A study on Arsenic in Irrigation Water and Plant-Soil Environment in Bangladesh

By
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A thesis approved as to style and content for the degree of M. Sc. Engineering (Civil)

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ABSTRACT

Arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh, India and several other countries. In Bangladesh tubewell water extracted from an estimated 7.5 to 8.0 million hand tubewells is the primary source of drinking/cooking water for most of its rural population. Besides domestic use, huge quantities of water from shallow aquifer are also used for irrigation during the dry season. A total of 865213 shallow tubewells and 23182 deep tubewells were used for irrigation during the 2001 boro season. Widespread use of groundwater for irrigation suggests that ingestion of irrigated crops could be another major exposure route for arsenic. Besides, phytotoxicity due to increased arsenic in soil/water and its long-term impact on agricultural yield is another major concern. According to the present study, an estimated 900 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 reletively high.

In this study, two arsenic affected areas (Srinagar and Sonargaon) have been selected for detailed characterization of irrigation water, soil and crop/vegetables produced in irrigated soils. A few samples were collected from arsenic affected Comilla and Noakhali districts. Water, soil and crop samples were also collected from an unaffected area in the Dinajpur district in northern Bangladesh. Besides, soil and plant samples were also collected from potato fields at Srinagar site and vegetable fields at Sonargaon site. Except for one, all these vegetable fields were irrigated by surface water.

Arsenic concentration in the well water used for irrigating the rice field site at Srinagar varied from 220 to 537 ppb; and for the Sonargaon site it varied from about 83 ppb to 354 ppb. At both sites, arsenic concentrations of irrigation well water varied significantly with time. Arsenic concentrations in all groundwater samples from the Dinajpur district were below detection limit (i.e., < 1ppb). Concentration of arsenic in the surface water bodies used for irrigation was significantly lower.

Arsenic profiles in the irrigated rice fields at the Srinagar, Sonargoan and Comilla sites show higher accumulation of arsenic primarily in the top layers (typically top 75 to 150 mm) of soil. In general, arsenic concentration in soil decreased with depth. Arsenic accumulation in the irrigation *canal* samples was relatively higher compared to the *field* samples. Compared to the rice field, arsenic concentrations in the soil samples collected from the vegetable fields were significantly lower. For example, mean arsenic concentration in the top soil layer (top 75 mm) at the Srinagar site was 7.8 mg/kg, compared to 14.5 mg/kg for rice field samples. For the Sonargoan site, the mean for the top layer (top 75 mm) of vegetable field samples was 3.5 mg/kg, compared to 8.9 mg/kg for the rice field samples. It is apparent that the higher arsenic concentration in the rice field soil samples, both at Srinagar and Sonargoan sites, is due to the presence of high level of arsenic in the irrigation water.

Analysis of arsenic content of rice plant samples collected from Srinagar, Sonargaon and Dinajpur sites showed that the roots of rice plants accumulated the maximum level of arsenic, followed by leaf and stem. Rice grain and husk accumulated the least amount of arsenic. Two grain samples (out of nine) from Srinagar and one (out of twelve) from Sonargaon exceeded the Australian food hygiene limit of 1.0 mg/kg. The level of arsenic in root, leaf and stem of the plant samples collected from Dinajpur (an arsenic-free area) were found to be lower compared to those found in the samples collected from the Srinagar and Sonargoan sites. However, statistically significant difference was found only for arsenic contents in rice plant roots. Thus it appears that arsenic present in irrigation water and soil results in higher level of arsenic especially in rice plant roots. There was no significant difference in arsenic levels present in the rice grains and rice husks.

Results of analysis of arsenic in different parts of potato and potato plant showed relatively lower level of accumulation. Highest accumulation of arsenic was found in the root of potato plants (up to 2.9 mg/kg). However, these levels were significantly lower than those found in rice roots. Arsenic concentration in the edible parts varied from 0.12 to 0.85 mg/kg [dry (oven dried at 65°C) weight basis], all below the Australian food hygiene standard. Results of arsenic concentration in different parts of *tomato, lalshak, datashak, cabbage* and *cauliflower* samples collected from the Sonargoan site also showed relatively low level of accumulation. Among the different parts, arsenic accumulation in roots was found to be the highest. Arsenic concentration in edible parts of *lalshak* ranged from < 0.39 to 0.96 mg/kg; for *datashak* it ranged from 0.56 to 1.06 mg/kg, for cabbage 0.38 to 1.6 mg/kg and for cauliflower 0.35 mg/kg. Arsenic concentrations in the five tomato samples ranged from 0.18 to 1.33 mg/kg. However, since all the vegetable fields (except one) were irrigated by pond or canal water, effect of arsenic bearing irrigation water on these vegetables could not be assessed from these results alone.

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Chapter 1

INTRODUCTION

1.1 GENERAL

Arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh, India and several other countries. In Bangladesh, an estimated 268 upazillas out of 465 have been affected with significantly high concentrations of arsenic. The southern, central and north-eastern regions of Bangladesh have been most severely affected by arsenic contamination of shallow tubewell water. In Bangladesh tubewell water extracted from shallow aquifers is the primary source of drinking/cooking water for most of its population. An estimated 7.5 to 8.0 million hand-tubewells constitute the backbone of the rural water supply in Bangladesh. The urban water supply is also heavily dependent on groundwater. Besides domestic use, huge quantities of water from shallow aquifer are also used for irrigation during the dry season. The situation is not much different in West Bengal, India. Since its detection in late 1993 in Bangladesh, much of the research works on arsenic have focused on its presence in and exposure through drinking/cooking water. However, widespread use of groundwater for irrigation suggests that ingestion of irrigated crops could be another major exposure route for arsenic. Besides, phytotoxicity due to increased arsenic in soil/water and its long-term impact on agricultural yield is another major concern.

1.2 OBJECTIVES

The major objectives of the present research include:

(i) Estimation of mass of arsenic extracted with groundwater (through both irrigation and domestic wells) in all over Bangladesh;

(ii) Evaluation of arsenic profile in irrigated (with arsenic bearing groundwater) as well as non-irrigated agricultural lands in study areas, and

(iii) Evaluation of arsenic in selected edible crops, both from irrigated and non-irrigated agricultural lands in study areas.

Specific tasks include: (i) Estimation (thana-wise) of mass of arsenic deposited on agricultural land each along with irrigation water; (ii) Estimation (thana-wise) of total mass of arsenic extracted through domestic tube wells; (iii) Determination of arsenic profile in irrigated (with arsenic bearing groundwater from shallow wells) agricultural lands, and its comparison with those in lands not receiving groundwater irrigation; (iv) Determination of arsenic concentration in different parts of selected edible crops (including paddy) and its relationship with the presence of arsenic in irrigation water and in soil.

1.3 SCOPE OF THE STUDY

In this study, estimation of mass of arsenic extracted with ground water was made from secondary information on distribution (thana-wise) of irrigation wells (BADC, 2002) and domestic wells (DPHE, 2000) and arsenic concentration database developed by DPHE/BGS (2000).

Due to resource constraints, only two field sites (in arsenic affected areas) were selected for intensive study on arsenic profile in agricultural lands and presence of arsenic in selected edible crops. Besides limited samples (both soil and crops) were also collected from another arsenic affected areas. In this study, only one field site was selected from the relatively arsenic free northern Bangladesh.

Since rice is the principal crop receiving irrigation water in Bangladesh, irrigated rice field sites were selected for this study. Besides rice fields, soil and plant samples were also collected from a number of vegetable fields, not receiving ground water irrigation.

1.4 METHODOLOGY

The first task of this study was to estimate the quantity of natural arsenic extracted with tubewell. Groundwater extracted both for irrigation and domestic purposes was considered for this estimation. Estimation of the number and distribution of tubewells used for domestic purpose was gathered from the department of public health engineering (DPHE) as well as other relevant government (e. g. LGED) and non-government organizations. Estimation on the number and distribution of irrigation wells was gathered from Bangladesh Agricultural Development Corporation (BADC) and Bangladesh Water Development Board (BWDB). The arsenic concentration database developed by DPHE/BGS (2000) was used to estimate the arsenic concentration in the tubewell water throughout Bangladesh. This information was utilized to estimate the mass of arsenic extracted from groundwater each year. The same procedure was adapted to estimate the quantity of arsenic deposited in agricultural soil through irrigation water.

Accumulation of arsenic in agricultural soil irrigated by arsenic bearing groundwater was evaluated in this study. For this purpose, root zone soil samples as well as irrigation water samples were collected from two different arsenic affected areas and were analyzed (for total arsenic). The two sites selected for this study are 1) Sonargaon and 2) Munshiganj, both highly arsenic affected and located close to Dhaka. Besides these two sites, water, soil and crop samples were collected from Comilla and Noakhali districts. To evaluate the uptake of arsenic into the food chain, key food items have been selected for this study: rice, potato, lalshak, datashak, cabbage, cauliflower and tomato. Samples of these crops and vegetables were collected from (irrigated) agricultural lands along with soil samples. These plant samples were analyzed for total arsenic. Arsenic concentrations in soil and plant samples were compared to those collected from Dinajpur, an area not affected by arsenic.

A database was developed incorporating available data on distribution of arsenic concentration in tube well water and distribution of irrigation wells. Maps showing distribution of arsenic concentration and irrigation wells were developed, with provision for quick updating as more data becomes available.

In this study arsenic concentration was measured using both GF-AAS and HG-AAS (Shimadzu AA6800). Total arsenic in soil samples was determined after digestion of the samples following the procedure adopted in Saha (2001). Total arsenic in crop/vegetable samples was analyzed following a procedure similar to that used by Bennett et al. (2000) and Chen and Folt (2000) and Shimadzu AAS Cookbook.

1.5 ORGANIZATION OF THE REPORT

There are five chapters including this chapter in this thesis. The first chapter provides a brief background of the study and describes the major objectives of the research. The second chapter presents estimates of mass of arsenic extracted with groundwater each year in Bangladesh. The third chapter presents results of the study on arsenic in agricultural soil. It summarizes results on the presence of arsenic in irrigation water and in soil both from arsenic-affected and unaffected areas. The fourth chapter presents the work on fate of arsenic in plants. It summarizes results on the presence of arsenic in soil and in different parts of the plants both from arsenic-affected and unaffected areas. Finally chapter five presents the overall conclusions and recommendations based on the findings of this study.

Chapter 2

ESTIMATION OF ARSENIC EXTRACTED WITH GROUNDWATER

2.1 INTRODUCTION

Widespread presence of arsenic in groundwater at levels above the drinking water standard is a major concern in Bangladesh, India and several other countries. In Bangladesh, high levels of arsenic have been detected in 59 out of 64 administrative districts; the southern, south-western and north-eastern regions of the country are worst-affected. In Bangladesh tubewell water extracted from shallow aquifers is the primary source of drinking/cooking water for most of its population, particularly the rural population. An estimated 7.5 to 8.0 million hand-tubewells constitute the backbone of the rural water supply in Bangladesh. Besides domestic use, huge quantities of water from shallow aquifer are also used for irrigation during the dry season. Although considerable work has been done on removal technologies of arsenic from contaminated groundwater and alternate water supply options, the presence of arsenic in irrigation water received relatively less attention. The dependency on groundwater for public water supplies and irrigation results in a huge quantity of arsenic being cycled through the environment each year with major implications on public health and environment. This chapter presents an assessment of the use of groundwater for irrigation in Bangladesh and provides an assessment of the amount of arsenic that is extracted with groundwater used for irrigation as well as domestic purpose. This chapter also provides an overview of the research needs for better understanding of the fate of arsenic in the environment.

2.2 GROUNDWATER IN IRRIGATION

In Bangladesh, in the absence of adequate surface water in the dry season, irrigation is heavily dependent on groundwater. Figure 2.1 shows increase in irrigated area in Bangladesh by different technologies during 1982-1997 (WARPO, 1999). As shown in Fig. 2.1, during the last fifteen years, the area under irrigation has been increased significantly to raise food production. Much of this increase has been accomplished through installation of shallow tube well (STW). As can be seen from Fig. 2.1, the area under irrigation by surface water has remained more or less static since the early eighties; while the area under irrigation by shallow tube wells has increased by a factor of about five. During each irrigation season, an estimated 27209 Mm^3 of water [considering a discharge of 10 l/s and 1200 hours of irrigation per season] is extracted through shallow tube wells. This quantity is order of magnitude higher than the amount of groundwater extracted for domestic purpose throughout the year.

In Bangladesh irrigation season is divided into two periods – Rabi season and Kharif season. In the 1996/97 Rabi season, the total irrigated area was 3.8 million hectares, among which 2.63 million hectares irrigated using ground water and 1.17 million hectares irrigated using surface water. In the Kharif season a total of 0.2 million hectares was irrigated, among which 0.158 million hectares was irrigated using ground water and 0.042 million-hectare using surface water.

In the Rabi 1996/97 season, STW irrigated 2.15 million hectares (63% of the total area under minor irrigation), among which *boro* field accounted for 1.68 million hectares, wheat field for 0.29 million hectare and other corps accounted for 0.18 million hectare. DTW irrigated 0.48 million hectare (14% of total area under minor irrigation), among which *boro* field accounted for 0.42 million hectare, wheat field accounted for 0.034 million hectare, and others accounted for 0.026 million hectare. In the Kharif 1996/97 season, STW irrigated 0.126 million hectare (66% of total area under minor irrigation), among which *aman* field accounted for 0.096 million hectare, and others accounted for 0.029 million hectare. DTW irrigated 0.032 million hectare (16% of total area under minor irrigation), among which *aman* field accounted for 0.029 million hectares and others accounted for 0.0027 million hectare.

According to a recent BADC survey (BADC, 2002), a total of 865213 shallow tube wells and 23182 deep tube wells were used for irrigation during the 2001 *boro* season. Shallow tube wells irrigated about 2.295 million hectares (about 61% of total area under irrigation) and deep tubewells accounted for about 0.538 hectare (about 14% of irrigated area). The contribution of surface and groundwater sources to total irrigated area has changed considerably over time. The contribution of groundwater to total irrigated area has increased from 41% in 1982/83 to 71% in 1996/97 and to over 75% in 2001. The contribution of surface water has, therefore, declined from 59% to less than 25% over this period.

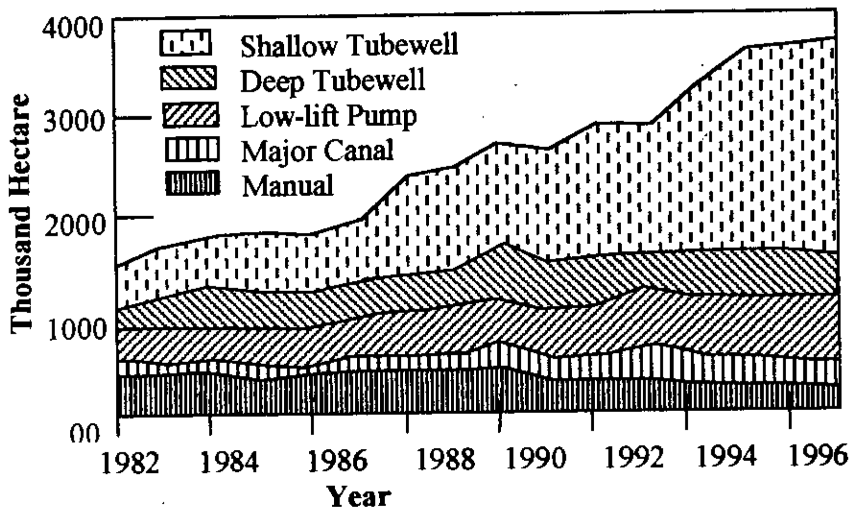


Figure 2.1: Increase in irrigated area in Bangladesh by different technology during 1982-1997 (WARPO, 1999).

In Bangladesh, *boro* rice (dry season rice) is the major recipient of irrigation water. Figure 2.2 shows total irrigation coverage as a function of time, along with contribution from FCDI (Flood Control, Drainage and Irrigation) coverage. It should be noted that in Bangladesh, total irrigation coverage accounts for over 60 percent of the net cultivable area. Figure 2.3 shows trends in growth of *boro* (dry season) rice production in Bangladesh. This figure shows that during 1973 – 94, *boro* registered a very high production growth, by a factor of over three. This 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 (Fig. 2.3) and growth in area covered under irrigation (Fig. 2.2) are strongly correlated with a correlation coefficient of 0.98 (Chowdhury et al., 1997). Currently *boro* rice accounts for about 37% of the total rice production in Bangladesh. Besides *boro* rice, wheat and a range of other crops and vegetables cultivated during dry season also need irrigation.

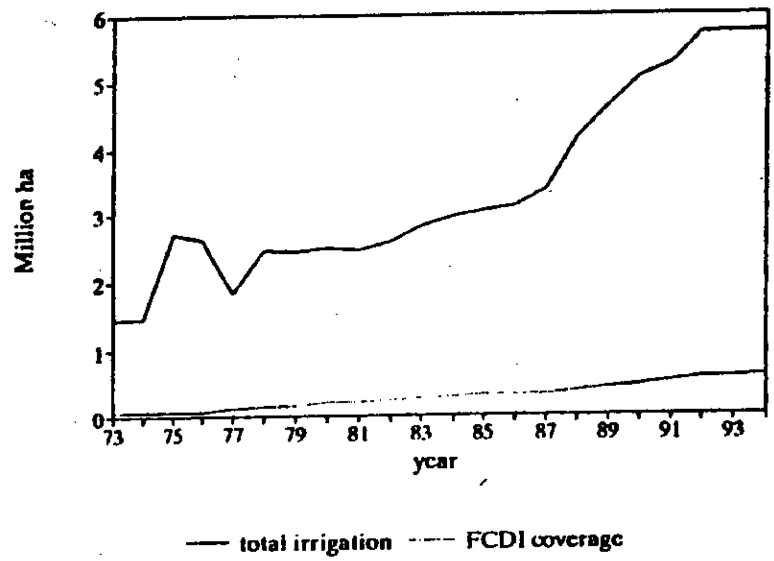


Figure 2.2: Growth in irrigation coverage in Bangladesh (Chowdhury et al., 1997)

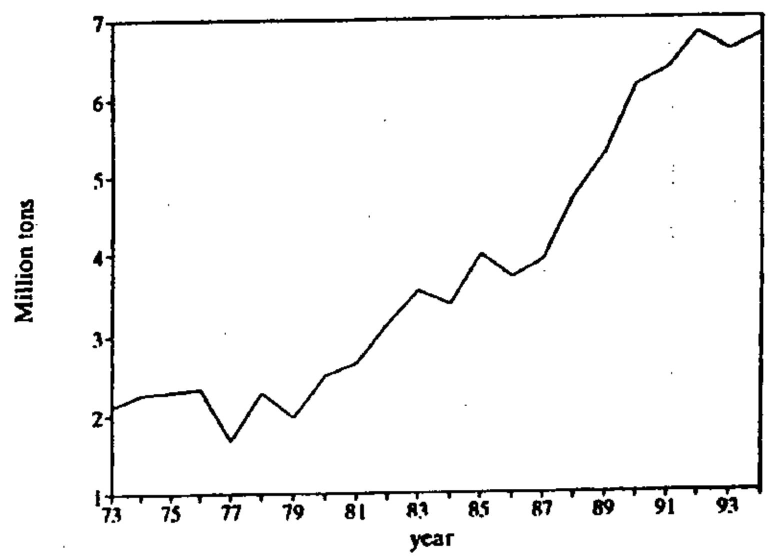


Figure 2.3: Growth in *boro* production in Bangladesh (Chowdhury et al., 1997)

Thus, 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. 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. For example, 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. Therefore, concerns have been raised about possible introduction of arsenic in the food chain as well as long-term implications (e.g., reduced yield) of increased arsenic in the agricultural fields.

2.3 AMOUNT OF ARSENIC EXTRACTED WITH GROUNDWATER

2.3.1 Arsenic Extracted with Irrigation Water

Figure 2.4 shows the arsenic concentration of ground water in Bangladesh and Figure 2.5 shows distribution (thana-wise) of shallow irrigation wells in Bangladesh. As shown in Fig. 2.5, high concentrations of shallow irrigation wells could be found in northern and north-western Bangladesh. A comparison between figure 2.4 and figure 2.5 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).

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 394 *thanas* and only these information were used in this estimation process. Figure 2.6 shows amount of arsenic extracted through irrigation wells every year for all the *thanas* in Bangladesh. Thus if all irrigable lands are irrigated, an estimated 900 metric tons of arsenic would be extracted each year through irrigation water. The estimates are particularly high for southwestern and south-central (excepting the hill districts) regions of Bangladesh, where both irrigation intensity and arsenic concentration in shallow wells are very high.

