mm cores were sealed by galvanized steel sheet cover. Different types of inundation water were then added on the top of the cores and then the cores were kept inundated under about 75 mm of water (see Fig.4.4). The depth of inundation water was adjusted every week by adding water in order to maintain a fixed depth of inundation. The cores were kept in this condition (open to sunlight) for a period of four months. This period is approximately equal to the time period during which paddy fields remain inundated with rain water/ flood water during rainy season, which immediately follow the *boro* season.

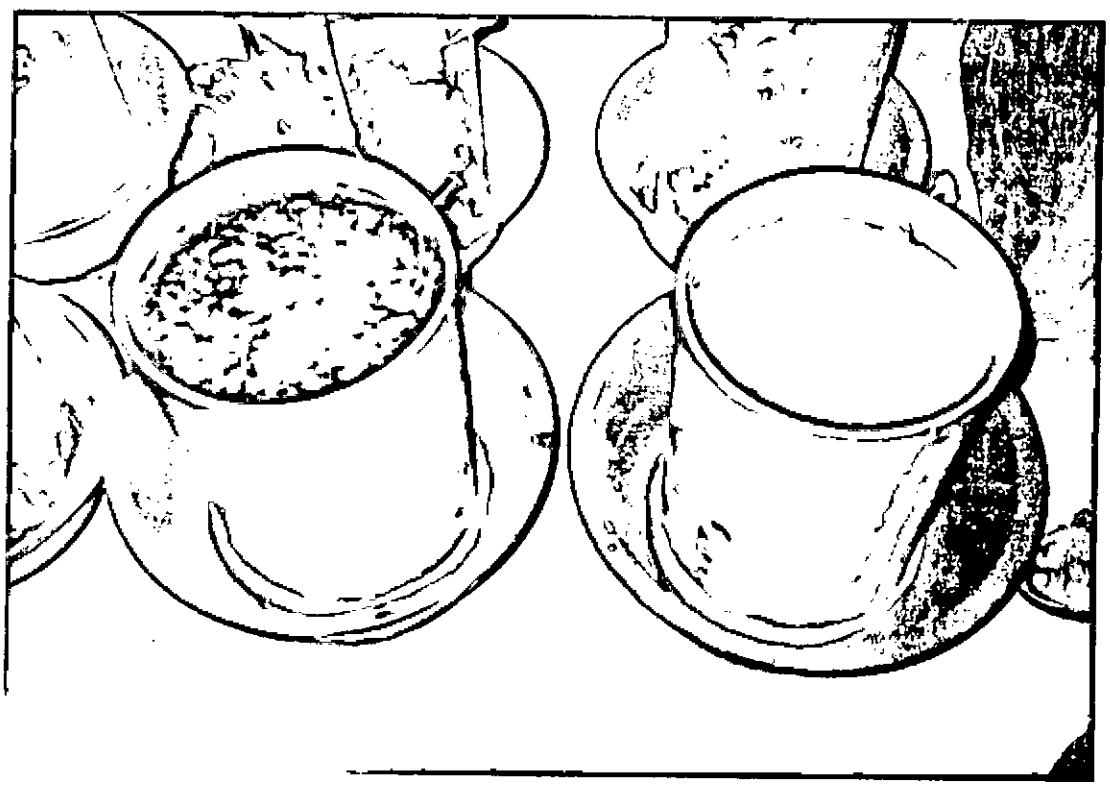


Figure 4.4: 250 mm soil cores inundated by 75 mm of water open to air with different "inundation water" in the laboratory

Among the six cores, two cores were inundated with rain water, two with canal water and the rest two with canal water amended with glucose and standard BOD dilution water as carbon and nutrient source, respectively. Canal water used for inundation was collected from a canal located close to the paddy field; rainwater was collected at the roof of the Civil Engineering building of BUET. Rainwater was used as inundation water because paddy fields often become inundated with rainwater; canal water and glucose amended canal water were used to simulate inundation with water rich in organic matter and nutrients. At the end of four-month inundation period, the water remaining on top of the cores were withdrawn with a pipette and its volume was measured. The water was then analyzed for a wide range of water quality parameter, including arsenic and iron. From each of the bigger i.e., 250 mm cores, three 37.5 mm diameter smaller core samples were then collected using 37.5 mm dia PVC pipes. These cores were then analyzed for the total (aqua-regia extractible) and oxalate extractible arsenic.

As noted earlier, in addition to the bigger core, six 37.5 mm core samples were also collected from the field (sub-area 'R'). After collection of the 37.5 mm soil core samples from the field, 3 cores were analyzed for total (aqua-regia extractible) and oxalate extractible arsenic and iron. The rest three cores were kept in freezing condition for a period of four months. Freezing was done to prevent any bacterial activity within the soil core that may lead to the possible biotransformation of arsenic. After the 4 months freezing period these 3 core samples were also analyzed for total (aqua-regia extractible) and oxalate extractible arsenic and iron.

4.3.8.2 Analysis of Water Samples

Rain and canal water collected for use as inundation water were analyzed for As and some other water quality parameters, including iron, pH, conductivity, ammonia, nitrate and phosphate. After the 4 months inundation period the water remaining on the top of each 250 m soil core was collected and analyzed also for a wide range of water quality parameters, including arsenic, iron, pH, conductivity, ammonia, nitrate and phosphate. Analysis of water samples was carried out following methods described in section 1.3

4.3.8.3 Analysis of 37.5 mm Soil Core Samples

Before analysis, each soil core sample was divided into five segments; the first segment consisting of the top 37.5 mm of soil, the second segment consisting of the next 37.5 mm, the third segment consisting of the next 75 mm, the fourth segment consisting of the next 150 mm, and the fifth segment consisting of the rest of the core. Each segment of soil was analyzed for total (aqua-regia extractable) and oxalate extractable arsenic and iron. Digestion of soil core samples were carried out following the procedure described in chapter 3. Oxalate extractable arsenic and iron in soil core samples were also determined following procedure described in Chapter 3.

4.4 RESULTS AND DISCUSSION

4.4.1 Estimate of Arsenic Added to Paddy Field

Estimate of the amount of arsenic added to the paddy field during the irrigation season was made from the estimated quantity of irrigation water added to paddy field and concentration of arsenic in the irrigation water.

A total of 8 irrigation water samples were colleted from the irrigation well of the paddy field during the period from January 2004 to April 2004. Concentrations of selected chemical constituents of water samples collected from the irrigation well are shown in Table 4.1. Arsenic concentration in irrigation water samples varied from 328 ppb to about 411 ppb. It is not clear why arsenic concentration of irrigation water varies so significantly with time. One possible reason for such variation could be the high flow rate of the irrigation wells and possible slower kinetics of arsenic mobilization. Table 4.1 shows that As mostly exist as As(III); As(V) ranged from 6 to 35% of total Arsenic. Mean total arsenic concentration in the well water was 366 µg/l.

Table 4.1: Concentration of selected chemical constituents of irrigation water samples

Sampling	pH	Conductivity (µS/cm)	As(III) (µg/l)	As(V) (µg/l)	As(T) (µg/l)	Fe (mg/l)	NH_3-N (mg/l)	PO_4 (mg/l)	NO_3-N (mg/l)
Sampling-1	6.98	596	252.06	76.19	328.25	7.80	6.35	2.68	0.85
Sampling-2	7.00	498	233.06	108.60	341.66	6.87	7.30	4.82	< 0.01
Sampling-3	6.88	637	234.92	124.80	359.72	9.90	6.61	3.84	2.56
Sampling-4	7.07	662	384.62	26.67	411.29	8.16	8.50	3.89	< 0.01
Sampling-5	7.27	536	340.15	68.16	408.31	8.92	7.58	4.65	1.27
Sampling-6	6.68	512	328.40	47.07	375.47	7.26	9.14	6.23	0.69
Sampling-7	7.09	698	322.54	57.61	380.15	5.84	6.37	4.68	2.67
Sampling-8	6.78	540	296.12	24.12	329.24	6.37	6.72	3.68	1.05

The volume of water added to the paddy field was estimated from records of pumping schedule and flow rate of irrigation water. According to the pumping records, the paddy field was irrigated for about 655 hours over the entire *boro* season. Rate of pumping from the irrigation well was estimated by recording the time required to fill a 80-L bucket and average pumping rate was found to be around 13 liters per second. Figure 4.5 shows calculated volumes of water added to the paddy field during the period from 24 December 2003 to 22 April 2004. Thus, on an average, the paddy field was irrigated with a total of about 0.96 m of water over the entire season, a number consistent with values (~1m) reported for *boro* paddy irrigation (e.g., Hossain et al., 2003). Therefore, an estimated 1.14 kg of arsenic was added to the sub-area 'R' of the paddy field with irrigation water during the *boro* season.

In making the above estimate, it was assumed that the arsenic concentration in irrigation water does not change significantly as it travels through the irrigation channels to different sub-areas of the paddy field. Results from a recent and related study (Roberts et al., 2006) suggest that this is a reasonable assumption. Roberts et al. (2006) showed that along the irrigation channels of this paddy field in Munshiganj, total As concentration remained virtually unchanged, though dissolved As decreased and colloid-bound As concentration increased with increasing distance from the irrigation well. Based on this study, Roberts et al. (2006) concluded that the arsenic input to a single paddy field through irrigation does not depend on its distance from the irrigation well along the irrigation canal.

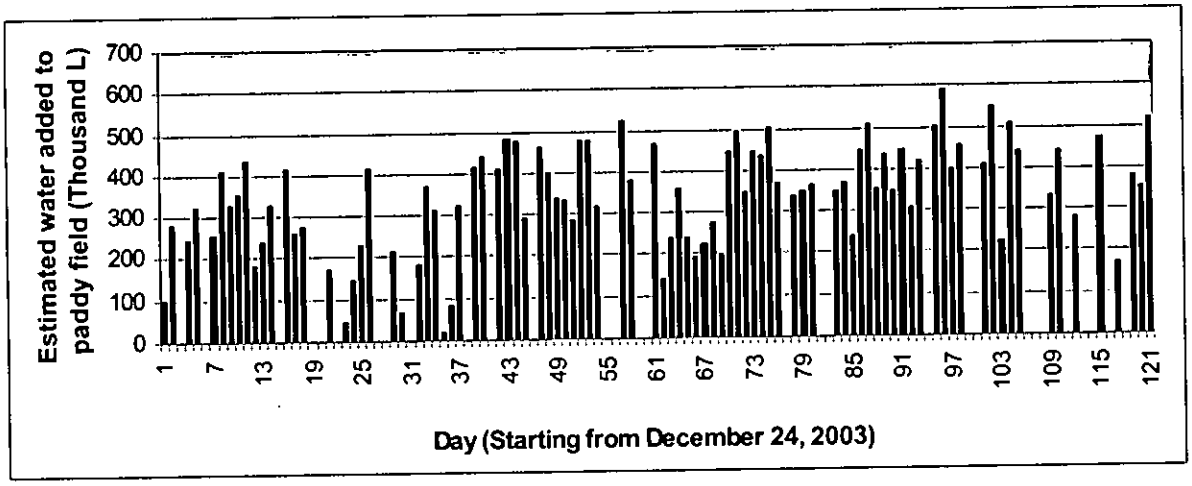


Figure 4.5: Estimated volumes of water added to the paddy field site during the period from 24 December 2003 to 22 April 2004

Results of analysis of fertilizer samples carried out at ITO-ETHZ are presented in Appendix C. These results show that arsenic content of TSP, urea, zinc and potash fertilizers are 3.8 mg/kg, 0.6 mg/kg, 0.7 mg/kg, and < 1 mg/kg, respectively. According to local farmers, these four fertilizers are added to the paddy fields approximately at the rate of 88 kg/ha, 141 kg/ha, 44 kg/ha and 70 kg/ha, respectively during the irrigation season. However, according to the local farmers, only TSP and urea are regularly used in the paddy field, while potash and zinc are rarely used. Considering application of all fertilizers, an estimated 1.6×10^{-4} kg of arsenic was added to the sub-area 'R' of the paddy field with fertilizers during the *boro* season. This amount is negligible compared to the arsenic input from irrigation water. Besides, there is considerable uncertainty regarding the quality of fertilizer actually used in the paddy field. Hence arsenic input from fertilizers to paddy field was considered negligible and was neglected in estimating arsenic input to agricultural soil.

4.4.2 Estimate of Arsenic Accumulation in Top Soil

Figure 4.6 shows the variations of arsenic concentration of soil core samples for different sampling times. Each data point in Fig. 4.6 represents the average concentration of arsenic for a particular segment of the soil core and has been plotted at a depth representing the mid-depth of the segment. Table 4.2 shows range, mean and standard deviation of arsenic content in the different segments of soil layer at different sampling times.

Table 4.2. Range, mean and standard deviation (SD) of arsenic content in the different segment of soil core samples collected from different sampling times.

Segment and Depth	Parameter	1st Sampling, December 2003 (mg/kg)	2nd Sampling, May 2004 (mg/kg)	3rd Sampling, June 2004 (mg/kg)	4th Sampling, November 2004 (mg/kg)
Segment-1 (0-37.5 mm)	Range (n=7)	7.46-16.27	6.48-20.34	7.64-18.35	6.31-18.07
	Mean ± SD	12..33 ± 2.81	14.57 ± 4.12	13.82 ± 3.31	12.64 ± 3.38
Segment-2 (37.5-75 mm)	Range (n=7)	5.34-15.64	6.42-18.08	5.37-16.65	6.87-14.45
	Mean ± SD	10.93 ± 2.87	12.79 ± 3.66	12.29 ± 3.20	11.44 ± 2.24
Segment-3 (75-150 mm)	Range (n=7)	5.03-10.97	4.54-12.27	5.21-10.25	6.05-10.22
	Mean ± SD	8.42 ± 1.82	8.73 ± 2.38	8.08 ± 1.52	8.50 ± 1.21
Segment-4 (150 -300mm)	Range (n=7)	3.25-9.66	3.76-10.57	4.35-11.35	5.64-10.64
	Mean ± SD	6.99 ± 1.96	6.95 ± 1.92	7.01 ± 2.16	7.54 ± 1.53
Segment-5 (300-450 mm)	Range (n=7)	4.05-6.87	3.91-7.85	4.12-7.97	5.02-7.45
	Mean ± SD	5.92 ± 0.87	6.02 ± 1.23	6.17 ± 1.22	5.94 ± 0.82

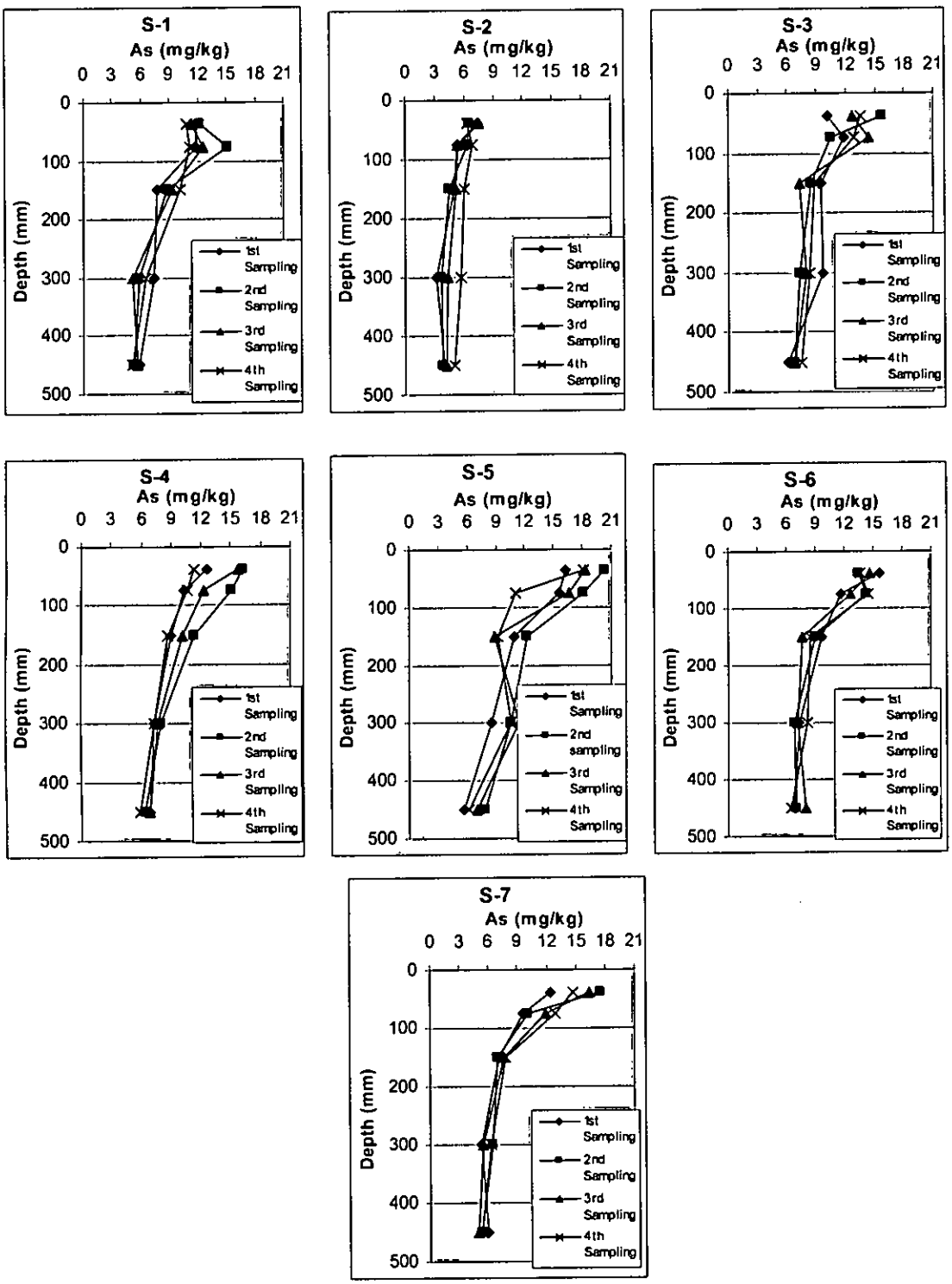


Figure 4.6: Arsenic profiles of soil cores collected from the sub-area "R" of the paddy field in Munshiganj

Figure 4.6 shows that arsenic levels of irrigated soils vary significantly with depth as well as with time of sampling. The results are similar to those found for another paddy field in Munshiganj and paddy fields in other arsenic affected areas, as presented in Chapter 3. In

general, arsenic concentrations in the top soil layers are high compared to those in the bottom layers. For example, in the 1st sampling average arsenic concentration in the 1st, 2nd, 3rd, 4th and 5th layers are 12.33, 10.93, 8.42, 6.99 and 5.92 mg/kg, respectively.

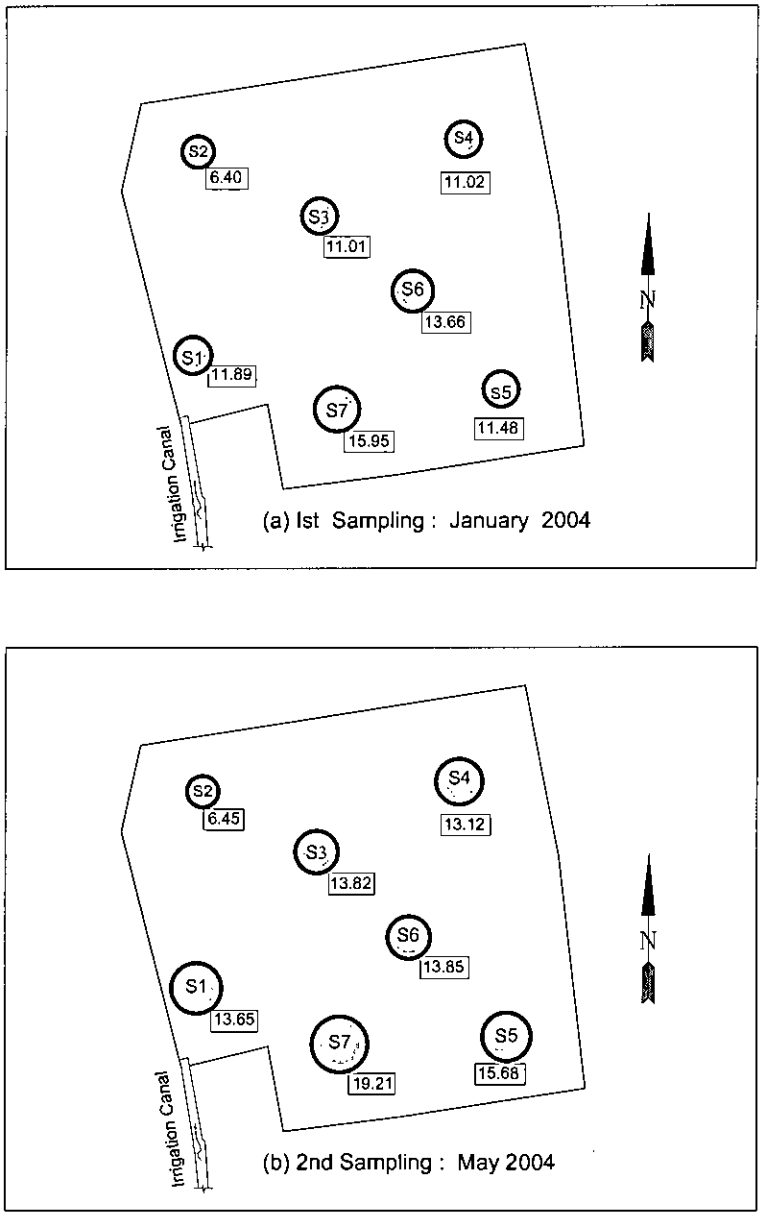


Figure 4.7: Schematic representation of sub-area "R" (identified in Fig. 4.3) of the paddy field in Munshiganj, along the approximate sampling locations and arsenic concentration in top 0-75 mm segment of soil

Average arsenic concentration in the top 0-75 mm segment of the seven soil cores collected in December 2003 varied from 6.40 to 15.95 mg/kg with an average of 11.6 mg/kg (see Fig. 4.7a). For samples collected at the end of the irrigation season in May

2004, average arsenic concentration in the top 0-75 mm varied from 6.45 to 19.21 mg/kg with an average of 13.7 mg/kg (see Fig. 4.7b). For samples collected during rainy season (3rd sampling) and after the rainy season (4th sampling), the average arsenic in top 0-75 mm in layer were 13.07 and 12.05 mg/kg, respectively. Thus, arsenic level in the top segments of soil cores increased at the end of the irrigation season and then decreased after the rainy season.

Average arsenic levels of the 7 soil core samples collected from the paddy field at the beginning and at the end of the irrigation season were used to estimate arsenic accumulation in the different soil layers during the irrigation season. Using average arsenic levels and a measured dry unit weight of 1.62 gm/cc for the soil, it is estimated that about 0.81 kg of arsenic was retained in the top 0-75 mm segment of soil up to the end of the irrigation season. Similarly the amount of arsenic retained in the next three segments i.e., 75-150 mm, 150-300 mm and 300-450 mm are 0.12, 0.03 and 0.07 kg, respectively. Thus, significant amount of arsenic is accumulated in the top 0-75 mm segment of soil, which accounted for about 71% of estimated total arsenic that is added to the paddy field with irrigation water. Accumulation in next three segments of soil accounted for about 10.5, 3.2 and 6.1%, respectively of the estimated total arsenic added to the field. Thus, arsenic accumulated in the top 0-450 mm of soil (1.03 mg) accounts for majority of the total arsenic (about 90%) that is added to the paddy field with irrigation water.

4.4.3 Arsenic Uptake by Paddy Plant

Figure 4.8 and Table 4.3 show the arsenic concentrations in paddy grains and different parts of paddy plants collected from the sub-area "R" of the paddy field. Figure 4.8 and Table 4.3 show that the roots of paddy plants accumulated the maximum level of arsenic, followed by leaf and stem. Paddy grain and husk accumulated the least amount of arsenic. These results are consistent with those obtained for another paddy field in Munshiganj and paddy field in other arsenic affected areas, as presented in Chapter 3. Average arsenic concentration of root, leaf and stem are 14.20, 6.83 and 5.09 mg/kg, respectively. These trends are also in agreement with those reported by Abedin et al. (2002), based on a greenhouse study, and Ali et al. (2003b) based on a study carried out in Munshiganj, Sonargaon and Dinajpur areas.

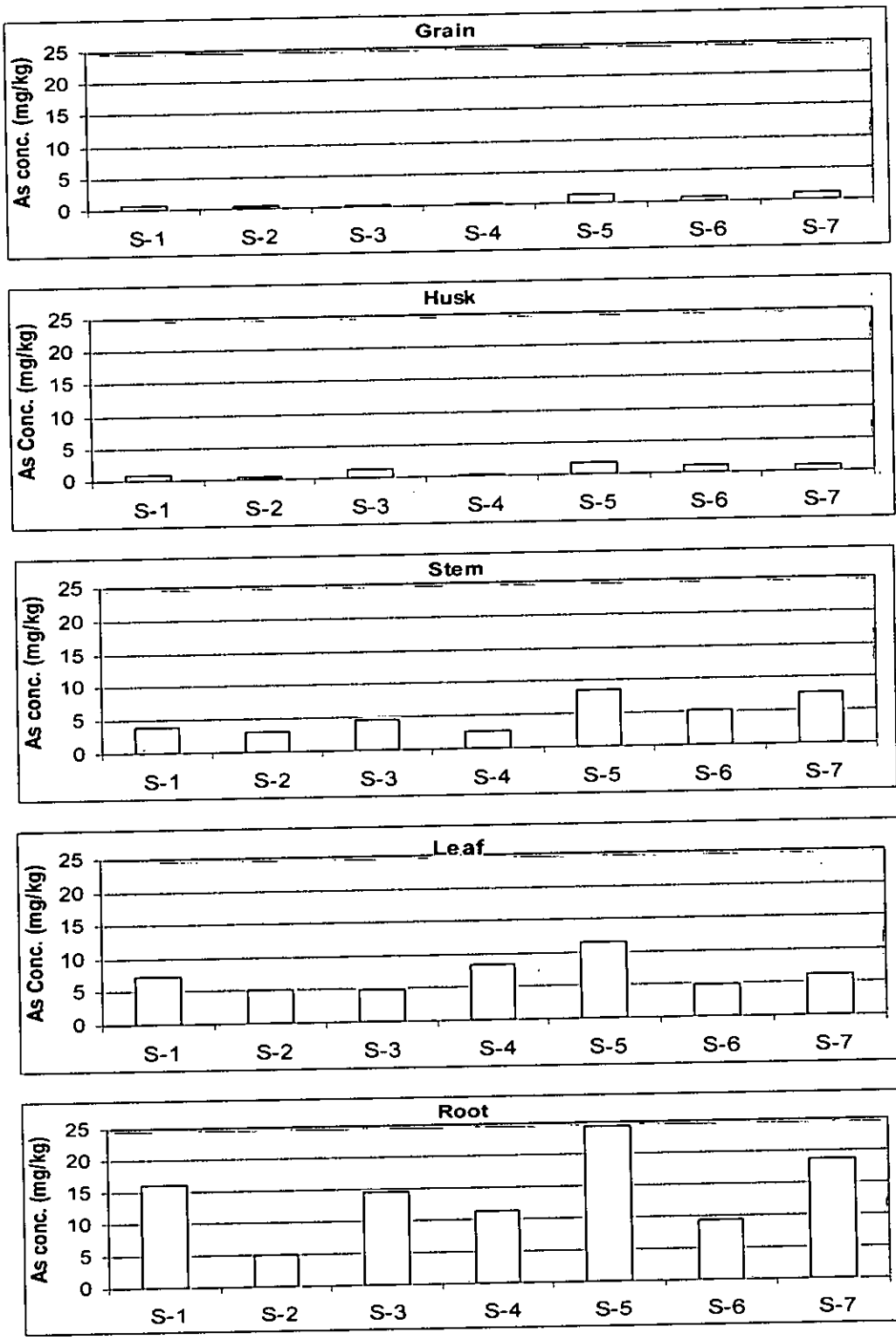


Figure 4.8: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants (S = Sample location)

Table 4.3. Arsenic content in different parts of paddy plants samples collected from the sub-area "R" of the paddy field in Munshiganj

Sample location	Root (mg/kg)	Leaf (mg/kg)	Stem (mg/kg)	Husk (mg/kg)	Grain (mg/kg)
S-1	16.02	7.21	4.02	0.92	0.62
S-2	5.04	5.04	3.03	0.56	0.55
S-3	14.65	4.82	4.65	1.45	0.28
S-4	11.41	8.32	2.56	0.25	0.18
S-5	24.33	11.42	8.46	1.72	1.32
S-6	9.24	4.79	5.36	1.22	0.71
S-7	18.76	6.24	7.57	0.95	1.02

Arsenic concentration in paddy grains varied from 0.28 mg/kg to 1.32 mg/kg, with a mean of 0.66 mg/kg. For two samples, arsenic concentration of grain exceeded the Australian food hygiene limit of 1.0 mg/kg. Average arsenic concentration in roots of paddy plant samples varied from 5.04 to 24.33 mg/kg, with a mean of 14.20 mg/kg.

In order to estimate the total mass of paddy plant, the number of plants per sq.m area of the paddy field was counted at different locations of the field and oven dried mass of different parts of paddy plants were determined (Table 4.4).

Table 4.4: Average (n=7) oven dried (65° C) mass of different parts of a paddy plant sample

Root (gm)	Leaf (gm)	Stem (gm)	Husk (gm)	Grain (gm)	Total (gm)
11	8	19	9	19	66

It was found that there were about 45 paddy plants per sq. meter area. Using average arsenic levels and measured dry weight of different parts of paddy plants, it was estimated that about 0.05 kg of arsenic was taken up by the paddy plants of sub-area "R" of the paddy field under investigation. This accounts for about 4.4% of arsenic added to the paddy field with irrigation water. Thus, the arsenic taken up by paddy plants accounts for about 4.4 % of the estimated total arsenic added to the paddy field with irrigation water.

Figure 4.9 shows arsenic uptake by different parts of paddy plant. Of the total uptake root accumulated for 47.27 %, stem 29.39 %, leaf 16.67%, husk 2.73% and grain 3.94%.