Figure 2.6 shows that although the north-eastern region of Bangladesh is an area 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).

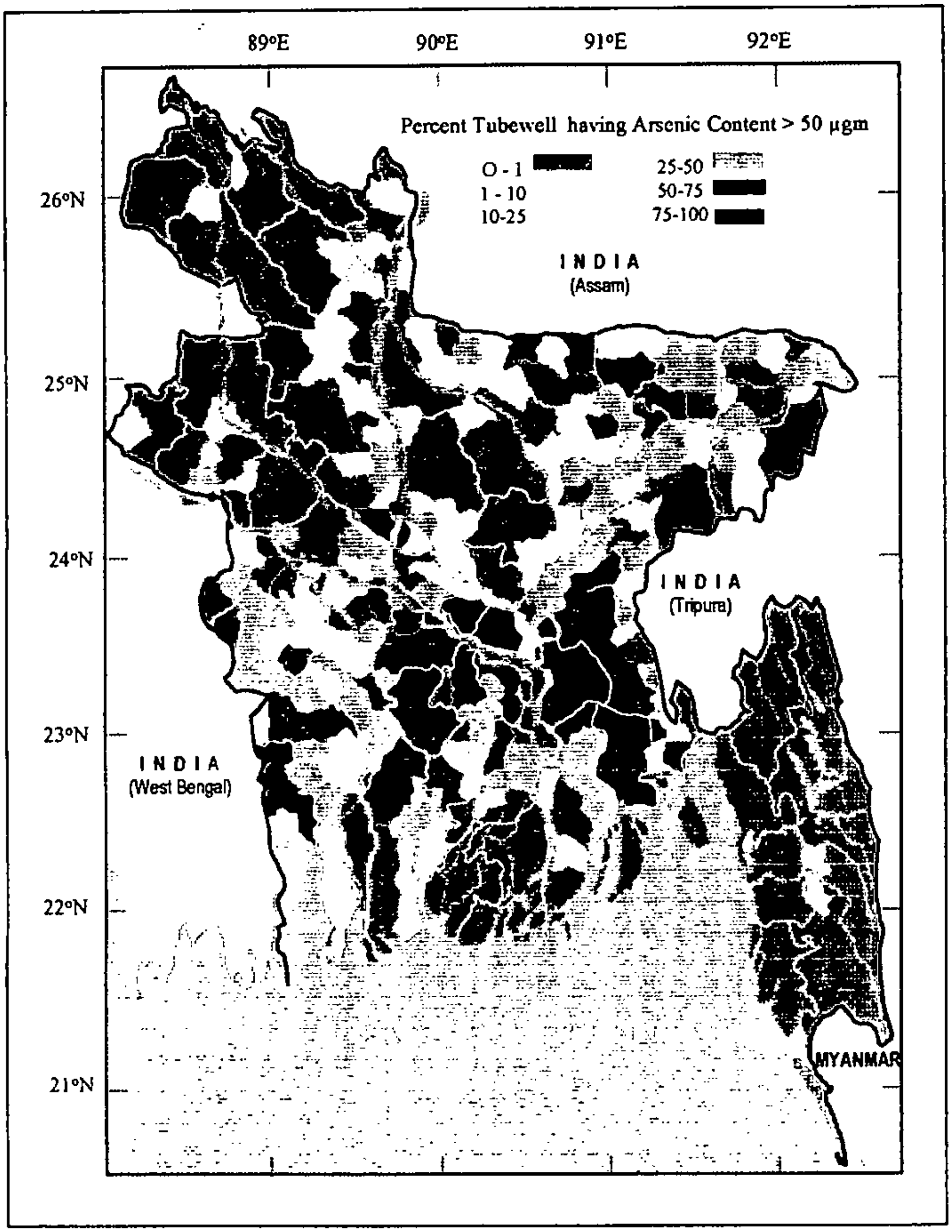


Figure 2.4: Arsenic concentration of groundwater in Bangladesh

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.

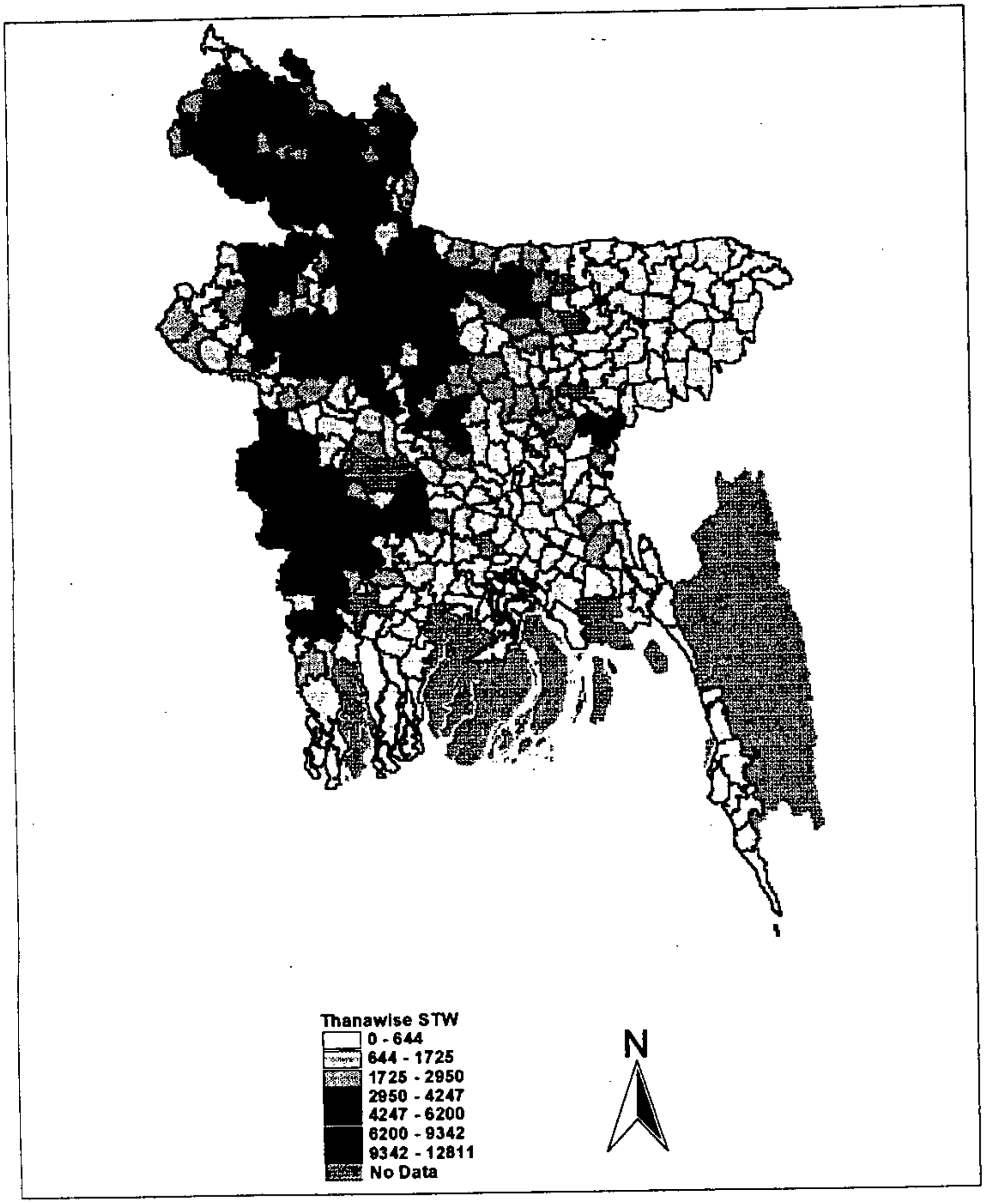


Figure 2.5: Distribution of shallow irrigation wells in Bangladesh (data: BADC, 2002)

Figure 2.7 shows thana-wise estimates of the amount of arsenic deposited in agricultural land per hectare of irrigated area. This estimate was made by dividing the estimated total arsenic for each thana (presented in Fig. 2.6) by the irrigated area for that thana (BADC, 2002). According to this estimate, the districts with high deposition of arsenic include Chandpur, Munshigonj, Comilla, Gopalgonj, Faridpur, Madaripur, Jessore, Jhenaidah, Bagerhat, and Kushtia.

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.

2.3.2 Arsenic Extracted with Domestic Well Water

In this study, an attempt has been made to develop a gross estimate of arsenic extracted with groundwater from domestic wells. Arsenic extracted from domestic tubewells were estimated by combining estimates of total population of each *thana*, percentage of population using shallow wells for domestic purpose and per capita use of water. Only rural area was considered in this estimation. Besides shallow tubewell, a number of technologies are used in the rural water supply, which include deep tubewell (DTW), pond sand filter (PSF), and VSST/SST. Since a significant fraction of shallow tubewells is privately owned, there is no good record of actual number of shallow tubewells in the country. On the other hand, all the other technologies are almost entirely owned by the Government and the statistics provided by the DPHE on these technologies can be considered to be reliable. It has been assumed that except for shallow tubewell, water derived from all other technologies is free from arsenic.

Thus the number of people using shallow tubewell was calculated as the total population minus the population using the other technologies. For this calculation, it was assumed that each deep tubewell serves 101 people (DPHE, 1999), each PSF serves 500 people and each VSST/SST serves 75 people. In the absence of *thana*-wise population data from the 2001 Census, it was assumed that the ratio of population of a particular *thana* to the total population is the same as it was in 1991 Census. Thus for each *thana*, the population using shallow tubewell was estimated.

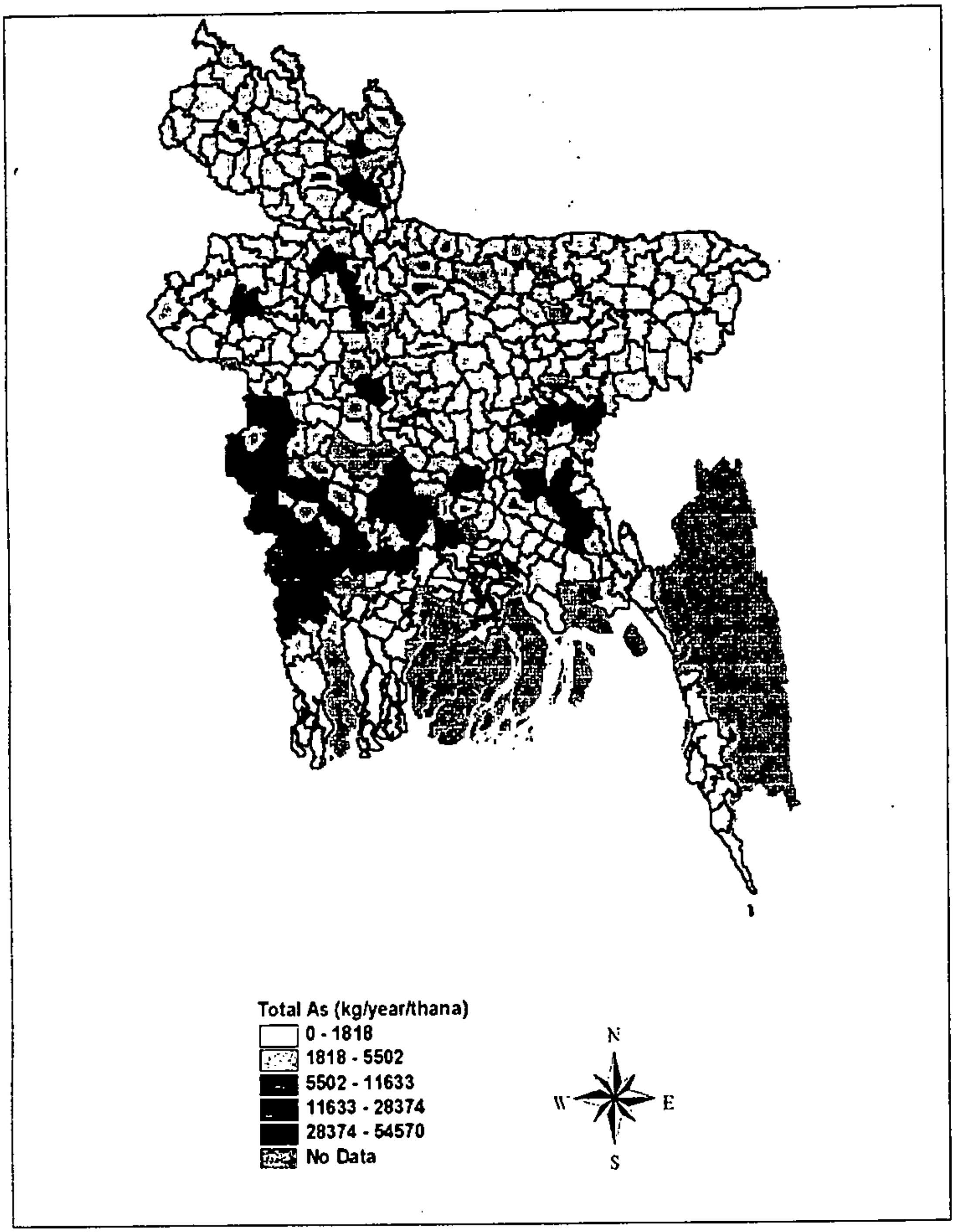


Figure 2.6: Estimates of arsenic extracted each year through shallow irrigation wells in Bangladesh

Based on the results of a study on water use (Ahmed and Smith, 1987), the average daily per capita use of water was assumed to be about 20 liters. Arsenic concentration in the well water was taken as the average of the values reported for that *thana* in the arsenic-database developed by DPHE/BGS (2000). Based on this simple methodology, it was estimated that about 46 metric tons of arsenic is extracted each year along with groundwater extracted from domestic tubewells. As expected, this amount is significantly lower compared to the estimated amount extracted with irrigation water.

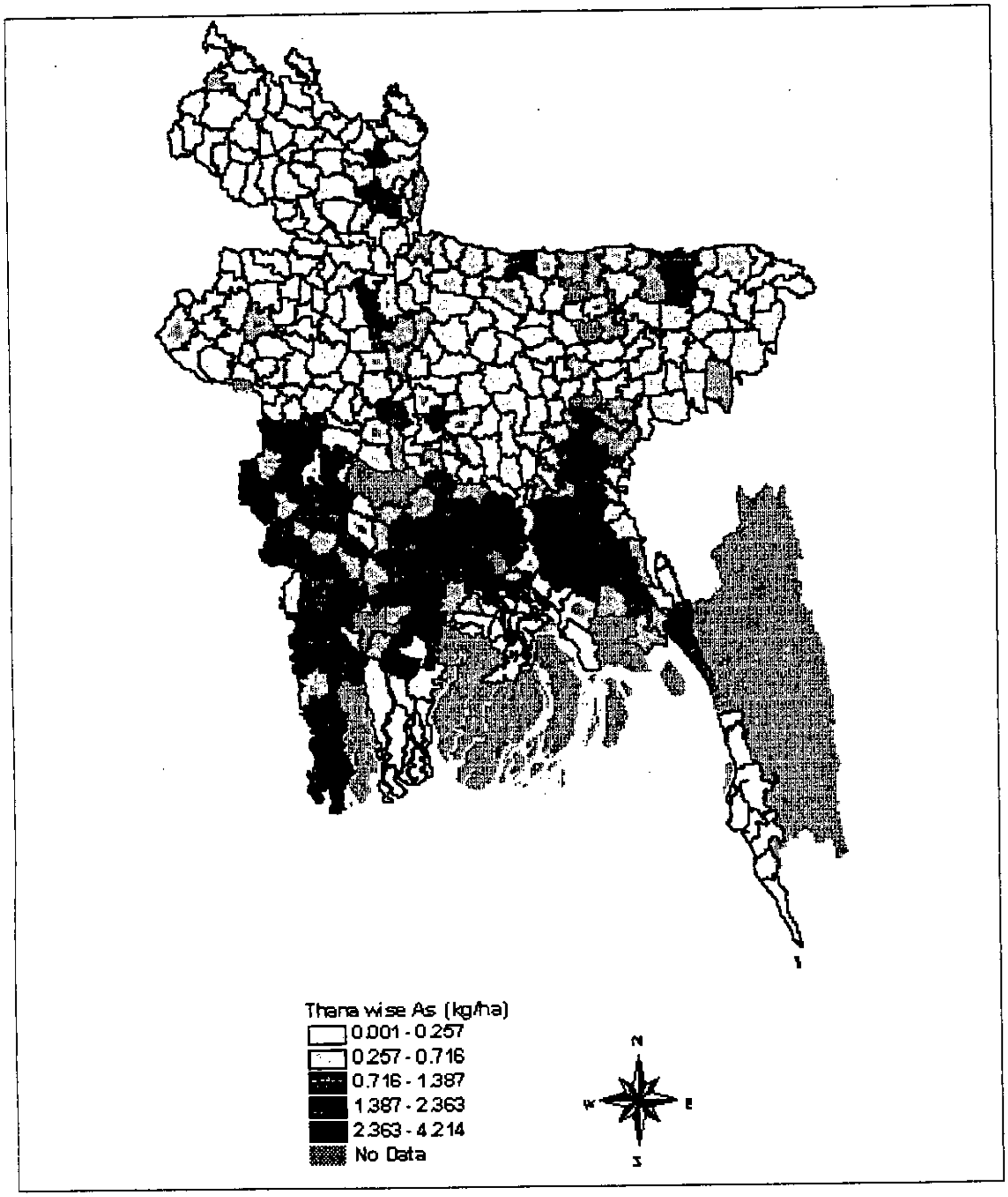


Figure 2.7: Estimates of arsenic deposition per hectare of irrigated area

2.4 FATE OF ARSENIC IN SOIL-WATER-PLANT ENVIRONMENT

Most research works on arsenic in Bangladesh have focused on its presence in and exposure through drinking/cooking water. Only limited research works have so far been carried out on understanding fate of arsenic in the soil-water-plant environment. 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.

Figure 2.8 schematically shows the fate of arsenic, extracted through groundwater, in the soil-water-plant environment. The arsenic pumped with tubewell water can (i) undergo transformation (e.g., through redox or microbial processes), (ii) volatilize into the atmosphere as a result of different biological transformations, (iii) undergo adsorption-desorption and thus become retained onto soil, washed away by surface runoff or leached into the groundwater, and (iv) be taken up by plants, and subsequently enter into the food chain. 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 MMA and DMA in agricultural soil.

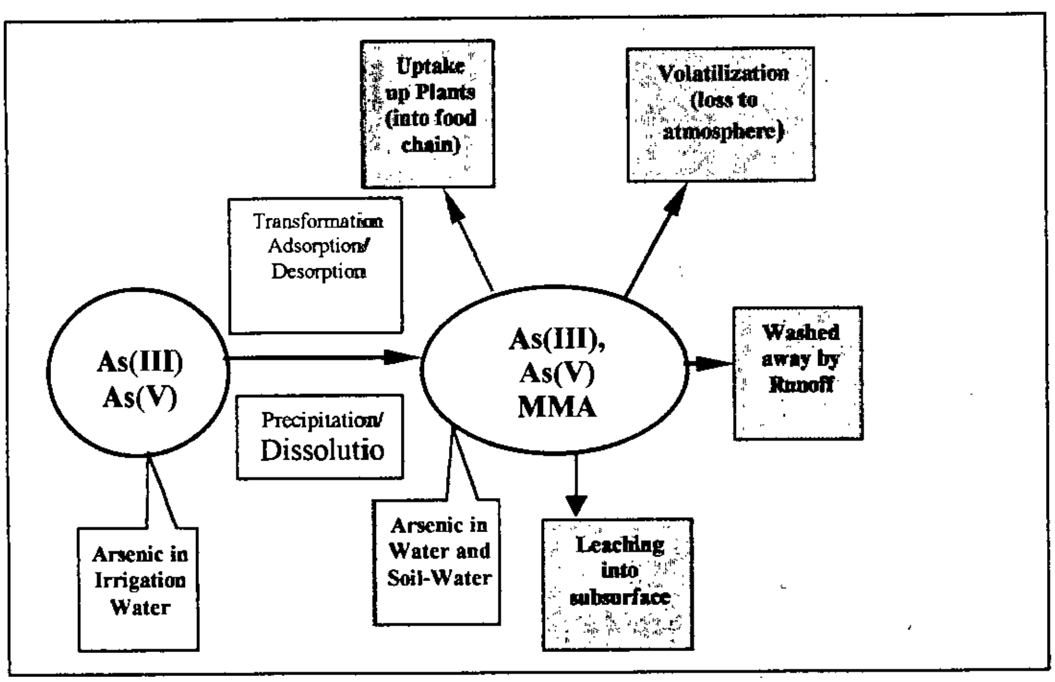


Figure 2.8: Fate of arsenic in soil-water-plant environment

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).

Adsorptoin-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, a cumulative accumulation of arsenic in surface soils is expected and some recent data (Huq et al., 2001; Alam and Sattar, 2000; Ullah, 1998) suggest arsenic concentration as high as 83 mg/kg in topsoil, against a background concentration of about 3-9 mg/kg. In general, higher arsenic concentrations have been reported in the top layer of soil (Huq et al., 2001). 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 not available. 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 leaching back into the subsurface. Microbial influences on adsorption-desorption is also unclear.

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 MMA and DMA were taken up to a lesser extent than the inorganic species. Since phosphate and arsenate are analogous in certain respects (e.g., adsorption characteristics), 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 effect of phosphate.

2.5 SUMMARY

Shallow tubewells are widely used for irrigation in Bangladesh. According to a recent BADC survey (BADC, 2002), a total of 865213 shallow tubewells and 23182 deep tubewells were used for irrigation during the 2001 boro season. The contribution of groundwater to total irrigated area was over 75% in 2001, and shallow tubewells accounted for over 60% of irrigated area. 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. 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.

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). According to the present study, an estimated 900 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. Amount of arsenic extracted with groundwater from domestic tubewells was estimated to be about 46 metric tons per year, which is about 20 times smaller than that extracted with irrigation water.

The huge quantity of arsenic being withdrawn with irrigation and domestic wells is a major concern. 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

ARSENIC IN AGRICULTURAL SOIL IN BANGLADESH

3.1 INTRODUCTION

Arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh, India and several other countries. In Bangladesh tubewell water extracted from shallow aquifers is the primary source of drinking/cooking water for most of its population. Besides domestic use, huge quantities of water from shallow aquifer are also used for irrigation during the dry season. Since its detection in late 1993 in Bangladesh, much of the research works on arsenic have focused on its presence in and exposure through drinking/cooking water. However, widespread use of groundwater for irrigation suggests that ingestion of irrigated crops could be another major exposure route for arsenic. Besides, phytoxicity due to increased arsenic in soil/water and its long-term impact on agricultural yield is another major concern.

Recent studies by Meharg *et al.* (2002) and Huq *et al.* (2001) demonstrate significant uptake of As by rice and a range of vegetables commonly grown in Bangladesh. Greenhouse studies by a number of researchers have revealed that an increase in As in soils leads to an increase in the levels of As in edible vegetables (Burló *et al.*, 1999; Carbonell-Barrachina *et al.*, 1999; Helgensen and Larsen, 1999) with many complex factors affecting bioavailability, uptake and phytotoxicity of As (Carbonell-Barrachina *et al.*, 1999). Like other heavy metals, arsenic is toxic to plant (Martin *et al.* 1993) and its discharge into the environment must be carefully controlled and minimized. Twenty percent loss of crop (cereal) production due to high concentration (20 ppm) of arsenic in plant body was reported by Davis *et al.* (1998).

Although arsenic in irrigated agriculture is a major concern, relatively limited research works have been carried out in this area. More studies are needed to develop a reliable database on the presence of arsenic in irrigation water, irrigated soil and food samples, and to assess their interrelationships.

This Chapter presents the results of studies done to assess the presence of arsenic in irrigation water and in agricultural soil. Detailed evaluations of arsenic profiles of both irrigated and non-irrigated agricultural soils have been presented in this chapter. Assessment of arsenic profile in soil has been made for both arsenic-affected and unaffected areas.

3.2 MATERIALS AND METHODS

In this study, two arsenic affected areas have been selected for detailed characterization of irrigation water, soil and crop/vegetables produced in the irrigated soils. These two locations are: (i) Sonargaon, Narayangonj and (ii) Srinagar, Munshiganj. Water, soil and crop samples have also been collected from a less affected (i.e., with low levels of arsenic in shallow wells) area in the Dinajpur district in northern Bangladesh. For intensive sampling, one rice field (i.e., the whole area under the influence of one irrigation well) was selected at each of the two sampling locations (Sonargaon and Srinagar). Besides these sites, water, soil and crop samples have been collected from Comilla and Noakhali districts.

3.2.1 Collection of Water and Soil Samples

3.2.1.1 Collection of Water Samples

At each of the two sites in Sonargaon and Srinagar, 10 irrigation wells were monitored over the entire irrigation season (about three months). During the first month of the irrigation season when the irrigation intensity was low (10 to 12 hours per day), groundwater samples from the irrigation wells were collected once every two weeks. Later in the season, when irrigation intensity increased (20 to 22 hours per day), water samples were collected every week. Besides, surface water samples were also collected from the ponds and canals, which are used for irrigating vegetable fields. At the Srinagar site, water samples were collected from two ponds used for irrigating potato fields. At the Sonargaon site, water samples were collected from two ponds and from three different sections of a canal used for irrigating vegetable fields. Water samples were also collected from a shallow hand-pump tube well used for irrigating a vegetable (cauliflower) field. Besides Srinagar and Sonargaon, five groundwater samples were also collected from Dinajpur site. At Comilla site, water samples were collected from two irrigation wells used for irrigating paddy fields and at the Noakhali site, water samples were collected from two ponds and two tube wells used for irrigating vegetable fields. At each location, water samples were collected in two pre-washed plastic bottles. One bottle was acidified in the field with concentrated hydrochloric acid for analysis of metal ions.

3.2.1.2 Collection of Soil Samples

In a typical rice 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. For intensive sampling, one rice field (i.e., the whole area under the influence of one irrigation well) was selected at each of the two sampling locations (Sonargaon and Srinagar). At the Srinagar site, the rice (BR-29 variety) field was about 3 hectares in size and it was divided into twenty-one sub areas (see Fig. 3.1). At the Sonargaon site, the rice (BR-29 variety) field was about 4 hectares in size and was divided into 45 sub-areas (see Fig. 3.2). At each rice field site, soil samples were collected both from agricultural land (referred to as *field* samples) as well as the shallow irrigation canals (referred to as *canal* samples).

While collecting soil samples, efforts were made to collect core samples with a depth close to the root zone depth for the particular crop. The root zone depths of various plants are shown in Table 3.1. Based on this data, it was decided that a 750mm sampler would be used for collecting soil core samples.

Soil samples were collected by inserting into the soil, a 37.5 mm diameter PVC pipe sampler, about 750 mm in height. A 3-pound hammer was used to insert the pipe sampler to required (root zone) depth. After withdrawing the sampler along with the soil core, its both ends were sealed with tapes to reduce contact with air and transported to the environmental engineering laboratory of BUET. Besides paddy fields, soil samples were also collected (following the same method) from other agricultural fields growing vegetables. These fields did not receive irrigation water from shallow wells. However, these were irrigated by water from nearby surface water bodies (ponds/canals).

Table 3.1: Root zone depth of various vegetable plants

Crop Type	Scientific name	Effective root zone depth (cm)
Wheat	Trticum aestidum	90 (80-120)
Pulse	Vigna mungo	50 (40-60)
Brinjal	Solanum meslonyena	70 (70-120)
Cabbage	Brassica capitata	40 (30-50)
Carrot	Daucus carota	60 (50-70)
Cauliflower	Brassica aleracea var.betrytis	40 (30-50)
Paddy	Oryza sativa	50 (50-60)
Potato	Solanum tuberosum	50 (40-60)
Sweat Potato	Ipomoea batatus	100 (90-150)
Tomato	Lucopersiem esculentum	70 (70-150)
Arum	Colocasia esculenta	40 (30-50)
Lalshak	Amaranthus gangeticus	40 (30-50)

Source: FAO 1984; Rashid 1990
Reference: Manual on Irrigation and Soil Water Engg. By
Md. Harun-ur-Rashid, Principal Scientific Officer,
Irrigation and Water management division,
Bangladesh Agricultural Research Institute, Gazipur.
June, 1997

Bangladesh, depending on location, dry season irrigation for rice commences between last week of December and first week of February and continues for a period of about three to three and a half months. At the Srinagar site, soil core samples were collected at three different times. The first sampling was carried out on 6th February 2002 (at the beginning of the 2001-2002 dry season), about one week after the commencement of irrigation at the site. During this time, a total of 29 soil core samples were collected. Among these, 11 are *field* samples, 12 are *canal* samples (see sampling locations in Fig. 1). The remaining 6 core samples were collected from four different potato fields at Srinagar. All these four fields were irrigated by water from ponds located close to the fields. The second sampling operation was carried out after the end of irrigation season and before the commencement of flood on 22nd June 2002.

During this time, a total of five *field* samples were collected from the rice field site at Srinagar. The third and final sampling operation was carried out at the beginning of the 2002-2003 dry season. As a part of this sampling operation, 8 *field* core samples from the rice field and five core samples from potato fields were collected on 26th November 2002.

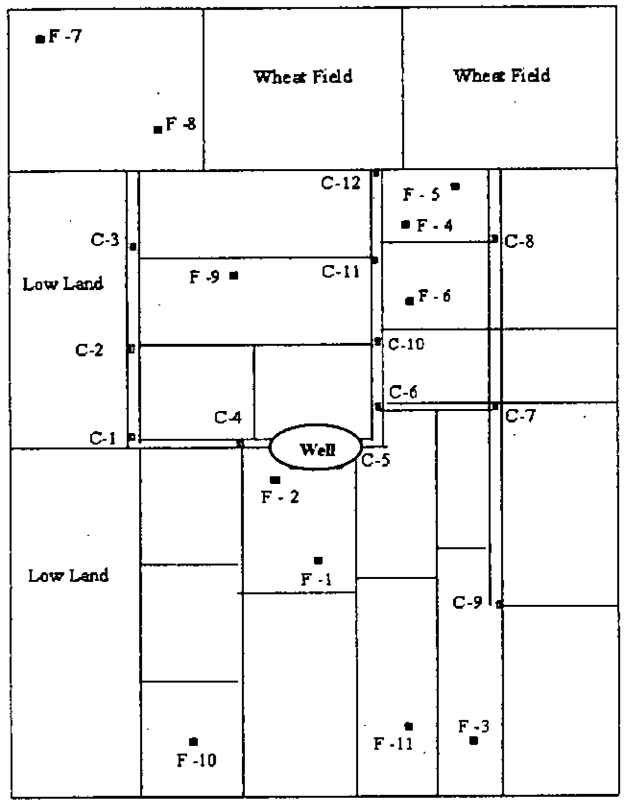


Figure 3.1: Schematic representation of Srinagar paddy field site along with sampling locations and identification numbers (F = Field Sample, C = Canal Sample)

At the Sonargaon site, the first sampling operation was carried out on 3rd March 2002 (at the beginning of 2001-2002 dry season), about 3 weeks after the commencement of irrigation at the site. During this time, a total of 42 soil core samples were collected. Out of these 42 samples, 14 are *field* samples, 16 are *canal* samples (see sampling locations in Fig. 2). The remaining 12 core samples were collected from 12 different vegetable fields. Among these, five were tomato fields, two *lalshak* fields, two *datashak* fields, two cabbage fields and one cauliflower field. Except for the cauliflower field, all vegetable fields were irrigated by pond or canal water located close to the fields. The cauliflower field was irrigated by water from a shallow hand-pump tubewell. The second and final sampling operation at the Sonargaon site was carried out at the beginning of the 2002-2003 dry irrigation season. As part of this sampling operation, 6 *field* core samples from the rice field and two core samples from vegetable fields were collected on 18th December 2002.

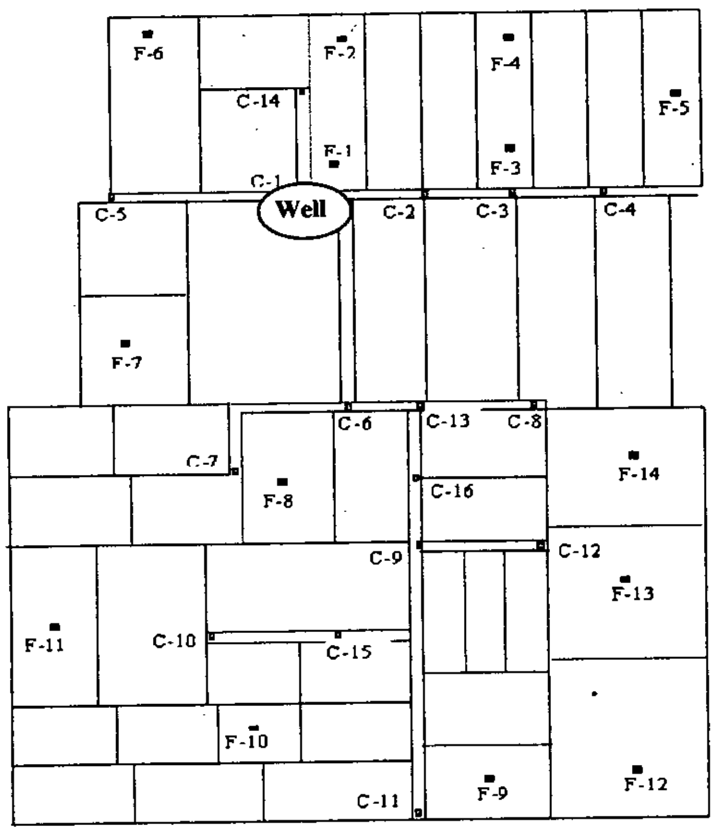


Figure 3.2: Schematic representation of Sonargaon paddy field site along with sampling locations and identification numbers (F = Field Sample, C = Canal Sample)

At the Dinajpur site, a total of ten soil core samples were collected from five different fields (two from each field). Four of the fields were growing *China Irri* variety of rice and one was growing *Chandina* variety of rice. Besides, two soil core samples were collected from two different paddy fields used for Irri variety of rice at Comilla site and four soil core samples were collected from vegetable fields (two arum and two datashak fields) at the Noakhali site.

3.2.2 Laboratory Analysis of Water and soil Samples

3.2.2.1 Water Samples

Groundwater and surface water samples were analyzed for arsenic and a range of other water quality parameters. Arsenic analysis was carried out with an AAS (Shimadzu, AA6800) attached with a graphite furnace.

3.2.2.2 Soil samples

Before analysis, each *field* soil sample core 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. The *canal* samples were divided into two segments, top 150 mm and the next 150 mm. The soil samples collected from the vegetable fields were also divided into four segments (like the *field* samples) before analysis. Each segment of soil sample was analyzed for total arsenic after digestion.

Briefly, the soil digestion procedure consisted of the following steps: (i) oven-dry each segment of soil sample at 110°C for 24 hours, (ii) take 5 gram oven-dried sample in a volumetric flask, add 2.5 ml concentrated nitric acid and 7.5 ml of concentrated hydrochloric acid to the soil sample and keep it overnight, (iii) heat the sample for 2 to 3 hours to boiling, then allow it to cool and adjust the volume to 500 ml by adding deionized water, and finally (iv) filter the sample and store it for analysis. Arsenic analysis was carried out with an AAS (Shimadzu, AA6800) attached with a graphite furnace.

3.3 RESULTS AND DISCUSSION

3.3.1 Arsenic in Irrigation Water

Arsenic concentration in groundwater samples from 10 irrigation wells (which were monitored) at Srinagar site varied from about 170 ppb to about 600 ppb. Arsenic concentration in the well water used for irrigating the rice field site at Srinagar varied from 220 to 537 ppb. At the Sonargaon site, arsenic concentrations in the 10 monitored irrigation wells varied from about 50 ppb to over 400 ppb. Arsenic concentration in the rice field irrigation water varied from about 83 ppb to 354 ppb. At both sites, arsenic concentrations of irrigation well water varied significantly with time.

It is not clear why arsenic concentration of irrigation water varies so significantly with time. One possible reason behind such variation could be the high flow rate of the irrigation wells and slower kinetics of arsenic mobilization. However more studies are needed to better reason behind such variation.

Arsenic concentrations in all groundwater samples from the Dinajpur district were below detection limit (i.e., below 1ppb). At the Comilla site, concentration of arsenic was 252ppb and 212ppb in the two irrigation wells respectively.

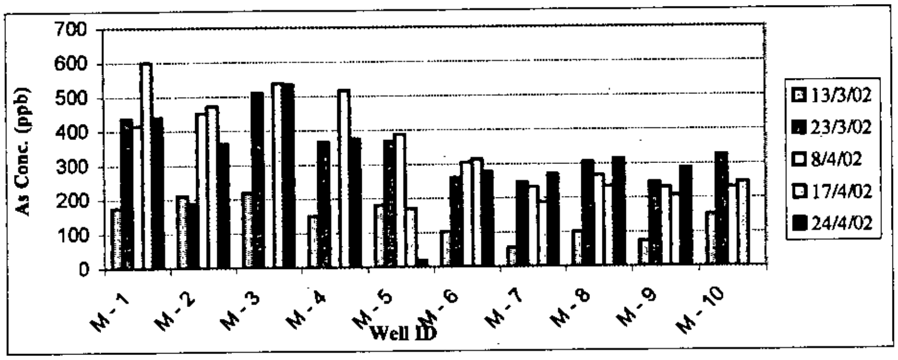


Figure 3.3: Arsenic concentrations of Srinagar monitoring irrigation wells.

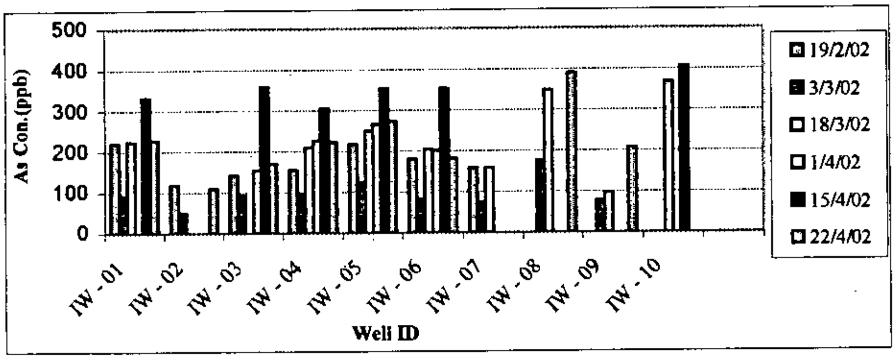


Figure 3.4: Arsenic concentrations of Sonargaon monitoring irrigation wells.

Of the two pond water samples (used for irrigating potato fields) collected from the Srinagar site, arsenic concentration in one was 37 ppb and in the other it was 1 ppb (which is also the machine detection limit). Surface water usually contains relatively lower level of arsenic. During field visits it was observed that the pond with higher level (37 ppb) of arsenic is located about 300 ft from an irrigation well, whose arsenic concentration varied from 187 to 472 ppb). The higher level of arsenic in this pond water may result from overflow of groundwater from this nearby irrigation well containing high levels of arsenic.

At the Sonargaon site, concentration of arsenic was 2 ppb in one pond water sample and 10 ppb in the other. Concentrations of arsenic in three canal water samples were < 1 ppb, 8 ppb and 35 ppb. Arsenic concentration in the shallow hand-pump tube well water used for irrigating a vegetable (cauliflower) field was 176 ppb. At the Noakhali site, concentration of arsenic was <1ppb in one pond water sample and 29ppb in the other. Concentrations of arsenic in two tube wells were 159 and 472ppb.

3.3.2 Arsenic in Irrigated agricultural Soil

3.3.2.1 Arsenic in soil of Irrigated Rice Field

Figures 3.5 and 3.6 show arsenic profiles of the eleven *field* and twelve *canal* soil core samples, respectively, collected from the Srinagar site one week after commencement of irrigation. This field was irrigated by groundwater from a shallow tube well, whose arsenic concentration varied from 220 ppb to 537 ppb. Figures 3.7 and 3.8 show arsenic profiles of the twelve *fields* and fifteen *canal* soil core samples, respectively, collected from the Sonargaon site about three weeks after commencement of irrigation. This field was irrigated by groundwater from a shallow tube well, whose arsenic concentration varied from 83 ppb to 354 ppb. Figure 3.9 shows arsenic profiles of the ten soil core samples collected from Dinajpur. These core samples were collected for rice fields irrigated with groundwater having arsenic concentration less than 1 ppb. Figure 3.10 shows arsenic profiles of the two soil core samples collected from Comilla site. These core samples were collected for two rice fields irrigated with groundwater having arsenic concentrations 252ppb and 212ppb, respectively.