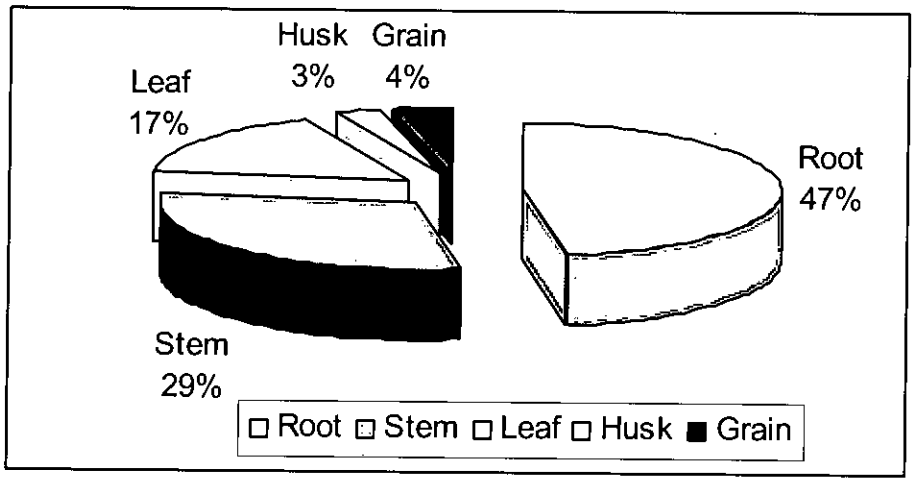


Figure 4.9: Arsenic uptake by different parts of paddy plant

4.4.4 Possible Loss of Arsenic from Soil by Microbial Methylation

In order to asses the possible loss of arsenic from soil by microbial methylation during inundation by rainwater/flood water, laboratory experiments were carried out in which 250 mm dia, 550 mm deep soil core samples were kept inundated under different conditions. The soil cores were kept in metallic (steel) cylindrical casings, the bottoms of which were sealed. Any loss of arsenic would therefore take place only by volatilization to the air. At the end of four-month inundation period, changes in mass of arsenic in each soil core was estimated by measuring arsenic levels in soil (as a function of depth) and in the inundation water.

Initial distribution of arsenic in the 250 mm soil cores were taken as same as those obtained for the 37.5 mm soil cores collected from the same field at close proximity of these bigger cores. Figure 4.10 shows average (n=3) arsenic profile of 37.5 mm core samples measured just after collection (refered to as "initial") and after 4 month freezing period (refered to as "Freezing"). It shows that as expected, arsenic levels in the freezed core samples are almost identical to those of the original samples measured right after collection. Since these cores were taken from the field at close proximity of the bigger cores, the arsenic profile presented in Fig. 4.10 was taken as the initial arsenic profile of the 250 mm dia soil cores.

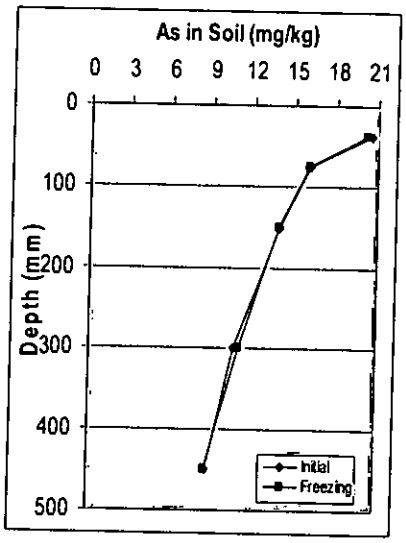


Figure 4.10: Average Arsenic profile of soil cores of "initial" and "freezed" condition

Figure 4.11 shows As profiles of the 250 mm soil core samples after 4-month inundation period for different inundation conditions, along with the initial As profile. Table 4.5 and Table 4.6 show the average total (aqua-regia extractable) and oxalate extractable As and Fe concentrations, respectively in different layers of soil cores after the 4-month inundated period. Figure 4.11 and Table 4.5 show that after the four-month inundation period, As profile of the 250 core samples did not change significantly. Table 4.6 shows that the 4-month inundation also did not cause any significant change in the Fe profile of the core samples as well. Table 4.5 also shows that on an average oxalate extractable As account for about 70% of total (aqua-regia extractable) arsenic for the top (0-75mm) layer and about 55 % of total arsenic for the bottom (300-450 mm) layer.

It appears that the soil arsenic profiles of the 250 mm soil cores after the 4-month inundation period do not differ significantly and it is difficult to identify differences among the different experimental conditions just by looking at the soil core arsenic profiles (Fig. 4.11). However, chemical composition of the inundation water is expected to provide a much better picture of arsenic mobilization under the different experimental set up. This is because of the fact that since the volume of inundation water is relatively small (2.05 to 2.89 liters), if a small fraction of soil arsenic is partitioned to water, it is likely to result in a significant increase of arsenic concentration in the inundated water. For example if 0.2 mg/kg of arsenic is partitioned from 0.75 mm layers of soil, it would cause a rise of arsenic concentration by 368 ppb in 2 liter of water.

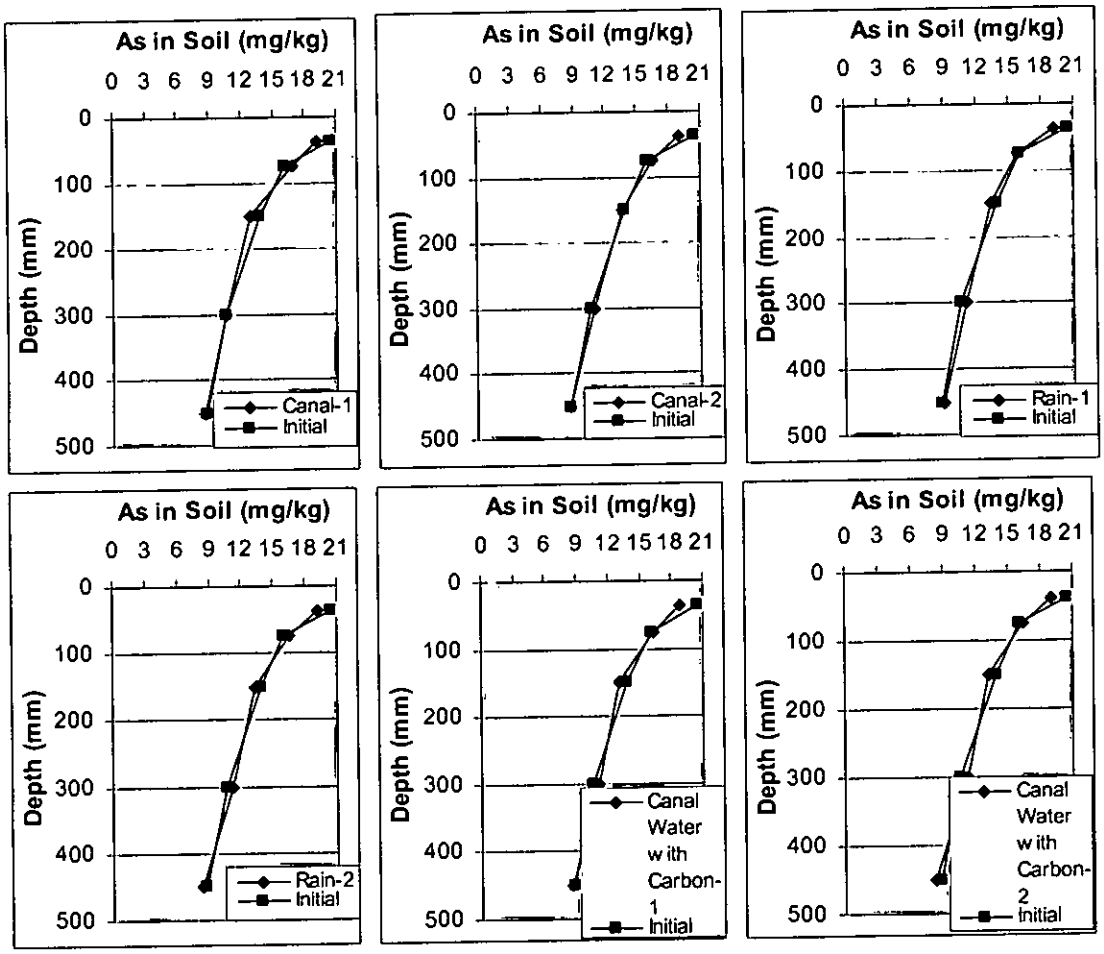


Figure 4.11: Average As profile of soil cores of different inundation condition

Table 4.5: Average total (aqua-regia) and oxalate extractable arsenic concentration of different layers of soil samples both initial and inundated condition in mg/kg

Layers (mm)	Initial Distribution		Inundation condition			
			Canal water-1		Canal water-2	
	Total	Oxalate	Total	Oxalate	Total	Oxalate
0-37.5	20.51	14.31	19.20	12.77	19.11	12.06
37.5-75	16.09	9.82	16.81	10.78	16.49	9.79
75-150	13.89	8.23	13.92	6.40	13.67	8.46
150-300	10.67	6.5	10.50	5.41	11.06	5.68
300-450	8.76	4.89	8.70	4.78	8.80	5.21

Layers (mm)	Inundation Condition							
	Rain water-1		Rain water-2		Canal water with glucose-1		Canal water with glucose-2	
	Total	Oxalate	Total	Oxalate	Total	Oxalate	Total	Oxalate
0-37.5	19.17	12.78	19.29	12.25	18.88	12.16	19.08	12.41
37.5-75	15.88	9.79	16.59	10.42	16.30	10.72	16.37	10.24
75-150	13.39	8.58	13.40	7.30	13.09	10.37	13.15	8.84
150-300	11.07	6.30	11.13	4.87	11.10	7.08	11.26	7.10
300-450	9.04	5.84	8.41	5.60	8.57	5.37	8.37	5.68

Table 4.6: Average total (aqua-regia) and oxalate extractable iron concentration of different layers of soil samples both initial and inundated condition in g/kg

Layers (mm)	Initial Distribution		Inundation condition			
			Canal water-1		Canal water-2	
	Total	Oxalate	Total	Oxalate	Total	Oxalate
0-37.5	34.59	12.36	33.99	12.56	34.00	11.59
37.5-75	32.80	11.50	32.98	11.68	33.14	10.35
75-150	30.81	10.01	31.16	10.53	30.34	10.88
150-300	32.37	7.78	29.38	7.01	29.60	8.56
300-450	29.47	7.23	29.33	6.69	29.33	6.33

Layers (mm)	Inundation Condition							
	Rain water-1		Rain water-2		Canal water with glucose-1		Canal water with glucose-2	
	Total	Oxalate	Total	Oxalate	Total	Oxalate	Total	Oxalate
0-37.5	33.00	12.76	34.29	12.32	33.13	12.33	33.29	12.80
37.5-75	30.78	11.80	33.19	10.35	33.21	10.12	33.50	10.95
75-150	32.06	10.87	30.37	8.79	31.81	9.39	31.78	9.45
150-300	31.08	8.19	30.56	8.24	30.19	8.24	28.65	6.74
300-450	30.56	6.86	30.28	6.70	29.38	6.51	30.17	6.91

Table 4.7 shows concentration of selected chemical constituents of rain water and canal water used as inundation water in the laboratory experiments. The rain water had low EC value with arsenic level below detection limit. The canal water had higher EC showing presence of dissolved solids and an arsenic concentration of 5.2 ppb.

Table 4.7: Concentration of selected chemical constituents of inundation water samples

Source of Water	pH	Conductivity (μS/cm)	As (μg/l)	Fe (mg/l)	NH_3-N (mg/l)	PO_4^{3-} (mg/l)	NO_3-N (mg/l)
Canal water	7.10	302	5.20	0.40	1.05	0.30	0.75
Rain water	7.25	38	<1.0	< 0.05	0.01	0.06	0.15

Table 4.8 shows concentration of selected chemical constituents of the inundated water after 4 month inundation period. Table 4.8 shows dramatic changes in the chemical composition of inundation water after the 4- month inundation period, when canal water amended with glucose and nutrients is used as inundation water (Experiment ID: Bio-5 and Bio-6 in Table 4.8). For these two cases, significant increase in Conductivity, As, Fe, NH_3, and PO_4 concentrations were observed after the 4-month inundation period. For example, for the four experiments without carbon and nutrient source in the inundation water (Experiment ID: Bio-1 to Bio-4 in Table 4.8), average arsenic and iron concentration in the inundation water after the 4-month inundation period were 11.25 μg/l

and 0.27 mg/l, respectively. Whereas for the two experiments with carbon and nutrient amended inundation water, the corresponding values were 457 μg/l and 23.8 mg/l, respectively (Table 4.8). Thus it appears that addition of a carbon source and nutrient causes significant mobilization of arsenic from the soil (solid) phase to the aqueous phase. This mobilization is most likely due to reductive dissolution of iron oxyhydroxides present in soil and concurrent oxidation of organic matter. Dissolution of iron would cause release of adsorbed arsenic and phosphate to the aqueous phase, while oxidation of soil organic matter may cause an increase of NH_3 concentration in water.

Table 4.8: Concentration of selected chemical constituents of collected water at the end of inundation period

Expt. ID	Inundation Water	Volume of water	pH	EC (μS/cm)	As (μg/l)	Fe (mg/l)	NH_3-N (mg/l)	PO_4^{3-} (mg/l)	NO_3-N (mg/l)
Bio-1	Canal water-1	2.05 L	8.27	419	4.30	0.24	0.31	0.13	0.70
Bio-2	Canal water-2	2.58 L	8.23	378	22.98	0.28	0.24	0.12	0.20
Bio-3	Rain water-1	2.33 L	8.14	444	11.24	0.21	0.26	0.23	1.05
Bio-4	Rain water-2	2.15 L	8.37	384	6.48	0.35	0.28	0.10	1.15
Bio-5	Canal water with glucose (5 g/L)-1	2.47 L	8.08	653	557.4	36.05	5.2	1.89	0.30
Bio-6	Canal water with glucose (2.5 g/L)-2	2.89 L	8.16	556	356.2	11.60	3.34	1.21	0.80

Possible loss of arsenic from the 250 mm soil cores was estimated by comparing the amount of arsenic remaining in the soil and water column of the cores after the 4-month inundation period with the initial amount of arsenic in soil. Table 4.9 shows estimate of arsenic in the experimental soil cores.

Table 4.9: Estimate of mass of arsenic in mg in the experimental soil cores

	Depth (mm)	Amount (mg) of arsenic in different segments of the experimental columns						
		Initial Condition	Bio-1	Bio-2	Bio-3	Bio-4	Bio-5	Bio-6
Water	0-75	0	0.008	0.059	0.026	0.013	1.376	1.029
Soil	0-37.5	61.160	57.253	56.985	57.164	57.522	55.299	56.896
	37.5-75	47.979	50.126	49.172	47.353	49.470	48.606	48.814
	75-150	82.839	83.018	81.527	79.857	79.916	78.067	78.425
	150-300	128.270	125.243	131.922	132.041	132.757	132.399	133.308
	300-450	104.488	103.773	104.965	107.828	100.313	102.222	99.836
Total		424.736	419.421	424.633	424.269	419.991	417.969	418.308
Amount Lost			5.315	0.103	0.046	4.745	6.767	6.428

Table 4.9 shows that change in the total mass of arsenic in between 0.10 to 6.77 mg after the 4-month inundation period (compared to initial mass). However, the most significant changes are noticed for the two experiments where inundation water was amended with a carbon source and nutrients. Maximum calculated loss of arsenic from soil column is about 1.6 %. Most of the loss appears to take place from the 0-150 mm soil layer. Thus, under the laboratory experimental conditions, possible loss of arsenic from soil by the microbial methylation process does not appear to be very significant in comparison to the total amount arsenic retained in the soil. However, the calculated loss of arsenic was significantly higher than the amount mobilized to the inundation water.

4.5 SUMMARY

From intensive monitoring of one sub-area of a paddy field during the *boro* season of 2004, it is estimated that about 90% arsenic added to the paddy field with irrigation water is accumulated in the top 0-450 mm of soil, of which the top 0-75 mm soil segment accounts for about 71%. The arsenic taken up by paddy plants accounts for about 4.5 % of total arsenic that is added to the paddy field with irrigation water. Of the total uptake by paddy plants, root accumulated 47.3 %, stem 29.4 %, leaf 16.7%, husk 2.7% and grain 3.9%.

In order to asses the possible loss of arsenic from soil by microbial methylation during inundation by rainwater/flood water, laboratory experiments were carried out in which 250 mm dia, 550 mm deep soil core samples were kept inundated under different conditions. Relatively insignificant changes in the total mass of arsenic were observed in the soil core samples after the 4-month inundation period, compared to the initial mass. However, the most significant changes were noticed for two experiments where the inundation water was amended with a carbon source (glucose) and nutrients. Under these conditions, significant amounts of arsenic, iron, phosphate and ammonia were detected in the inundation water after the 4-month period. This is most likely due to reductive dissolution of iron oxy-hydroxides present in soil; dissolution of iron would cause release of adsorbed arsenic and phosphate to the aqueous phase, while oxidation of soil organic matter may cause an increase of NH_3 concentration in water.

For these two laboratory experimental conditions, maximum calculated loss of arsenic from soil column is about 1.6 %. Most of the loss appears to take place from the 0-150 mm soil layer. However, the importance of such methylation process under actual field condition needs to be evaluated.

From the experimental results, it appears that during inundation of paddy fields in the rainy/flood season (that follows the *boro* season), a significant amount of arsenic could be partitioned from top soil to the inundation water in actual paddy fields, which are usually inundated under a significant depth of water during rainy/flood season. This is probably an important mechanism responsible of lowering of arsenic concentration of top soil layers after the rainy/flood season. The arsenic partitioned to the inundation water may be transported away from the site with percolation water or receding rain/flood water. More studies are needed to better understand these processes.

Chapter 5

Accumulation of Arsenic in Irrigated Vegetable Field Soil and Selected Vegetables

5.1 INTRODUCTION

The widespread presence of arsenic in groundwater at levels above the drinking water standard is a major concern in Bangladesh, India and several other countries (Nordstrum, 2002; BGS and DPHE, 2001; Smith et al., 2000). In Bangladesh, groundwater extracted from shallow aquifers using hand-tubewells is the primary source of drinking and cooking water for most of the population. Besides domestic use, huge quantities of groundwater are also used for irrigation during dry season. Thus, accumulation of arsenic in root zone soil, introduction of arsenic into the food chain, and impact of arsenic bearing irrigation water on crop yield are major concerns. Though groundwater irrigation is primarily used for growing dry season rice (called *boro*) and wheat (Ali *et al.*, 2003a), vegetable fields also receive groundwater irrigation during the dry season. A number of recent studies (e.g., Ullah,1998; Huq et al., 2001a; Huq et al., 2003; Ali et al., 2003b; Saha and Ali, 2004) have shown that high concentration of arsenic in irrigation water results in higher level of arsenic in the top soil layers. Larsen et al., (1992) reported that in arsenic contaminated soil, the uptake of arsenic by the plant tissue is significantly elevated, particularly in vegetables and edible crops.

Ali et al. (2003b) found higher concentration of arsenic in root, stem and leaf of rice plants grown with high arsenic bearing irrigation water; however accumulation of arsenic in rice grains has been found to be relatively low. Available data suggest that arsenic concentrations in different parts of certain common vegetables grown with arsenic bearing irrigation water are relatively high (Alam et al., 2003; Farid et al., 2003; Ali *et al.*, 2003b; Huq *et al.*, 2001b; Das et al., 2004). However, it is not clear whether these levels are significantly different from the background arsenic levels for these vegetables (i.e., arsenic levels of these vegetables grown in arsenic-unaffected areas). Most available data, however, are based on random sampling and hence it is difficult to correlate arsenic

concentrations in water, soil and plant samples. Available data also suggest significant variations of arsenic content among different varieties of crop/vegetable and also among different parts of the same plant. In the present study, effect of arsenic bearing irrigation water on accumulation of arsenic in vegetable field soil and some selected common vegetables have been assessed. This chapter presents results of laboratory analysis of water, soil and vegetable plant samples, collected from three different areas of Bangladesh, and provides an assessment of the effect of arsenic bearing irrigation water on vegetable field soil and some common vegetables.

5.2 METHODOLOGY

5.2.1 Selection of Sampling Sites and Vegetable Types

In this study, effect of irrigation water on arsenic contents of six different types of vegetables (Tomato, *lal shak*, *data shak*, cabbage, cauliflower and potato), commonly grown during dry season with the help of irrigation water, have been assessed. Local, English, scientific and family names of these vegetables are shown in Table 5.1. As shown in Fig. 5.1, three different areas of Bangladesh have been selected in this study as sampling sites. Among these, Sonargaon *upazilla* of Narayanganj district and Kachua *upazilla* of Chandpur district are arsenic affected areas; whereas the third field site at Sherpur *upazilla* of Bogra district has not been affected by arsenic contamination of groundwater. At each sampling location, each of the six types of vegetable samples was collected from three different fields.

Table 5.1: Local, English, scientific and family names of vegetables analyzed in this study

Local name of Vegetable (Bengali)	English Name	Scientific Name	Family
Alu	Potato	*Solanum tuberosum*	Solanaceae
Tomato	Tomato	*Lycopersicon esculentum*	Solanaceae
Data Shak	Stem Amaranth	*Amaranthus lividus*	Amaranthaceae
Lal Shak	Red Amaranth	*Amaranthus gangeticus*	Amaranthaceae
Badha Copi	Cabbage	*Brassica oleracea* L. Var. *capitata*	Brassicaceae
Ful Copi	Cauliflower	*Brassica oleracea* L. Var. *botrytis*	Brassicaceae

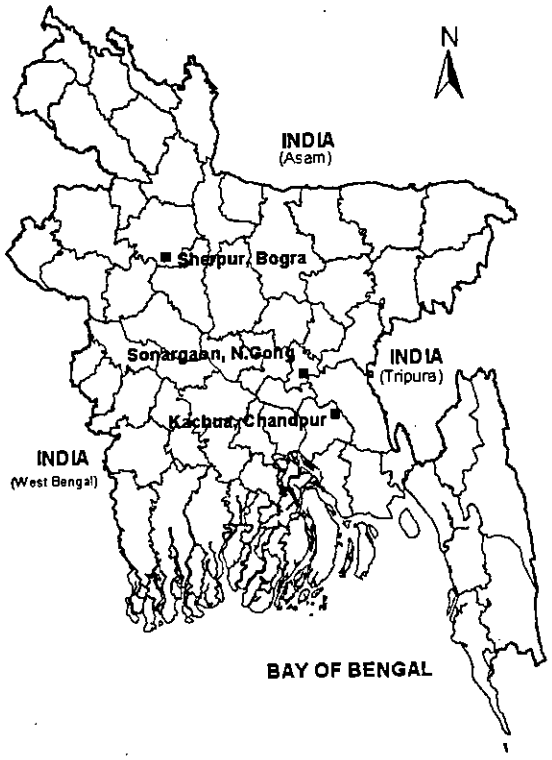


Figure 5.1: Bangladesh map showing sampling locations

5.2.2 Sample Collection

5.2.2.1 Collection of Water Sample

Irrigation water used in each of the 18 vegetable fields was collected during January to March, 2004. Groundwater samples were collected directly from wells and surface water samples were collected from respective ponds / canals. Water samples were collected in pre-washed plastic bottles and which was acidified in the field with 1 ml concentrated hydrochloric acid for analysis of metal ions.

5.2.2.2 Collection of Soil Samples

From each vegetable field, two to three soil core samples were collected. Soil core 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 required depth. After withdrawing the sampler along with the soil core, both its ends were sealed with plastic tape to reduce contact with air.

5.2.2.3 Collection of Vegetable Samples

From each site, samples of each of the six vegetables were collected from three different fields during January to March, 2004. At least three different vegetable plant samples including root and root soil (soil associated with root) were collected from each field.

5.2.3 Analysis of Sample

5.2.3.1 Analysis of Water Samples

Irrigation water samples collected from the field sites were analyzed for total arsenic. Acidified water samples were used for arsenic analysis, following the method described in section 1.3.

5.2.3.2 Analysis of Soil Samples

Division of Core Sample: Before analysis, each soil core sample was divided into four segments; the first segment consisting of the top 75 mm of soil, the second segment consisting of the next 75 mm, the third segment consisting of the next 150 mm, and the fourth segment consisting of the rest of the core. Besides, soil associated with the roots of each plant sample, referred to here as "root-soil", was collected by washing the roots with deionized water. The root-soil and each segment of the soil core samples were analyzed for total (aqua-regia extractable) arsenic and iron.

Digestion of Soil Sample: Digestion of soil samples were carried out following methods described in Chapter-3.

5.2.3.2 Analysis of Vegetable samples

Division of Plant Samples: Vegetable plant samples were divided into four parts: (1) root (2) stem (3) leaf and (4) edible part. For cabbage, the edible part was further divided into outer layer and inner layer.

Digestion of Plant Samples: Digestion of Plant samples were carried out following methods described in Chapter 3.

5.3 RESULTS AND DISCUSSION

5.3.1 Arsenic in Irrigation Water

As expected, As concentrations in all irrigation water samples (both from surface water and groundwater sources) collected from Bogra were found to be very low, mostly below the machine detection limit of 1 μg/l (see Table 5.2 through 5.7). On the other hand, As concentrations of irrigation water from the arsenic affected areas of Chandpur and Narayanganj have been found to be significantly higher when they came from groundwater source; whereas As contents of irrigation water from ponds and canals, i.e., from surface water sources, have been much lower (see Table 5.2 though 5.7). Compared to Chandpur, much higher As concentrations were detected in the groundwater samples (irrigation water) from Narayanganj. Arsenic concentration in groundwater samples collected from Chandpur varied from 73 to 132 μg/l; for Narayanganj it varied from 63 to 267 μg/l. Surface water (irrigation water) samples from Narayanganj have been found to contain relatively higher As (up to 25.3 μg/l), compared to those from Bogra (up to 2.5 μg/l) and Chandpur (up to 6.7 μg/l). Arsenic concentration in surface water samples collected from Chandpur varied from less than 1 ppb up to 6.7 μg/l; for Narayanganj it varied from 11 to 25.3 μg/l.

5.3.2 Arsenic in Vegetable Field Soil

Figures 5.2a, 5.2b and 5.2c show the As profile of soil core samples collected from vegetable fields of Bogra, Chandpur and Narayanganj, respectively. Each data point in the figures represents average As concentration (n = 3 to 6) for a particular segment of soil and has been plotted at a depth representing the mid-depth of the segment. The figures also show As concentration of irrigation water for each field. Average As concentrations of irrigation water of the three sampling areas are 3.1 μg/l (n = 12), 89 μg/l (n = 7) and 198 μg/l (n = 11), respectively for groundwater; and 1.1 μg/l (n = 6), 3.1 μg/l (n = 11) and 17.7 μg/l (n = 7), respectively for surface water. Figure 5.2a shows that in Bogra, where irrigation water (from both surface and groundwater sources) contained little As, average arsenic concentrations in the soil layers are relatively low (compared to those in samples from Chandpur and Narayanganj), and do not vary significantly with

depth. In Bogra, As concentrations in "root-soil" have been found to be comparable to those found in the top 75mm segment of soil.

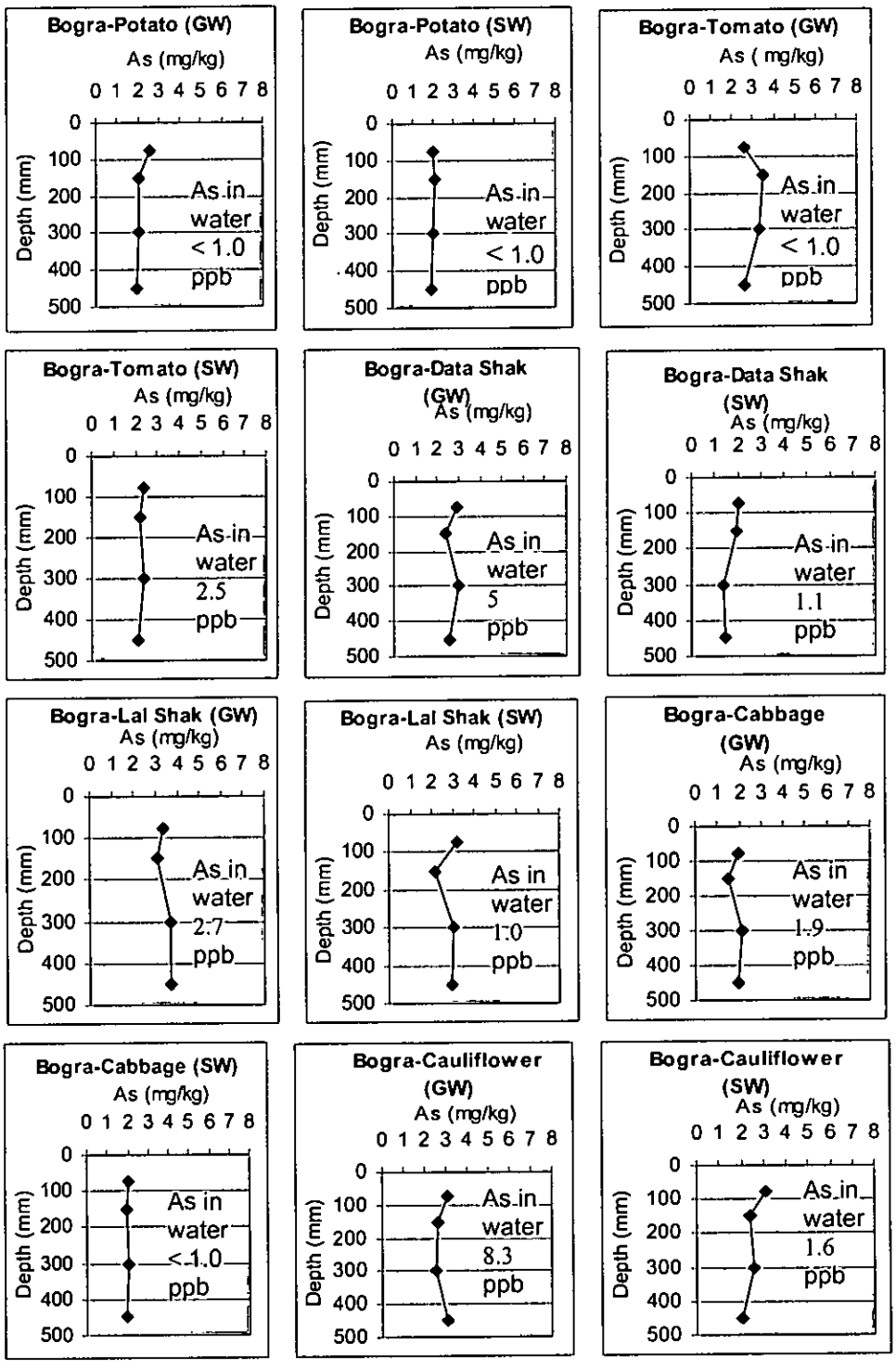


Figure 5.2a: As profile of soil cores collected from different vegetable fields irrigated with groundwater (GW) and surface water (SW) in Bogra

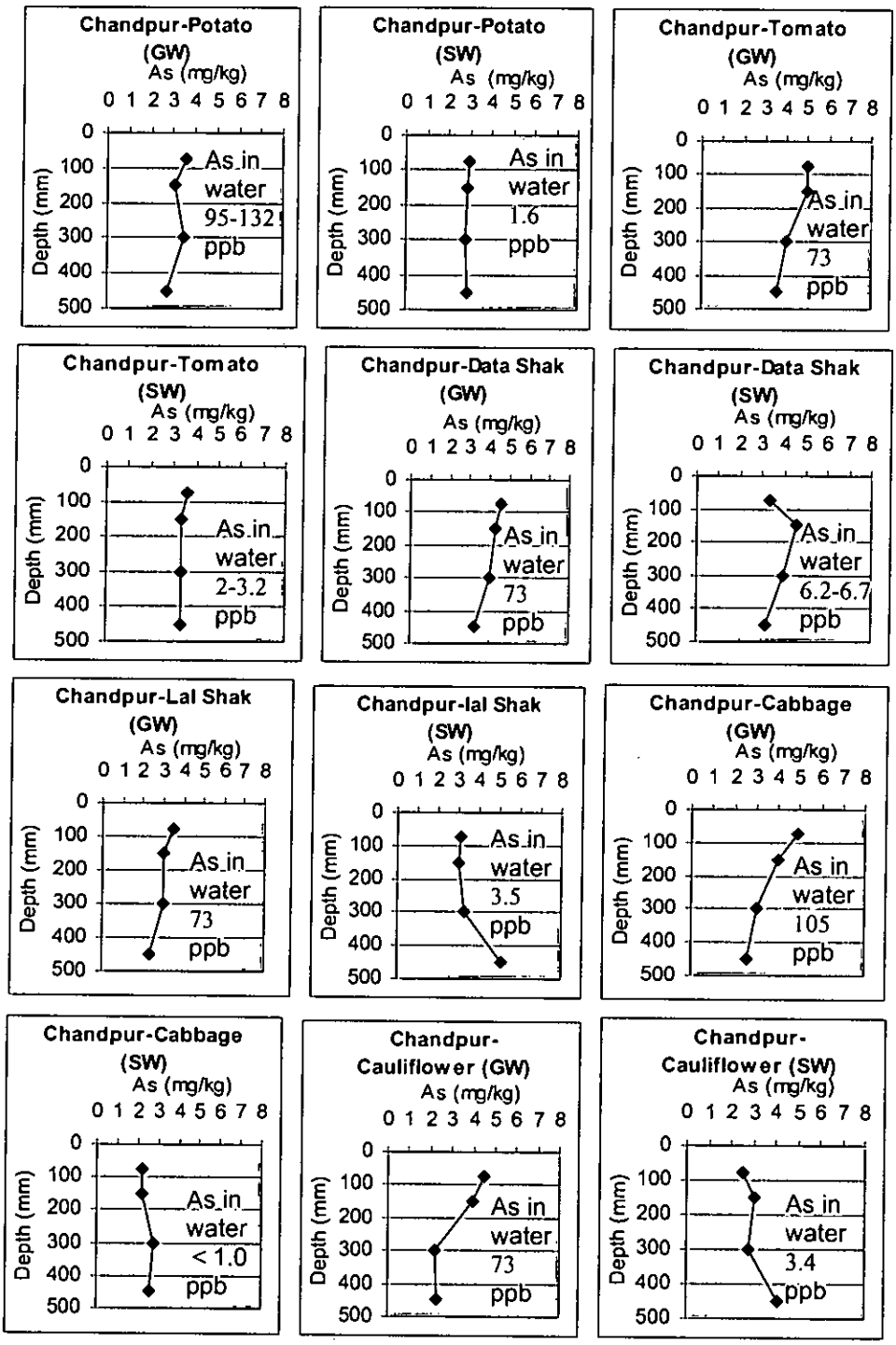


Figure 5.2b: As profile of soil cores collected from different vegetable fields irrigated with groundwater (GW) and surface water (SW) in Chandpur

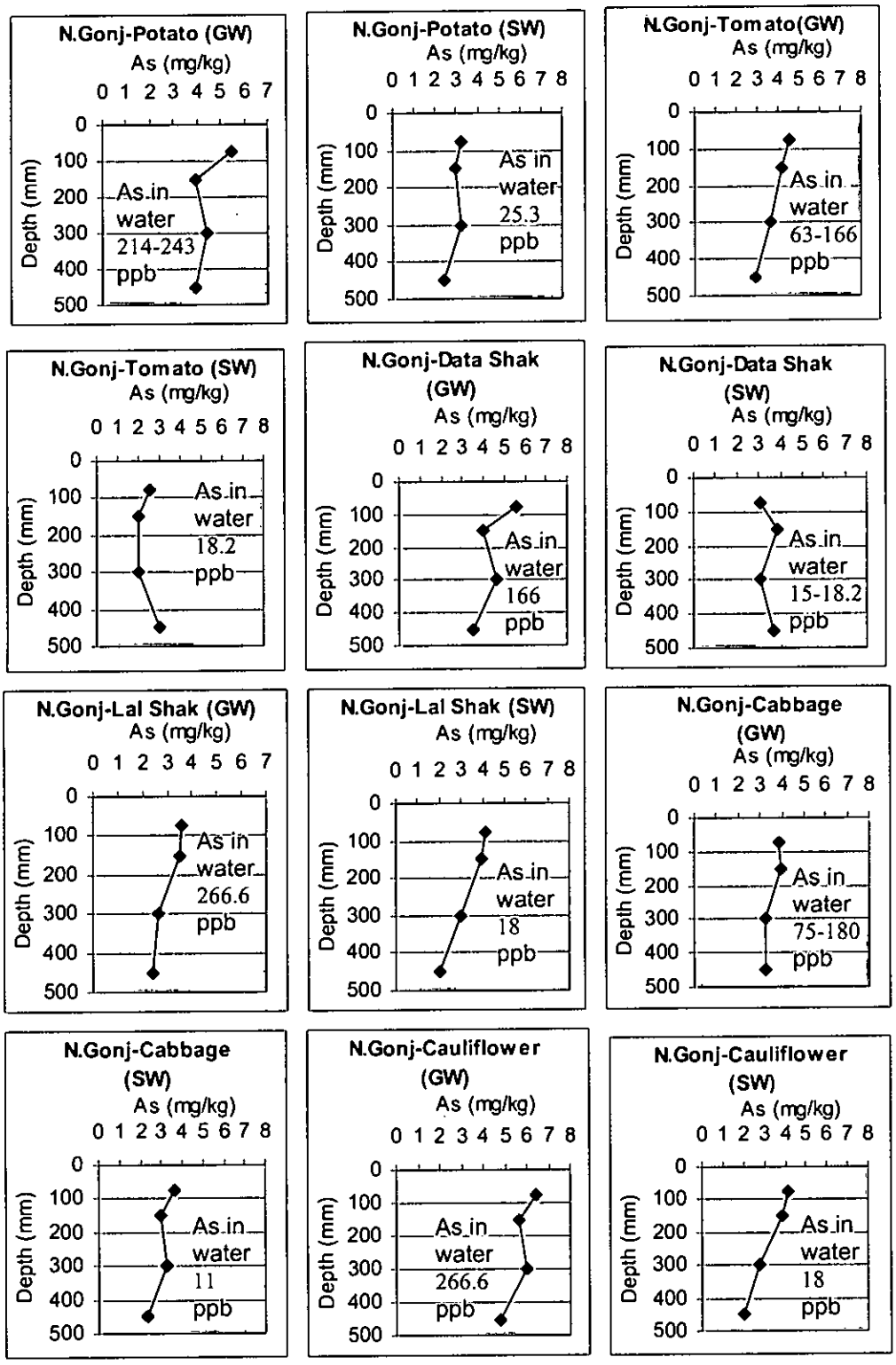


Figure 5.2c: As profile of soil cores collected from different vegetable fields irrigated with groundwater (GW) and surface water (SW) in Narayanganj (N. Gonj)

In Chandpur and Narayanganj, arsenic contents of top soil layers of vegetable fields irrigated with surface water are relatively lower, compared to those irrigated with high arsenic bearing groundwater (see Figs. 5.2b, 5.2c). For vegetable fields irrigated with groundwater, arsenic content in soil appears to decrease with depth. The highest arsenic (7.6 mg/kg) in top 0-75mm segment of soil was recorded for a cauliflower field in Narayanganj, where arsenic content of irrigation water was also the highest (267 μg/l) among all the water samples collected. In Chandpur and Narayanganj, root-soils have been found to contain slightly higher arsenic compared to the top 75 mm segment soil layer, especially for vegetable fields irrigated with groundwater.

Figures 5.3a and 5.3b show the relationships between arsenic content in irrigation water and arsenic content in root-soil and top 75 mm segment of soil, respectively, for all the vegetable fields. The figures show that, in general, arsenic contents of root-soil and top 0-75 mm segment of soil increase with increasing concentration of arsenic in the irrigation water. Arsenic in root-soil has been found to be strongly correlated with arsenic in irrigation water, with a correlation coefficients of $R^2 = 0.676$; arsenic in the top 0-75 mm segment of soil has been found to be moderately correlated with arsenic in irrigation water, with a correlation coefficients of $R^2 = 0.407$. In a study conducted in Hajiganj upazilla of Chandpur district and Sharishabari upazilla of Jamalpur district, Das et al. (2004) also observed a positive correlation ($R^2 = 0.74$) between arsenic in tubewell water and arsenic in soil; samples were collected randomly in this study.

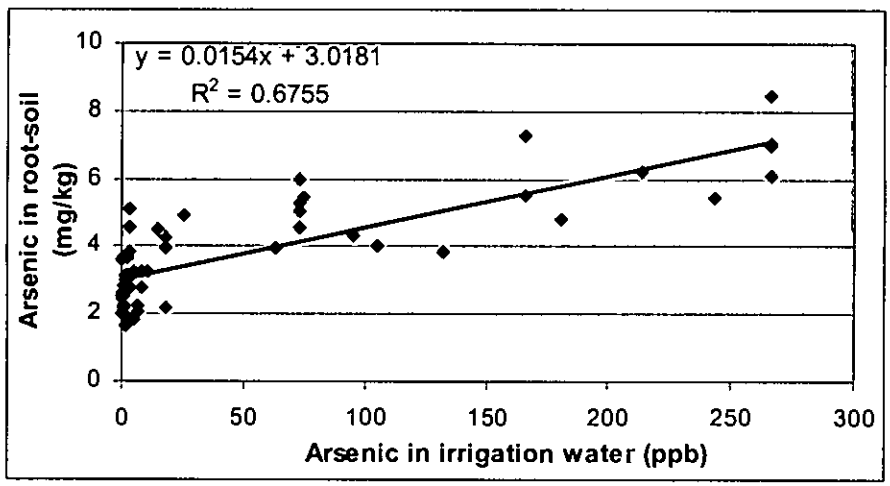


Figure 5.3a: Relationship between arsenic in irrigation water and arsenic in root-soil of vegetable fields

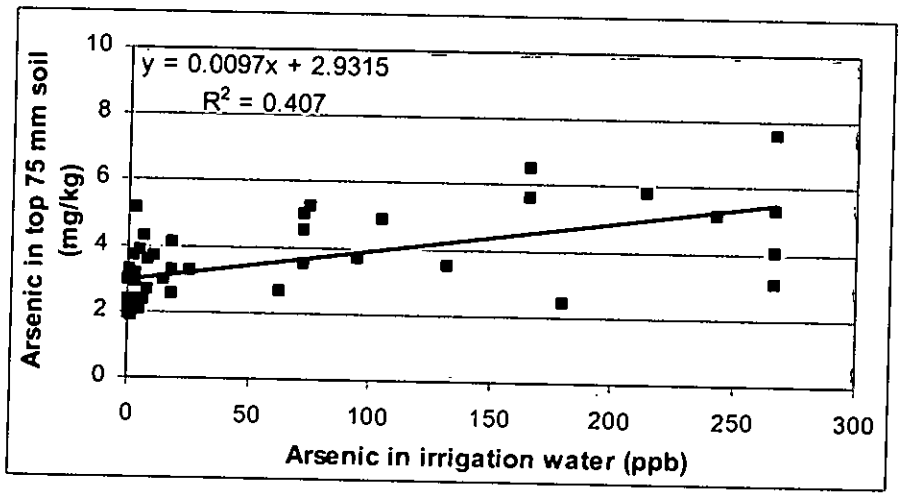


Figure 5.3b: Relationship between arsenic in irrigation water and arsenic in top 75 mm segment of soil layer of vegetable fields

5.3.3 Arsenic in Vegetable

5.3.3.1 Arsenic in Potato

Results of analysis of arsenic concentrations in different parts of potato samples show that root accumulated the highest arsenic and the edible part accumulated the least. Table 5.2 shows source and arsenic concentration of irrigation water, and arsenic concentration in root, stem, leaf and edible part of potato samples collected from the three sampling areas. It clearly shows that arsenic content in the edible part as well as root of potato samples increases with increasing arsenic concentration in the irrigation water. In Bogra, where all irrigation water contained very little arsenic (<1 μg/l), mean arsenic content in the edible part of potato was very low (up to 0.035 mg/kg). In both Chandpur and Narayanganj, arsenic content of edible part has been found to be much higher (by a factor of over 2) for potato grown with irrigation water having high arsenic content, compared to potato grown with surface water irrigation having relatively low arsenic. Ali et al. (2003b) found mean arsenic content in edible part of potato grown with pond water (having arsenic concentration of up to 37 μg/l) in Srinagar, Munshigonj to be 0.45 mg/kg, a value similar to those found in the present study. In a study conducted in Kachua and Hajiganj upazillas of Chandpur district and Sharishabari upazilla of Jamalpur district, Das et al. (2004) found arsenic concentrations in potato to vary from 0.07 to1.36 mg/kg.

As shown in Figs. 5.4 (a) and 5.4(b), arsenic content in edible part of potato is strongly correlated with arsenic content in irrigation water (R^2=0.60) and arsenic content in root-soil (R^2=0.75).

Table 5.2: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of potato

Groundwater Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	< 1.0	2.55 (n=6)	0.16 (n=6)	0.09 (n=6)	0.07 (n=6)	0.02 (n=6)
Chandpur	95 – 132	4.09 (n=6)	1.78 (n=6)	0.34 (n=6)	0.25 (n=6)	0.23 (n=6)
Narayanganj	214 - 243	5.82 (n=6)	2.62 (n=6)	1.45 (n=6)	2.06 (n=6)	1.15 (n=6)
Surface Water Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	< 1.0	2.59 (n=3)	0.35 (n=3)	0.12 (n=3)	0.25 (n=3)	0.04 (n=3)
Chandpur	1.6	3.12 (n=3)	0.45 (n=3)	0.24 (n=3)	0.25 (n=3)	0.10 (n=3)
Narayanganj	25.3	4.90 (n=3)	1.58 (n=3)	0.85 (n=3)	1.03 (n=3)	0.51 (n=3)

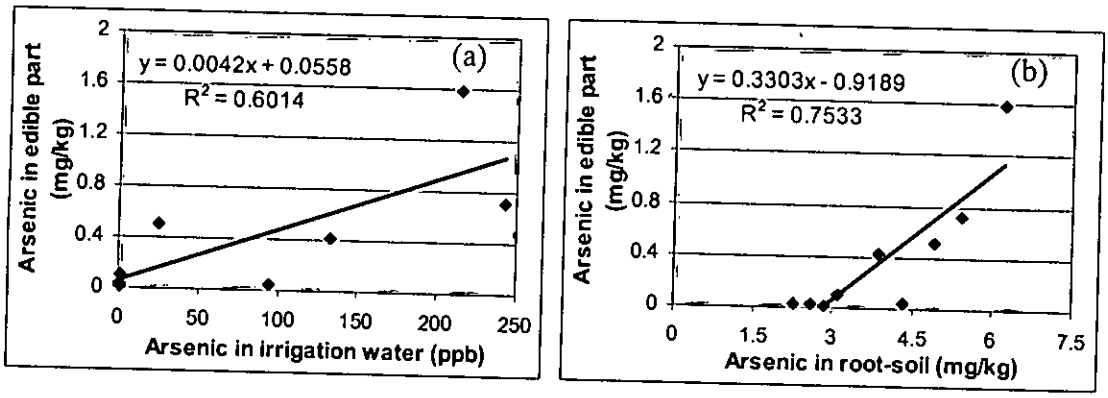


Figure 5.4: Relationship between arsenic in edible part of potato with: (a) As in irrigation water, and (b) As in root-soil

5.3.3.2 Arsenic in Tomato

Unlike potato, accumulation of arsenic in different parts of tomato samples did not show any clear trend. In some cases, mean arsenic concentration in edible part, stem and leaf exceeded that found in the root. Table 5.3 shows arsenic concentration in root, stem, leaf and edible part of tomato samples along with source and arsenic concentration of irrigation water. In general, arsenic contents in both edible part and root of tomato samples increased with increasing arsenic concentration in the irrigation water. In Bogra, where all irrigation water contained very little arsenic, mean arsenic content in the edible part of tomato was low (up to 0.465 mg/kg) compared to those for Chandpur and Narayanganj. In tomato samples from Chandpur and Narayanganj, arsenic content of edible part has been found to be relatively higher (by a factor of 1.3 to 1.7) for tomato grown with irrigation water having higher arsenic content, compared to those grown with surface water irrigation having relatively low arsenic. Similar results have been reported by Ali et al. (2003b). Burlo et al. (1999) also found that concentration of arsenic in tomato plants, grown under soil-less culture conditions, increased with increasing arsenic concentration in solution. Arsenic concentration in tomato has been found to be positively correlated with arsenic concentration in water (R^2=0.61) and root-soil (R^2=0.55) (Fig. 5.5).

5.3.3.3 Arsenic in Data Shak

For *data shak,* leaf and stem are the main edible part. As shown in Table 5.4, root of *data shak* samples have been found to accumulate relatively higher arsenic compared to stem and leaf (i.e., edible part). In general, arsenic content of edible part has been found to be higher (up to 1.41 mg/kg) in *data shak* grown in Chandpur and Narayanganj with groundwater irrigation having higher arsenic content. Arsenic content of edible part was relatively lower for *data shak* grown with surface water irrigation having low arsenic. Similar results have been reported by Ali et al. (2003b). Fig. 5.6 shows that arsenic concentration in edible part of *data shak* is very strongly correlated with arsenic concentration in root-soil (R^2=0.832).

Table 5.3: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of tomato.

Groundwater Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	<1.0	3.03 (n=6)	0.33 (n=6)	0.13 (n=6)	0.39 (n=6)	0.27 (n=6)
Chandpur	73.0	4.53 (n=3)	1.69 (n=3)	0.99 (n=3)	0.85 (n=3)	1.05 (n=3)
Narayanganj	63 - 166	5.63 (n=6)	1.99 (n=6)	1.15 (n=6)	2.82 (n=6)	1.70 (n=6)
Surface Water Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	2.5	3.67 (n=3)	1.72 (n=3)	0.55 (n=3)	0.33 (n=3)	0.47 (n=3)
Chandpur	2.0 - 3.2	3.53 (n=6)	0.48 (n=6)	0.23 (n=6)	0.36 (n=6)	0.78 (n=6)
Narayanganj	18.2	2.21 (n=3)	1.03 (n=3)	1.09 (n=3)	0.93 (n=3)	0.99 (n=3)

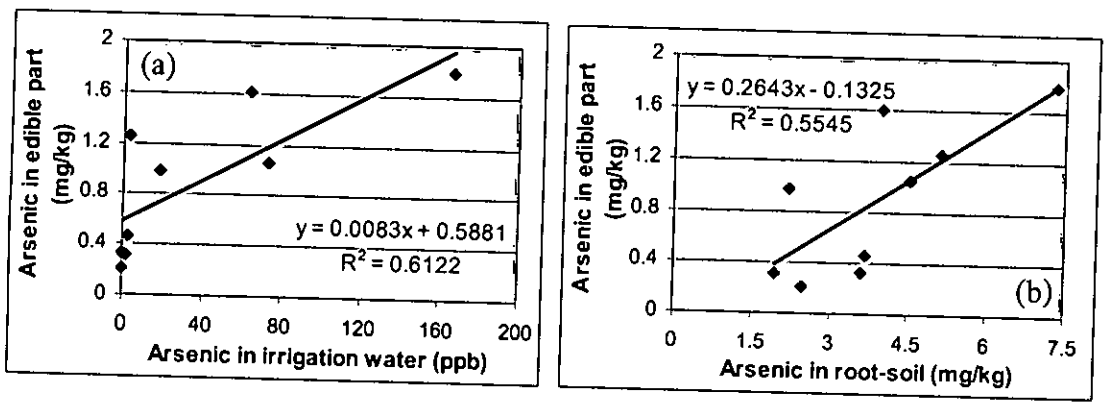


Figure 5.5: Relationship between arsenic in tomato with: (a) As in irrigation water and (b) As in root-soil.

Table 5.4: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of *data shak*

Groundwater Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (avg. of stem and leaf) (mg/kg)
Bogra	5	2.55 (n=6)	1.08 (n=6)	0.99 (n=6)	0.62 (n=6)	0.80 (n=6)
Chandpur	73	5.03 (n=3)	2.04 (n=3)	1.70 (n=3)	0.87 (n=3)	1.28 (n=3)
Narayanganj	166	5.52 (n=3)	1.55 (n=3)	1.41 (n=3)	1.40 (n=3)	1.41 (n=3)
Surface Water Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part(avg. of stem and leaf) (mg/kg)
Bogra	1.1	2.54 (n=3)	1.27 (n=3)	0.24 (n=3)	0.56 (n=3)	0.40 (n=3)
Chandpur	6.2 - 6.7	2.16 (n=6)	0.81 (n=6)	0.25 (n=6)	0.42 (n=6)	0.33 (n=6)
Narayanganj	15 - 18.2	4.23 (n=6)	2.40 (n=6)	1.00 (n=6)	1.47 (n=6)	1.24 (n=6)

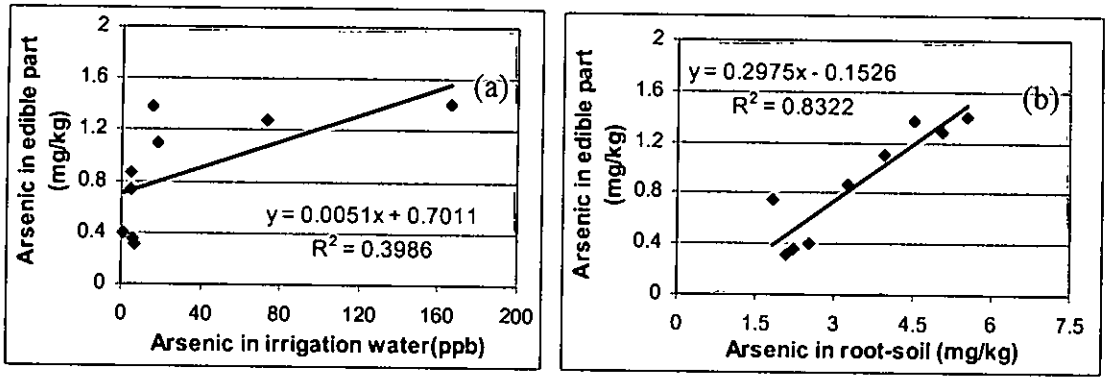


Figure 5.6: Relationship between arsenic in edible part of *data shak* with: (a) As in irrigation water, and (b) As in root-soil.

5.3.3.4 Arsenic in Lal Shak

For *lal shak,* leaf is the main edible part. Results of analysis of arsenic in different parts of *lal shak* show that root accumulated the highest arsenic and leaf (i.e., edible part) the

least. Table 5.5 shows source and arsenic content of irrigation water, and arsenic concentration in root and edible part of *lal shak* samples collected from the three sampling areas. It shows that arsenic contents in root and edible part of *lal shak* increased with increasing arsenic content of groundwater that is used for irrigation; the trend is not clear for plants grown with surface water irrigation.

In Bogra, where all irrigation water contained very little arsenic (1-3 μg/l), mean arsenic content in the edible part of *lal shak* varied from 0.306 to 0.469 mg/kg, and these values were much lower compared to those found for plants grown in Chandpur and Narayanganj, especially when groundwater with high arsenic has been used for irrigation. In Narayngonj arsenic content of edible part have been found to be much higher (by a factor of over 2.5) for *lal shak* grown with irrigation water having high arsenic content, compared to those grown with surface water irrigation having relatively low arsenic. But this general trend was absent in case of Chandpur. In fact, here arsenic contents in both root and edible part of *lal shak* have been found to be lower for plants grown with groundwater with higher arsenic content, compared to those grown with surface water having relatively low arsenic. Arsenic concentrations in the edible parts of *data shak* and *lal shak*, found in this study, are comparable and similar to those reported for *kalmi shak* (*Ipomoea reptoms*) (0.1 – 1.53 mg/kg) by Das et al. (2004); much higher values (0.09 – 3.99 mg/kg), however, have been reported for *kachu shak* (*Colocasia antiquorum*) (Das et al., 2004).

Arsenic concentration in edible part of *lal shak* has been found to be moderately correlated with arsenic concentration in irrigation water (R^2=0.32) and root-soil (R^2=0.54) (Fig. 5.7).

5.3.3.5 Arsenic in Cabbage

For cabbage, roots accumulated higher arsenic compared to stem and edible part (i.e., leaf), except for the cabbage samples grown with groundwater irrigation in Chandpur, where the edible parts have been found to contain slightly higher arsenic compared to root (see Table 5.6). Mean arsenic concentration in edible part of cabbage grown either with surface water or groundwater having low arsenic content has been found to be much lower (0.20 to 0.335 mg/kg) compared to those grown with groundwater having high

arsenic content (0.659 to 0.946 mg/kg). However, no clear trend could be observed for arsenic in root of cabbage samples.

Table 5.5: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of *lal shak*.

Groundwater Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part(avg. of stem and leaf) (mg/kg)
Bogra	2.7	3.07 (n=6)	0.94 (n=6)	0.48 (n=6)	0.14 (n=6)	0.31 (n=6)
Chandpur	73	5.27 (n=3)	1.24 (n=3)	0.97 (n=3)	0.84 (n=3)	0.90 (n=3)
Narayanganj	266.6	6.59 (n=6)	2.05 (n=6)	1.30 (n=6)	1.18 (n=6)	1.24 (n=6)
Surface Water Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part(avg. of stem and leaf) (mg/kg)
Bogra	1.0	2.17 (n=3)	0.69 (n=3)	0.58 (n=3)	0.35 (n=3)	0.47 (n=3)
Chandpur	3.5	4.21 (n=6)	1.84 (n=6)	1.74 (n=6)	0.72 (n=6)	1.23 (n=6)
Narayanganj	18	4.26 (n=3)	0.65 (n=3)	0.25 (n=3)	0.66 (n=3)	0.46 (n=3)

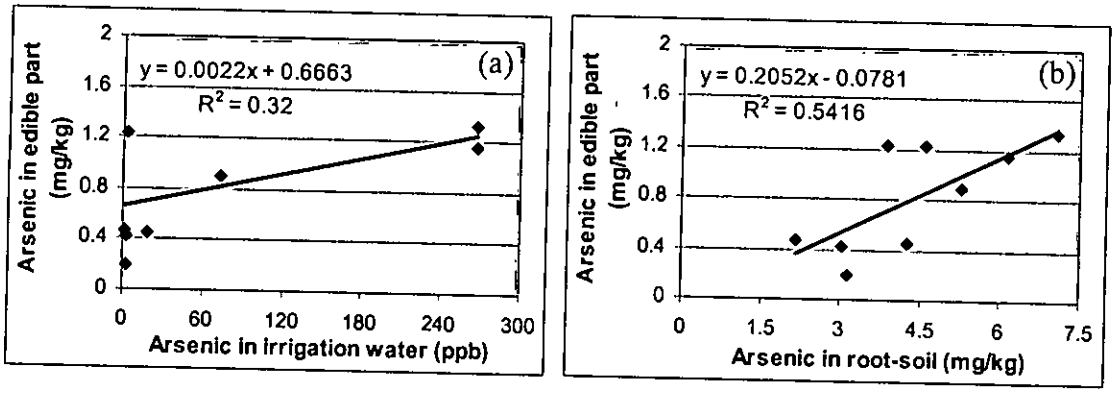


Figure 5.7: Relationship between arsenic in edible part of *lal shak* with: (a) As in irrigation water, and (b) As in root-soil

Similar to the other vegetable samples, arsenic concentration in edible part of cabbage has been found to be moderately correlated with arsenic concentration in irrigation water (R^2= 0.39) and root-soil (R^2= 0.54) (Fig. 5.8).