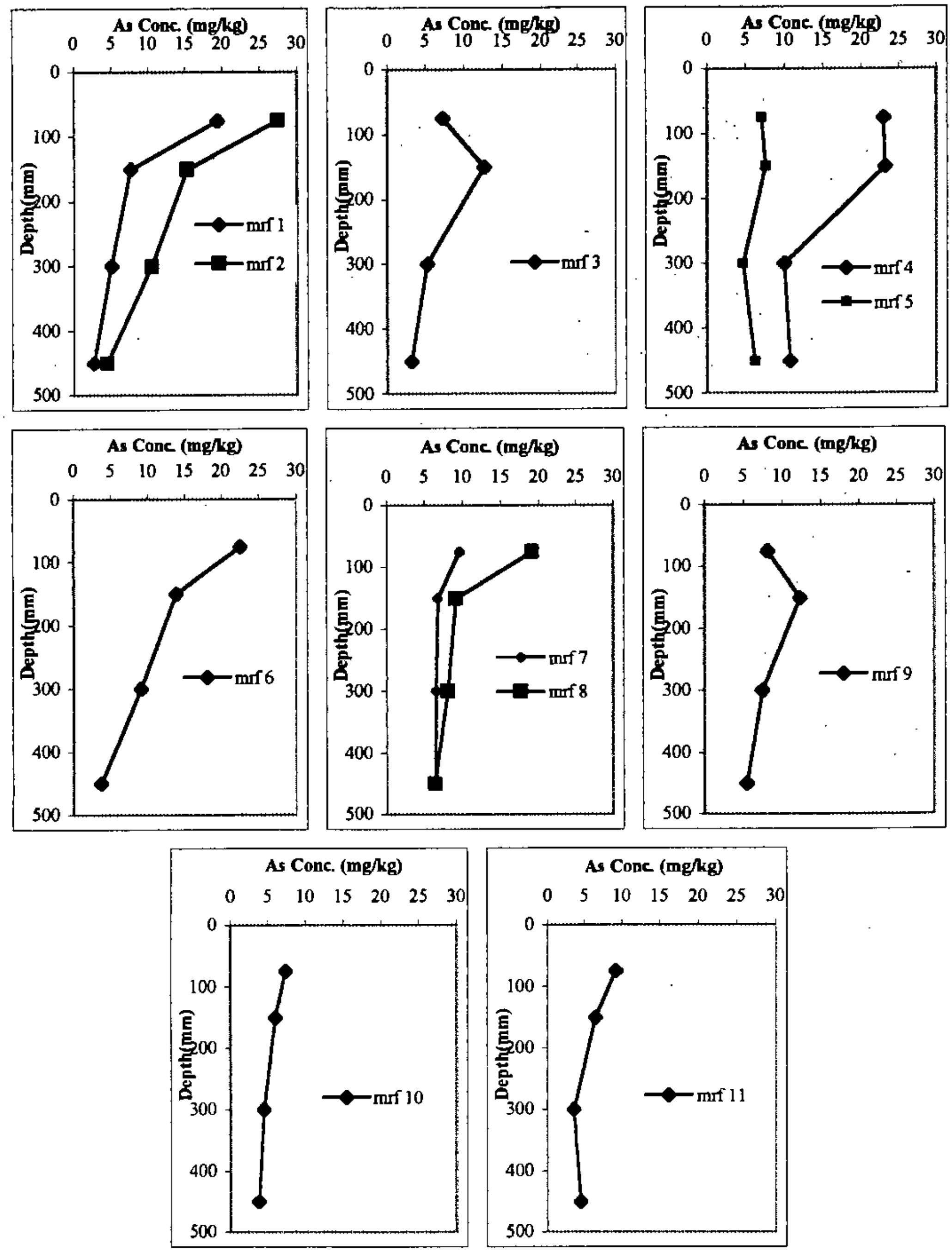


Figure 3.5: Arsenic profiles of "field" samples collected from Srinagar, Munshigonj site (mrf =Munshigonj Rice Field)

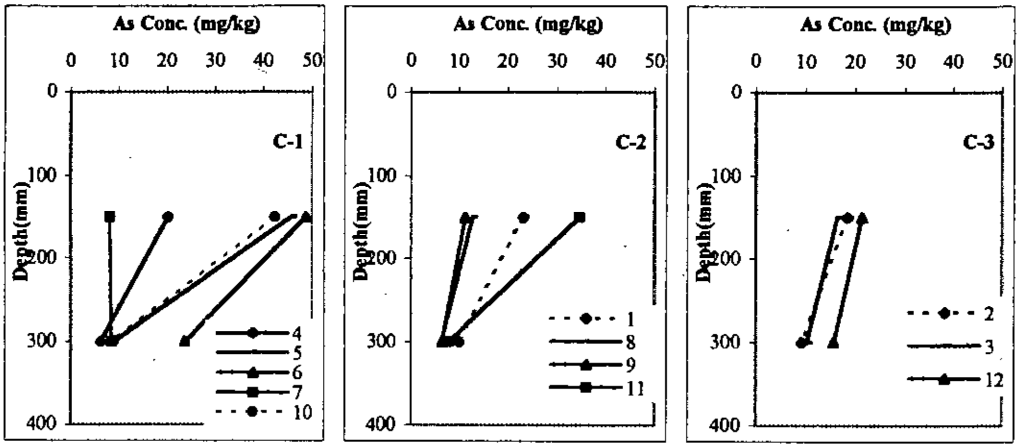


Figure 3.6: Arsenic profiles of "canal" samples collected from Srinagar site

Arsenic profiles in the irrigated rice fields at the Srinagar and Sonargoan sites show accumulation of higher levels of arsenic primarily in the top layers (typically top 75 to 150 mm) of soil. In general, arsenic concentration in soil decreased with depth. Arsenic accumulations in the canal samples were relatively higher compared to the *field* samples. Among the *field* samples at the Srinagar site, arsenic concentration in the topsoil layer (top 75 mm) varied from about 7 to 27.5 mg/kg. The mean arsenic concentration in the top layer (top 75 mm) was 14.5 mg/kg, while that in the layer (300 to 450 mm) was 4.9 mg/kg. As expected, arsenic concentration in the *canal* samples were relatively much higher compared to the *field* samples, with a mean arsenic concentration of 25.3 mg/kg in the top layer (top 150 mm) of canal samples.

At the Sonargaon site, arsenic concentration in the topsoil layer varied from about 3.2 to 19 mg/kg. The mean arsenic concentration in the topsoil layer (top 75 mm) was 8.9 mg/kg, while that at the bottom layer was 6.07 mg/kg. Like the Srinagar site, arsenic concentrations in the *canal* samples were much higher compared to the *field* samples. Mean arsenic concentration in the top (top 150 mm) layer of canal samples was found to be about 15.4 mg/kg. The higher arsenic concentration in the upper soil layers in the rice field samples appears to be due to irrigation with arsenic-rich groundwater. The higher accumulation of arsenic at the Srinagar site (compared to the Sonargoan site) is probably partly related to higher arsenic concentration in the irrigation water at Srinagar site.

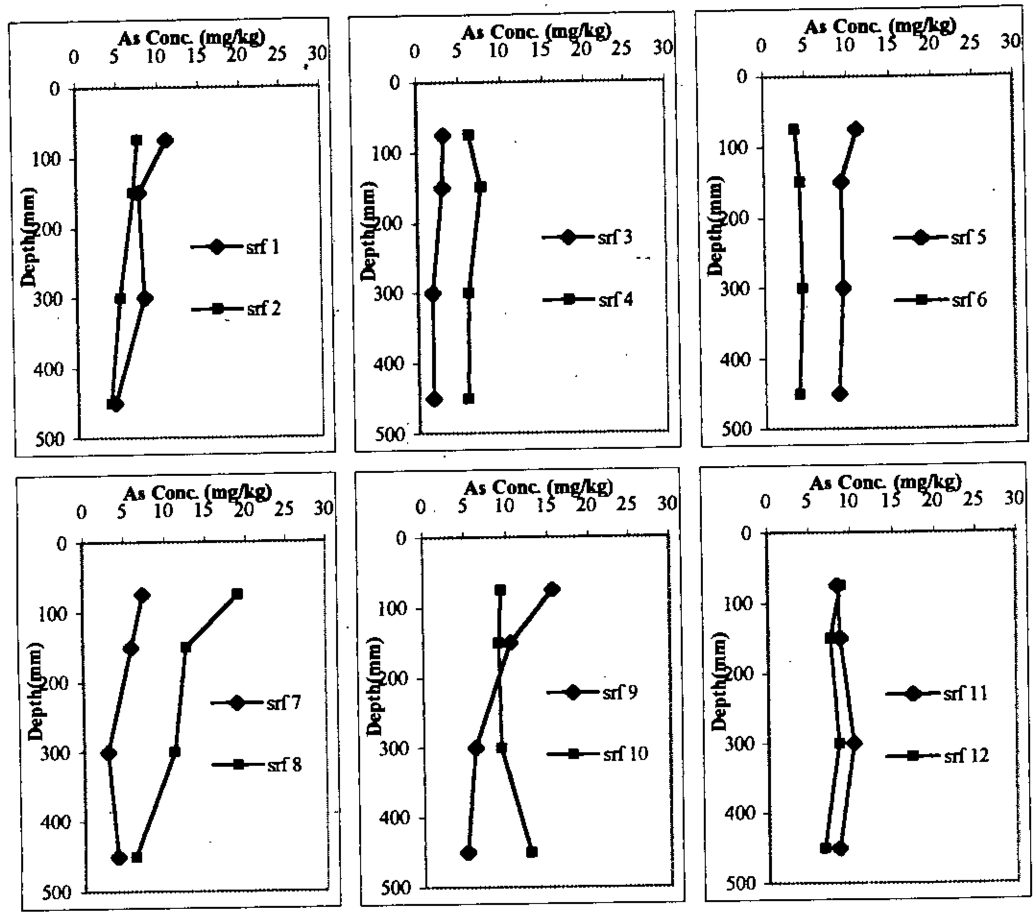


Figure 3.7: Arsenic profiles of "field" samples collected from Sonargaon site (srf = Sonargaon Rice Field)

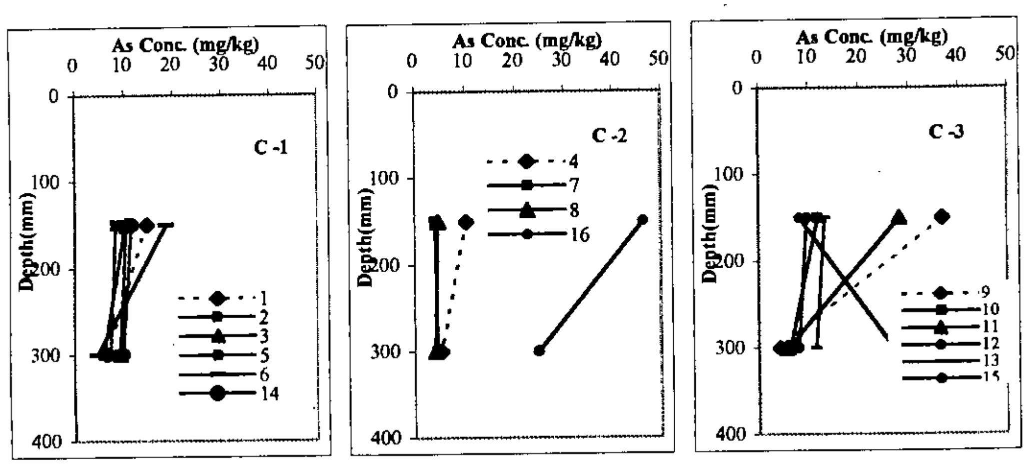


Figure 3.8: Arsenic profiles of "canal" samples collected from Sonargaon site

At the Dinajpur site where irrigation water contained arsenic at below detection level (i.e., less than 1 ppb), accumulation of arsenic in the soil core samples were insignificant compared to those at Srinagar and Sonargaon sites. The arsenic concentration in the top soil layers (top 75 mm) varied from 0.10 to 2.75 mg/kg. The mean arsenic concentration in the top soil layer (top 75 mm) was 1.04 mg/kg, and that for the bottom layer (300 to 450 mm) was 2.22 mg/kg. As can be seen from Fig. 7, unlike the Srinagar and Sonargaon sites, a slight increase of arsenic concentration with depth was observed for the samples from Dinajpur site. As discussed later, a similar trend was also observed for the soil core samples collected from vegetable fields at the Srinagar and Sonargaon sites that were not irrigated by arsenic contaminated well water.

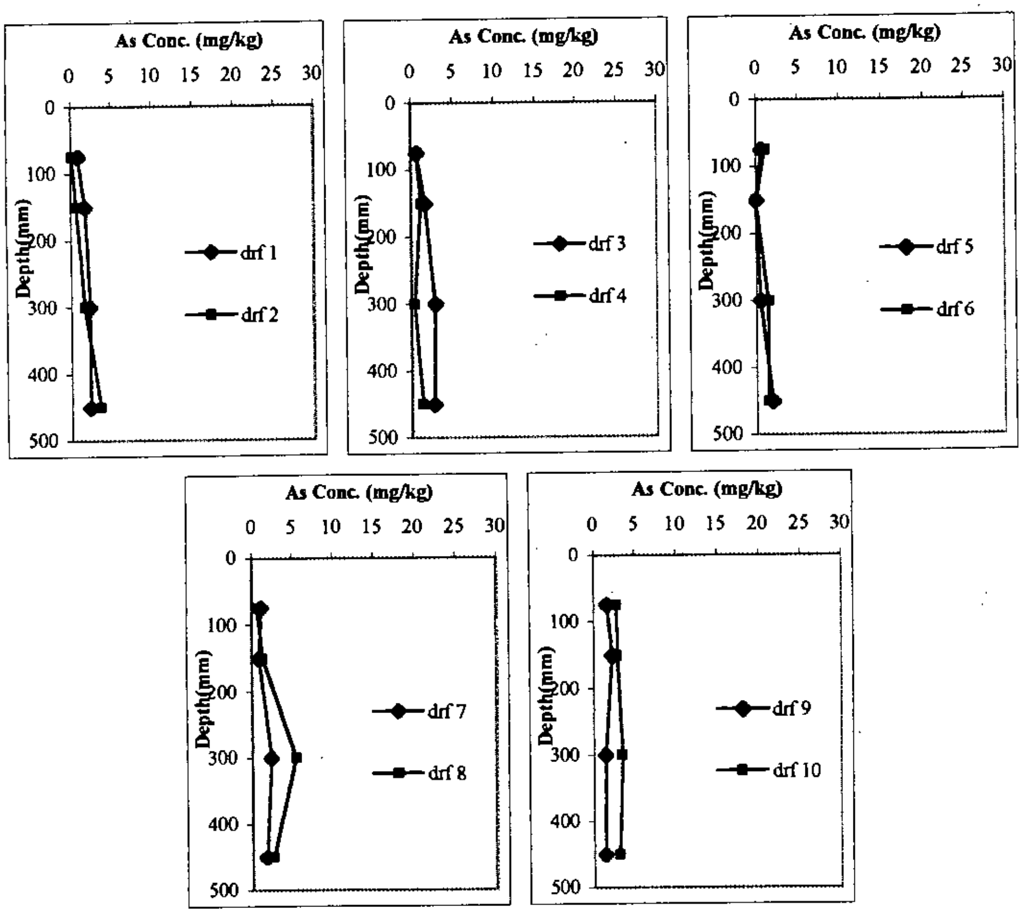


Figure 3.9: Arsenic profiles of soil samples collected from Dinajpur site

At the Comilla site where irrigation water contained arsenic 252ppb and 212ppb, accumulation of arsenic in the soil core samples was low compared to those at Srinagar and Sonargaon sites. The arsenic concentration in the topsoil layers (top 75 mm) varied from 3.54 to 2.13 mg/kg. As can be seen from Fig.3.10, like the Srinagar and Sonargaon sites, a slight decrease of arsenic concentration with depth was observed for the samples from Comilla site.

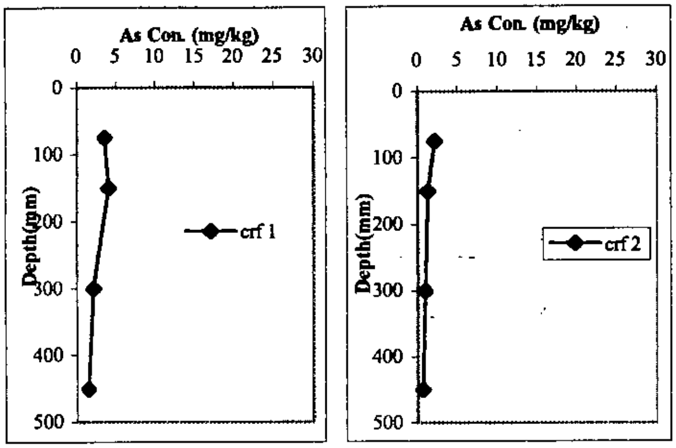


Figure 3.10: Arsenic profiles of soil samples collected from Comilla site (crf = Comilla Rice Field)

3.3.2.2 Arsenic in soil of Vegetable Fields

Figure 3.11 shows arsenic profile of six soil cores collected from potato fields in Srinagar. These fields were irrigated by surface water (from pond) with relatively low level of arsenic. Four of these six vegetable fields were irrigated by water from a pond with arsenic concentration of 37 ppb; and the rest two were irrigated by another pond water with arsenic concentration of 1 ppb. Figure 3.12 shows arsenic profiles of soil core samples collected from the vegetable fields from Sonargaon. Figure 3.13 shows arsenic profiles of soil core samples collected from the vegetable fields from Noakhali.

Compared to the rice field, arsenic concentrations in the soil samples collected from the vegetable fields were significantly lower. For example, mean arsenic concentration in the topsoil layer (top 75 mm) at the Srinagar site was 7.8 mg/kg, compared to 14.5 mg/kg for rice field samples. For the Sonargoan site, the mean for the top layer (top 75 mm) of vegetable field samples was 3.5 mg/kg, compared to 8.9 mg/kg for the rice field samples. It is apparent that the higher arsenic concentration in the rice field soil samples, both at Srinagar and Sonargoan sites, is due to the presence of high level of arsenic in the irrigation water. It is interesting to note that unlike the rice fields at Srinagar and Sonargaon, arsenic concentrations of soils in the vegetable fields in most cases either did not vary significantly with depth or increased slightly with depth. A similar trend was also observed for the rice field samples collected from Dinajpur where irrigation water contained very little arsenic.

At Noakhali site, arsenic concentration in topsoil layer (0-75mm) varies 1.99 to 4.68mg/kg. Though high arsenic concentration in tube well water, vegetable fields are not high contaminated because water is used for irrigating vegetable fields in insignificant amount. Arsenic concentration in vegetable fields increases slightly with depth like Srinagar and Sonargaon vegetable fields.