Table 5.6: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of cabbage

Groundwater Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	1.9	1.81 (n=6)	0.91 (n=6)	0.32 (n=6)	0.19 (n=6)	0.26 (n=6)
Chandpur	105	4.03 (n=3)	0.76 (n=3)	0.55 (n=3)	0.66 (n=3)	0.95 (n=3)
Narayanganj	75 - 180	5.11 (n=6)	1.30 (n=6)	0.20 (n=6)	0.69 (n=6)	0.66 (n=6)
Surface Water Irrigation						
Sampling Location	As in Water (µg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	<1.0	2.54 (n=3)	0.86 (n=3)	0.58 (n=3)	0.13 (n=3)	0.23 (n=3)
Chandpur	<1.0	2.30 (n=6)	0.34 (n=6)	0.30 (n=6)	0.33 (n=6)	0.34 (n=6)
Narayanganj	11	3.25 (n=3)	0.33 (n=3)	0.25 (n=3)	0.29 (n=3)	0.20 (n=3)

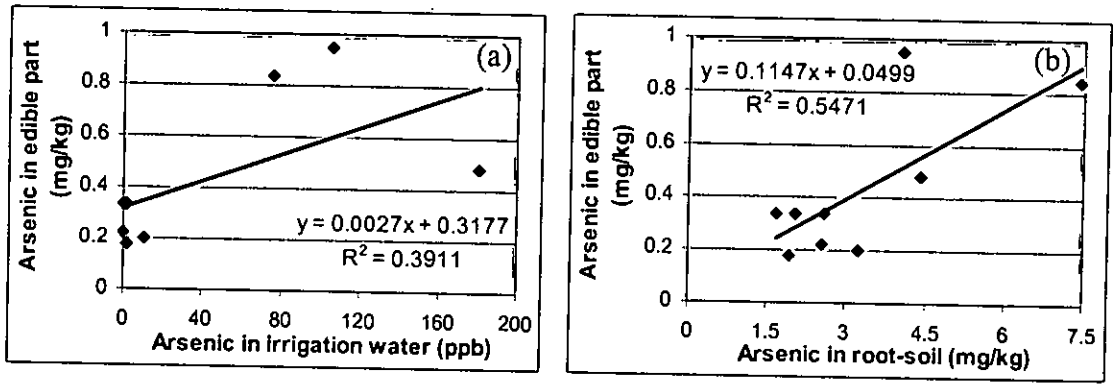


Figure 5.8: Relationship between arsenic in edible part of cabbage with: (a) As in irrigation water, and (b) As in root-soil

5.3.3.6 Arsenic in Cauliflower

As shown in Table 5.7, roots of cauliflower samples have been found to accumulate relatively higher arsenic compared to stem, leaf and the edible part. In general, arsenic contents of different parts of cauliflower samples increased with increasing arsenic content of irrigation water (see Table 5.7).

In Bogra, where all irrigation water contained very little arsenic (up to 8.3 μg/l), mean arsenic content in the edible part of cauliflower was very low (up to 0.083 mg/kg) compared to those found for cauliflower grown in Chandpur and Narayanganj. In both Chandpur and Narayanganj, arsenic content in edible part have been found to be higher (by a factor of approximate 1.5) for cauliflower grown with irrigation water having high arsenic content, compared to cauliflower samples grown with surface water irrigation having relatively low arsenic.

Table 5.7: Source and arsenic concentration of irrigation water and mean arsenic in root-soil, root and different parts of cauliflower.

Groundwater Irrigation						
Sampling Location	As in Water (μg/l)	Mean As in Root Soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	8.3	3.03 (n=6)	0.95 (n=6)	0.39 (n=6)	0.19 (n=6)	0.08 (n=6)
Chandpur	73.0	5.41 (n=3)	1.87 (n=3)	0.37 (n=3)	0.73 (n=3)	0.62 (n=3)
Narayanganj	266.6	7.72 (n=6)	2.18 (n=6)	0.52 (n=6)	0.99 (n=6)	0.78 (n=6)
Surface Water Irrigation						
Sampling Location	As in Water (μg/l)	Mean As in Root soil (mg/kg)	Mean As in Root (mg/kg)	Mean As in Stem (mg/kg)	Mean As in Leaf (mg/kg)	Mean As in Edible Part (mg/kg)
Bogra	1.6	3.03 (n=3)	0.96 (n=3)	0.21 (n=3)	0.13 (n=3)	0.01 (n=3)
Chandpur	3.4	2.91 (n=6)	1.27 (n=6)	0.45 (n=6)	0.92 (n=6)	0.41 (n=6)
Narayanganj	18.0	3.60 (n=3)	1.04 (n=3)	0.52 (n=3)	0.68 (n=3)	0.58 (n=3)

Strong positive correlation has been observed (Fig. 5.9) between arsenic in edible part of cauliflower and arsenic concentration in irrigation water and root-soil, with correlation coefficient of 0.68 and 0.59, respectively.

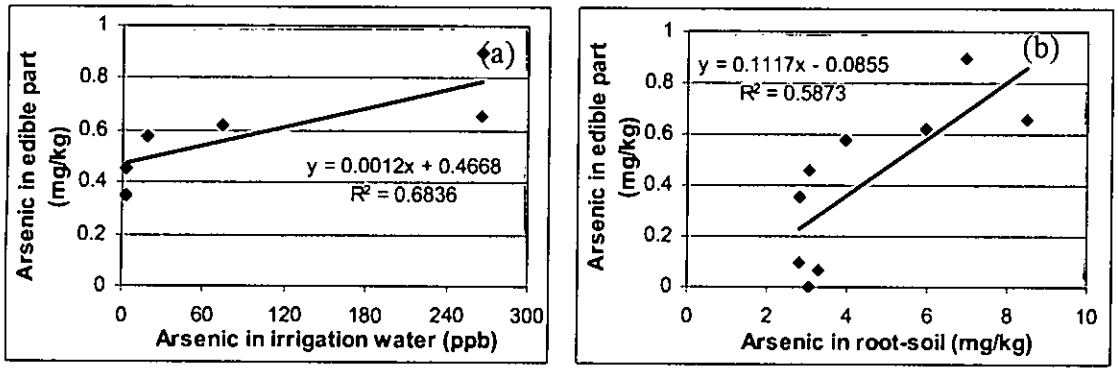


Figure 5.9: Relationship between arsenic in edible part of cauliflower with: (a) As in irrigation water, and (b) As in root soil

5.4 SUMMARY

In this study, effect of arsenic bearing irrigation water on accumulation of arsenic in vegetable field soil and in six common vegetables grown in Bangladesh has been assessed. Irrigation water, soil core samples and vegetable plant samples have been collected from three different areas of Bangladesh – Bogra, Narayanganj and Chandpur. Bogra has not been affected by arsenic contamination of groundwater and all irrigation water samples, both from surface and groundwater sources, collected from Bogra contained little arsenic (maximum concentration was 8.3 μg/l). Arsenic concentrations of irrigation water from the arsenic affected areas of Chandpur and Narayanganj have been found to be significantly higher when they came from groundwater source (63 to 267 μg/l); whereas arsenic contents of irrigation water from ponds and canals have been much lower (less than 1 to 25.3 μg/l).

In general arsenic content of top soil layer of vegetable fields has been found to increase with increasing concentration of arsenic in the irrigation water. The highest arsenic content (7.6 mg/kg) in top 75 mm segment of soil was recorded for a cauliflower field in Narayanganj, where arsenic content of irrigation water was also the highest (267 ppb) among all the water samples collected. Good correlation was observed between arsenic

concentration in irrigation water and arsenic contents of root-soil and the top 75-mm segment of soil.

In general, for all six types of vegetable samples, arsenic accumulation in the root was higher compared to other parts of the vegetable plants. Arsenic accumulation in the edible parts of these commonly grown vegetables is of particular concern. In this study, it has been found that accumulation of arsenic in the edible parts of all six types of the same vegetables are much lower for samples collected from Bogra, where irrigation water contained little arsenic. Whereas, accumulation was found to be much higher in edible parts of the same vegetables collected from the arsenic affected areas of Chandpur and Narayanganj, especially where irrigation was carried out with groundwater having high arsenic. Arsenic concentration in edible parts of these vegetable have been found to be relatively strongly correlated with arsenic content in irrigation water and arsenic content in root-soil.

Thus, it appears that high arsenic concentration in irrigation water is causing an increase in the arsenic contents of different parts, including the edible part, of commonly grown vegetables. For example, average arsenic concentrations of all six vegetables grown in Narayanganj with groundwater and surface water irrigation are 1.157 mg/kg and 0.66 mg/kg, respectively; whereas the corresponding value of vegetables grown in Bogra is 0.28 mg/kg. Considering vegetable consumption of 130 g/person/day (Alam et al., 2003; Hasan and Ahmed, 2000) and using the average arsenic concentration of all six vegetables, this corresponds to an estimated daily intake of about 150 μg of arsenic for vegetables grown with arsenic bearing groundwater in Narayanganj. In comparison, the estimated arsenic intake is about one-half (86 μg) for vegetables grown with surface water irrigation in Narayanganj and about one-fourth (36 μg) for vegetables grown in Bogra. Thus, it appears that intake from vegetables could constitute an important part of the overall arsenic intake for population living in the arsenic affected areas. On the other hand, for unaffected areas like Bogra, arsenic intake from vegetables, though small, appears to be much higher than that from drinking water (e.g., 4 μg, if As in water is 1 μg/l and daily consumption is 4 liter).

It should be noted that the quantities of organic and in organic arsenic in vegetable should always be quantified, since the form of arsenic affects its bioavailability and thus its toxicity to humans. Unlike water, where arsenic exists in the more toxic inorganic form, vegetable can contain either organic or inorganic arsenic. An EPA study found the percentage of inorganic arsenic in vegetable to be only 5% (EPA, 1988); a study conducted in West Bengal also found the percentage of inorganic arsenic in vegetable to be about 5% (Roychowdhury et al., 2003). Thus, vegetables would account for a very small fraction of overall inorganic arsenic exposure through food chain.

It also should be noted however that during field visits, it was observed that groundwater irrigation is not widely used for growing vegetables in the study areas; pond or canal waters were found to be more widely used for irrigating vegetable fields. Hence care should be taken in estimating possible arsenic intake from vegetables.

Among the six vegetables studied, relatively higher levels of arsenic (approaching or exceeding 1 mg/kg, the Australian food standard) were found in the edible parts of potato, tomato, data *shak*, and lal *shak*. If arsenic levels in vegetables grown in Bogra are taken as background levels, then potato and cauliflower appear to have the least background levels of arsenic (0.03 and 0.045 mg/kg, respectively) among the six vegetables studied. Data *shak* was found to have the highest background level (0.60 mg/kg). However, from the results of this study, it appears that potato and cauliflower have significantly higher tendency to accumulate arsenic (in edible part). For example, compared to the background (i.e., Bogra) level, arsenic concentration in edible parts of potato and cauliflower grown with arsenic bearing groundwater in Narayanganj were higher by a factor of 38 and 17, respectively. More studies are needed to assess the relative tendency of different vegetables to accumulate arsenic and to evaluate possible impact of arsenic bearing irrigation water on yield of vegetables.

Chapter 6

Mobilization of Arsenic from Agricultural Soil due to Adsorption-Desorption and Reductive Dissolution

6.1 INTRODUCTION

Understanding the fate of arsenic extracted through tube well water in soil-water-plant environment is vital for assessing its impacts on the food chain and the environment in general. The arsenic pumped with tubewell water can go through the following processes: (i) undergo adsorption and Co-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 retained on soils may undergo desorption/ dissolution and partition back into aqueous phase (i.e., stagnant water/ flood water/ rainwater) and subsequently transported away from the site with runoff or percolating water.

Adsorption-desorption of arsenic onto soil are key to the understanding its fate in the environment. 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, aluminium 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., Ullah, 1998; Huq et al., 2001; Meharg and Rahman, 2003; Ali et al., 2003b; Masud, 2003; Ahmed, 2005; Jahiruddin et al., 2005) have reported relatively higher levels of arsenic in paddy field soils irrigated with arsenic bearing groundwater. Results presented in Chapters 3 and 4 show that arsenic concentration in paddy field soils irrigated with high arsenic bearing groundwater varies significantly with time. In general, average arsenic levels in the top 0-150 mm soil layer of paddy fields increases 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 level in the top soil layer decreases significantly and come down to levels comparable to those found at the beginning of the irrigation season.

In this study, adsorption-desorption characteristics of arsenite, the principal form of As in groundwater, on agricultural soil has been assessed in batch experiments carried out with paddy field soil from three arsenic-affected areas and one unaffected area. Effect of soil composition and phosphate content of water on arsenic adsorption has also been assessed. Possible mobilization of arsenic from As-rich soil in paddy fields under reducing environment has also been assessed in batch experiments. This Chapter presents results of these laboratory investigations.

6.2 PREVIOUS STUDIES

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. However, limited information is available in the literature on adsorption characteristics of arsenite, As(III) (the principal chemical form of arsenic in groundwater) on agricultural soil. There appears a lack of information on desorption kinetics of arsenic from agricultural soil. Soil and water quality parameters affecting adsorption-desorption characteristics are also not clearly understood. Desorption of arsenic is known to be promoted in the presence of competing anions such as phosphate. Groundwater in many areas of the country also contains high concentration of phosphate, which could compete with arsenic for adsorption on soil. Phosphate may also come to paddy field soil from the addition of phosphate fertilizer. It is therefore important to assess the effect of phosphate on arsenic adsorption-desorption of arsenic on paddy field soil.

Available information on adsorption-desorption of arsenic are mostly concentrated on adsorption of arsenate [As(V)] and effect of phosphate on arsenate adsorption-desorption. 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 (Fordham and Norrish, 1974, 1983; Huang, 1975; Livesey and Huang, 1981; Pierce and Moore, 1982). Arsenate can also sorb 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). 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). 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 (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).

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). Sakata (1987) reports distribution coefficients (K_d) for arsenite for 15 subsurface soils from different sites in Japan with K_d values ranging from 75 to 1200. The distribution coefficient was significantly correlated with the extractable iron content of the soils.

Arsenate is not easily desorbed 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% 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_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-}. Phosphate-

released As was not significantly resorbed in the presence of added PO_4^{3-} (Amacher and Amacher, 1994; Peryea, 1991).

The ability of PO_4^{3-} to compete with arsenate for goethite surface sites was somewhat expected since PO_4^{3-}, 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). Phosphate is considered an analog of arsenate (they have similar chemical properties and behaviors). They are both oxyanions in aqueous solution with three similar acid dissociation constants. 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.

Phosphate substantially suppresses arsenate adsorption by soil, with the extent of the suppression varying from soil to soil (Livesey and Huang, 1981). Roy et al. (1986) found that the adsorption of arsenate was significantly reduced by competitive interactions with PO_4^{3-} in three different soil types (clay, silt loam and ultisol). 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. Approximately 40% 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. 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) (Hayakawa and Watanabe, 1982).

The amount of As 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 As sorption capacity of the soil (Dickens and Hiltbold, 1967; Jacobs et al., 1970a; Galba, 1972; Wauchope, 1975; Livesey and Huang, 1981). Barry et al. (1995) examined the adsorption characteristics of a forest soil profile. The greatest sorption capacity for As 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 aluminium. 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.

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). Carey et al. (1996) 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.

Richardson et al. (1978) 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% of the amount applied would be 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.

6.3 METHODOLOGY

6.3.1 Site Selection and Collection of Agricultural Soil Sample

For assessing arsenic adsorption-desorption characteristics, paddy field soil were collected from four different areas of the country. These included three arsenic affected areas – Srinagar-Munshiganj, Vanga-Faridpur and Nabinagar-Brahmanbaria; and one unaffected area – Nazipur-Naogaon. The paddy field site at Munshiganj is the same as the one used for intensive monitoring during 2004 (described in Chapter 4). The paddy field sites at Faridpur, Brahmanbaria and Naogaon are the same as the "Field 2" sites in these respective areas (described in Chapter 3) that were used for monitoring of soil and paddy arsenic levels.

Soil samples from the Faridpur, Brahmanbaria, and Naogaon field sites were collected during May-June 2003; soil samples from the Munshiganj site was collected in May 2004. Soil samples were collected by inserting into the soil, 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 and transported to the laboratory.

6.3.2 Laboratory analysis

6.3.2.1 Initial Arsenic and Iron Contents of Agricultural Soil

Initial total (aqua-regia extractable) and oxalate-extractable arsenic and iron contents of the agricultural soil samples were determined following the same procedure described in Chapter 3. For this purpose, soils of the top 0-75mm layer of the soil cores were used. Oxalate-extractable iron gives an estimate of the quantity of amorphous iron oxy-hydroxide contents of soil, which is often thought to be the principal adsorbent in the soil matrix. Oxalate-extractable arsenic is expected to provide an estimate of the quantity of arsenic associated with the amorphous iron oxy-hydroxides.

6.3.2.2 Analysis of Water and Soil Samples

Arsenic concentration of water and soil samples (after appropriate digestion) was determined using an atomic absorption spectrophotometer (Shimadzu, AA6800) attached with a graphite furnace (GF). Iron concentration of water and soil samples (after

digestion) was measured with flame emission atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800), pH, ammonia, nitrate, and phosphate concentrations were measured following methods described in section 1.3.

6.3.3 Batch Adsorption-Desorption Experiments

6.3.3.1 Adsorption of As and PO_4

Adsorption characteristics of arsenic and phosphate on agricultural soil were assessed in batch experiments carried out in 15 ml centrifuge tubes. Adsorption characteristics of agricultural soil samples collected from the four different areas of the country were evaluated by equilibrating known mass of soil sample with aqueous solution containing varying arsenic (250 to 17000 μg/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.

6.3.3.2 Effect of Phosphate on Adsorption of Arsenic

Effect of phosphate concentration on adsorption of arsenic on paddy field soils from the four areas was evaluated 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.

6.3.3.3 Desorption of Arsenic from Soil

Desorption characteristics were evaluated using the soil samples remaining in the centrifuge tubes after completion of the batch adsorption experiments described above (in Section 6.2.3.2). After completion of the batch adsorption experiments (where As concentration was varied from 150 to 2500 μg/l, and phosphate from 2 to 6 mg/l), the supernatant liquid in each centrifuge tube was decanted. Then 12.5 ml of arsenic free (As < 1μg/l) groundwater was added to each centrifuge tube. Then the centrifuge tubes were equilibrated for 24 hours in 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 24-hour equilibration periods.

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

Mobilization of arsenic from paddy field soils was evaluated using the soil samples collected from the paddy field sites at the end of the irrigation season. Mobilization of arsenic from arsenic-rich natural paddy field soil 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 aqueous solutions (12.5 ml) containing different concentrations of organic matter (added in the form of glucose) were added. The carbon source (glucose) was added in order to induce reducing condition on the centrifuge tubes for simulating a situation where a paddy field is inundated with flood/rain water rich in organic content. The tubes were equilibrated for different time periods (24 hours and 7 days) in end-over-end rotators, following which the tubes were centrifuged and arsenic of the supernatant liquid were determined. The data were then used to assess mobilization of arsenic from agricultural soil under reducing condition. For one set of experiment with Munshiganj soil, external organic matter content was fixed at 0, 10, 15, 20 and 25 mg/l of carbon (added in the form of glucose).

For subsequent batch experiments using paddy soil from all four areas, higher concentration of external 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 $NaH_2PO_4.2H_2O$.

6.3.4 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, the hydrometer is used. Hydrometer analysis was carried out for soil samples collected from all four sampling areas. Combined curve for soil of different areas are shown in Appendix D. 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.

6.4 RESULTS AND DISCUSSION

6.4.1 General Characteristics of Soil and Water used in Experiments

In this study, arsenic adsorption-desorption characteristics on paddy field soil from four different areas of the country were assessed. Table 6.1 shows composition of soil from the four sampling areas, 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 contents of irrigation water used for irrigating the paddy fields from which the soil samples were collected are also shown in Table 6.1.

Table 6.1 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 (15.8%), Naogaon (10.4%), and Munshiganj (8.0%).

Data presented in Table 6.1 suggest that composition of irrigation water strongly influences the chemical composition of top soil of paddy field. Arsenic and iron contents of top soils appear to be strongly correlated to the arsenic and iron 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.

Table 6.1: 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 = 69.4% Clay = 23.2%	Sand = 6.6% Silt = 77.6% Clay = 15.8%	Sand = 19.10% Silt = 70.5% Clay = 10.4%
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

Concentrations of selected chemical constituents of water used in batch adsorption-desorption experiments in this study are shown in Table 6.2. 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 6.2: 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

6.4.2 Adsorption of Arsenic and PO_4 on Paddy Field Soil

6.4.2.1 Adsorption of As on Paddy Field Soil

Figure 6.1 shows adsorption isotherm of arsenic on paddy field soils from four different areas of the country. Figure 6.1 shows a plot of initial concentration of arsenic (µg/l) in water vs. quantity of As partitioned to soil (expressed as mg/kg, dry weight basis).

Available data on arsenic adsorption suggest that As adsorption on iron oxyhydroxides is relatively rapid, with majority of adsorption taking place within 24 hours. For example, results of the As (V) sorption kinetics on goethite at pH 6 (Fuller et al., 1993) showed that initial arsenate sorption was very rapid, with over 93% sorbed within a 24-h period. After one year, almost 100% of the added As (V) sorbed to the goethite. These results were similar to those obtained by Fuller et al. (1993) who also observed a period of rapid As(V) uptake followed by continual adsorption, and McGeehan et al. (1992) who saw rapid initial adsorption followed by a plateau phase.

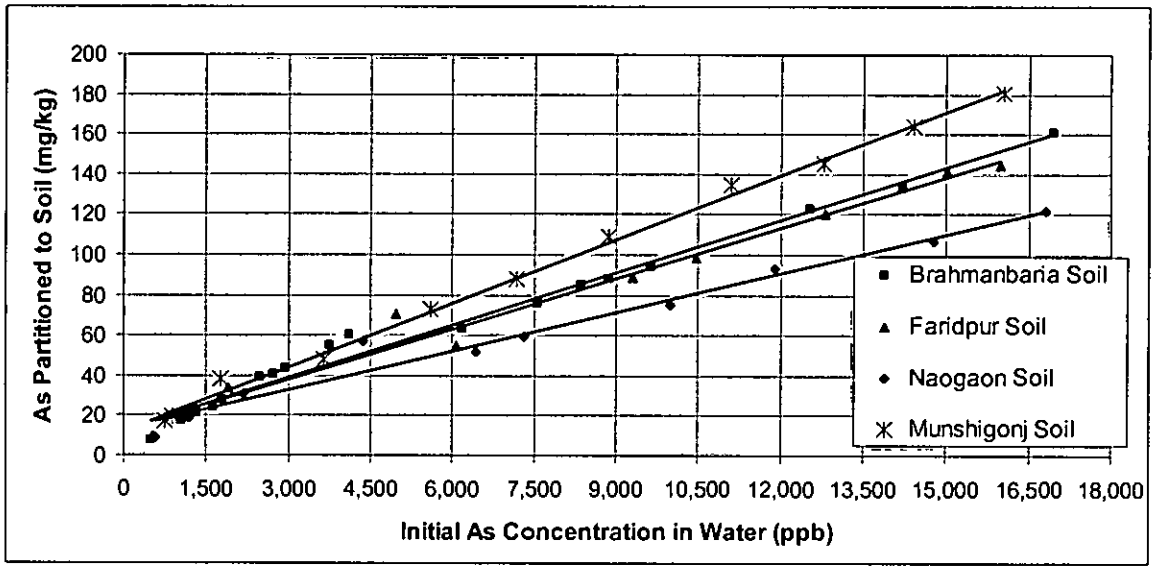


Figure 6.1: Arsenic partitioning to paddy field soil in batch adsorption experiments as a function of initial As concentration in water

Figure 6.1 shows that in all cases arsenic partitioning to soil increases with increasing concentration of arsenic in water in contact with the soil. Figure 6.1 shows that for any initial arsenic concentration (up to 17000 μg/l), partitioning of As to soil was highest for Munshiganj soil and least for the Naogaon soil. Brahmanbaria and Faridpur paddy field soil lie in between. A closer look at the data presented in Table 6.1 shows that As partitioning to soil is strongly correlated to both the total and oxalate extractable iron contents of soil. 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. As shown in Fig. 6.2, calculated distribution coefficients (slope of adsorption curves in Fig. 6.1) correlate very well with oxalate extractable iron contents of soils. Initial concentration of As of soil did not appear to have any influence on limiting adsorption of arsenic onto soil. Other soil parameters, including composition of soil, do not appear to have any major influence on As partitioning to soil.

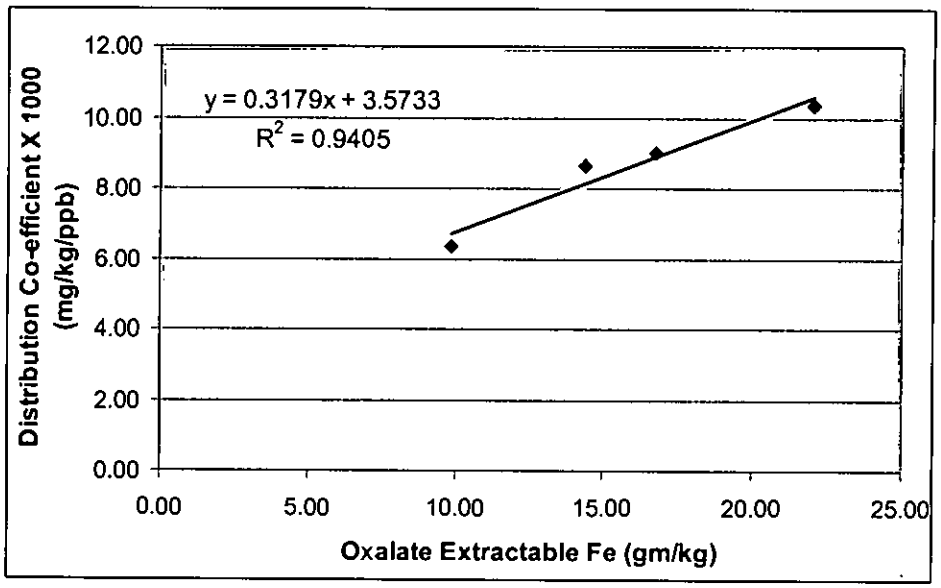


Figure 6.2: Correlation between calculated distribution coefficient for As adsorption and oxalate-extractable iron in paddy field soil

Metal oxyhydroxides, primarily of Fe and Al, are the principal adsorbents in natural soil. The increasing partitioning of As to soil with increasing soil iron content probably 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 portioning of arsenite has been observed in the batch experiments

conducted in this study. Figure 6.1 shows very high 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 supports such high adsorption densities of arsenic on paddy field soils. Thus, very high adsorption densities are achieved even under field conditions where As concentration in irrigation water are much lower compared to those employed in the batch experiments.

If oxalate extractable iron is considered to be the principal contributor of adsorption sites, then its concentration in soil varies from 0.1766 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 quoted 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 calculated 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.

6.4.2.2 Adsorption of PO_4 on Agricultural Soil

Figure 6.3 shows adsorption isotherm of phosphate on paddy field soils from Brahmanbaria, Faridpur, and Naogoan. It shows that in all cases phosphate partitioning to soil increases with increasing concentration of phosphate in water. Among the three soils, phosphate partitioning is highest for Brahmanbaria soil and least for Naogaon soil. Similar to the case for arsenic, it could be easily seen that phosphate partitioning to 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.

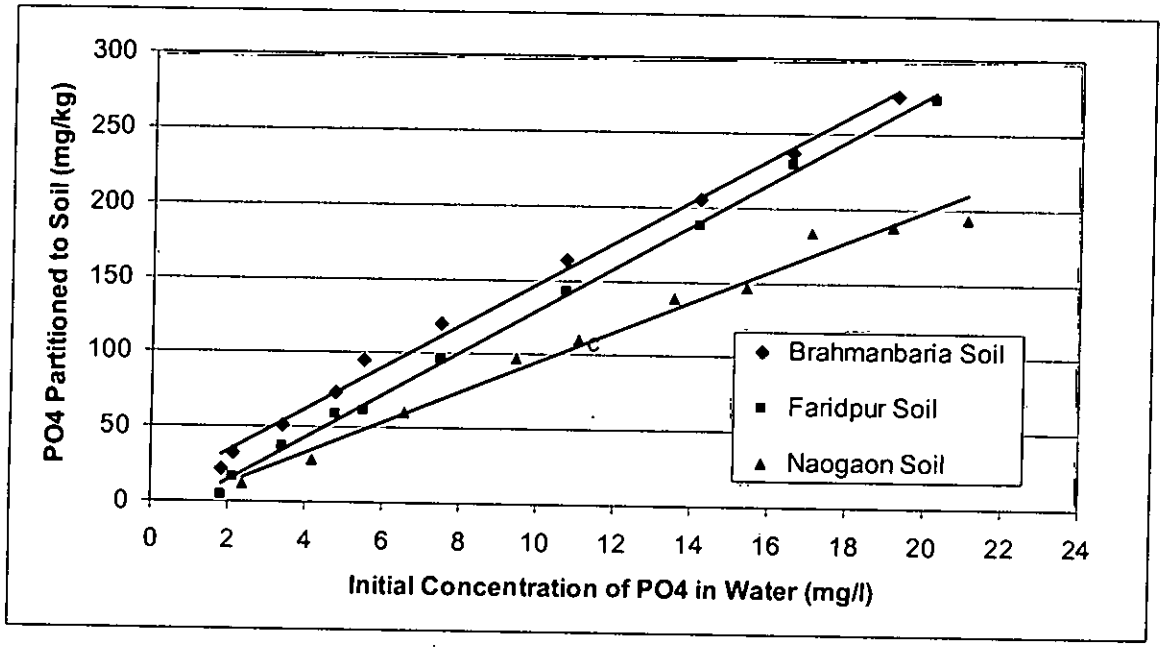


Figure 6.3: Phosphate partitioning to paddy field soil in batch adsorption experiments as a function of initial phosphate concentration in water

6.4.3 Effect of Phosphate on Arsenic Adsorption

Figures 6.4a-d show arsenic partitioning to 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 raw groundwater used in this study) to 6 mg/l. 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 most likely due to occupation of adsorption sites by phosphate, which is known to have stronger affinity for iron oxyhydroxides compared to arsenite. Since available adsorption surface sites appear to be 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. Such condition, i.e., very high concentration of phosphate, also exists in actual paddy field sites. 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).

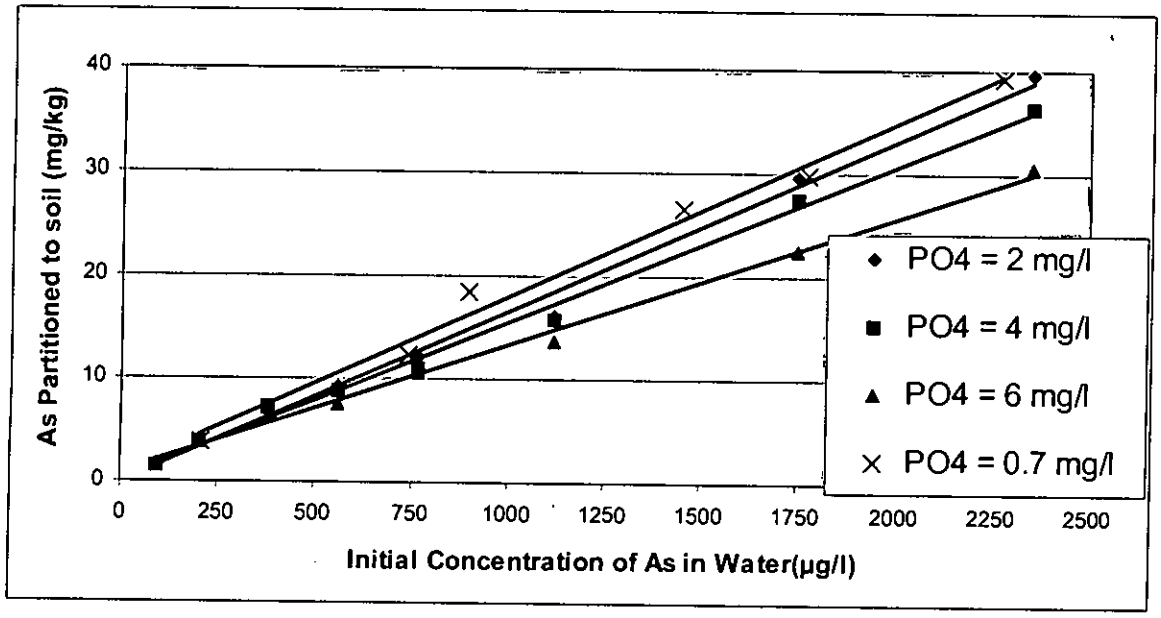


Figure 6.4a: Partitioning of As to paddy field soil from Munshiganj in the presence of phosphate

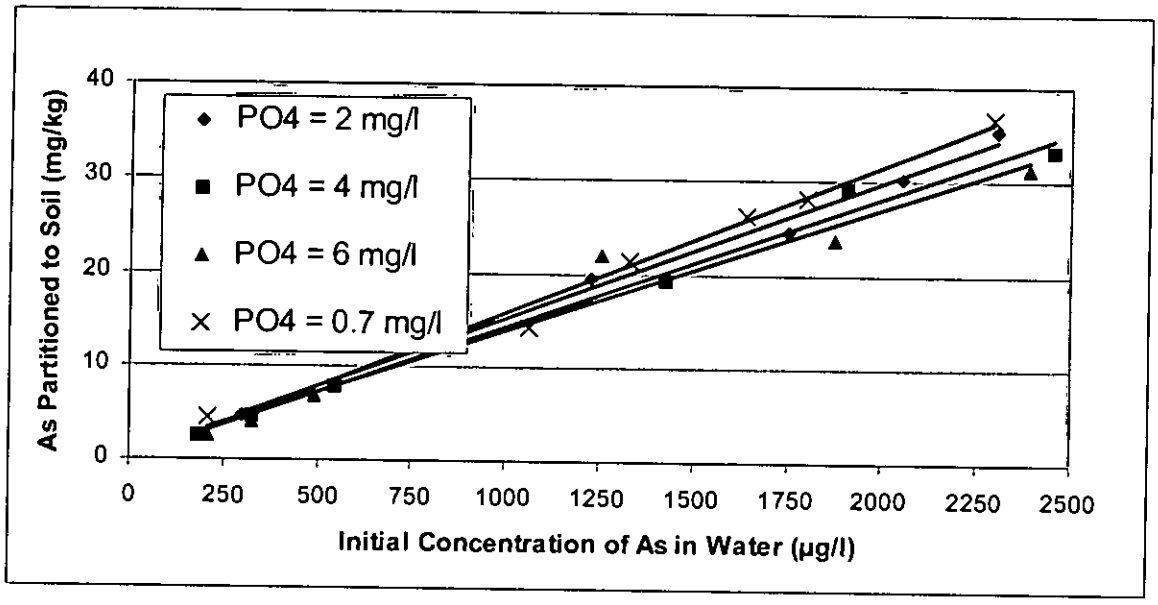


Figure 6.4b: Partitioning of As to paddy field soil from Brahmanbaria in the presence of phosphate

In order to induce stronger effect 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 over a wider range – from 2 to 42 mg/l, and As (arsenite) concentration was fixed at 1000 µg/l.

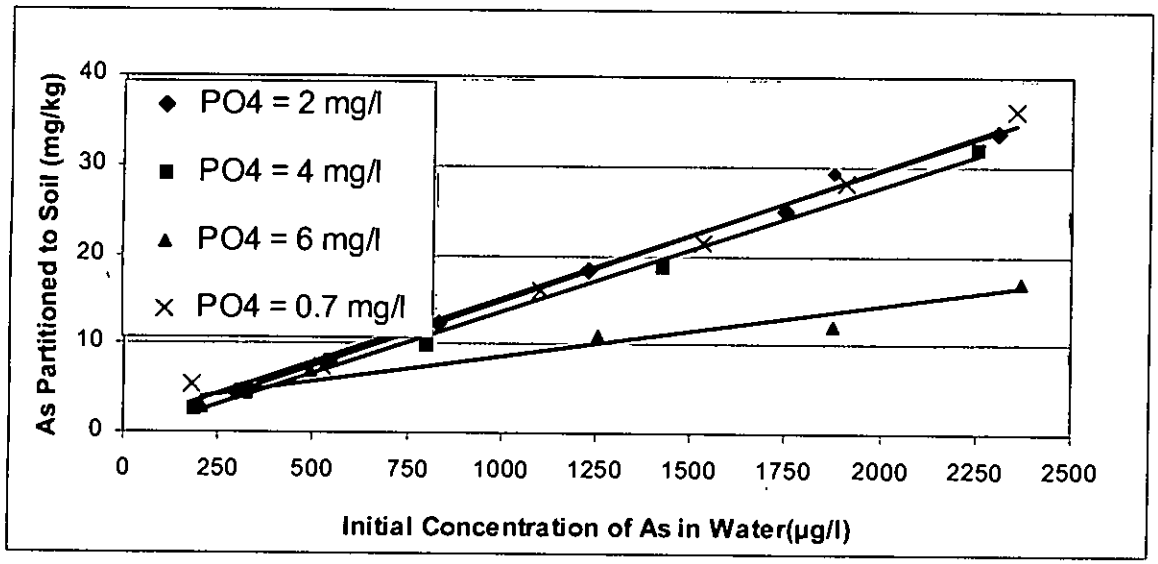


Figure 6.4c: Partitioning of As to paddy field soil from Faridpur in the presence of phosphate

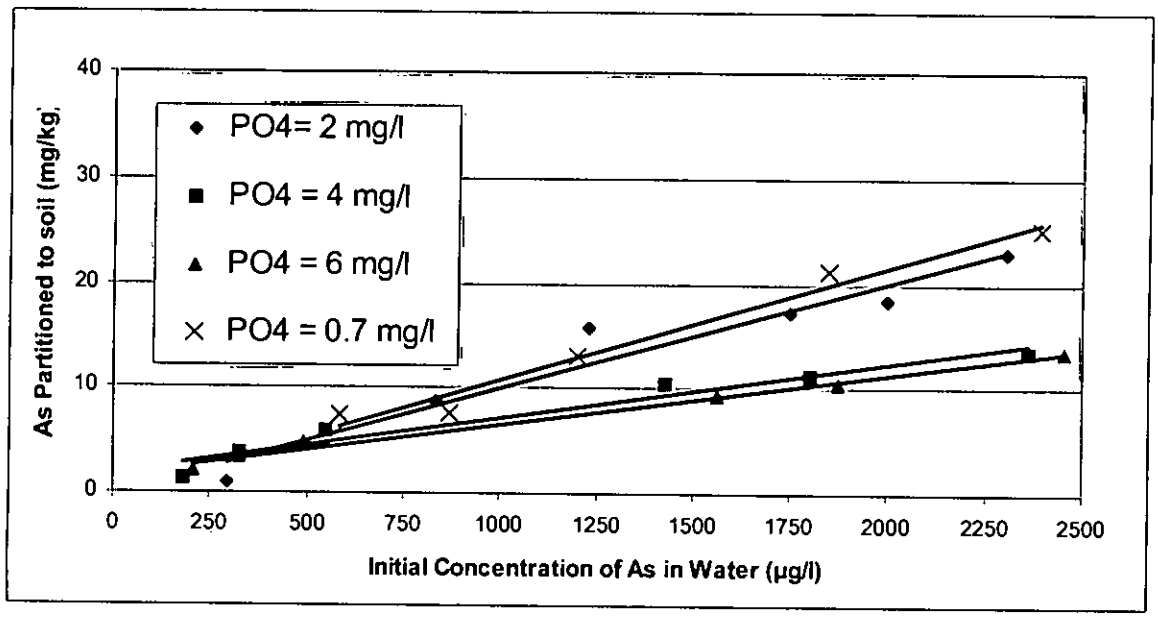


Figure 6.4d: Partitioning of As to paddy field soil from Naogaon in the presence of phosphate

The results of these experiments are plotted in Fig. 6.5, where partitioning of As to soil as a function of initial phosphate concentration in water. Figure 6.5 shows that high concentration of phosphate could significantly reduce partitioning of As to soil. For example, for Naogaon soil, As partitioning came down from about 8 mg/kg to around 3 mg/kg as phosphate concentration in water increased from 2 to 42 mg/l.

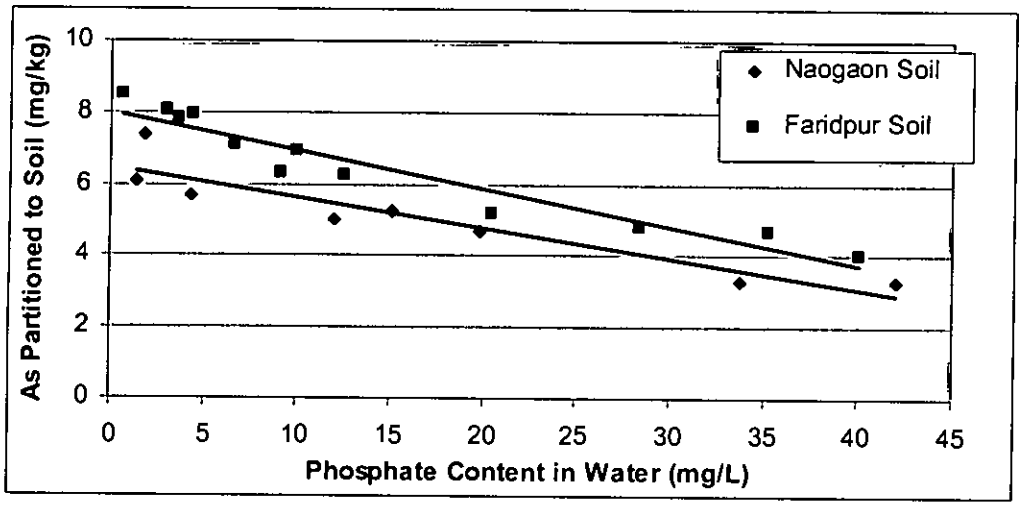


Figure 6.5: Partitioning of As to paddy field soil from Faridpur and Naogaon in the presence of phosphate

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 as expected. 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. Roy et al. (1986) used the Steindorf-Rebhun-Sheintuch equation to model adsorption of binary-solute concentrations and concluded that arsenate replacement by phosphate was more probable than the reverse. Research has demonstrated that As adsorption to mineral surfaces may be reduced in the presence of oxyanions such as PO_4^{3-}, SO_4^{2-}, and MoO_2 (Manning and Goldberg, 1996). The presence of specifically sorbed ligand ions such as phosphate have been reported to suppress the sorption of As. Darland and Inskeep (1997) conducted transport studies using free iron oxides in a sand column and found that PO_4^{3-} effectively competes with arsenate. Additionally, Barrow (1992) also concluded that PO_4^{3-} becomes more competitive over time since it is capable of slow sorption.

6.4.4 Desorption of Arsenic from Soil

Desorption characteristics were assessed in batch experiments carried out with soil samples which were earlier used to assess effect of phosphate on arsenic adsorption (results described in Section 6.3.3). In these experiments, arsenic concentration was varied from 150 to 2500 μg/l, and for each initial arsenic concentration phosphate concentration was fixed at 2 mg/l, 4 mg/l, and 6 mg/l. Thus, for the desorption experiments, initial total As contents of the soils used was calculated as the sum of initial As content of original soils (as listed in Table 6.1) and the amount of As partitioned to soil during adsorption experiment.

Figures 6.6a-d show results of desorption experiments for Munshiganj, Brahmanbaria, Faridpur and Naogaon soils, respectively. Here quantity of desorbed has been expressed as mg/kg of soil (dry wt. basis) and plotted against initial total As content of soil. The major observations from Figs. 6.6a-d are as follows: (i) Quantity of As desorbed from soil (to As-free water in contact with the soil) is relatively small compared to the initial concentration of As in soil; (ii) Quantity desorbed is more or less proportional to the initial As concentration in soil; (iii) For any particular initial soil As-concentration, desorption of arsenic is higher from soils with higher phosphate content.

Figure 6.6 shows that the highest desorption (~2-6 mg/kg) were obtained for the Munshiganj soil, which had initial total arsenic content of ~70 mg/kg. 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. Thus it appears that As adsorbed to paddy field soil does not desorb readily to water within the 24 hour equilibration used in this study. However, since desorption kinetics are usually slow (as reported for arsenate by McGeehan et al.,1992; Fuller et al., 1993; and McBride, 1994), more arsenic is likely to come off from soils under longer equilibration times.

The soils that went through adsorption experiments with higher phosphate concentrations (e.g., 6 mg/l) (and subsequently used for desorption experiments) obviously had higher phosphate contents. Figure 6.6 shows that for a particular initial soil As content, more As is desorbed from soils with higher initial phosphate content. This 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.

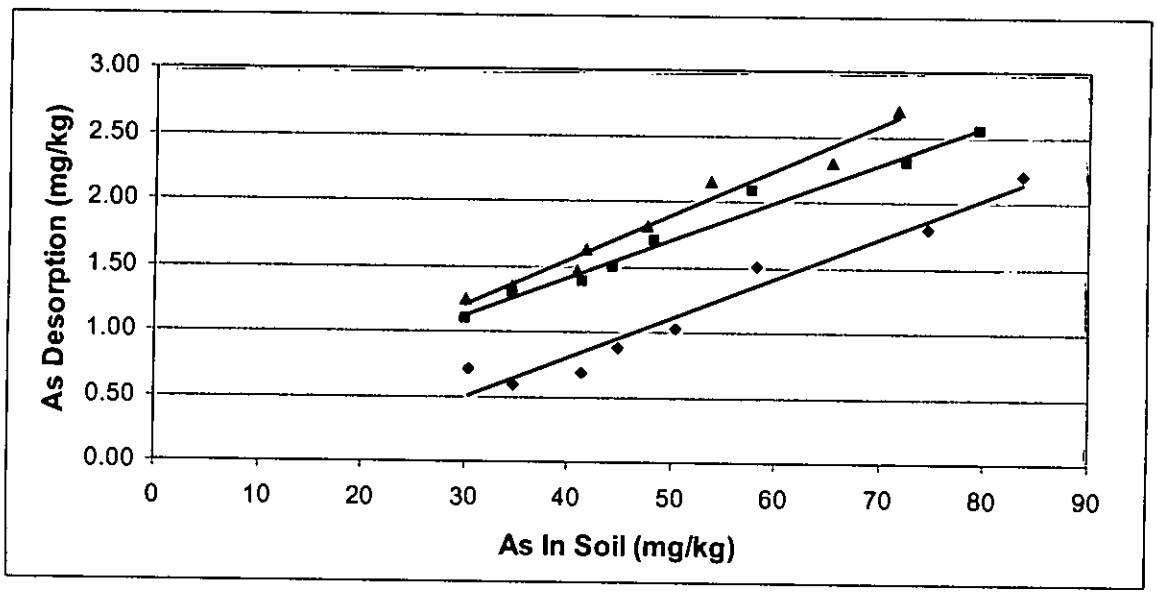


Figure 6.6a: Arsenic desorption from Munshiganj soil [soils undergoing As adsorption with 2 mg/l phosphate (♦), 4 mg/l phosphate (■), and 6 mg/l phosphate (▲)]

The experiments carried out in this study are similar to that was conducted by McGeehan et al. (1992), Fuller et al. (1993), and McBride (1994). Desorption (in the presence of phosphate) studies were conducted on goethite samples, which were reacted with arsenate for times ranging from 45 min to 7 months. In desorption experiments, it was found that initially desorption was very fast, with >35% being desorbed within 24 h. After the initial rapid desorption, the release slowed down.

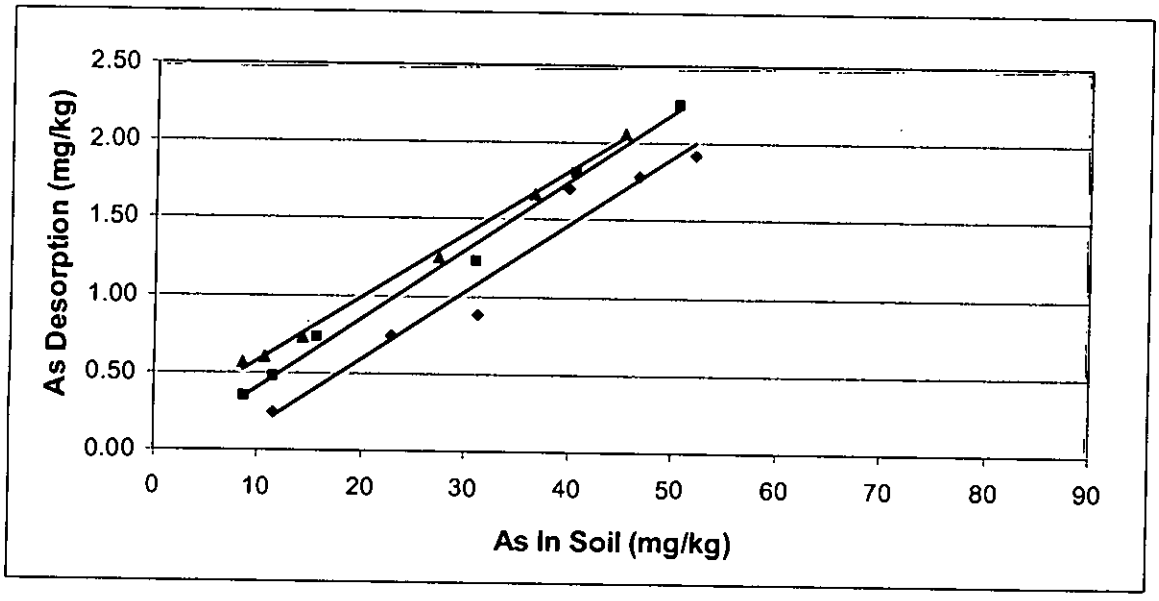


Figure 6.6b: Arsenic desorption from Brahmanbaria soil [soils undergoing As adsorption with 2 mg/l phosphate (♦), 4 mg/l phosphate (■), and 6 mg/l phosphate (▲)]

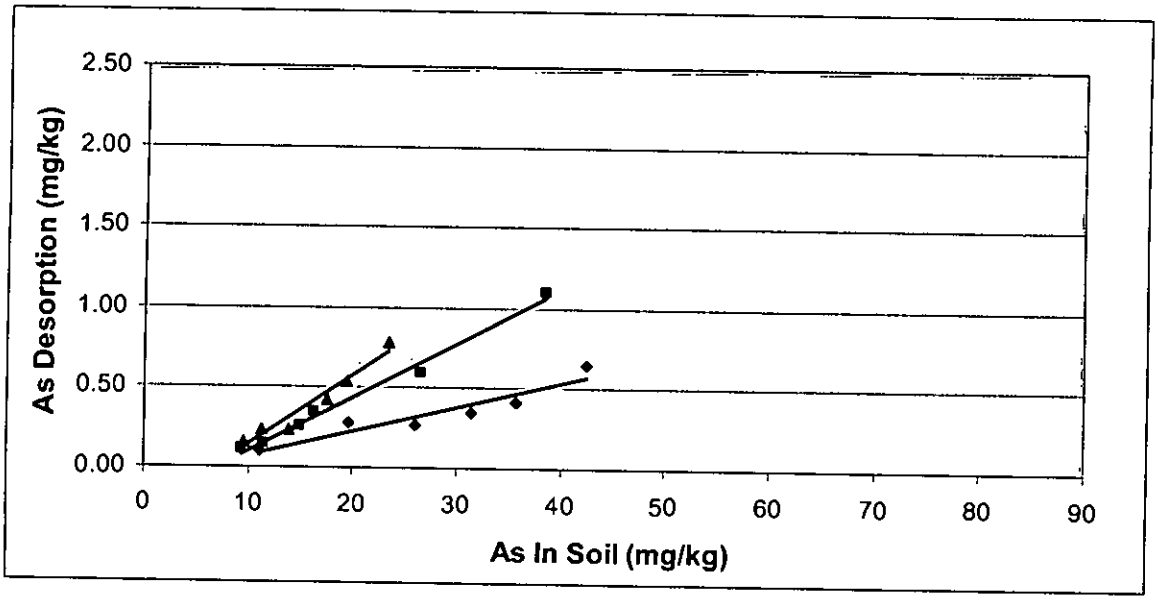


Figure 6.6c: Arsenic desorption from Faridpur soil [soils undergoing As adsorption with 2 mg/l phosphate (♦), 4 mg/l phosphate (■), and 6 mg/l phosphate (▲)]

Total desorption increased with time reaching about 65% total desorption after 5 month. These results showed that a significant amount of arsenate was still retained on the goethite after 5 month of desorption even though the PO_4^{3-} desorptive solution was three times more concentrated than the initial arsenate sorptive solution.

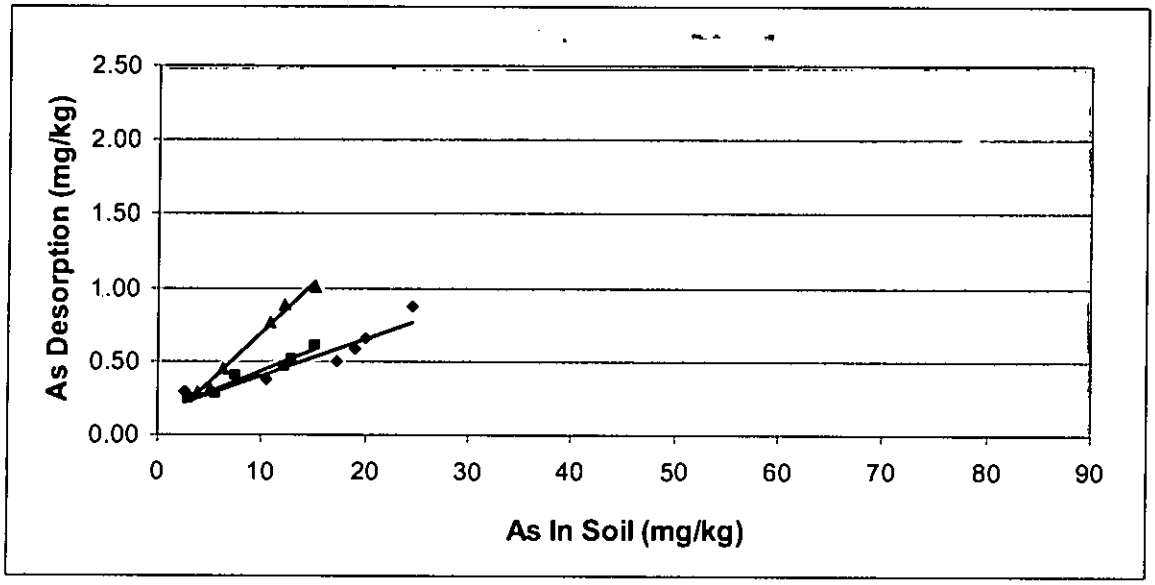


Figure 6.6d: Arsenic desorption from Naogaon soil [soils undergoing As adsorption with 2 mg/l phosphate (♦), 4 mg/l phosphate (■), and 6 mg/l phosphate (▲)]

Desorption kinetics in the presence of PO_4^{3-} at pH 4 also showed initial arsenate desorption to be rapid with about 45% desorbed within the first 24 h. Desorption then leveled off and the total percentage arsenate desorbed at pH 4 after one month was 53%. Similar to the pH 6 desorption data, there was no effect of sorption residence time on arsenate desorption at pH 4. These results indicate that desorption is much slower than sorption, which is expected for a ligand-exchange reaction (McBride, 1994).

6.4.5 Mobilization of Arsenic from Soil under Reducing Condition

Results presented in Chapters 3 and 4 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. Mobilization of arsenic from paddy field soil under reducing condition was evaluated using fresh soil samples collected from the paddy fields of the four study areas at the end of the irrigation season.

The first set of experiment was carried out with soil from the Munshiganj paddy field. Mobilization under reducing condition was evaluated in batch experiments where 1 gm of soil was equilibrated with water having varying 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 simulate presence of organic matter in inundation water under actual field condition. These carbon concentration ranges (10 to 25 mg/l) are similar to those reported for river, eutrophic lake and marsh (Thurman, 1985). Experiments conducted in the absence of organic carbon are likely to provide an estimate of As mobilized primarily due to desorption.

Figure 6.7a shows partitioning of As to water from Munshiganj paddy field soil for at the end of 24 hours and 7 days. It shows very little mobilization of As from natural soil within 24-hour equilibration period. Besides slower desorption kinetics, there could be other reasons for this lack of mobilization. First of all, a significant fraction of As in the paddy field soil is likely to exist as As(V), which adsorbs much more strongly to soil in comparison to As(III). Secondly, 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 (~ 2.5 mg/kg) occurred in the presence of 25-mg/l carbons. In the absence of the carbon source, about 1.5 mg/kg of As was mobilized from the soil at the end of 7-day period, which could be attributed to direct desorption of As from soil (assuming the natural soil had little or no organic matter content that could promote reductive dissolution of iron oxyhydroxides). Additional mobilization (i.e., in excess of 1.5 mg/kg) may be attributed to mobilization due to reductive dissolution of iron oxyhydroxides, which appears to increase with increasing concentration of carbon.

In order to assess possible 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 6.7b, 6.8a, 6.8b and 6.8c show mobilization of As from paddy field soils from Munshiganj, Brahmanbaria, Faridpur and Naogaon, respectively. As before (Fig. 6.7a), relatively little mobilization was recorded at the end of 24-hour inundation period. As explained earlier, this is not unexpected. However, relatively higher mobilization was recorded at the end of 7-day inundation period. Mobilization in excess of 4 mg/kg was recorded for the Munshiganj soil, which accounts for about 20% of oxalate-extractable As (18.58 mg/kg) initially present in the soil. Fig. 6.7b shows that about 2 mg/kg of this has been mobilized from the Munshiganj soil in the absence of the carbon source, which could be attributed to direct desorption of As from soil.

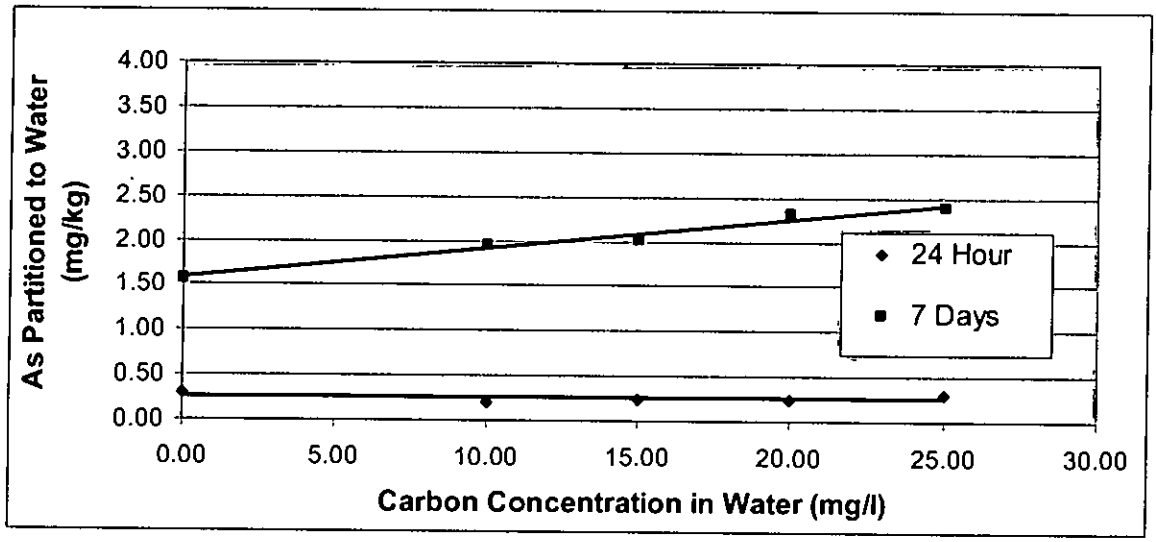


Figure 6.7a: Mobilization of As from Munshiganj paddy field soil in presence of organic carbon (glucose)

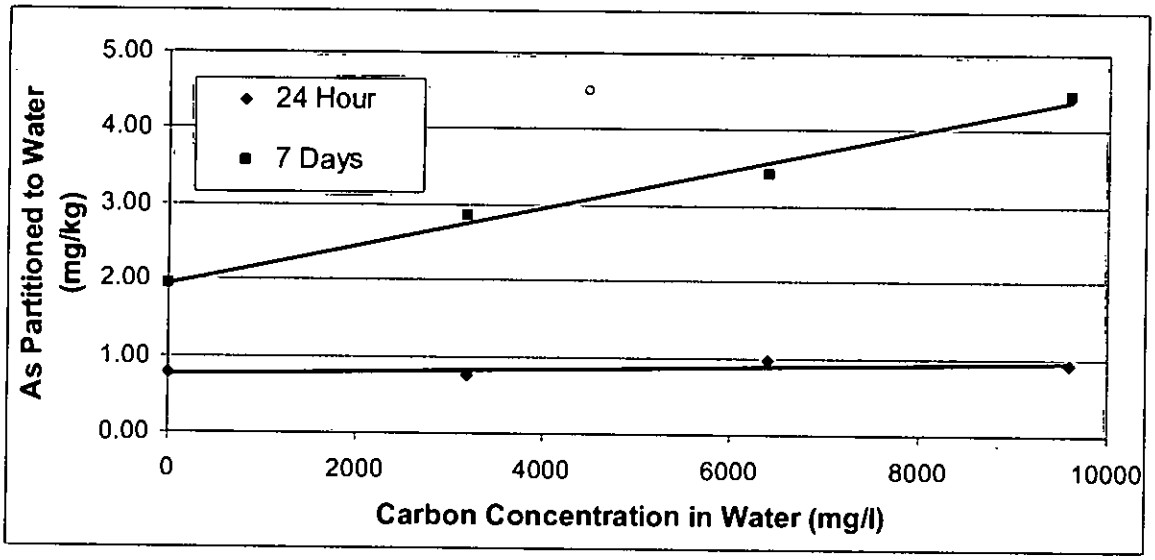


Figure 6.7b: Mobilization of As from Munshiganj paddy field soil in presence of organic carbon (glucose)

Maximum mobilization recorded for Brahmanbaria and Faridpur soils (Figs. 6.8a, b) are about 3 mg/kg, a significant part of which (~ 1 mg/kg) may be attributed to direct desorption from soil. Oxalate-extractable As in soils from these two areas were 3.85 mg/kg and 6.53 mg/kg, respectively. Thus, it appears that a significant fraction of the oxalate-extractable arsenic has been mobilized from these soils within the 7-day period. Despite significant variation in initial oxalate-extractable As contents (18.53 mg/kg for

Munshiganj and 3.85 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 for these soils (varying from about 3 mg/kg for Brahmanbaria to 4 mg/kg for Munshiganj).