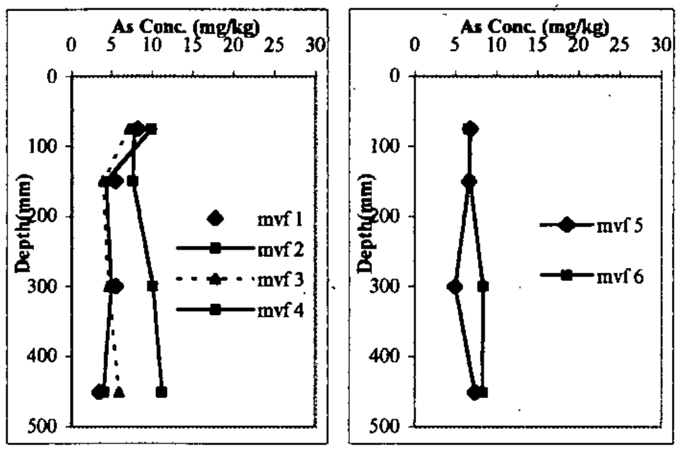


Figure 3.11: Arsenic profiles of potato field soil samples collected from Srinagar, Munshigonj site. (mrf = Munshigonj Vegetable Field)

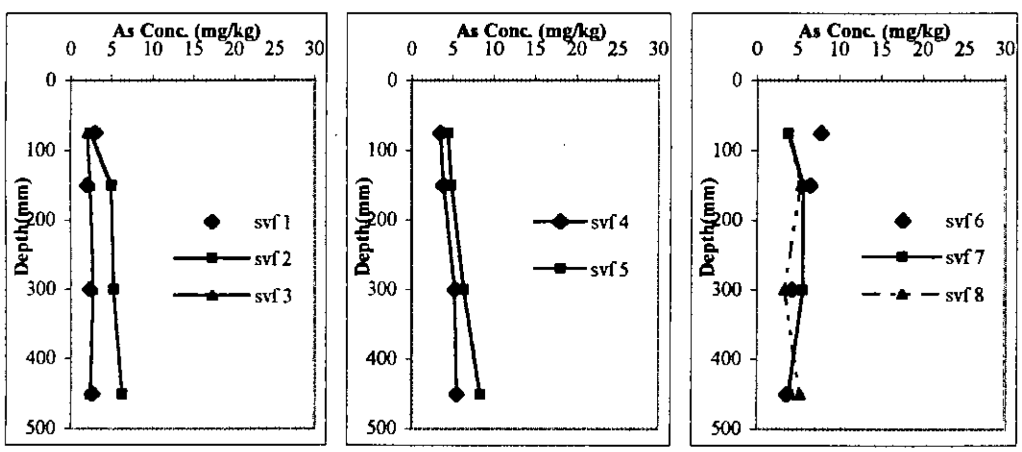


Figure 3.12: Arsenic profiles of vegetable field soil samples collected from Sonargaon site. (svf = Sonargaon Vegetable Field)

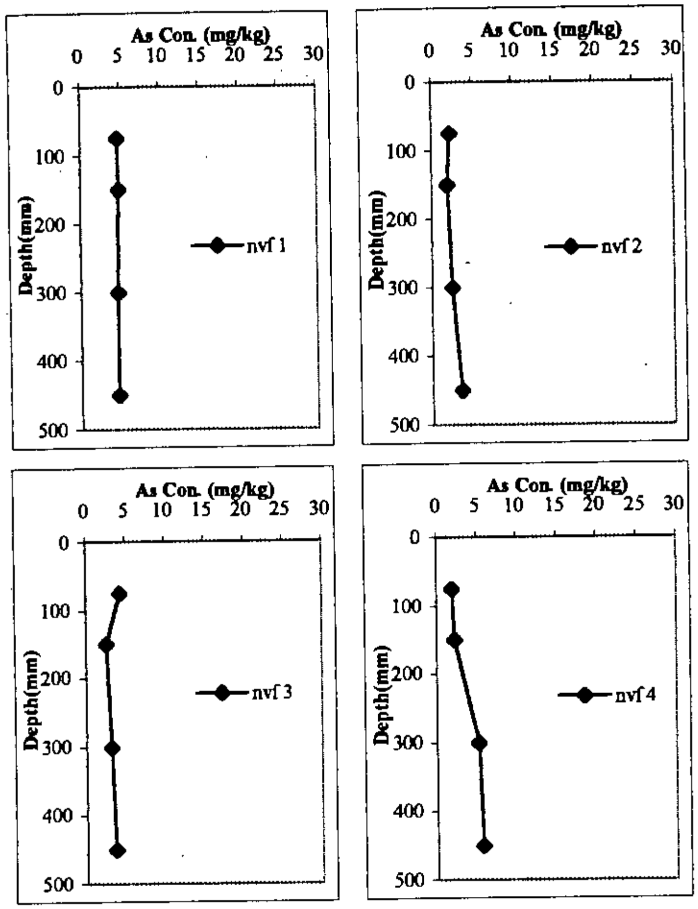


Figure 3.13: Arsenic profiles of Vegetable field samples collected from Noakhali site

3.3.3 Variation of Arsenic with distance from irrigation well

Groundwater from the irrigation well is carried to the sub-areas of paddy field through shallow irrigation canals. In order to assess the variation of the concentration of arsenic of soil with distance from irrigation well, soil samples from shallow irrigation canals (referred to as canal samples) were collected. Figure 3.14 and 3.15 show the variation of arsenic concentrations in canal soil samples with distance from irrigation well for Srinagar and Sonargaon sites, respectively. At Srinagar site, arsenic concentration of canal samples decreases with distance from irrigation well but at Sonargaon site, it shows slightly increasing. So no correlation between arsenic concentration of soil and distance from the well is found. It should be noted that retention of arsenic by soil depends on a number of factors including chemical form of arsenic, characteristics of soil, p^H, presence of complexity ions (for adsorption), etc.

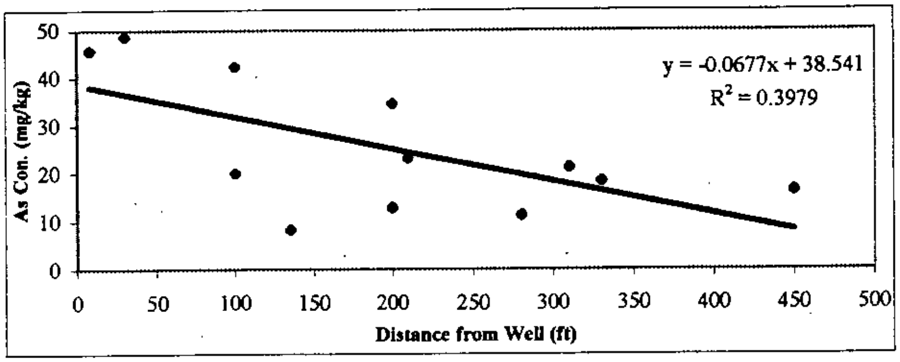


Figure 3.14: Vriation of arsenic concentration of Srinagar canal samples with distance along the canal from irrigation well.

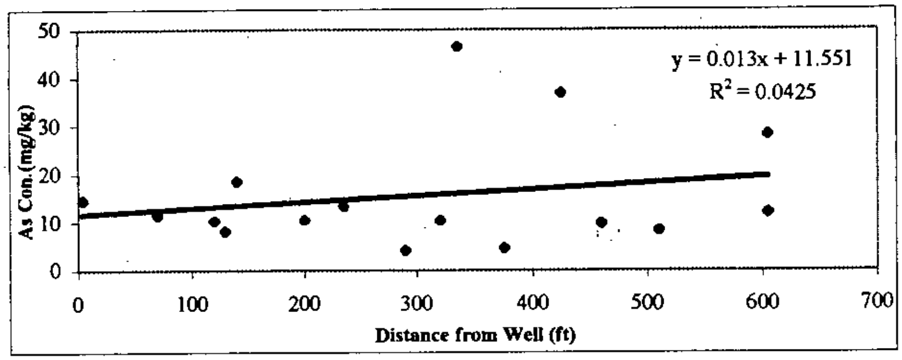


Figure 3.15: Vriation of arsenic concentration of Sonargaon canal samples with distance along the canal from irrigation well.

3.3.4 Accumulation of Arsenic in Soil Over Time

In order to assess the accumulation of arsenic in soil over time, soil core samples from rice and vegetable fields were collected at the end of the 2001-2002 irrigation season and also at the beginning of the 2002-2003 irrigation season. At the Srinagar site, core samples were first collected on the 6th February 2002 (at the beginning of the 2001-2002 dry season), about one week after the commencement of irrigation at the site. The second sampling operation was carried out on the 22nd June 2002, just before commencement of flood. During this time, five soil core samples were collected from five sub-areas of the rice field, from where core samples were also collected during the first sampling. The third and final sampling operation was carried out on the 26th November 2002 at the beginning of the 2002-2003 dry season. During this time core samples were collected from 8 sub-areas (including the five sub-areas covered during the second sampling) of the rice field. In addition, five core samples were also collected from potato fields, which were covered during the first sampling. Figure

3.16 shows arsenic profiles of soil core samples collected from the Srinagar rice fields at three different times.

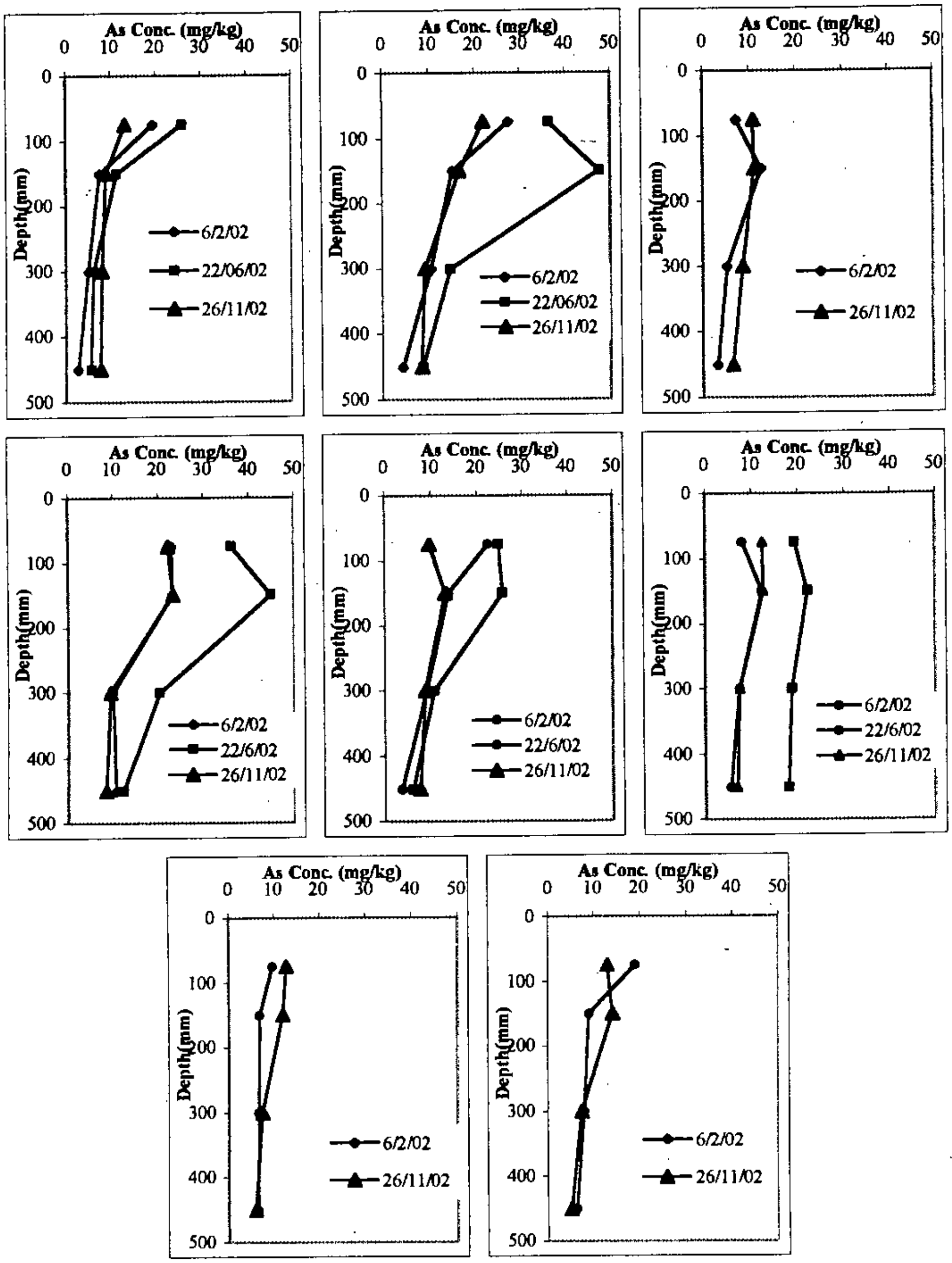


Figure 3.16: Arsenic profiles of soil samples from Srinagar rice field at different times

Figure 3.16 shows that, in general, arsenic concentration in soil was significantly higher at the end of the irrigation season, compared to concentrations at the beginning of the season. However, after the flood (during which the rice field at the Srinagar site was under floodwater for prolonged periods of time), arsenic concentration in soil came down to levels comparable to those at the beginning of the (2001-2002) irrigation season. The reduction in arsenic concentration in soil after the flood may result from bio-geochemical processes (e.g., bio-methylation, dissolution/ desorption) occurring in the rice fields. Thus it appears that over the monitoring period of about one year, arsenic concentration in the rice field at Srinagar did not increase significantly.

At the Sonargaon site, the first sampling operation was carried out on 3rd March 2002 (at the beginning of 2001-2002 dry season), about 3 weeks after the commencement of irrigation at the site. The second and final sampling operation at the Sonargaon site was carried out on 18th December 2002 at the beginning of the 2002-2003 dry irrigation season. During this time, six core samples from the rice field and 2 core samples from vegetable fields were collected. Core samples were also collected from these eight areas during the first sampling.

Figure 3.17 shows arsenic profiles of six sets of soil core samples collected from the Sonargaon rice fields at two different times. Of the six sets, three showed significant increase of arsenic concentration over the one-year monitoring period; while the other three sites did not show any significant increase in arsenic concentration. Unlike the Srinagar site, soil core samples were not collected from the Sonargaon site before the commencement of flood, and so it is not clear whether flood had any impact on arsenic profile at the Sonargoan site.

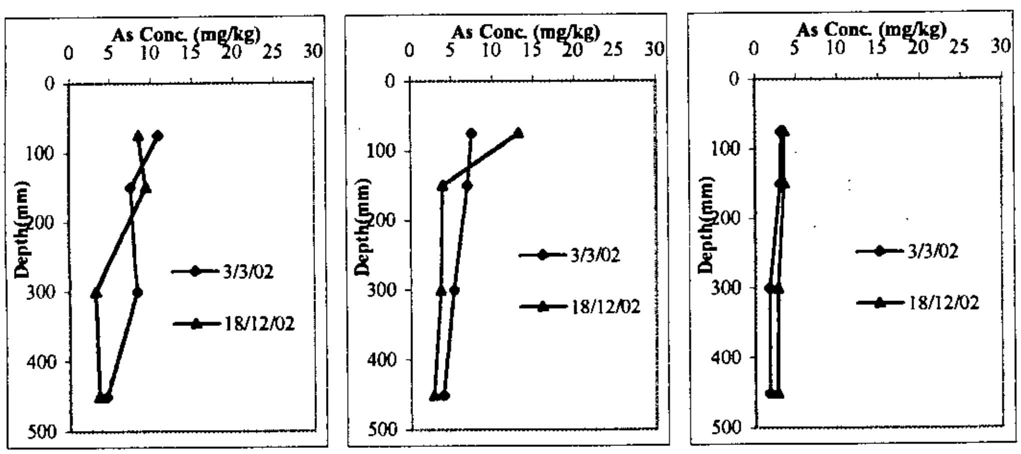


Figure 3.17(a): Arsenic profiles of soil samples from Sonargaon rice field at different times

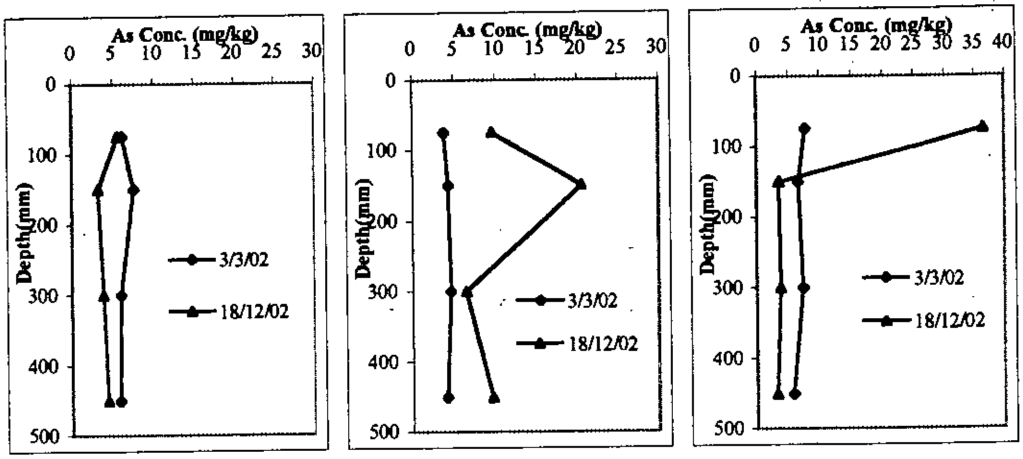


Figure 3.17(b): Arsenic profiles of soil samples from Sonargaon rice field at different times

During field visits, it was gathered that *boro* rice cultivation with groundwater irrigation at the Srinagar field site started about 14 years ago. Before this time, this field was not used for agriculture. *Boro* cultivation using groundwater irrigation at the Sonargoan site began about 9 years back. Before that, the field was used only for *aman* (wet season rice) cultivation. In the absence of data, it is not clear whether the irrigation water at these sites contained arsenic in the past. So it is not possible to estimate how long it took for the arsenic in the soil to reach this level. From the limited results gathered in this study, it appears that the rate of accumulation of arsenic in soil at the Srinagar site is relatively slow. For the Sonargoan site, accumulation of arsenic appears to be significant for some plots of the rice field, while not so significant for the others. More studies are needed for better understanding of the processes leading to accumulation of arsenic in soil.

Figures 3.18 and 3.19 show arsenic profiles of soil core samples collected from the vegetable fields at Srinagar and Sonargoan sites, respectively, at two different times. These figures show little variation of arsenic concentration over the one-year monitoring period.

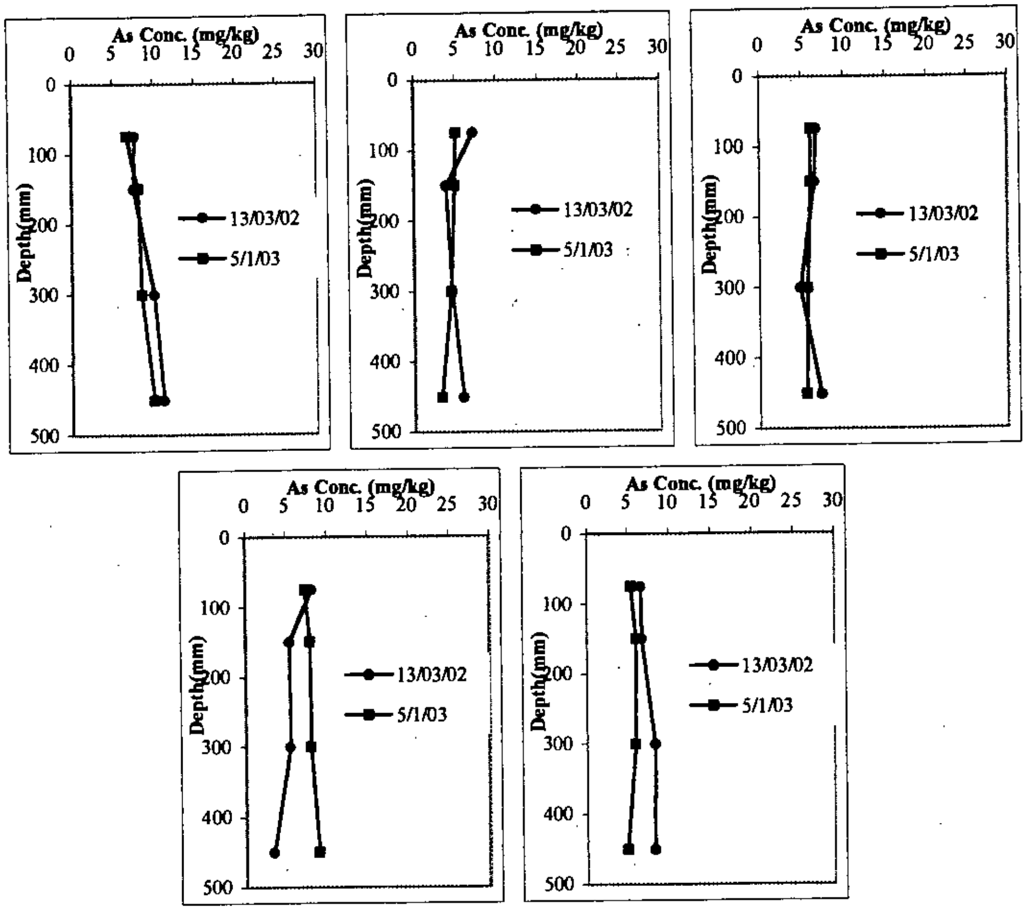


Figure 3.18: Arsenic profiles of soil samples collected from Srinagar vegetable fields at two different times

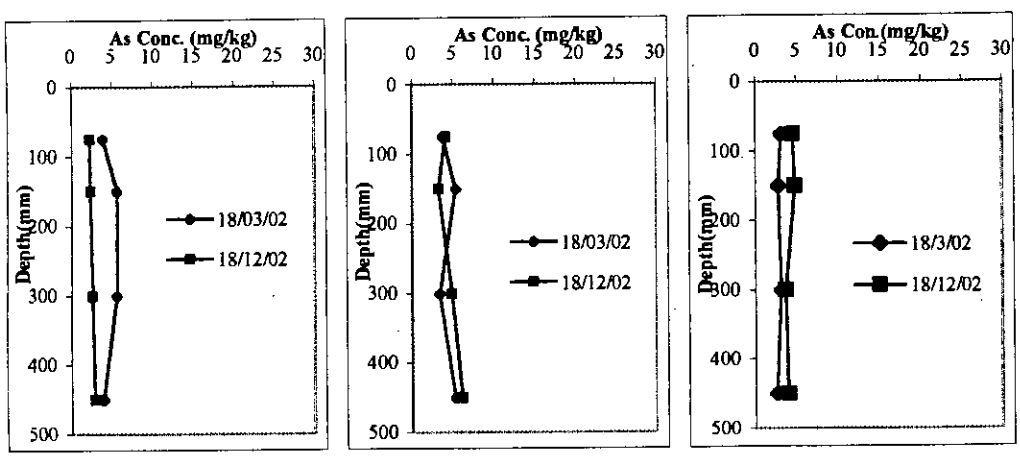


Figure 3.19(a): Arsenic profiles of soil samples collected from Sonargaon vegetable fields at two different times