Very little mobilization was recorded for the paddy field soil from Naogaon (Fig. 6.8c), which is an area unaffected by As contamination. This is probably due to the fact that Naogaon soil had the least oxalate-extractable As (1.68 mg/kg), and it is this fraction of As that is likely to be mobilized due to desorption and reductive dissolution. It should be noted that results presented in Chapter 3 also showed very little change in As content of paddy field soils in Naogaon, in agreement with the results of the batch experiments.

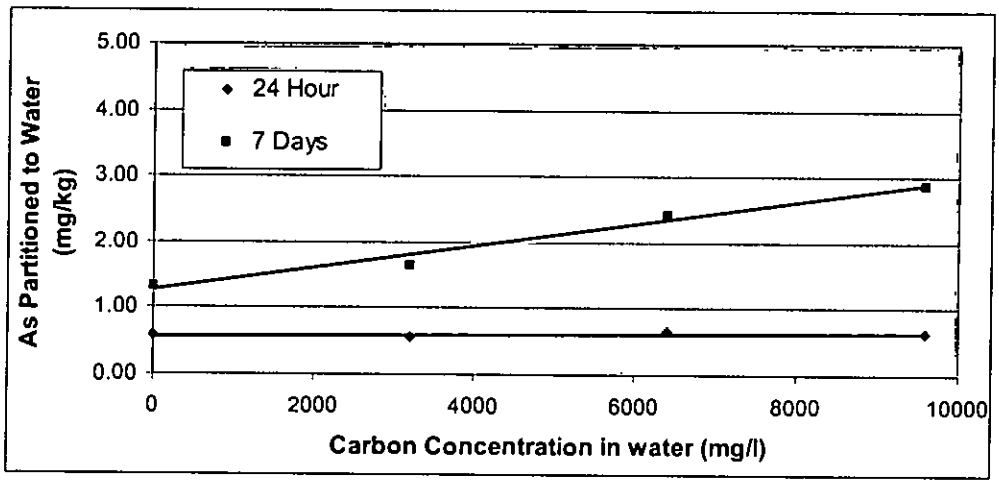


Figure 6.8a: Mobilization of As from Brahmanbaria paddy field soil in presence of organic carbon (glucose)

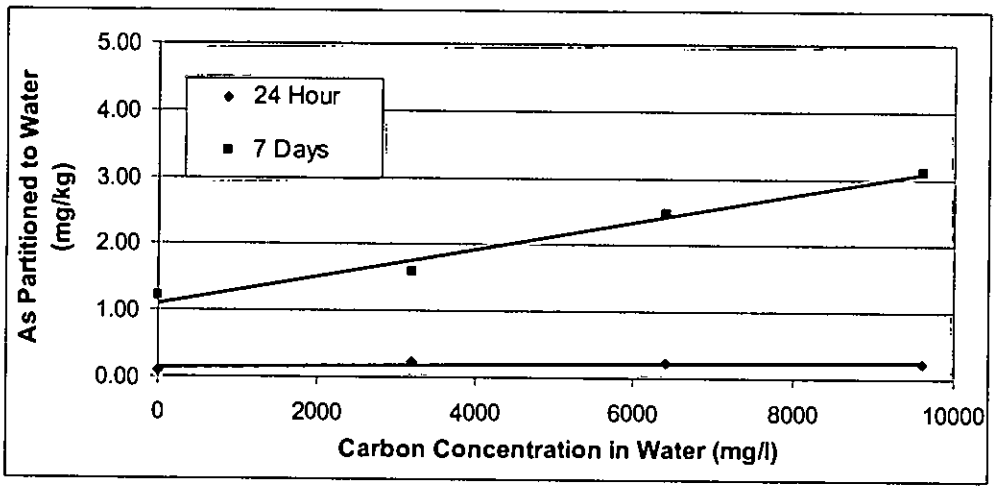


Figure 6.8b: Mobilization of As from Faridpur paddy field soil in presence of organic carbon (glucose)

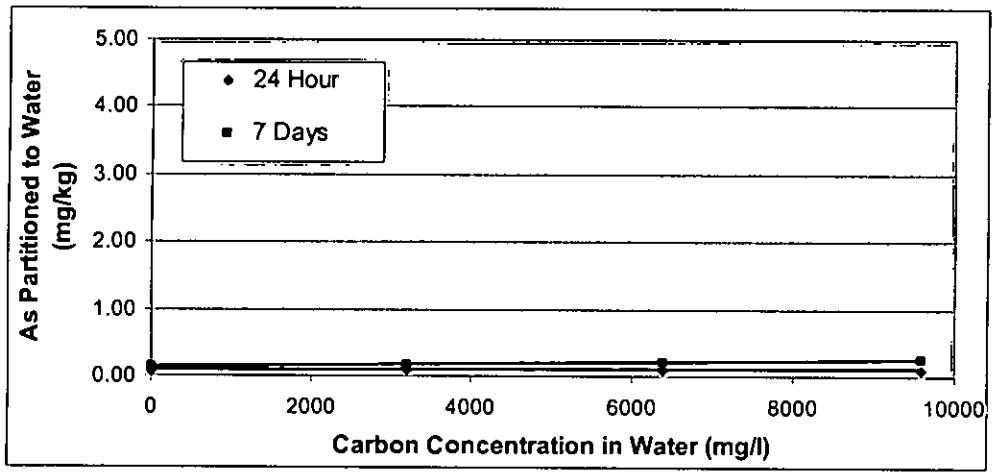


Figure 6.8c: Mobilization of As from Naogaon paddy field soil in presence of organic carbon (glucose)

Figures 6.7a and 6.7b, showing mobilization of As from Munshiganj soil, provide some insight into the effect of organic carbon concentration on the mobilization of As from soil. Figure 6.7a shows that As mobilization attributable 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 6.7b shows that As mobilization to increase from ~ 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.

6.5 SUMMARY

Results from this study shows that arsenite adsorption to paddy field soil is a strong function of oxalate-extractable 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, arsenite adsorption to paddy field soil depends, not only on the characteristics of soil, but also on the quality 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 recorded for paddy field soil. This indicates that paddy field

soil is capable of accumulating very high concentration of As. In fact, 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 quite alarming because adverse effects on growth of plants and yield of crops have been recorded at similar and lower soil arsenic levels. However, as noted in Chapters 3 and 4, As accumulation in agricultural soil is counteracted and limited by biogeochemical pathways leading to arsenic removal from soil.

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; but since the batch experiments were carried out with low sorbate to sorbent ratios, the effects were apparent only at very high concentrations of both As and phosphate.

Arsenic adsorbed onto paddy field soils desorbed into As-free water, but only to a limited extent, within the 24-hour equilibration period used in this study; desorption was found to be proportional to initial concentration of As in soil. Higher desorption was recorded for soils having higher phosphate contents. Though desorption of As appear to be insignificant in the laboratory batch experiments, under actual field condition where a paddy field may be inundated under a meter of water for about three months during the rainy season, arsenic release by desorption could be significant.

Significant mobilization of arsenic, beyond that achieved by desorption alone, was recorded for soil samples equilibrated with water containing organic carbon (glucose). This appears to be due to reductive dissolution of iron oxyhydroxides and consequent partitioning of adsorbed As to water. Such mobilization appears to be a strong function of time. Since paddy fields are inundated in flood/rain water for periods of up to three months, significant amount of soil arsenic could be mobilized during this time. Both desorption and reductive dissolution of iron oxyhydroxides appear to be important processes in governing fate of arsenic in irrigated paddy fields. These natural processes appear to be preventing arsenic concentration in soil to reach toxic levels.

Chapter 7

Conclusions and Recommendations

7.1 INTRODUCTION

This Chapter summarizes the major conclusions based on the results of this study. Some policy issues based on the results of this study have also been addressed. Recommendations for future studies have also been made.

7.2 CONCLUSIONS

Major conclusions from this study may be summarized as follows:

- Close to 1000 metric tons of arsenic could be cycled each year through irrigation water. The estimates are particularly high for south-western and south-central regions of Bangladesh, where both irrigation intensity and arsenic concentration in shallow wells are very high.

- Comparison of arsenic contents of paddy field and village soils in both arsenic-affected and unaffected areas suggest that irrigation with arsenic-bearing groundwater is definitely causing an increase of arsenic content of paddy field soils.

- Arsenic contents of soils, irrigated with arsenic-bearing irrigation water, varies significantly over a paddy field, with depth and with time. In general, average arsenic concentration in the top soil layers (up to 150 mm) increases significantly at the end of the irrigation season (by a factor varying from 1.26 to 2.2 for the paddy fields monitored in this study). In general, higher increase in soil arsenic content was observed for sampling points located close to the entry points of water into different sub-areas of the paddy fields.

- In the unaffected areas, arsenic contents of irrigated soils do not vary significantly either with depth or sampling time; arsenic levels in paddy field soils and village soils are comparable for the unaffected areas.

- Arsenic levels in the paddy field soils are quite dynamic. After the flood/rainy season and before the beginning of the next irrigation season, arsenic levels in the top soil layer of paddy field decreases significantly and comes down to levels comparable to those found at the beginning of the previous season.

- Thus, although paddy field soils are capable of accumulating very high concentrations of arsenic (as shown by both field measurements and in laboratory adsorption experiments), long-term As accumulation in soil appears to be counteracted by biogeochemical pathways leading to arsenic removal from soil during inundation of paddy fields by flood/rain water.

- In both arsenic affected and unaffected study areas, the roots of paddy plants accumulated the maximum level of arsenic, followed by leaf and stem. Paddy grain and husk accumulated the least amount of arsenic. Arsenic content in top soil was found to be strongly correlated with arsenic concentration in root and moderately correlated with arsenic concentration in leaf and stem. The level of arsenic in root, leaf and stem of the paddy plant samples collected from unaffected areas have been found to be significantly lower (by a factor of almost 2) compared to those found in the samples collected from the arsenic affected areas. Since paddy straw is used as cattle feed, arsenic exposure of cattle through straw and its impact should be carefully assessed.

- Average arsenic concentrations in husk and grain of samples from affected and unaffected areas do not differ significantly, though arsenic concentration in both grain and husk have been found to be statistically higher in samples from the affected areas.

- Irrigation with arsenic-bearing groundwater appears to be causing a minor increase in human exposure to arsenic. Considering average arsenic contents of rice grains from affected and unaffected areas and average rice consumption of 450 gm/person/day, daily As intake in affected areas is estimated to be slightly

higher (233 μg) compared to that in unaffected areas (176 μg). Since arsenic toxicity depends on its chemical form and the reported values for organic and inorganic fractions of arsenic in rice grains vary widely, speciation of As in rice grains of Bangladeshi rice varieties should be determined more carefully for making an assessment of arsenic exposure through rice and its possible health impacts

- For a paddy field in Munshigonj, it is estimated that about 90% arsenic added to the field with irrigation water is accumulated in the top 0-450 mm of soil; the top 0-75 mm soil segment accumulated about 71% of added arsenic. The arsenic taken up by paddy plants accounted for about 4.5% of total arsenic that is added to the paddy field with irrigation water. Of the total uptake by paddy plants, root accounted for 47.3%, stem 29.4%, leaf 16.7%, husk 2.7% and grain 3.9%.

- Results of laboratory experiments, designed to simulate field conditions during inundation by flood water, showed a maximum arsenic loss of about 1.6% (of initial amount present in soil column), which could be attributed to microbial methylation of arsenic into volatile forms.

- Arsenite adsorption to paddy field soil is a strong function of oxalate-extractable iron content of soil. Iron content of paddy field soil, in turn, has been found to be related to the iron content in irrigation water. Thus, arsenic adsorption to paddy field soil depends, not only on the characteristics of soil, but also on the quality (e.g., iron content) of irrigation water.

- Significant mobilization of arsenic, beyond the level that could be explained by desorption alone, was recorded for soil samples equilibrated with water containing organic carbon (glucose). This appears to be due to reductive dissolution of iron oxyhydroxides and consequent partitioning of adsorbed As to water. Such mobilization appears to be a strong function of time. Since paddy fields are inundated in flood/rain water for periods of up to three months, significant amount of soil arsenic 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 be preventing arsenic concentration in soil to reach toxic levels.

- Like the paddy field soils, arsenic content of top soil layer of vegetable fields increase with increasing concentration of arsenic in the irrigation water. Good correlation (R^2=0.68) was observed between arsenic concentration in irrigation water and arsenic contents of root-soil and the top 75-mm segment of soil.

- Arsenic concentration in edible parts of vegetables have been found to be relatively strongly correlated with arsenic content in irrigation water and arsenic content in root-soil. Among the six vegetables studied, relatively higher levels of arsenic (approaching or exceeding 1 mg/kg, the Australian food standard) were found in the edible parts of potato, tomato, data *shak*, and lal *shak*. If arsenic levels in vegetables grown in Bogra (an unaffected area) are taken as background levels, than potato and cauliflower appear to have the least background levels of arsenic, but they also appear to have significantly higher tendency to accumulate arsenic.

- Considering vegetable consumption of 130 g/person/day and average As concentration of all six vegetables, this corresponds to an estimated daily intake of about 150 μg of As for vegetables grown with As bearing groundwater in Narayangonj; the estimated As intake is about one-half (86 μg) for vegetables grown with surface water irrigation in Narayangonj and about one-fourth (36 μg) for vegetables grown with As-free (< 1 μg/l) in Bogra. Since groundwater irrigation is not widely used for growing vegetables and reported inorganic fractions of As in vegetables is relatively low (~ 5%), vegetables appear to account for a very small fraction of overall inorganic arsenic exposure through food chain.

- While more studies are needed on arsenic in agricultural soil and the food chain, results from this study suggest that at present there is no reason to worry about the current practice of groundwater irrigation in the arsenic affected areas.

7.3 RECOMMENDATIONS FOR FUTURE STUDIES

- It should be noted that only limited information is available on the chemical forms of arsenic (e.g., inorganic and organic) in paddy/ vegetable, which is needed for estimating its toxicity. Some recent studies suggest that a significant portion of arsenic in paddy exist as As(V). However, in the present study, speciation of arsenic present in paddy/vegetable samples could not be performed due to analytical limitations. Studies are needed to better understand the forms of arsenic in paddy/ vegetables.

- In this study variation in arsenic uptake among different paddy varieties was not assessed. The BR-29 (a high-yielding variety, HYV) was the predominant paddy variety in the areas covered in this study. More studies are needed to better understand the uptake of arsenic by different varieties of paddy, including the local varieties.

- The effect of residual soil arsenic on *aman* paddy (wet season paddy that is grown with flood/rain water) needs to be assessed for fields where both paddy varieties are cultivated.

- From results of laboratory experiments, it appears that during inundation of paddy fields in the rainy/flood season (that follows the *boro* season), significant amount of arsenic could be partitioned from top soil to the inundation water due to desorption and reductive dissolution of iron oxyhydroxides. This arsenic appears to be transported away from the paddy fields either with percolating water or receding flood/rain water. This is probably the principal mechanism responsible of lowering of arsenic concentration of top soil layers after the rainy/flood season. Appropriate field studies needs to be carried out to better understand these processes and their relative importance in regulating arsenic contents of paddy field soils.

- Adsorption-desorption depend on a wide range of factors, including soil characteristics (e.g.,, sand, silt and clay contents), pH of both soil and water, extractable iron and aluminum oxides (acetate or oxalate extractable), As species [As(III), As(V)], heavy metal content (Fe, Mn content), DOC, presence of

oxyanions and other sorbates (such as PO_4, SO_4, silica, bicarbonate), sorption sites on soil surface (specific surface area), sorbate-sorbent ratio, equilibration time, etc. Only a few of these variables were considered in this study. The effect of other relevant factors on arsenic adsorption-desorption in agricultural soil should be carefully studied.

- Monitoring of selected paddy field soils in arsenic affected areas is necessary to assess rate of arsenic accumulation in agricultural soils.

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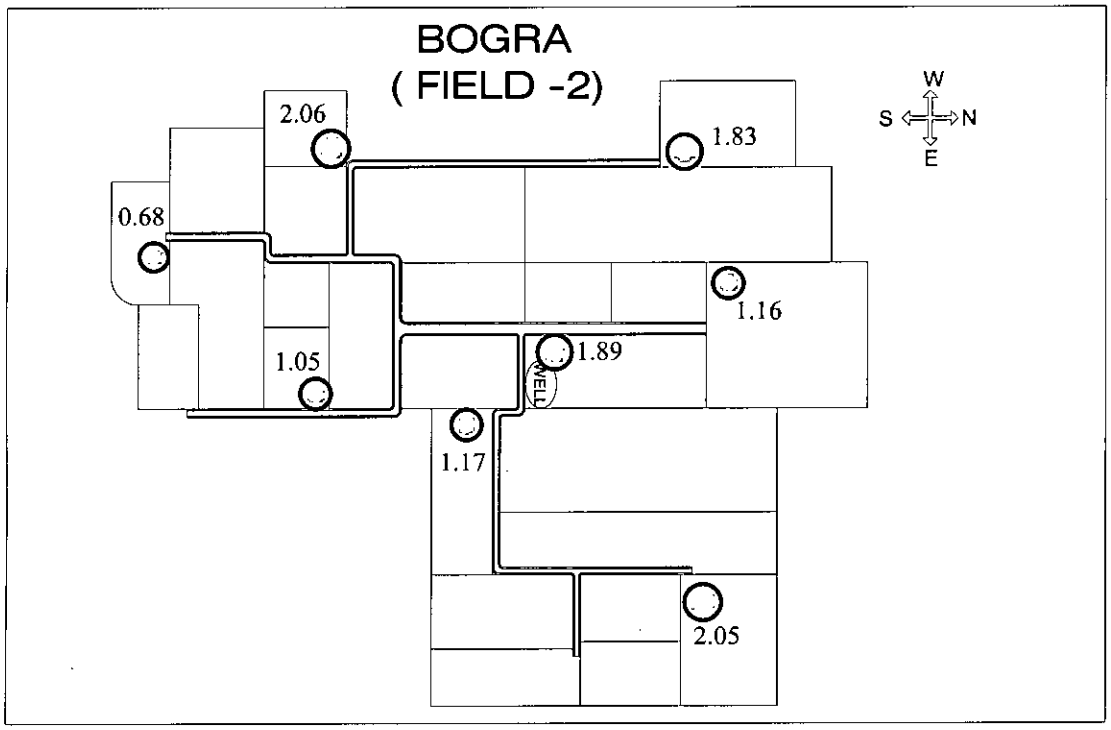
APPENDICES

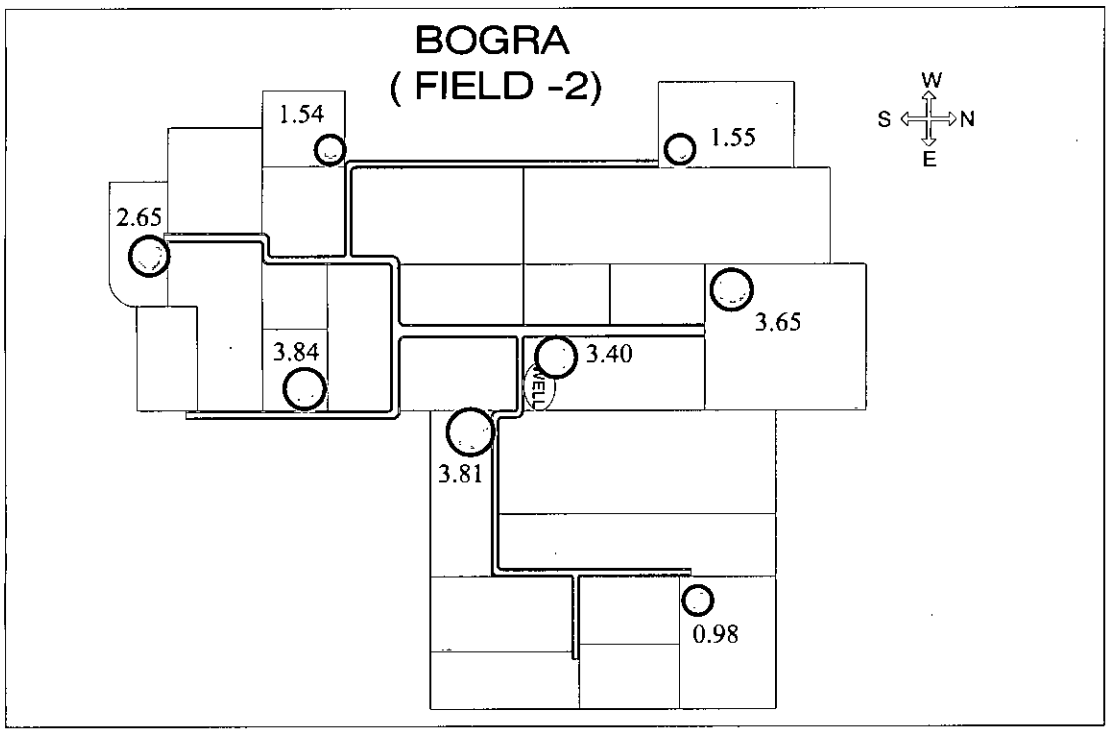
Appendix-A: Schematic Representation of the Paddy Field-2 in Different Field Sites along with Concentration of As in Top 0-75 mm Soil During 1st & 2nd Sampling

and

Arsenic Concentration of Different Parts of Paddy Plant Samples collected from Field-2 in Different Field Sites

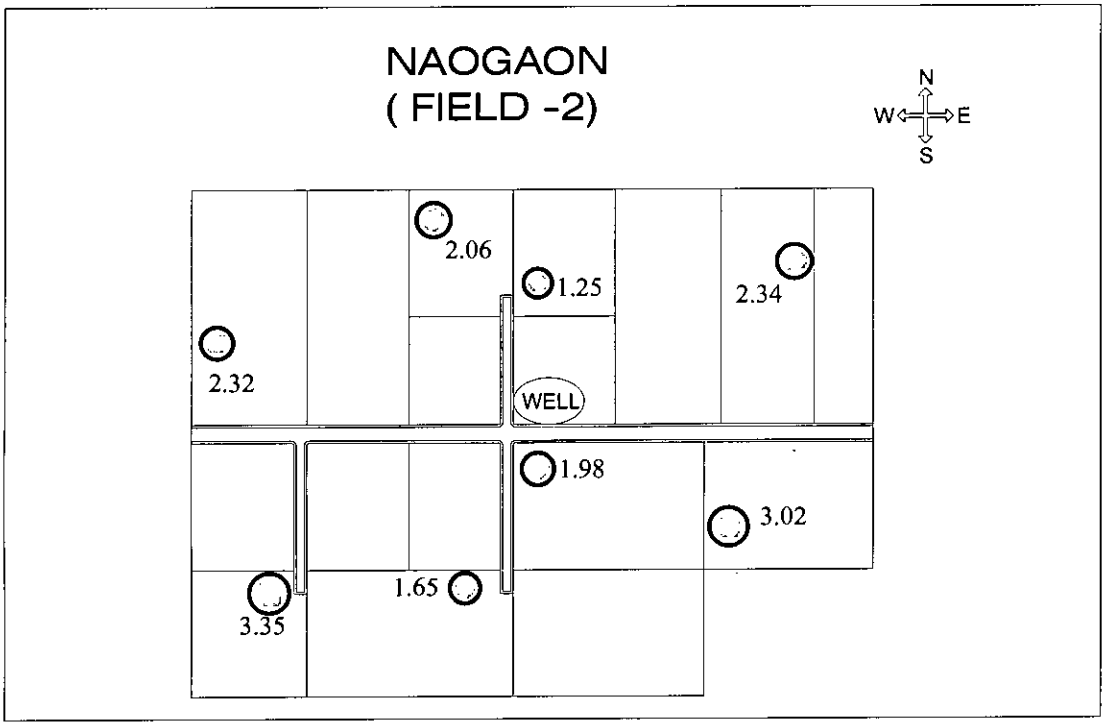


(i)

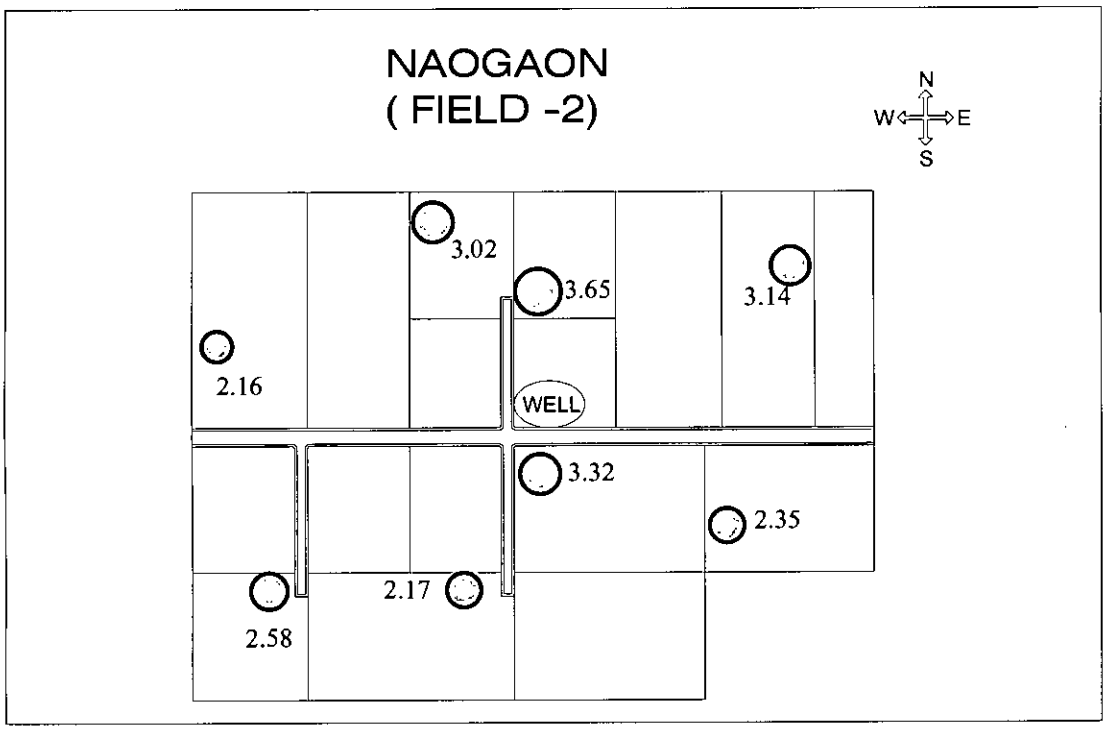


(ii)

Figure A-1: Schematic representation of the paddy field-2 in Bogra along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

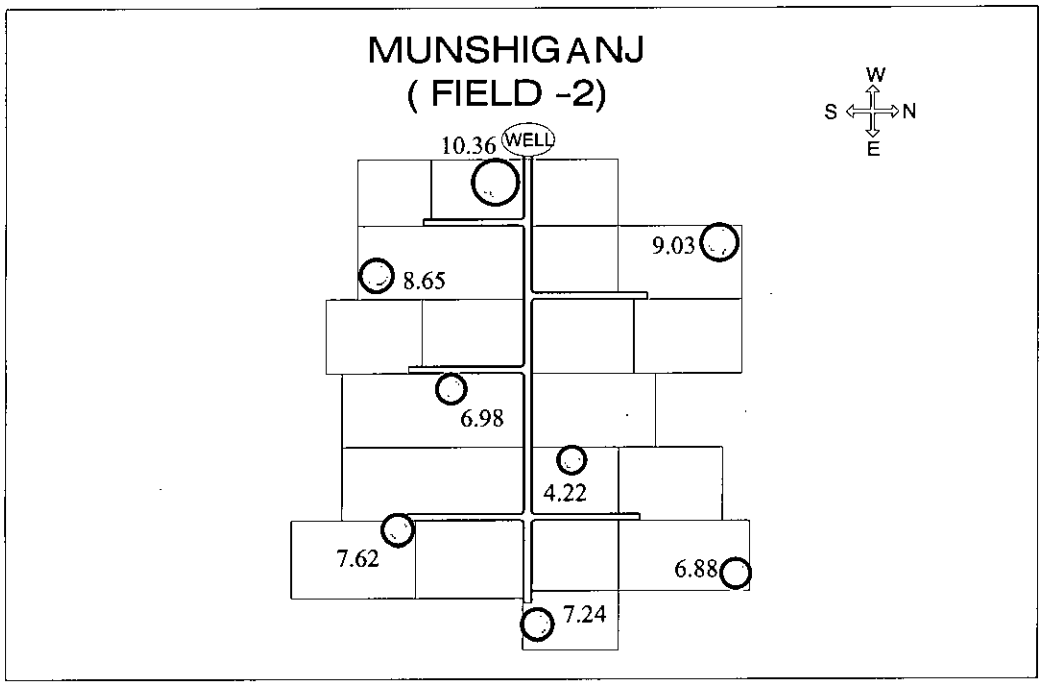


(i)