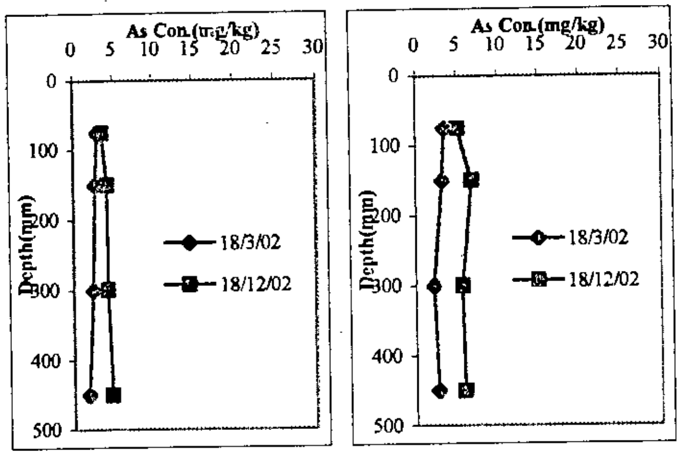
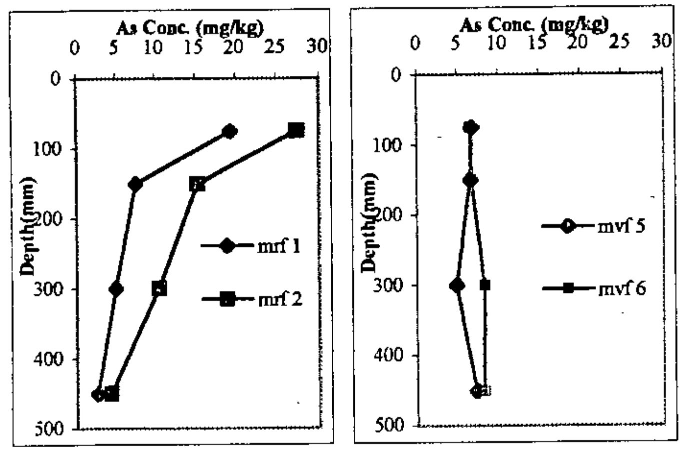


Figure 3.19(b): Arsenic profiles of soil samples collected from Sonargaon vegetable fields at two different times

3.4 SUMMARY

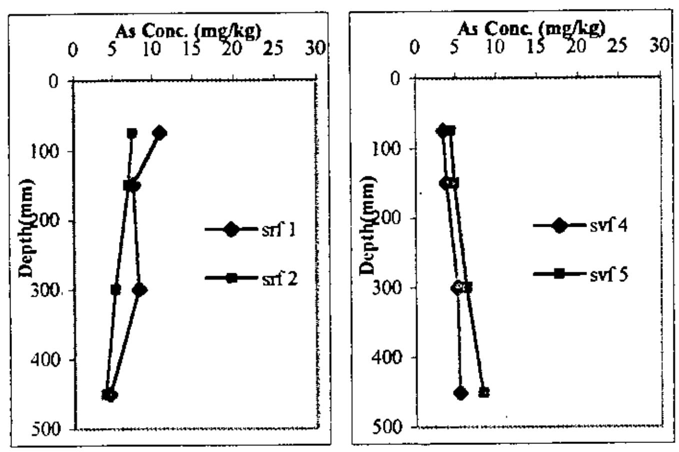
Concentration of arsenic in irrigation water varies with time but the reasons of this variation are not clear. Arsenic concentrations of groundwater samples collected from Dinajpur district are very low (<1 ppb), while those from arsenic affected regions of Srinagar, Sonargaon, Noakhali and Comilla are much higher. Arsenic concentration in surface water samples are generally low. Figure 3.20 and 3.21 show the comparison of arsenic profile of rice field with vegetable field at Srinagar and Sonargaon sites respectively. Figure 3.22 shows the comparison of irrigated rice fields at Srinagar, Sonargaon and Dinajpur sites respectively. So clearly As in irrigation water is causing accumulation of arsenic in topsoil

At the Srinagar site, average arsenic concentration in top (0-75mm) soil layer of rice fields was 14.5 mg/kg. This field was irrigated with groundwater having arsenic concentration varying from 220 to 537 ppb. On the other hand, average arsenic concentration in top (0-75mm) soil layer of vegetable field, not irrigated by arsenic affected groundwater, was 7.8mg/kg, about one half of that in the rice field in the same area. Similarly at the Sonargaon site, average arsenic concentration in top (0-75mm) soil layer of rice fields was 8.9 mg/kg. This field was irrigated with groundwater having arsenic concentration varying from 83 to 354 ppb. On the other hand, average arsenic concentration in top (0-75mm) soil layer of vegetable field, not irrigated by arsenic affected groundwater, was 3.5 mg/kg, about one half of that in the rice field in the same area. This result is in agreement with that reported by Huq *et al.* (2003).



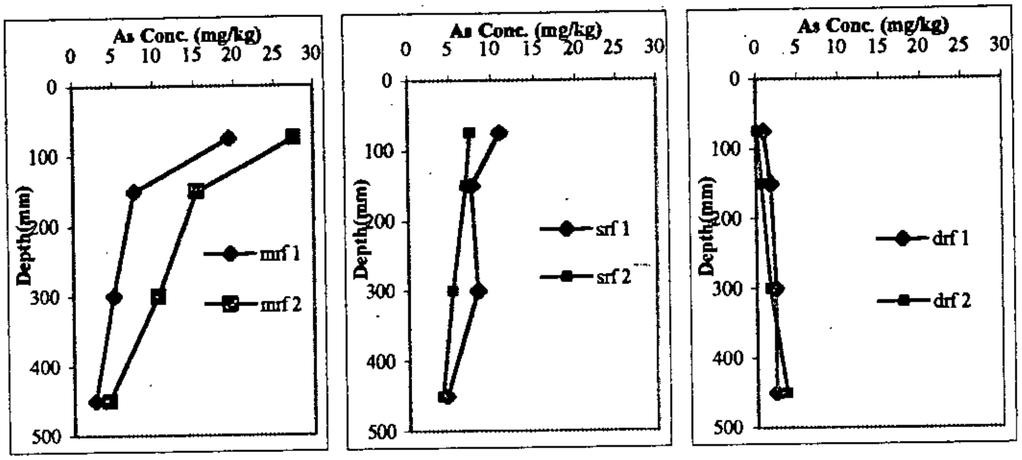
Rice field (As : 220-537ppb) Potato field (As : 1ppb)

Figure 3.20: Comparison of typical arsenic profile of rice field with vegetable (potato) field at Srinagar



Rice field (As : 83-354ppb) Potato field (As : <1-10 ppb)

Figure 3.21: Comparison of typical arsenic profile of rice field with vegetable field at Sonargaon



Srinagar (As:220-537 ppb)	Sonargaon (As:83-354 ppb)	Dinajpur (As: <1 ppb)
As in top soil : 14.5 mg/kg	As in top soil : 8.9 mg/kg	As in top soil : 1.04 mg/kg
(n = 11, std = 7.74)	(n = 14, std = 4.28)	(n = 10, std = 0.72)

Figure 3.22: Comparison of typical arsenic profile of rice fields at Srinagar, Sonargaon and Dinajpur

In this study arsenic concentration in irrigated soil was found to vary significantly with time at the Srinagar site. It was found that arsenic concentration at the topsoil layer were significantly higher at the end of the irrigation season, compared to that at the beginning. However, after floods concentration of arsenic came down almost to the pre-irrigation levels. More studies are needed to better understand the process affecting accumulation of arsenic in soil.

Chapter 4

ARSENIC IN PLANTS IN BANGLADESH

4.1 INTRODUCTION

As Bangladesh is struggling to mitigate arsenic toxicity in drinking water with nearly 40 million people feared to have been exposed to arsenic contaminated groundwater, recent concern of the presence of arsenic in the food chain has added a new dimension to the arsenic problem in Bangladesh. This concern stems from the fact that groundwater is widely used for irrigation in Bangladesh, a significant part of which comes from the arsenic affected shallow aquifer. The country is heavily dependent on its agricultural sector for its gross domestic product. National growth relies heavily on the growth of agricultural output. More than 80% of the population depends on agriculture for its livelihood. The agricultural sector employs about 90% of rural males as well as 80% of rural females (World Development Indicators, 1998) of the country. The population growth rate is still quite high and therefore the demand for food grain production; especially rice production has always been a challenging issue for our country. To ensure food security Bangladesh Government has emphasized on increasing rice production. To become self-sufficient in food grain, Bangladesh Government has encouraged production of HYV rice, which requires a large volume of irrigation water. The use of groundwater for irrigation has increased abruptly over the last couple of decades. About 86% of total groundwater withdrawn is utilized in agricultural sector (WRI, 2000).

As described in chapter 2, preliminary estimates suggest that a significant amount of arsenic (about 900 metric tons per year) is cycled through the environment each year. Results of the present study, presented in chapter 3, showed that arsenic in irrigation water is causing an increase in the arsenic concentration in top soils in agricultural lands irrigated with arsenic contaminated groundwater. Presence of arsenic in irrigation water as well as soil can cause an increase in the arsenic concentration of plants grown on such soil. Some recent studies have shown relatively high levels of arsenic in plant samples either irrigated with arsenic bearing water or grown in soil with high arsenic content. The uptake of arsenic by plant, however, depends on a wide range of factors including the species of interest, soil characteristics etc.

This chapter presents results of analysis of arsenic content in different parts of selected edible crops, both from arsenic affected and unaffected areas. Comparison of arsenic contents in samples from affected and unaffected areas have been made. Besides, possible correlation between the presence of arsenic in irrigation water-soil and plant has been made.

4.2 MATERIALS AND METHODS

In this study, two arsenic affected areas have been selected for detailed characterization of crop/vegetables produced in the irrigated soils. These two locations are: (i) Sonargaon, Narayangonj and (ii) Srinagar, Munshiganj as explained in chapter 3, irrigation water and soil core samples were collected from these sites. Besides, these sites crop/vegetable samples have been collected from Comilla and Noakhali districts. Crop samples have also been collected from a less affected (i.e., with low levels of arsenic in shallow wells) area in the Dinajpur district in northern Bangladesh. For intensive sampling, one rice field (i.e., the whole area under the influence of one irrigation well) was selected at each of the two sampling locations (Sonargaon and Srinagar).

4.2.1 Collection of Plant Samples

Paddy samples were collected just before harvest time. Entire rice plants (including roots) were collected. Samples were collected from the different sub-areas under the same irrigation well. A total of 33 rice plant samples were collected, 12 from Srinagar site, 11 from the Sonargaon site, and 10 from the Dinajpur site. Besides rice, five tomato plant samples, two *lal shak* plant samples, two *data shak* plant samples, one cauliflower plant sample, and two cabbage plant samples were collected from the vegetable fields at Sonargaon site. These twelve samples were collected from twelve different vegetable fields at the Sonaraon site. Six potato plant samples (from four different fields) were collected from the Srinagar site.

4.2.2 Laboratory Analysis of Plant Samples

Before analysis, the rice plant samples were divided into five parts: (i) root, (ii) stem, (iii) leaf, (iv) grain, and (v) husk. Vegetable samples were divided into four parts: (i) root, (ii) stem, (iii) leaf, and (iv) edible part. For cabbage, the edible part was further divided into outer layer and inner layer.

For analysis of total arsenic, the different parts/segments of the rice and vegetable 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). 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 crop/vegetable samples with distilled water, (ii) divide the crop/vegetable 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 dry crop/vegetable 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 crop and vegetable samples were carried out with hydride generation atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800).

4.3 RESULTS AND DISCUSSION

4.3.1 Arsenic in Rice Samples

Figures 4.1, 4.2, 4.3 and 4.4 show arsenic concentrations in rice grains and different parts of rice plants collected from the Srinagar, Sonargoan, Dinajpur and Comilla sites, respectively. These figures show that the roots of rice plants accumulated the maximum level of arsenic, followed by leaf and stem. Rice grain and husk accumulated the least amount of arsenic. These trends are in agreement with those reported by Abedin et al. (2002) based on a greenhouse study.

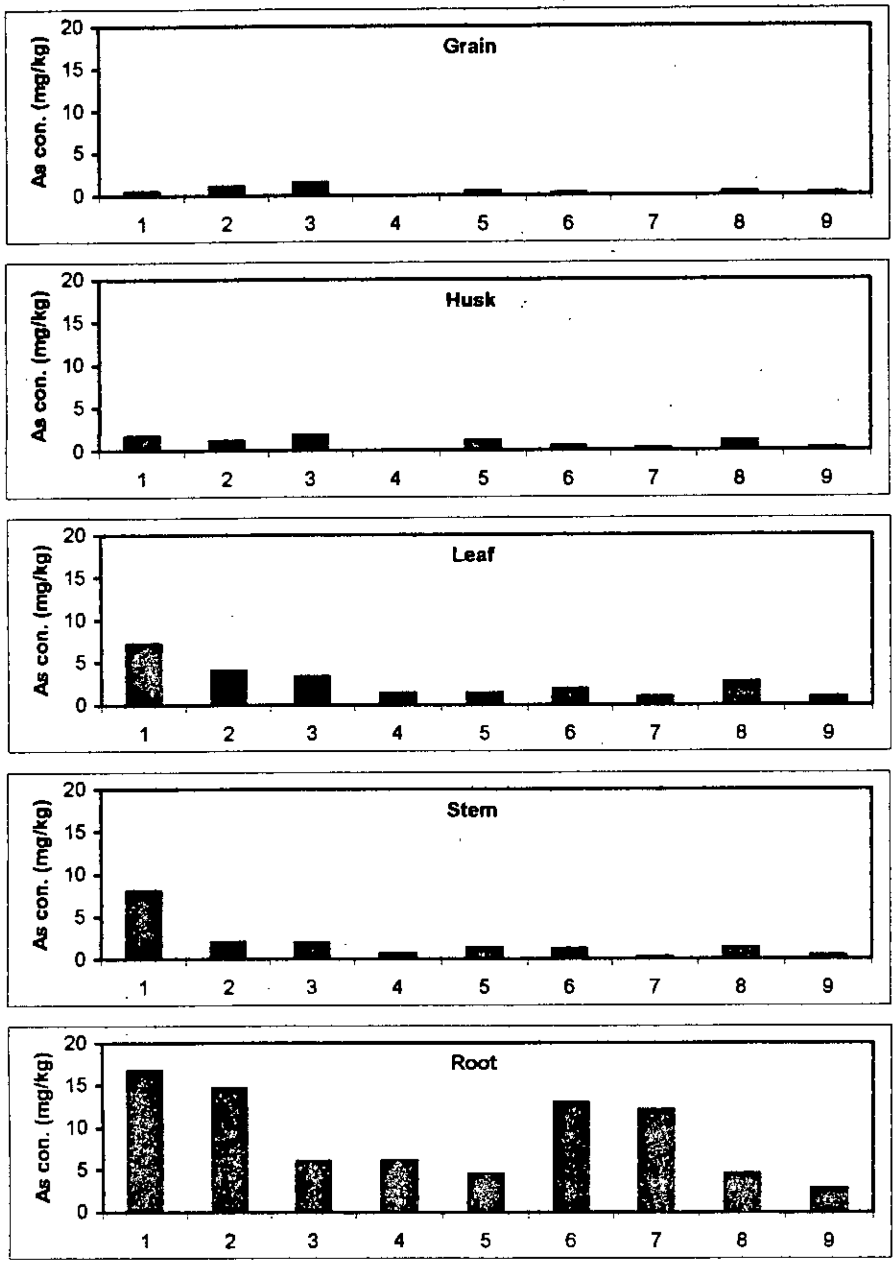


Figure 4.1: Arsenic concentrations in grain, husk, stem, leaf and root of rice plants collected from Srinagar site

Arsenic concentration in roots of rice plant samples collected from the Srinagar site varied from 2.81 to 16.8 mg/kg (with a mean of 8.9 mg/kg), while that in the rice grain varied from < 0.05 mg/kg (lowest detectable limit for this study) to 1.52 mg/kg (with a mean of 0.48 mg/kg). For the samples collected from the Sonargoan site, arsenic in root varied from 2.88 to 26.1 mg/kg (with a mean of 11.9 mg/kg), while that in the rice grain varied from < 0.05 mg/kg to 1.23 mg/kg (with a mean of 0.46 mg/kg). Two grain samples (out of nine) from

Srinagar and only one (out of twelve) from Sonargaon exceeded the Australian food hygiene limit of 1.0 mg/kg. Arsenic concentration in roots of rice plant samples collected from the Comilla site varied from 9.1 to 18.56 mg/kg (with a mean of 13.83 mg/kg), while that in the rice grain varied from .23 mg/kg to .36 mg/kg (with a mean of 0.3 mg/kg).

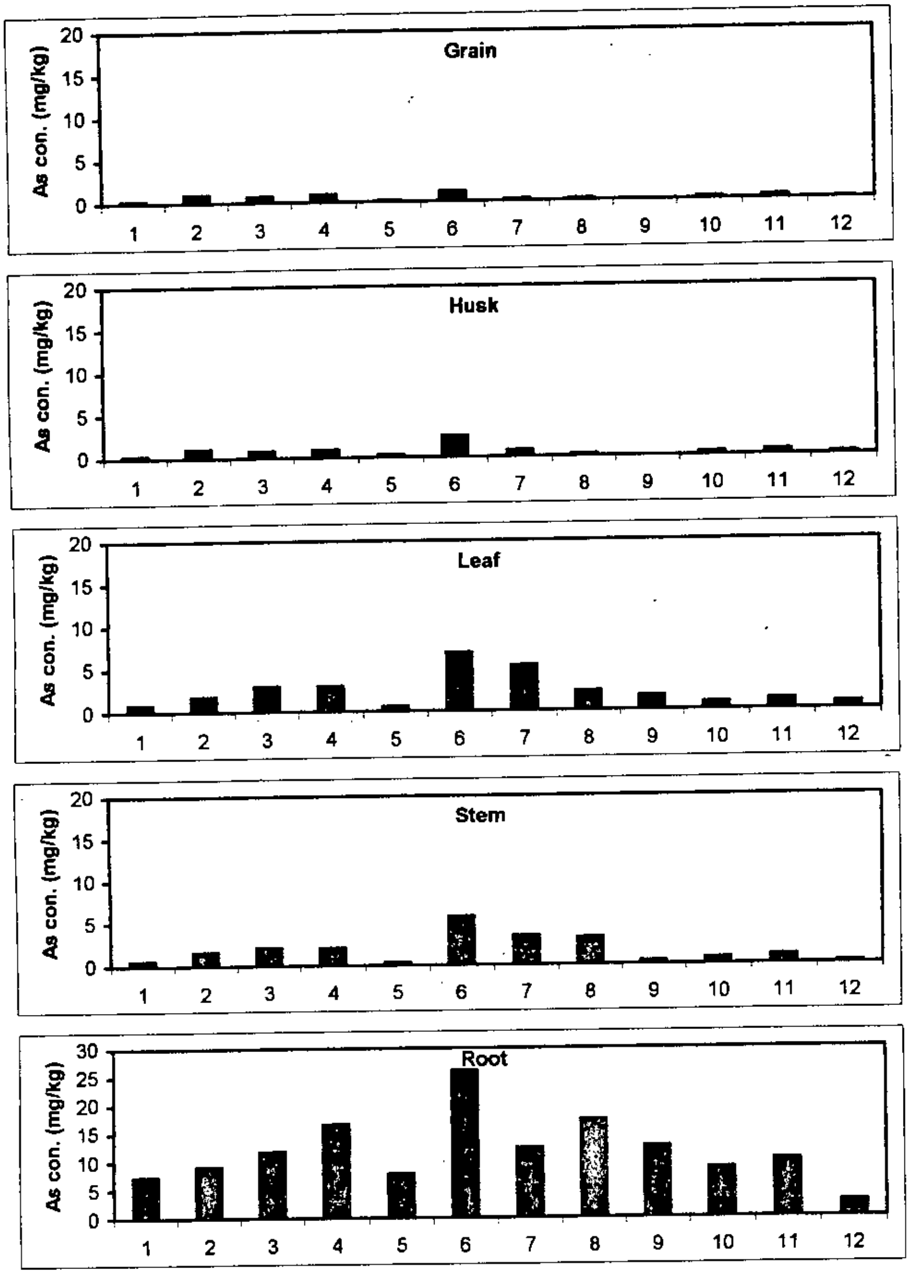


Figure 4.2: Arsenic concentrations in grain, husk, stem, leaf and root of rice plants collected from Sonargaon site

The level of arsenic in root, leaf and stem of the plant samples collected from Dinajpur (an arsenic-free area) were found to be significantly lower compared to those found in the samples collected from the Srinagar and Sonargoan sites. For example, average arsenic concentration in the root samples from Dinajpur was 6.76 mg/kg, compared to 8.9 and 11.9 mg/kg for the Srinagar and Sonargoan sites, respectively.

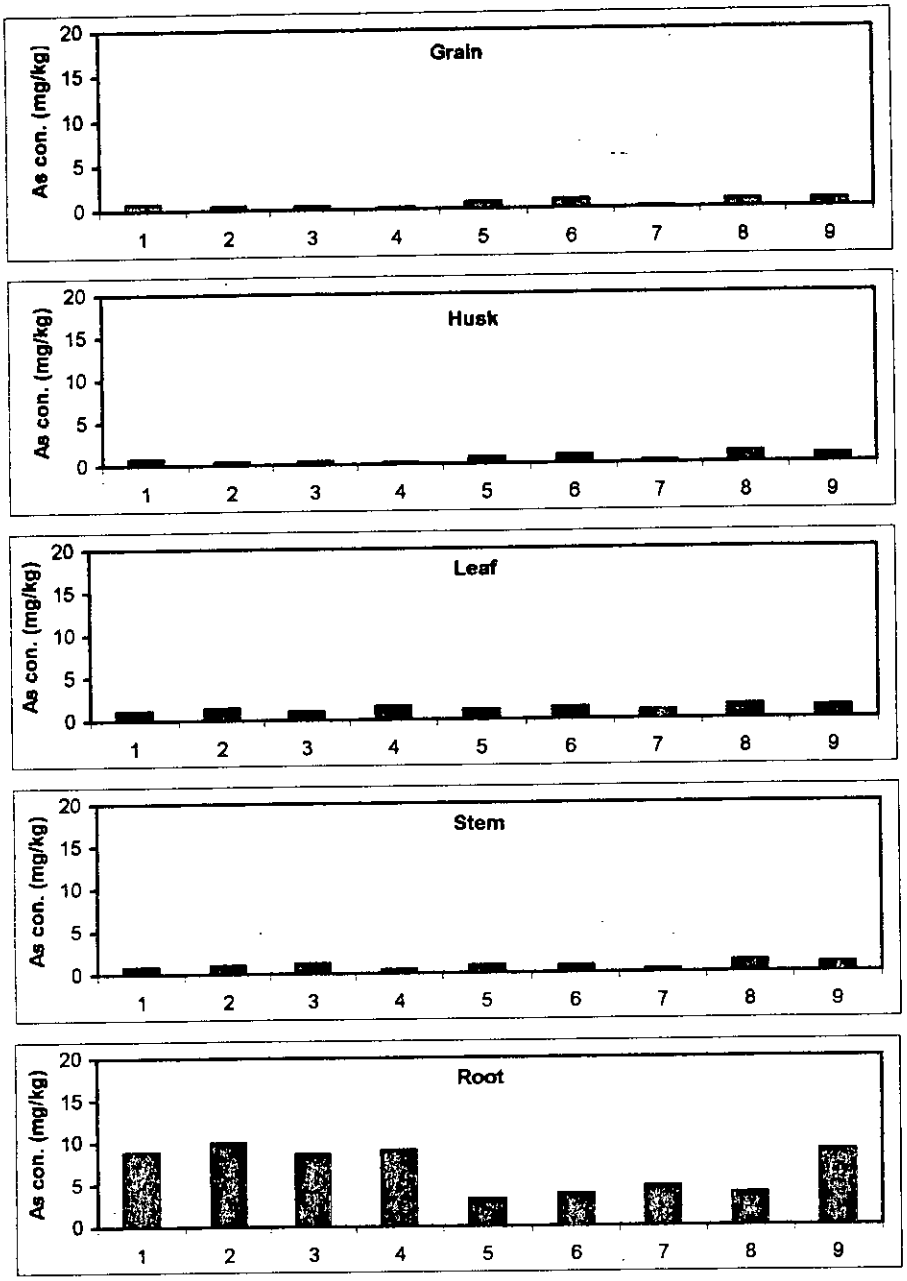


Figure 4.3: Arsenic concentrations in grain, husk, stem, leaf and root of rice plants collected from Dinajpur site

Thus it appears that arsenic present in irrigation water and soil results in higher level of arsenic in rice plant root, leaf and stem. However, as shown in Fig. 4.5, no strong correlation could be observed (R^2=0.21) between the presence of arsenic in soil and rice plant root (as well as leaf and stem).

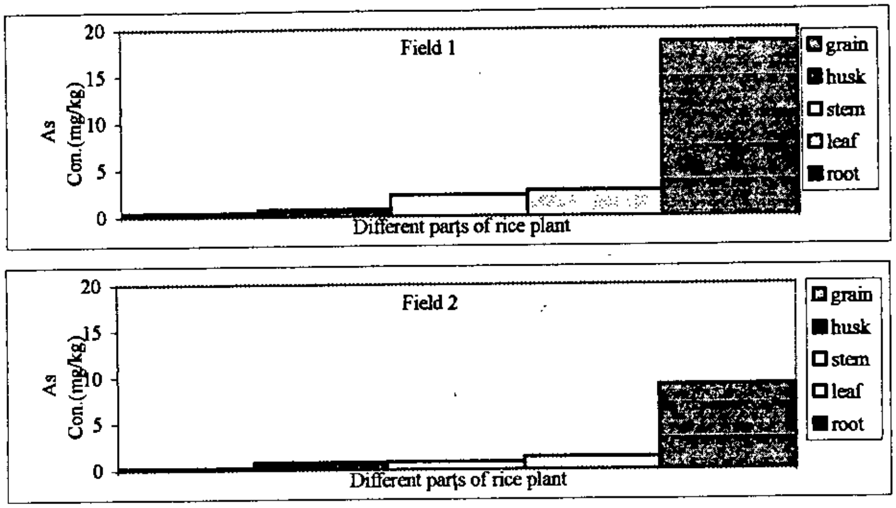


Figure 4.4: Arsenic concentrations in grain, husk, stem, leaf and root of rice plants collected from Comilla site

There was no significant difference in arsenic levels present in the rice grains and rice husks from the different sites. In fact, the mean arsenic concentration in the rice grain samples from the Dinajpur site was found to be 0.54 mg/kg, slightly higher than those from the Srinagar and Sonargaon sites, although none of the grain samples from Dinajpur exceeded the Australian food hygiene standard of 1.0 mg/kg. It should be noted, however that the rice cultivated at both Srinagar and Sonargaon site were of BR-29 variety, whereas those at Dinajpur site were of *China Irri* and *Chandina* varieties. As shown in Fig. 4.6, no correlation exists between the arsenic concentration in soil and in rice grains (R^2=0.017). Thus it appears that arsenic present in irrigation water and soil is not translocated to rice grain.

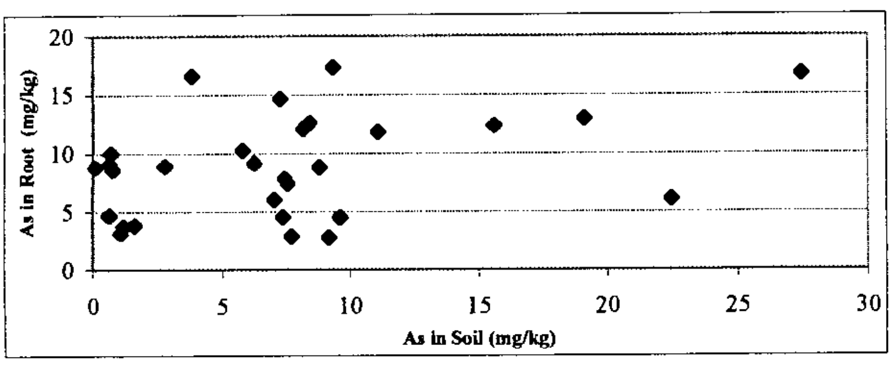


Figure 4.5: Arsenic concentrations in root versus arsenic in top soil layer (all samples)

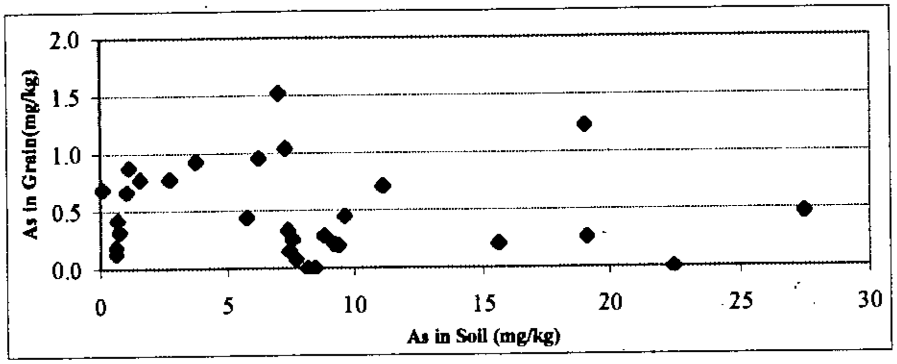


Figure 4.6: Arsenic concentrations in grain versus arsenic in top soil layer (all samples)

Figure 4.7 shows correlations between the arsenic present in grains and other parts of rice plants for the BR-29 variety of rice collected from Srinagar and Sonargaon sites. Relatively strong correlation was observed between arsenic in grains and husks (R^2=0.68); but correlations between arsenic in grains and arsenic in root, stem and leaf were poor.

4.3.2 Comparison of Arsenic in Rice Plants from Different Sites: Statistical Analysis

In order to assess the difference in arsenic concentration in various parts of rice plant samples collected from the arsenic affected areas of Srinagar and Sonargaon and unaffected area of Dinajpur, a statistical analysis was done by performing a non-parametric test. A non-parametric test is one in which (a) it is not necessary to assume that the population is normally distributed; no other strong assumption regarding the population distribution is required, (b) categorical or ranked data are used. Various types of rank tests are available such as Sign test, Rank test, and Spearman rank correlation test. In this chapter the rank test is used for the analysis purpose.

4.3.2.1 The Rank Test

Rank test is a non-parametric test and it is characterized by being distribution free. No assumption is made regarding the distribution. In rank test the observations are ranked and on the basis of ranking a statistic is calculated to test a hypothesis. Rank tests are very efficient, and so very popular. These are easy to understand and calculate. Rank tests have a crucial advantage for data, which are originally ranked and not in numerical form. In such data, numerical calculations such as mean and standard deviation is not possible. If there are some outlier which are likely to create problems, then also the observations can be transformed into ranks and rank test can be performed.

The Wilcoxon Rank Test

For the analysis of arsenic concentration, Wilcoxon rank test has been used. It is a typical and popular form of rank tests.

To do the analysis it was tested whether (i) the concentrations of arsenic in different parts of rice plant samples from the Srinagar and Dinajpur, (ii) the concentrations of arsenic in different parts of rice plant samples from the Srinagar and Sonargaon and (iii) the concentrations of arsenic in different parts of rice plant samples from the Sonargaon and Dinajpur, are identical or not, for each case, the task was to test the following hypothesis (assumed level of significance,$\alpha = 0.05$)

H_0 = Concentration of the two sites are equal

H_a = Concentration of the two sites is different

The alternative hypothesis tells that it is two-tail test. So it was compared the probability with $\alpha/2$ or 0.025.

Two steps are important here. Identification of the smaller sample is one and the ranking is another. Ranking should start from the smaller sample and it should start at the end where the smaller sample is concentrated. The test statistic Wilcoxon rank sum W is the sum of the ranks of the smaller samples. This value is compared with the table value provided in Appendix C (table C2) and the corresponding probability is noted. If this probability is lower than α, reject the null hypothesis. If this probability is larger than α, do not reject the null hypothesis. Results of the tests are summarized in Appendix C(Table C1). Results shown in Appendix C (Table C1) show that significant difference in arsenic concentration exists only between the root samples from Sonargaon and Dinajpur.

4.3.2.2 Student's t Distribution

Generally it is concerned for the most part with making probability statements, determining confidence intervals, and testing hypotheses in the situation where the appropriate statistics is normally distributed. In all cases it is assumed (1) that the variance is known and (2) that it is either selecting a sample from a normal population or that the sample size is sufficiently large to enable us to the central limit theorem. If either of the assumptions is not satisfied, it must determine other possibilities. This is precisely what was done by W.S.Gossett, a statistician who wrote under the pseudonym "Student".

Gossett derived the exact distribution of the statistics for the situation where a sample of any size *n* is selected from a normal population for which the variance is unknown. This distribution is known as Students t distribution or student's distribution or simply the distribution. Results of Students t test are summarized in Table 4.1

Table 4.1 Comparison of arsenic concentrations of different parts of paddy plants of the three sites by t distribution.

Samples	Comparison	t	$t_{critical}$	Comment
Grain	Srinagar vs Sonargaon	0.136	2.093	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	0.306	2.12	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	0.529	2.093	Concentrations of two sites are equal/identical
Husk	Srinagar vs Sonargaon	0.849	2.093	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	0.934	2.12	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	0.035	2.093	Concentrations of two sites are equal/identical
Stem	Srinagar vs Sonargaon	0.193	2.093	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	1.329	2.12	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	1.601	2.093	Concentrations of two sites are equal/identical
Leaf	Srinagar vs Sonargaon	0.333	2.093	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	1.985	2.12	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	1.615	2.093	Concentrations of two sites are equal/identical
Root	Srinagar vs Sonargaon	1.201	2.093	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	1.113	2.12	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	2.393	2.093	Concentration in Sonargaon is higher

Results shown in Table 4.1 show that significant difference in arsenic concentration exists only between the root samples from Sonargaon and Dinajpur.

Thus table C1 and Table 4.1 Show almost same trend about the comparison of arsenic concentration of the five parts of paddy plants of Srinagar, Sonargaon and Dinajpur sites. These results show that

(1) The arsenic concentrations of *Grain* samples of arsenic affected areas (Srinagar, Sonargaon) and unaffected area (Dinajpur) are identical.

(2) The arsenic concentrations of *Husk* samples of arsenic affected areas (Srinagar, Sonargaon) and unaffected area (Dinajpur) are identical.

(3) The arsenic concentrations of *Stem* samples of arsenic affected areas (Srinagar, Sonargaon) and unaffected area (Dinajpur) are identical.

(4) The arsenic concentrations of *Leaf* samples of arsenic affected areas (Srinagar, Sonargaon) and unaffected area (Dinajpur) are identical.

(5) The arsenic concentrations of *Root* samples of arsenic affected areas (Sonargaon) are higher than unaffected area (Dinajpur).

So there does not appear to be a strong correlation between the presence of arsenic in rice grain, husk, stem and leaf with the presence of arsenic in irrigation water and soil.

4.3.3 Arsenic in Vegetable Samples

Results of analysis of arsenic in different parts of potato (Table 4.2) and potato plant showed relatively lower level of accumulation. It should be noted that the potato fields were irrigated by pond water with relatively low levels of arsenic. Highest accumulation of arsenic was found in the root of potato plants (up to 2.9 mg/kg). However, these levels were significantly lower than those found in rice roots. Arsenic concentration in the edible parts varied from 0.12 to 0.85 mg/kg [dry (oven dried at 65°C) weight basis], all below the Australian food hygiene standard.

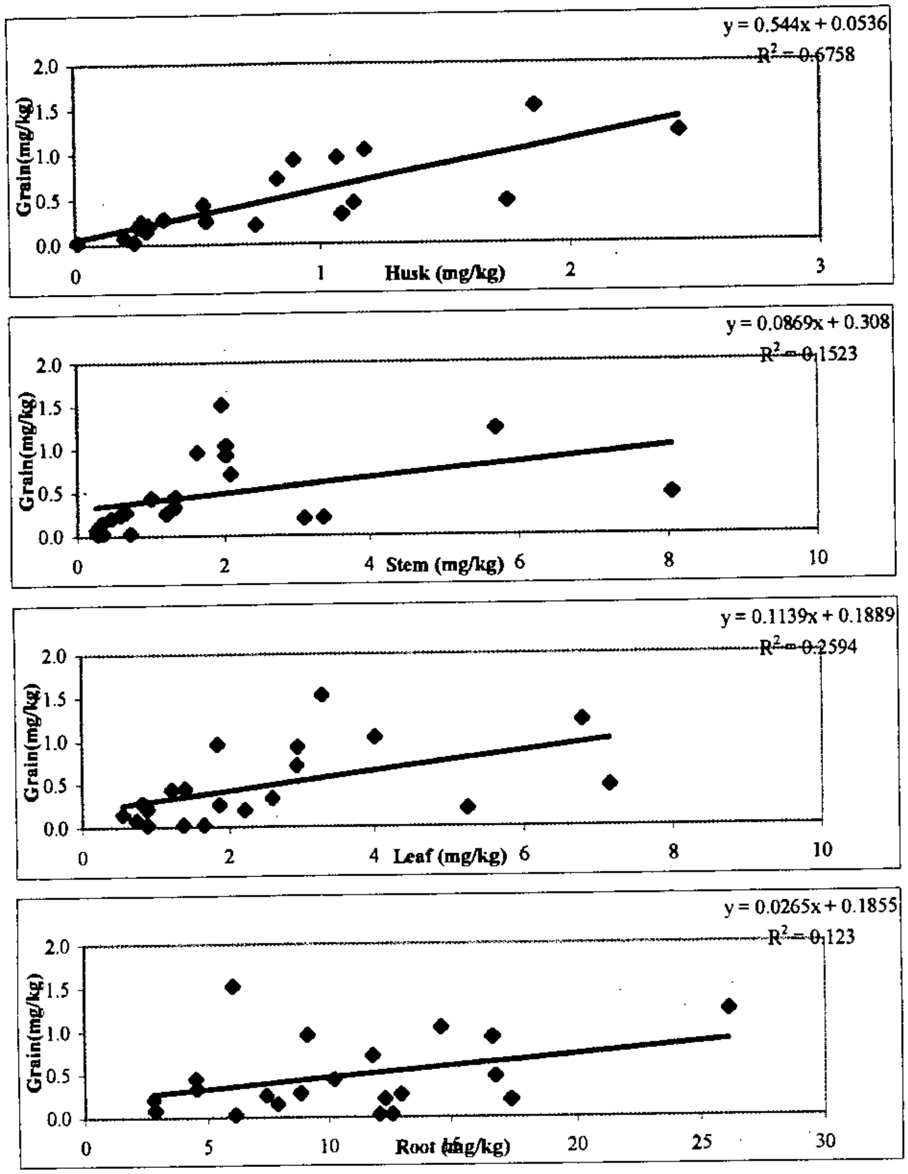


Figure 4.7: Correlations between arsenic in present grains and arsenic in other parts of rice plants (BR-29 variety) collected from Srinagar and Sonargaon

Results of arsenic concentration in different parts of tomato, *lalshak*, *datashak*, cabbage and cauliflower samples collected from the Sonargoan site also showed (Table 4.3) relatively low level of accumulation. All these fields (except the cauliflower field) were irrigated by pond or canal water with relatively low levels of arsenic. Among the different parts, arsenic accumulation in roots was found to be the highest, although the levels (maximum 1.8 mg/kg) were very low compared to the rice roots. Arsenic concentration in edible parts of *lalshak* ranged from < 0.39 to 0.96 mg/kg; for *datashak* it ranged from 0.56 to 1.06 mg/kg, for cabbage 0.38 to 1.6 mg/kg and for cauliflower 0.35 mg/kg. Arsenic concentrations in the five tomato samples ranged from 0.18 to 1.33 mg/kg. However, since all the vegetable fields (except one) were irrigated by pond or canal water, effect of arsenic bearing irrigation water on these vegetables could not be assessed from these results alone. Results of arsenic concentration in different parts of data shak and arum samples collected from the Noakhali site also showed (Table 4.4) relatively low level of accumulation.