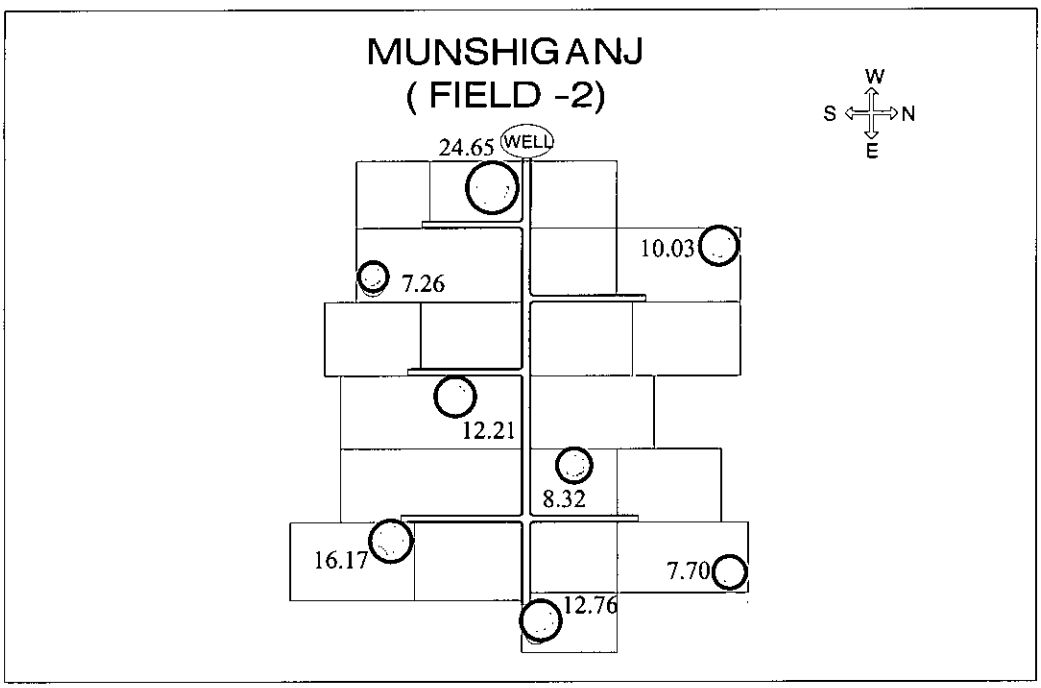


(ii)

Figure A-2: Schematic representation of the paddy field-2 in Naogaon along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

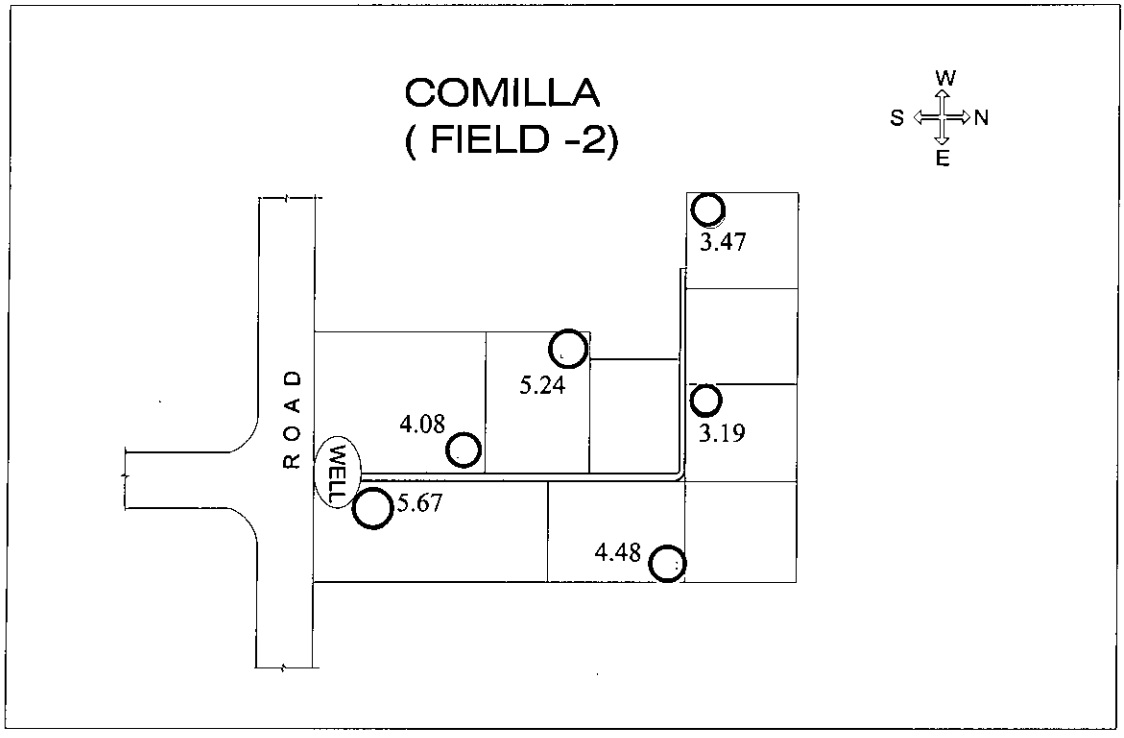


(i)

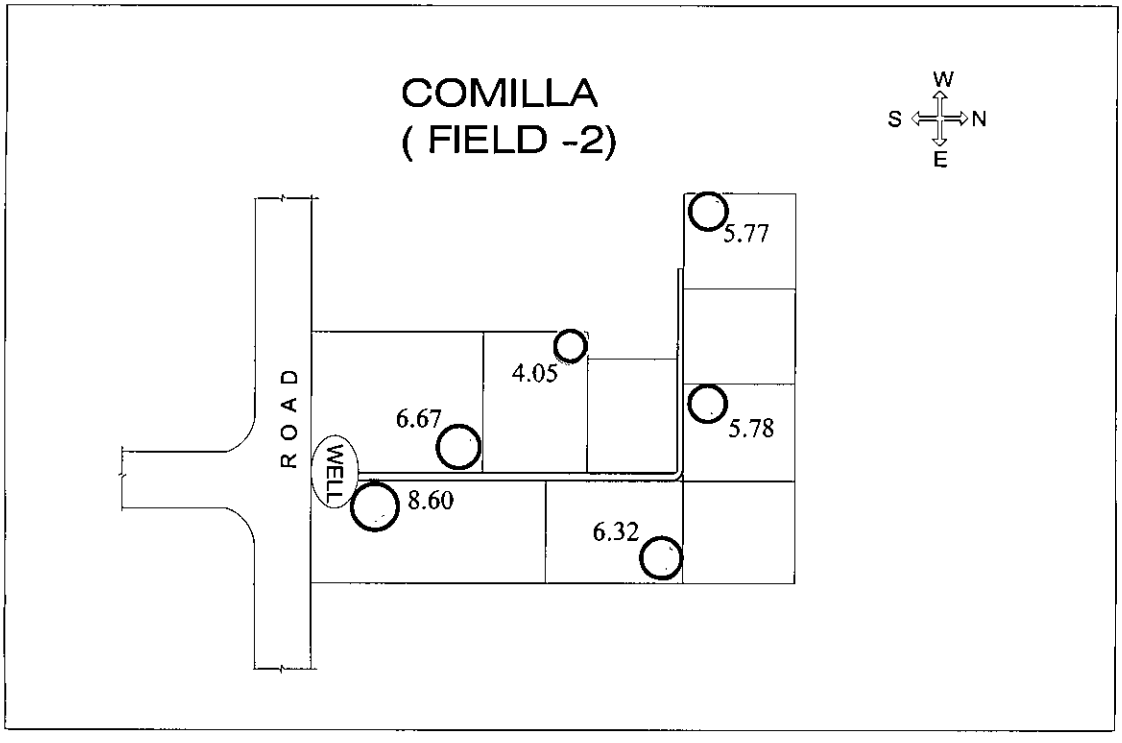


(ii)

Figure A-3: Schematic representation of the paddy field-2 in Munshiganj along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

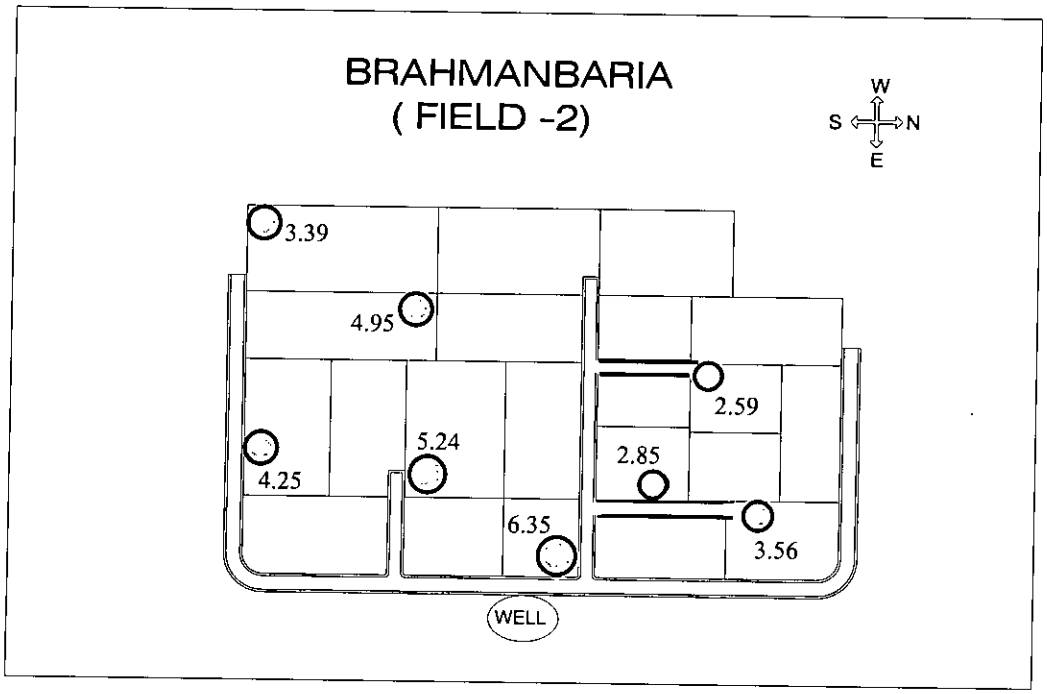


(i)

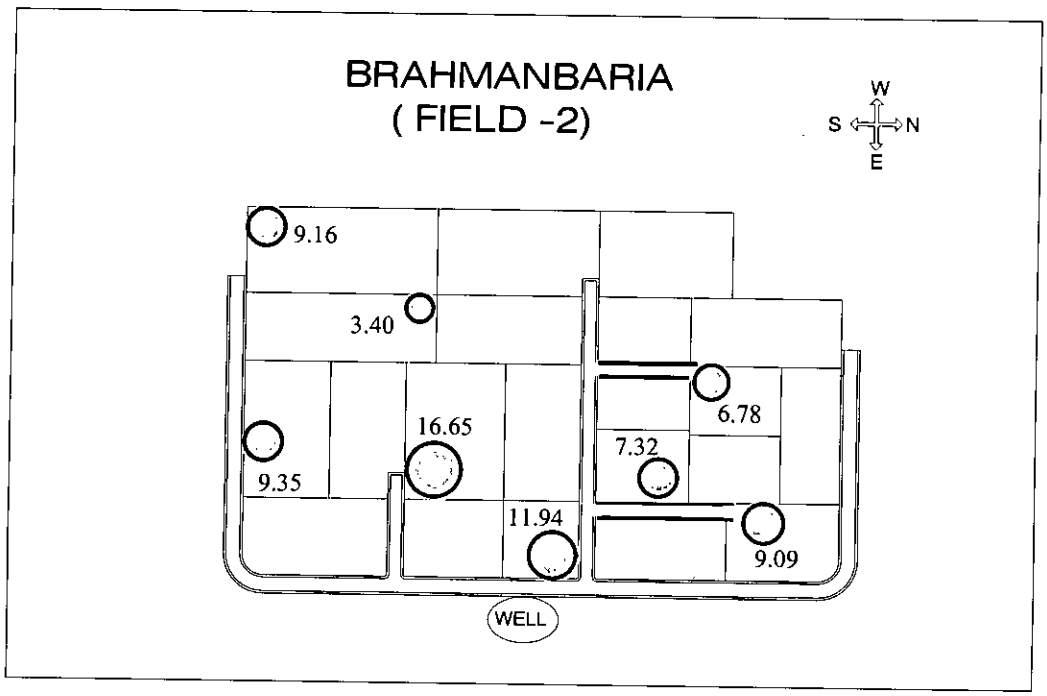


(ii)

Figure A-4: Schematic representation of the paddy field-2 in Comilla along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

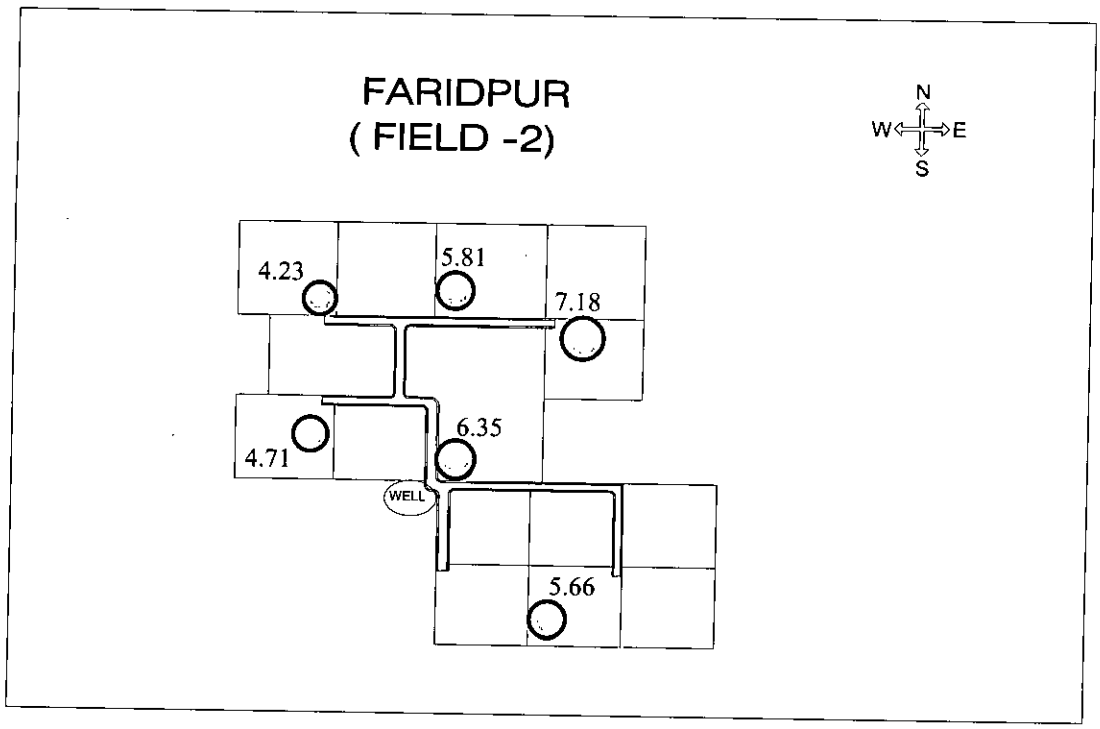


(i)

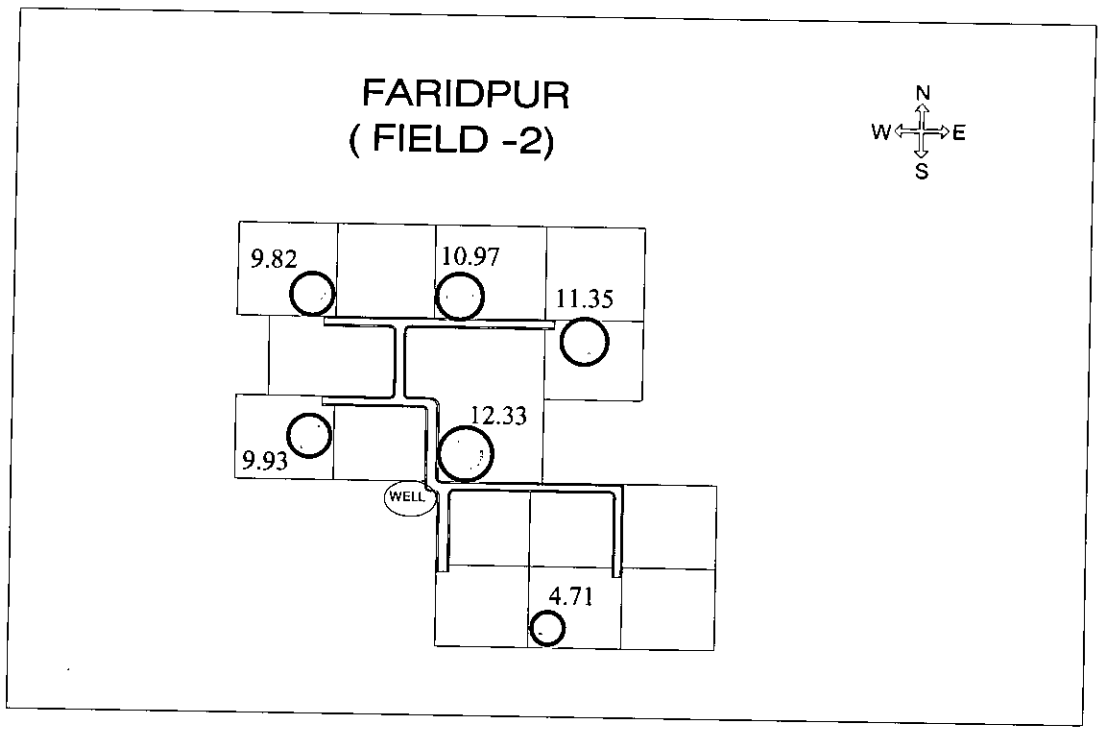


(ii)

Figure A-5: Schematic representation of the paddy field-2 in Brahmanbaria along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)



(i)



(ii)

Figure A-6: Schematic representation of the paddy field-2 in Faridpur along with concentration of As in top 0-75 mm soil (in mg/kg) for cores collected during (i) 1st sampling (March 2003), (ii) 2nd sampling (May-June 2003)

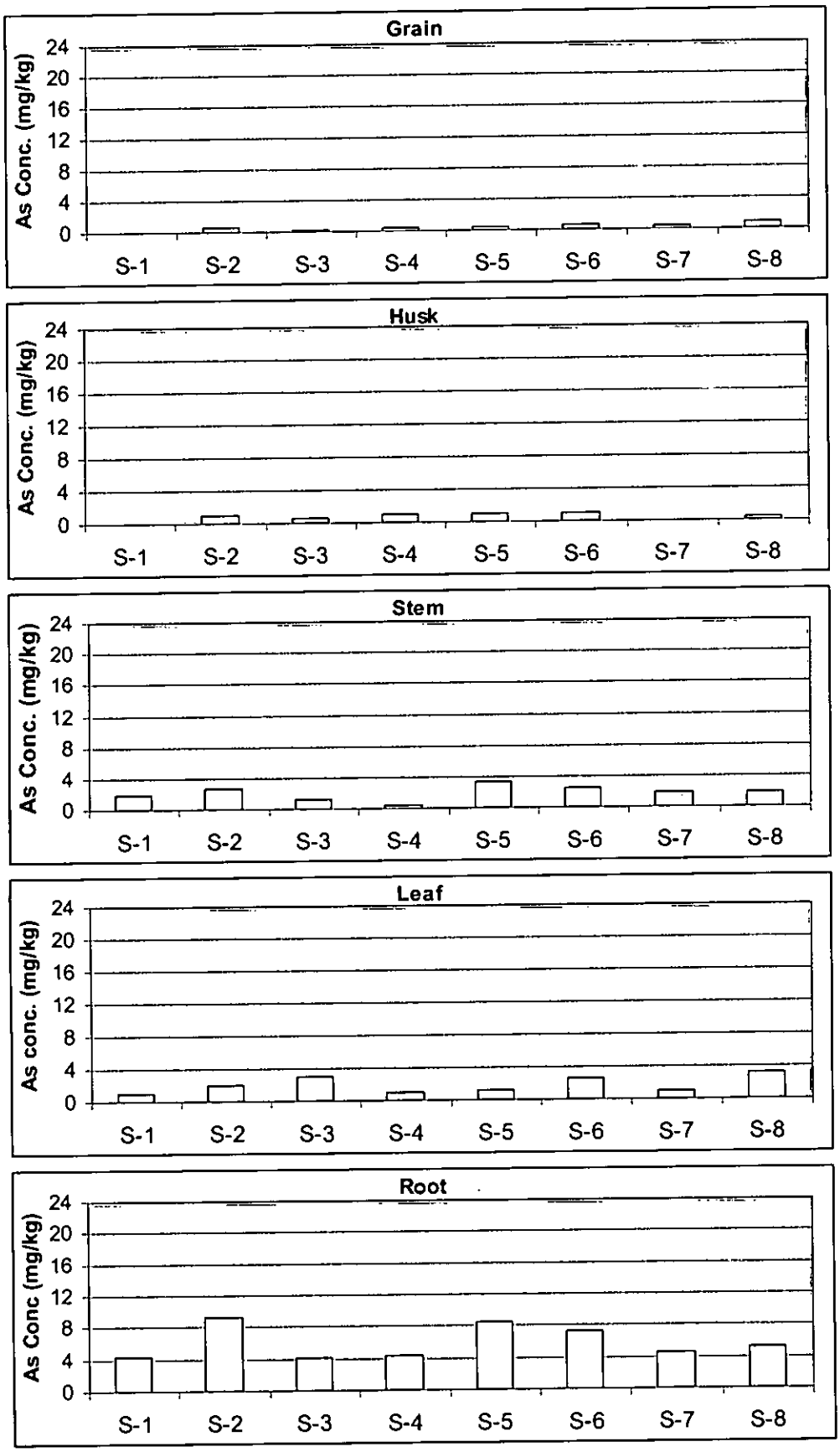


Figure A-7: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Bogra (S = sample number)

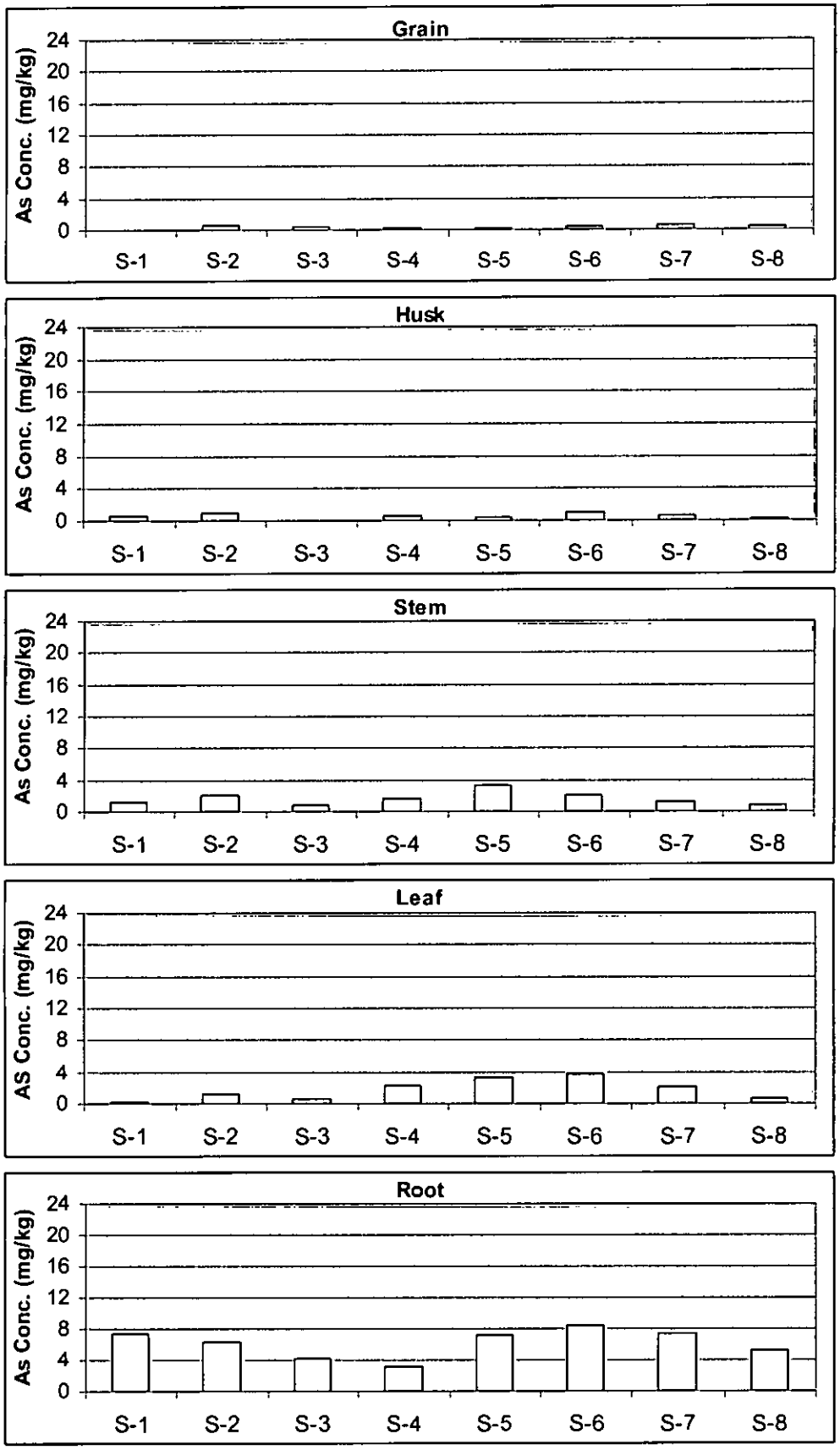


Figure A-8: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Naogaon (S = sample number)

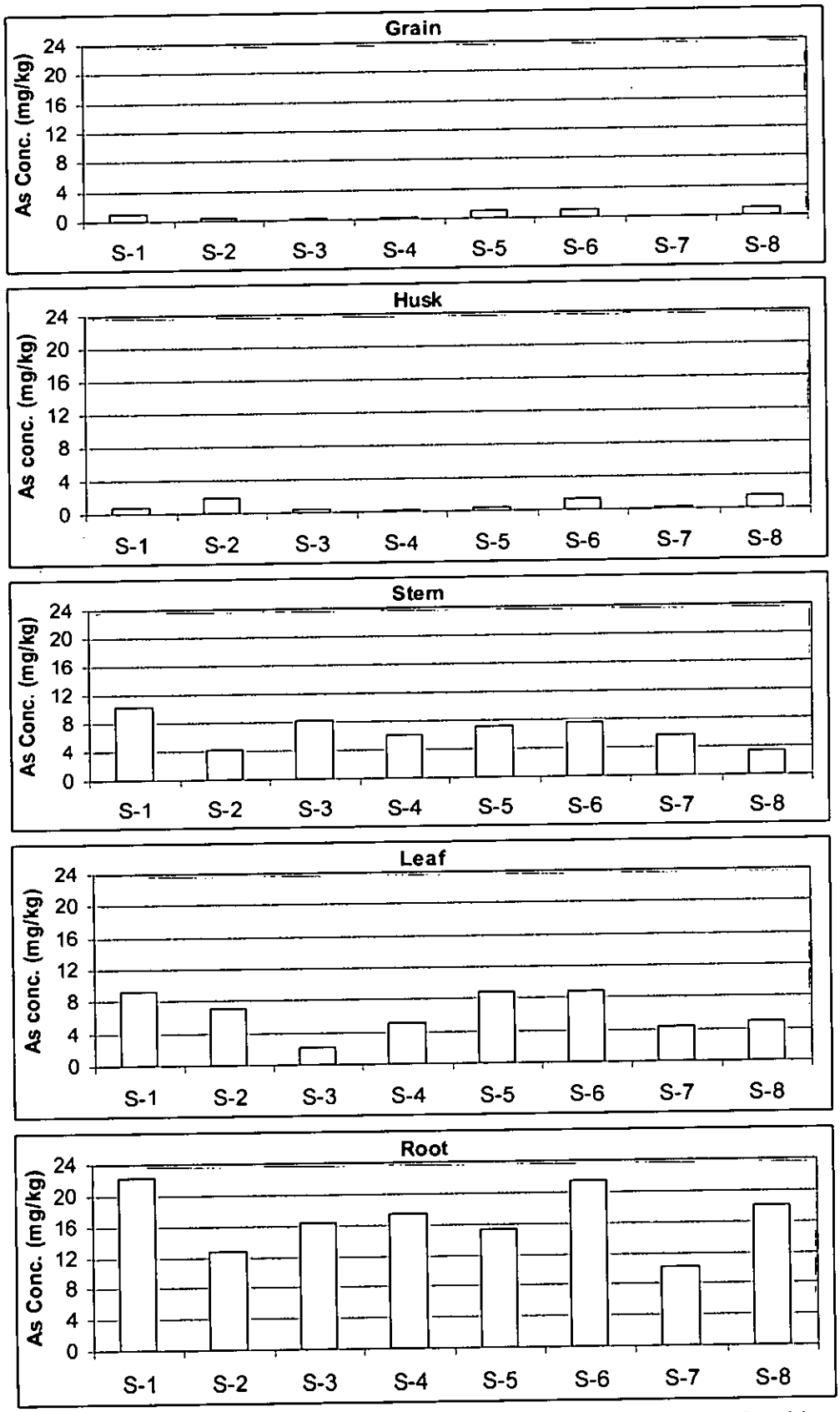


Figure A-9: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Munshiganj (S = sample number)

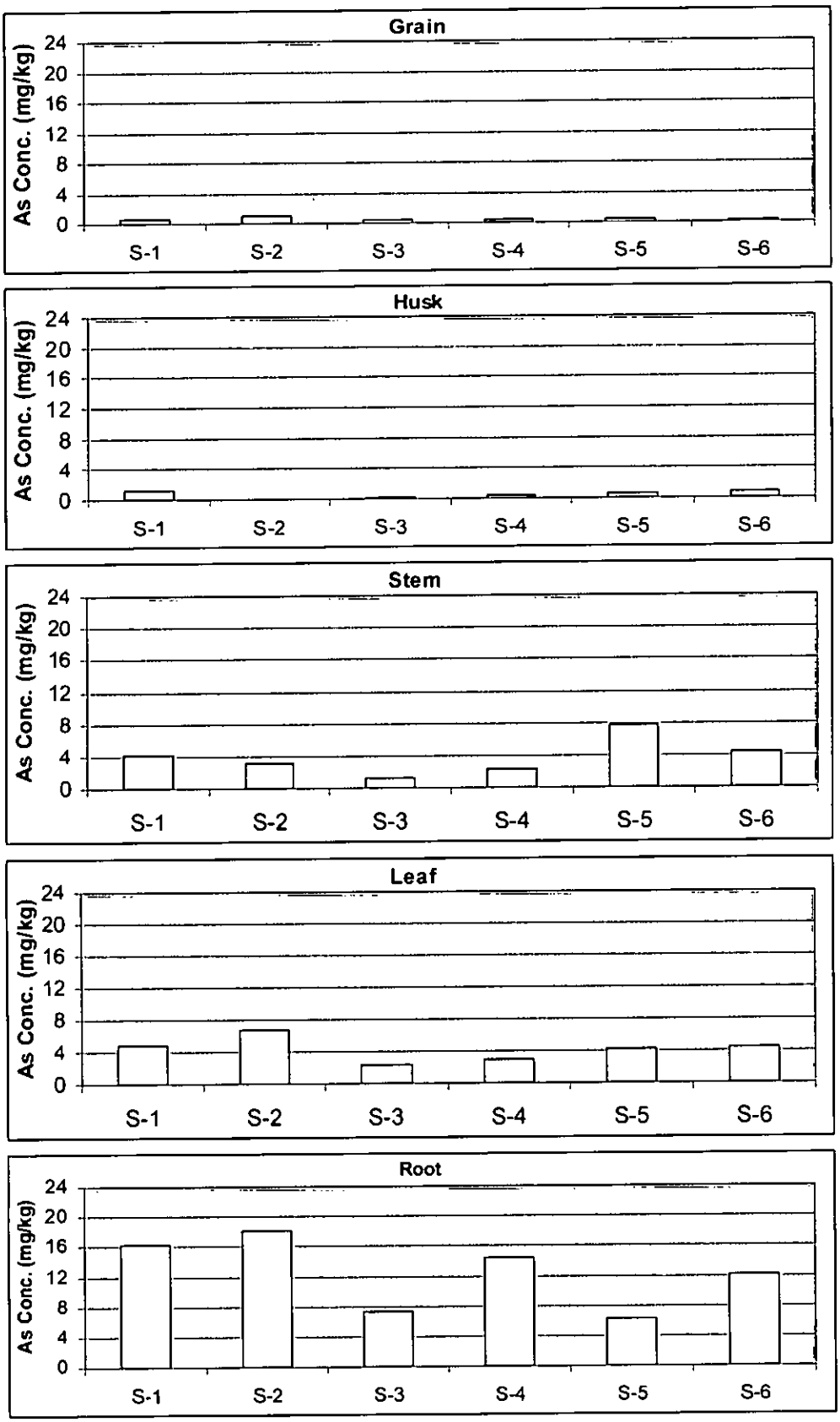


Figure A-10: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Comilla (S = sample number)

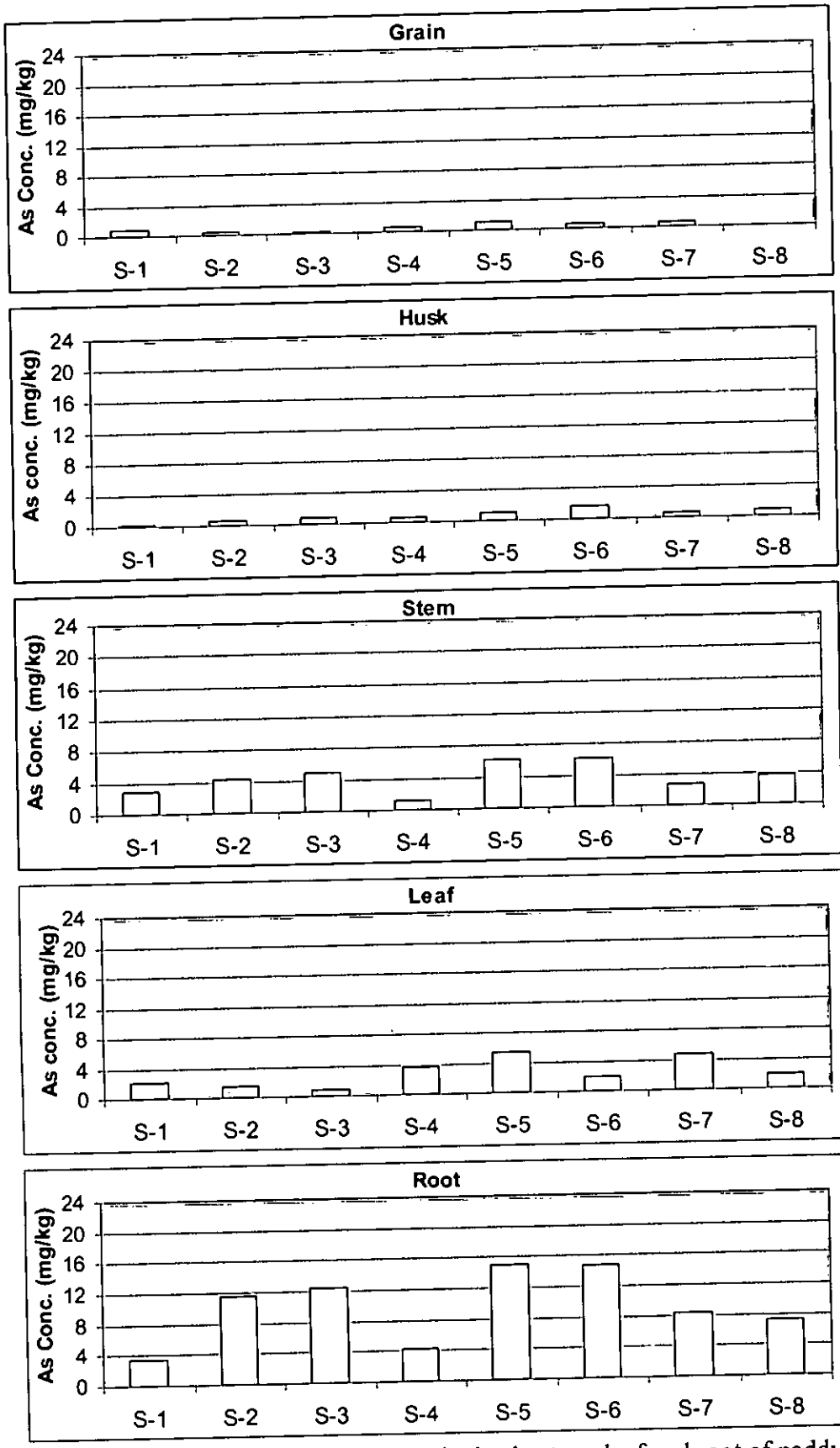


Figure A-11: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Brahmanbaria (S = sample number)

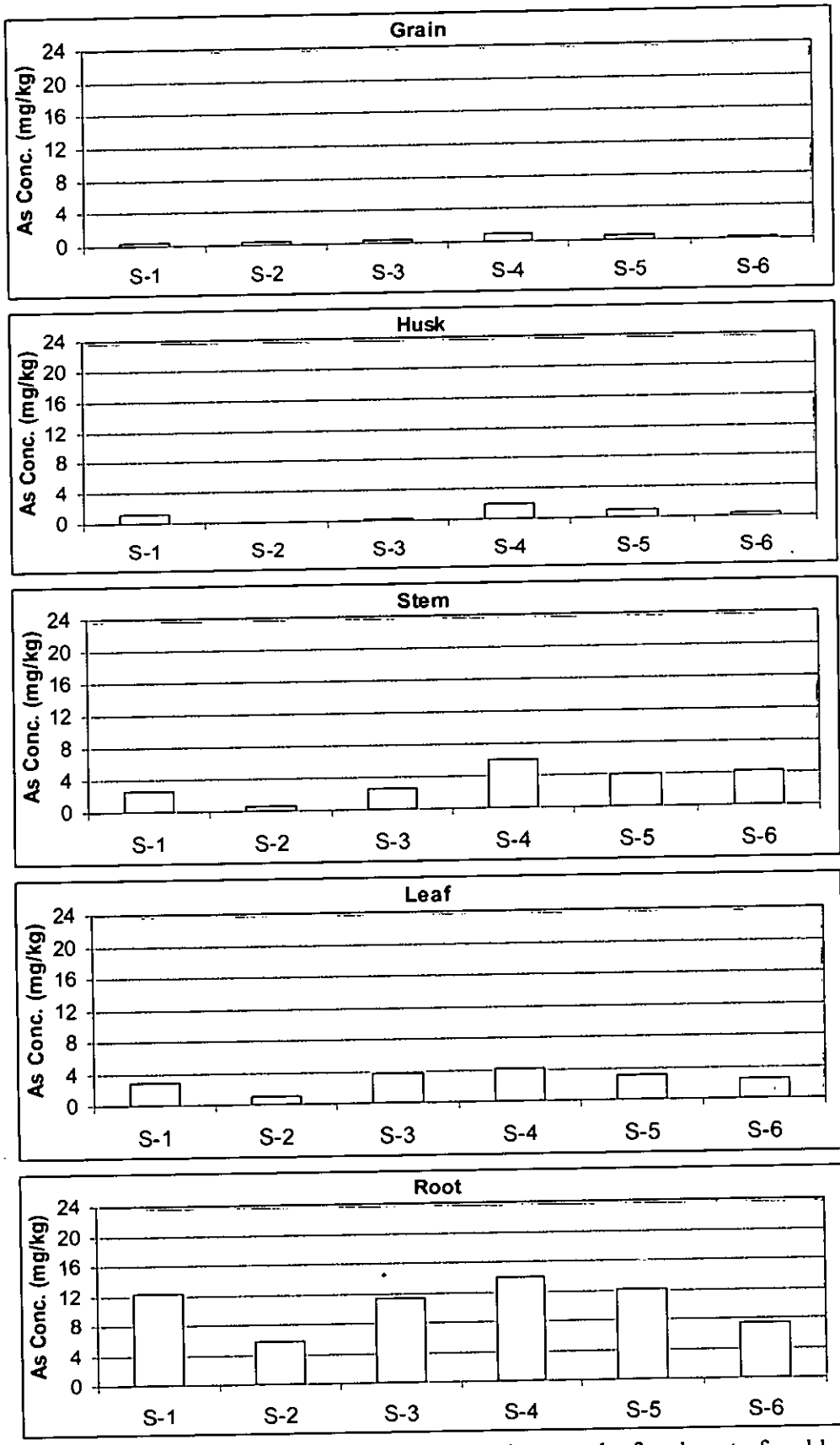


Figure A-12: Arsenic concentrations in grain, husk, stem, leaf and root of paddy plants collected from Field-2 in Faridpur (S = sample number)

Appendix-B: Concentration of Different Chemical Parameters in Fertilizer Samples Required in Boro Paddy Cultivation.

Table B-1 Concentration of different chemical parameters (including arsenic) in fertilizer samples required in boro paddy cultivation.
(Analyzed by EAWAG, Swiss Federal Institute of Aquatic Science and Technology, Switzerland.)

Chemical parameter	Fertilizer			
	Potash (mg/kg)	Urua (mg/kg)	TSP (mg/kg)	Zink (mg/kg)
As	<1	0.6	3.8	0.7
Na	>8390	<47	3070	1330
Mg	1250	42.8	3616	<110
Al	1710	<18	>6930	<380
Si	500	131.3	19270	13750
P	1820	<30	>74910	341.2
S	1860	76.2	>40450	>145100
Cl	>368200	111.6	>83380	736.3
K	>430300	119.7	>123000	1786
Ca	1570	41.7	>82290	>225000
Cr	9.1	3.0	56.2	20.8
Mn	47.8	6.8	308.7	24.3
Fe	1536	9.7	4920	2125
Ni	4.5	0.4	12.1	3.2
Cu	<1	0.4	1.9	<1.0
Zn	5.2	2.9	114.9	14.4
Pb	4.5	1.8	12.0	10.6
Br	>697.6	0.5	240.5	3.8
Ag	<0.8	<0.8	<0.8	<0.8
Cd	0.9	<0.7	3.0	0.5
Ba	<1.5	<1.5	199.3	>402.6

Appendix-C: Figures Show that the Correlation of Arsenic Concentration in Edible Part of Different Vegetable with Root and Leaf.

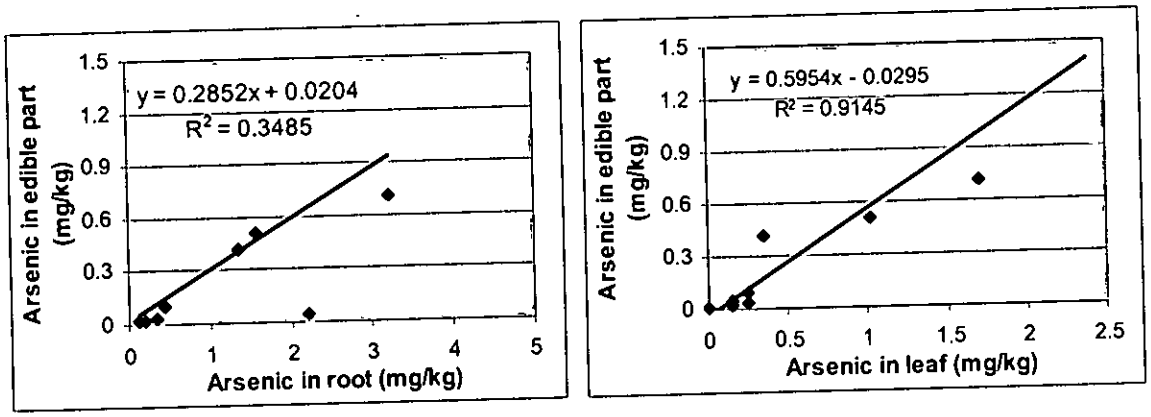


Figure C-1: Relationship between arsenic in edible part of Potato with:
(a) As in root, and (b) As in leaf

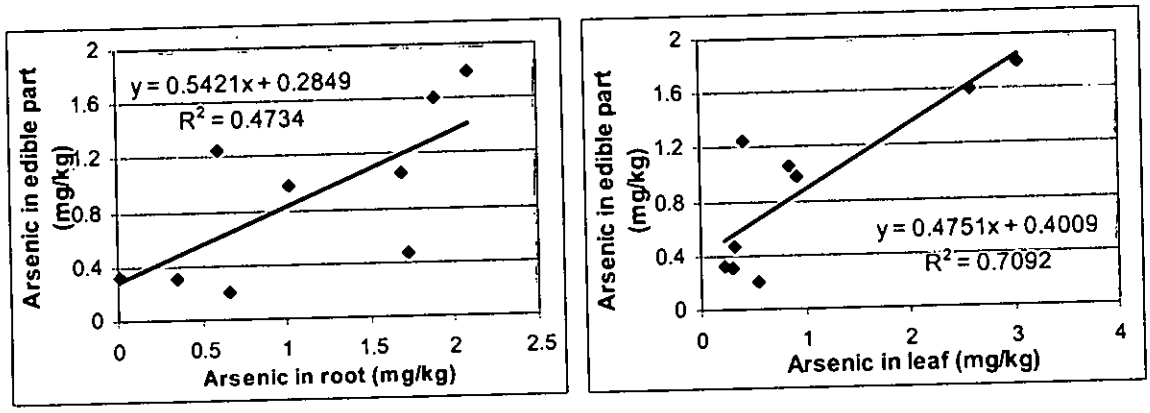


Figure C-2: Relationship between arsenic in edible part of Tomato with:
(a) As in root, and (b) As in leaf

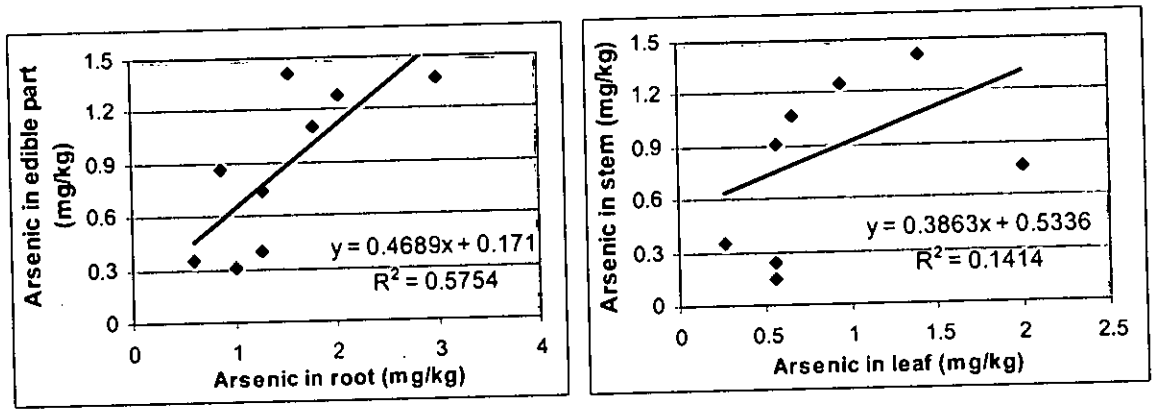


Figure C-3: Relationship between arsenic in edible part of Data Shak with:
(a) As in root, and (b) As in leaf

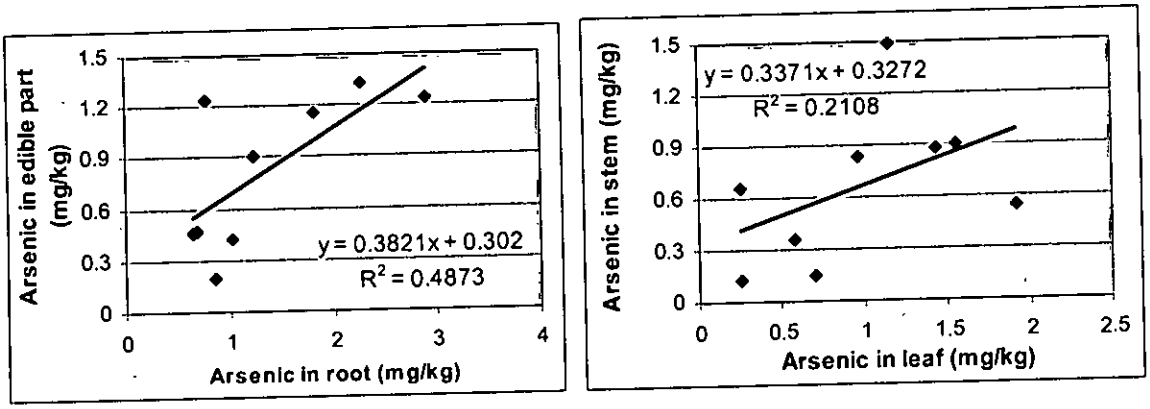


Figure C-4: Relationship between arsenic in edible part of Lal Shak with:
(a) As in root, and (b) As in leaf

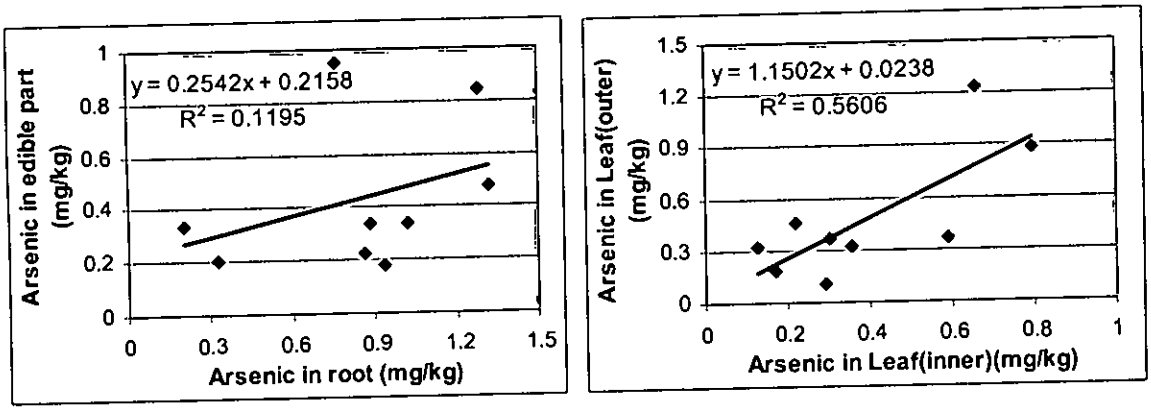


Figure C-5: Relationship between arsenic in edible part of Cabbage with:
(a) As in root, and (b) As in leaf

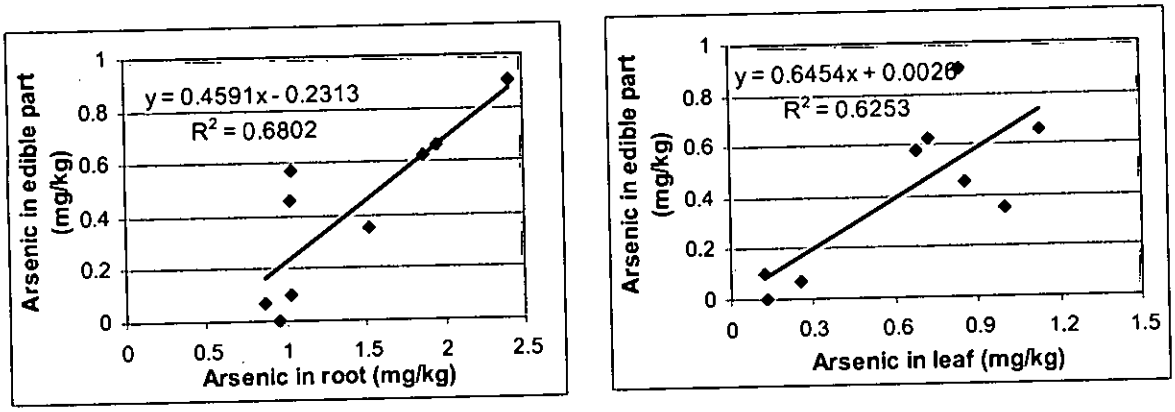


Figure C-6: Relationship between arsenic in edible part of Cauliflower with:
(a) As in root, and (b) As in leaf

Appendix-D: Grain Size Analysis Curve - Hydrometer Method

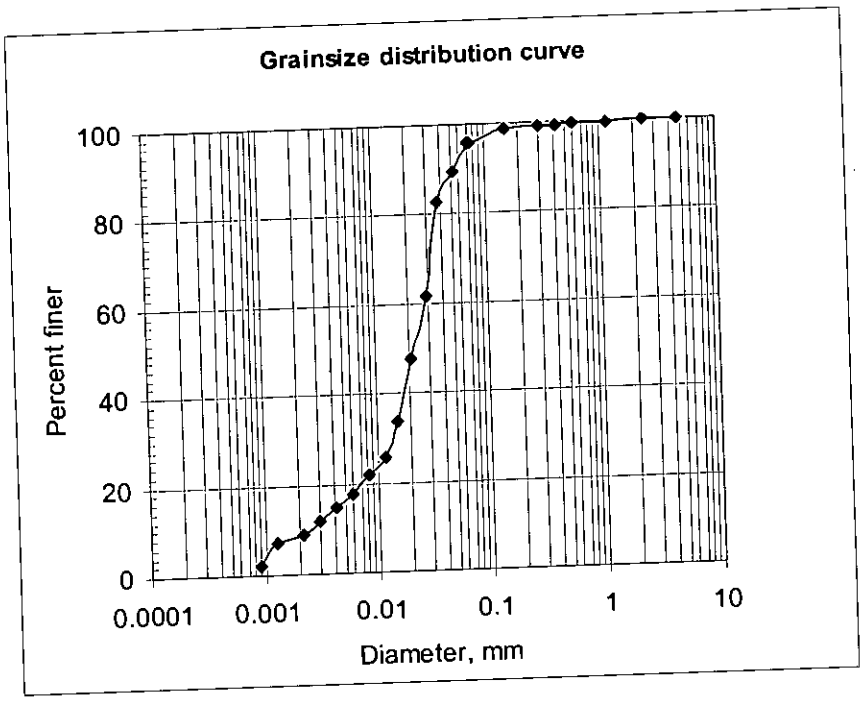


Figure D-1: Grain Size Analysis Curve for Munshigonj field Soil

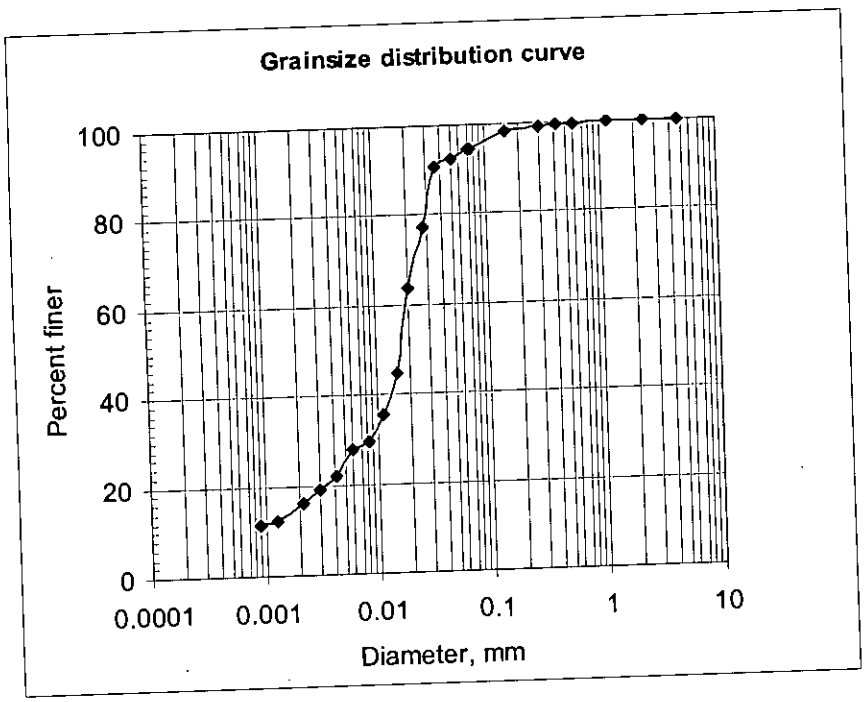


Figure D-2: Grain Size Analysis Curve for Brahmabaria field Soil

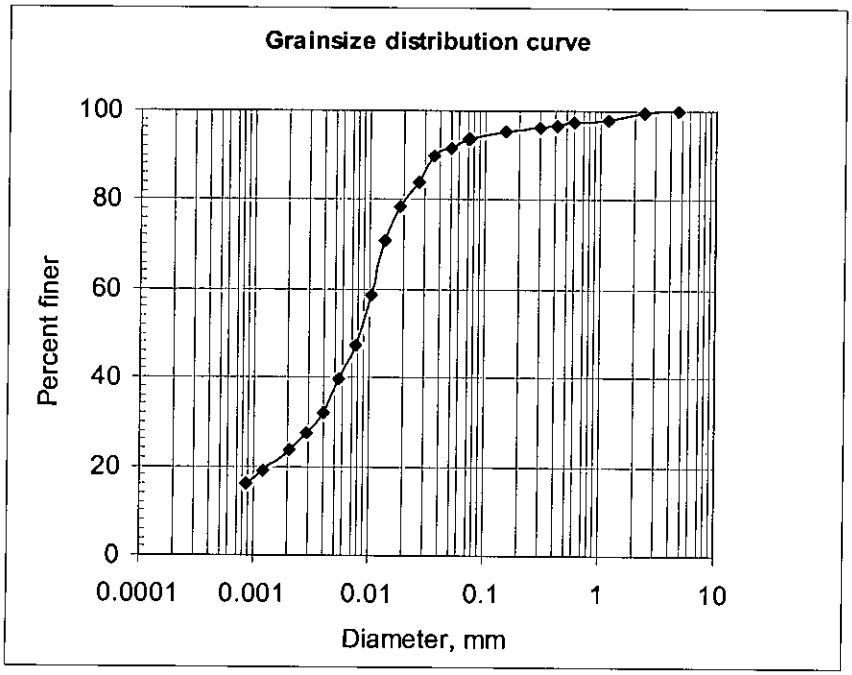


Figure D-3: Grain Size Analysis Curve for Faridpur field Soil

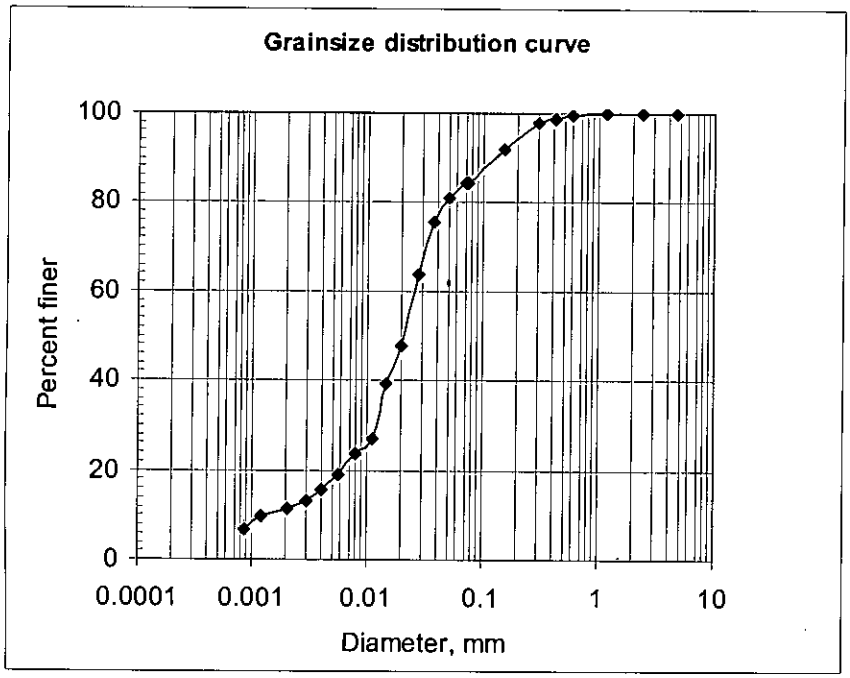


Figure D-4: Grain Size Analysis Curve for Naogaon field Soil