Table 4.2: Arsenic concentration in different parts of potato plant samples from Srinagar

Sample ID	As in Irrigation Water (ppb)	Arsenic in different parts of potato plants			
		Root	Stem	Leaf	Edible Part
Potato-1	37	1.8	0.42	0.81	0.81
Potato-1		2.8	0.51	0.65	0.26
Potato-1		1.0	0.21	0.54	0.12
Potato-1		2.9	0.69	0.29	0.85
Potato-1	1	2.1	0.72	0.79	0.39
Potato-1		-	0.26	0.48	0.27

Table 4.3: Arsenic concentration in different parts of plant samples from Sonargaon

Sample ID	As in Irrigation Water (ppb)	Arsenic in different parts of potato plants			
		Root	Stem	Leaf	Edible Part
Tomato-1	8	0.65	0.63	1.04	1.33
Tomaot-2	<1	1.27	0.66	0.88	0.63
Tomato-3	1.5	0.72	0.58	1.11	0.8
Tomato-4		-	0.47	0.50	0.63
Tomato-5		0.48	0.81	1.38	0.18
Lalshak-1	10	1.22			Stem: 0.58
Lalshak-2		0.84			Stem: 0.39, Leaf: 0.96
Datashak-1	35	1.84			Stem: 0.56, Leaf: 0.91
Datashak-2		1.29			Stem: 0.76, Leaf: 1.06
Cabbage-1		0.88			Inner: 1.6, Outer: 0.38
Cabbage-2		1.36			Inner: 0.62, Outer: 0.49
Cauliflower	176	1.24	0.34	0.66 - 2.5	0.35

Table 4.4: Arsenic concentration in different parts of plant samples from Noakhali

Field ID	As in irrigation water(ppb)	Vegetable Type	Root (mg/kg)	Edible Part	
				Stem (mg/kg)	Leaf (mg/kg)
1	Pond (1 ppb)	Datashak	0.76	1.61	0.18
2	Tube well (159 ppb)	Datashak	0.44	0.34	0.46
3	Pond (28.29 ppb)	Arum	1.48	0.85	0.98
4	Tube well (472.45 ppb)	Arum	1.05	0.7	0.73

4.4 SUMMARY:

Analysis of arsenic content of rice plant samples collected from Srinagar, Sonargaon and Dinajpur sites showed that the roots of rice plants accumulated the maximum level of arsenic, followed by leaf and stem. The level of arsenic in root of the plant samples collected from Dinajpur (an arsenic-free area) were found to be lower compared to those found in the samples collected from the Srinagar and Sonargoan sites. However, statistically significant difference was found only for arsenic contents in rice plant roots. Thus it appears that arsenic present in irrigation water and soil results in higher level of arsenic in rice plant root, leaf and stem. There was no significant difference however, in arsenic levels present in the rice grains and rice husks. Results of analysis of arsenic in different parts of potato and potato plant showed relatively lower level of accumulation. Highest accumulation of arsenic was found in the root of potato plants (up to 2.9 mg/kg). However, these levels were significantly lower than those found in rice roots. Results of arsenic concentration in different parts of tomato, *lalshak*, *datashak*, cabbage and cauliflower samples collected from the Sonargoan site also showed relatively low level of accumulation.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSIONS

Major conclusions and findings from the present study are summarized below:

1. According to the present study, an estimated 900 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. Amount of arsenic extracted with groundwater from domestic tubewells was estimated to be about 46 metric tons per year, which is about 20 times smaller than that estimated for irrigation water.

2. Arsenic profiles of soils in the irrigated rice fields at the Srinagar and Sonargoan sites show higher accumulation of arsenic primarily in the top layers (typically top 75 to 150 mm) of soil. In general, arsenic concentration in soil decreased with depth. Arsenic accumulation in the irrigation canal samples was relatively higher compared to the *field* samples. Compared to the rice field, arsenic concentrations in the soil samples collected from the vegetable fields were significantly lower. It appears that the higher arsenic concentration in the rice field soil samples, both at Srinagar and Sonargoan sites, is due to the presence of high level of arsenic in the irrigation water.

3. Analysis of arsenic content of rice plant samples collected from Srinagar, Sonargaon and Dinajpur sites showed that the roots of rice plants accumulated the maximum level of arsenic, followed by leaf and stem. The level of arsenic in root, stem and leaf of the rice plant samples collected from Dinajpur (an arsenic contamination free area) were found to be significantly lower compared to those

found in the samples collected from the Srinagar and Sonargoan sites. Thus it appears that arsenic present in irrigation water and soil results in higher level of arsenic in rice plant root, leaf and stem. There was no significant difference however, in arsenic levels present in the rice grains and rice husks. Since rice straw is widely used as cattle feed in Bangladesh and India, high arsenic in rice stem and leaf (i.e., in straw) may result in adverse health impacts on cattle and increase human arsenic exposure via the plant-animal-human pathway.

4. Results of analysis of arsenic in different parts of potato plants showed relatively lower level of accumulation. Highest accumulation of arsenic was found in the root of potato plants (up to 2.9 mg/kg). However, these levels were significantly lower than those found in rice roots. Arsenic concentration in the edible parts varied from 0.12 to 0.85 mg/kg [dry (oven dried at 65°C) weight basis], all below the Australian food hygiene standard of 1 mg/kg. Results of arsenic concentration in different parts of *tomato, lalshak, datashak, cabbage* and *cauliflower* samples collected from the Sonargoan site also showed relatively low level of accumulation. Among the different parts, arsenic accumulation in roots was found to be the highest, although the levels (maximum 1.8 mg/kg) were significantly lower compared to the rice roots. Since all the vegetable fields (except one) were irrigated by pond or canal water, effect of arsenic bearing irrigation water on these vegetables could not be assessed from these results alone.

5.2 RECOMMENDATIONS FOR FUTURE STUDIES

1. Arsenic concentrations of irrigation water collected from Srinagar and Sonargaon sites vary significantly with time. Further study should be carried out to identify the reasons of such variation of arsenic concentration with time.

2. More studies are needed to better understand the processes leading to accumulation of arsenic in soil. Specifically study is needed to find out the reasons of observed reduction of arsenic concentrations of irrigated soil after the flood season. This is important because phytotoxicity (i.e., reduced growth/yield of plants), due to increased arsenic in soil-water is a major concern.

3. In this study, speciation of arsenic present in food samples could not be performed due to analytical limitations. It is important to identify the chemical forms of arsenic (e.g., inorganic and organic) in crop/vegetable, which in turn is needed for estimating its toxicity.

4. More studies are needed to better understand the uptake of arsenic by different varieties of rice as well as other plants. Effects of soil characteristics as well as water quality on arsenic uptake should also be studied in more detail.

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APPENDIX-A

(Arsenic concentration of monitoring wells)

Table A1: As Concentrations of Srinagar , Munshiganj Monitoring Irrigation Wells

Sample ID	Date of Collection	AsConc.(ppb)	Date of collection	As Conc. (ppb)	Date of Collection	AsConc. (ppb)	Date of Collection	AsConc. (ppb)	Date of Collection	AsConc. (ppb)
M - 1	13.03.2002	175.75	23.03.2002	437.52	08.04.2002	416.78	17.04.2002	600.3	24.04.2002	441.26
M - 2	13.03.2002	210.12	23.03.2002	187.54	08.04.2002	452.21	17.04.2002	472.17	24.04.2002	361.39
M - 3	13.03.2002	219.61	23.03.2002	509.72	-	-	17.04.2002	537.09	24.04.2002	532.7
M - 4	13.03.2002	150.27	23.03.2002	365.71	-	-	17.04.2002	517.21	24.04.2002	376.04
M - 5	13.03.2002	181.64	23.03.2002	367.78	08.04.2002	386.73	17.04.2002	170.92	24.04.2002	20.1
M - 6	13.03.2002	102.67	23.03.2002	260.06	08.04.2002	304.97	17.04.2002	315.08	24.04.2002	277.07
M - 7	13.03.2002	54.27	23.03.2002	247.54	08.04.2002	232.48	17.04.2002	187.07	24.04.2002	270.89
M - 8	13.03.2002	100.11	23.03.2002	305.07	08.04.2002	267.17	17.04.2002	234.42	24.04.2002	316
M - 9	13.03.2002	72.78	23.03.2002	245.47	08.04.2002	231.01	17.04.2002	208.21	24.04.2002	286.49
M - 10	13.03.2002	152.62	23.03.2002	326.32	08.04.2002	230.5	17.04.2002	247.09	-	--

Table A2: As Concentrations of Sonargaon , Narayanganj Monitoring Irrigation Wells

Well ID	Date	Con.(ppb)	Date	Con.(ppb)	Date	Con.(ppb)	Date	Con.(ppb)	Date	Con.(ppb)	Date	Con.(ppb)
IW - 01	19.02.02	219.64	03.03.02	92.34	18.03.02	224.61	-	-	15.04.02	332.22	22.04.02	228.06
IW - 02	19.02.02	118.64	03.03.02	48.61	-	-	-	-	-	-	-	108.72
IW - 03	19.02.02	142.27	03.03.02	93.38	-	-	1/4/02	154.93	15.04.02	358.52	22.04.02	170.3
IW - 04	19.02.02	153.96	03.03.02	96.88	18.03.02	211.24	1/4/02	227	15.04.02	305.13	22.04.02	221.27
IW - 05	19.02.02	217.31	03.03.02	123.24	18.03.02	249.8	1/4/02	267.3	15.04.02	354.32	22.04.02	273.58
IW - 06	19.02.02	179.86	03.03.02	83.15	18.03.02	204.91	1/4/02	201.69	15.04.02	354.09	22.04.02	182.88
IW - 07	19.02.02	158.1	03.03.02	73.69	18.03.02	157.64	-	-	-	-	-	-
IW - 08	-	-	03.03.02	175.28	18.03.02	348.02	-	-	-	-	22.04.02	389.62
IW - 09	-	-	03.03.02	78.5	18.03.02	97.65	-	-	-	-	22.04.02	207.01
IW - 10	-	-	-	-	18.03.02	367.52	-	-	15.04.02	405.32	-	-

APPENDIX-B

(Arsenic concentration of different parts of soil and plant samples)

Table B1: Arsenic Concentrations (mg/kg) of different layers of Srinagar Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Srinagar, Munshiganj.	mrf 1	19.39	7.62	5.04	2.7
	mrf 2	27.47	15.30	10.55	4.42
1st Sampling	mrf 3	7.27	12.68	5.26	3.16
	mrf 4	22.98	23.24	10.00	10.70
	mrf 5	7.01	7.57	4.68	6.21
(06/02/2002)	mrf 6	22.45	13.91	9.11	3.68
	mrf 7	9.62	6.76	6.53	6.49
Irrigation Water	mrf 8	19.10	9.14	8.06	6.39
	mrf 9	8.16	12.29	7.47	5.51
Concentration	mrf 10	7.37	6.04	4.50	3.82
(220-537 ppb)	mrf 11	9.19	6.47	3.59	4.50

Table B2: As Concentrations of Different Parts of Srinagar Paddy Samples

Field ID	Grain (mg/kg)	Husk (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Root (mg/kg)
mrf 2	0.47	1.75	8.05	7.15	16.75
mrf 3	1.04	1.18	2.02	4.02	14.62
mrf 5	1.52	1.86	1.96	3.29	6.02
mrf 6	0.03	0.01	0.72	1.38	6.09
mrf 7	0.45	1.14	1.33	1.40	4.52
mrf 8	0.26	0.53	1.21	1.86	12.98
mrf 9	0.03	0.24	0.27	0.90	12.10
mrf 10	0.33	1.09	1.32	2.58	4.57
mrf 11	0.21	0.30	0.46	0.89	2.81

Table B3: Arsenic Concentrations (mg/kg) of different layers of Sonargaon Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Sonargaon, Narayangonj. 1st Sampling (03/03/2002) Irrigation Water Concentration (83-354 ppb)	srf 1	11	7.63	8.29	4.54
	srf 2	7.54	6.99	5.28	4.03
	srf 3	3.17	3.01	1.74	1.73
	srf 4	6.23	7.58	5.98	5.87
	srf 5	11.12	9.32	9.41	8.80
	srf 6	3.80	4.32	4.59	4.11
	srf 7	7.42	5.92	2.98	4.07
	srf 8	19.02	12.62	11.06	6.25
	srf 9	15.59	10.50	6.21	5.17
	srf 10	9.37	9.04	9.31	12.77
	srf 11	8.44	8.74	10.27	8.53
	srf 12	8.81	7.58	8.55	6.72
	srf 13	5.76	9.70	9.01	6.65
	srf 14	7.69	6.69	7.37	5.80

Table B4: As Concentrations of Different Parts of Sonargaon Paddy Samples

Field ID	Grain (mg/kg)	Husk (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Root (mg/kg)
srf 2	0.25	0.27	0.59	0.87	7.38
srf 4	0.96	1.07	1.63	1.84	9.14
srf 5	0.71	0.82	2.08	2.93	11.82
srf 6	0.93	0.89	2.02	2.94	16.64
srf 7	0.15	0.29	0.33	0.56	7.84
srf 8	1.23	2.44	5.70	6.78	26.11
srf 9	0.21	0.73	3.37	5.27	12.34
srf 10	0.20	0.26	3.10	2.20	17.35
srf 11	0.03	0.01	0.35	1.65	12.61
srf 12	0.28	0.36	0.66	0.82	8.82
srf 13	0.44	0.52	1.01	1.22	10.23
srf 14	0.08	0.20	0.26	0.74	2.88

Table B5: Arsenic Concentrations (mg/kg) of different layers of Dinajpur Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Dinajpur. 1st Sampling (03/03/2002) As con. of water (0 ppb)	drf 1	0.92	1.81	2.36	2.35
	drf 2	0.10	0.65	1.68	3.62
	drf 3	0.69	1.67	2.88	2.72
	drf 4	0.76	1.2	0.35	1.38
	drf 5	0.63	0	0.5	1.9
	drf 6	1.07	0	1.44	1.44
	drf 7	1.16	0.93	2.37	1.75
	drf 8	0.63	1.34	5.44	2.58
	drf 9	1.59	2.19	1.39	1.36
	drf 10	2.75	2.83	3.52	3.14

Table B6: As Concentrations of Different Parts of Dinajpur Paddy Samples

Field ID	Grain (mg/kg)	Husk (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Root (mg/kg)
drf 2	0.69	0.78	0.81	1.1	8.83
drf 3	0.42	0.43	0.98	1.42	10.01
drf 4	0.32	0.38	1.19	1.01	8.61
drf 5	0.19	0.21	0.45	1.55	9.03
drf 6	0.67	0.78	0.88	1.1	3.2
drf 7	0.88	0.95	0.81	1.37	3.76
drf 8	0.13	0.28	0.33	0.91	4.7
drf 9	0.78	1.28	1.33	1.57	3.82
drf 10	0.78	0.88	1.01	1.35	8.91

Table B7: Arsenic Concentrations (mg/kg) of different layers of Comilla Paddy Field Samples

Location and Date	As con.of water (ppb)	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-50mm)	3rd layer (150-00mm)	4th layer (300-50mm)
Comilla. 1stsampling (8/5/02)	252	crf 1	3.54	4.06	2.13	1.45
	212	crf 2	2.13	1.24	0.93	0.67

Table B8: As Concentrations of Different Parts of Comilla Paddy Samples

Field ID	'Grain (mg/kg)	Husk (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Root (mg/kg)
crf 1	0.3674	0.68	2.25	2.78	18.56
crf 2	0.2248	0.75	0.83	1.38	9.1

Table B9: As Concentrations (mg/kg) of two layers of Paddy Canal Samples

Location and Date	Canal Samples (CS) ID	Distance from Well (ft)	Top Layer (0-150mm)	Bottom Layer (150-300mm)
Srinagar, Munshiganj. Sampling Date 06/02/2002 As Concentration of Irrigation water (220-537 ppb)	CS - 1	210	23.21	10.01
	CS - 2	330	18.42	9.17
	CS - 3	450	16.31	10.31
	CS - 4	100	20.15	6.23
	CS - 5	8	45.73	8.85
	CS - 6	30	48.77	23.63
	CS - 7	135	8.23	8.40
	CS - 8	200	12.82	6.41
	CS - 9	280	11.31	6.55
	CS - 10	100	42.34	8.79
	CS - 11	200	34.6	7.98
	CS - 12	310	21.33	15.64

Table B10: As Concentrations (mg/kg) of two layers of Paddy Canal Samples

Location and Date	Canal samples (CS) ID	Distance from Well (ft)	Top Layer (0-150mm)	Bottom layer (150-300mm)
Sonargaon, Narayanganj. Sampling Date 03/03/2002 As Concentration of Irrigation water (83-354 ppb)	CS - 1	4	14.65	6.54
	CS - 2	120	10.3	5.85
	CS - 3	200	10.52	9.22
	CS - 4	320	10.42	5.35
	CS - 5	130	8.21	7.27
	CS - 6	140	18.54	4.55
	CS - 7	290	4.14	4.53
	CS - 8	375	4.63	4.11
	CS - 9	425	36.77	4.29
	CS - 10	605	11.94	6.39
	CS - 11	605	28.14	5.92
	CS - 12	510	8.29	27.1
	CS - 13	235	13.39	11.6
	CS - 14	70	11.48	9.73
	CS - 15	460	9.76	8.11
	CS - 16	335	46.47	24.84

Table B11: Arsenic Concentrations (mg/kg) of Different Parts of Srinagar, Munshigonj Vegetable Field Samples

Field ID	Source of water and As con(ppb)	Vegetable Type	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
mvf 1	Pond(37ppb)	Potato	8.25	5.51	5.52	3.46
mvf 2	Pond(37ppb)	Potato	7.76	7.65	10.13	11.22
mvf 3	Pond(37ppb)	Potato	7.20	3.92	4.67	5.91
mvf 4	Pond(37ppb)	Potato	9.95	4.31	4.99	-
mvf 5	Pond(1ppb)	Potato	6.82	6.64	4.91	7.38
mvf 6	Pond(1ppb)	Potato	6.64	6.77	8.38	8.31

Table B12: As Concentrations of Different Parts of Srinagar, Munshigonj Potato Samples

Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Edible (mg/kg)
mvf 1	Potato	1.81	0.42	0.81	0.81
mvf 2	Potato	2.8	0.51	0.65	0.26
mvf 3	Potato	1.01	0.21	0.54	0.12
mvf 4	Potato	2.89	0.69	0.29	0.85
mvf 5	Potato	2.05	0.72	0.79	0.39
mvf 6	Potato	-	0.26	0.48	0.27

Table B13: Arsenic Concentrations (mg/kg) of different layers of Sonargaon vegetable Field Samples

Field ID	Source of water and As con(ppb)	Vegetable Type	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
svf 1	Canal(8ppb)	Tomato	3.02	2.09	2.34	2.63
svf 2	Canal(< 1 ppb)	Tomato	2.44	5.03	5.24	6.29
svf 3	Pond(10 ppb)	Lalshak	3.48	3.8	5.24	5.51
svf 4	Pond(10 ppb)	Lalshak	4.35	4.78	6.35	8.39
svf 5	Pond(2 ppb)	Tomato	7.63	6.44	4.3	3.65
svf 6	Pond(2 ppb)	Tomato	3.82	5.6	5.6	3.95
svf 7	Pond(2 ppb)	Tomato	3.75	5.39	3.4	5.29
svf 8	Canal(35ppb)	Datashak	3.13	2.77	3.12	2.56
svf 9	Canal(35ppb)	Datashak	3.04	2.7	2.39	1.85
svf 10	Canal(35ppb)	Cabbage	2.22	2.11	1.81	2.33
svf 11	Canal(35ppb)	Cabbage	3.45	3.18	2.17	2.67
svf 12	Hand pump(176ppb)	Cauliflower	2.12	2.48	2.69	2.39

Table B14: As Concentrations of Different Parts of Sonargaon Tomato Samples

Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Edible (mg/kg)
svf 1	Tomato	0.65	0.63	1.04	1.33
svf 2	Tomato	1.27	0.66	0.88	0.63
svf 5	Tomato	0.72	0.58	1.11	0.28
svf 6	Tomato	-	0.47	0.5	0.63
svf 7	Tomato	0.48	0.81	1.38	0.18

Table B15: As Concentrations of Different Parts of Sonargaon vegetable Samples

			Edible Part	
Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)
svf 3	Lalshak	1.22	0.58	-
svf 4	Lalshak	0.84	0.39	0.96
svf 8	Datashak	1.84	0.56	0.91
svf 9	Datashak	1.29	0.76	1.06

Table B16: As Concentrations of Different Parts of Sonargaon vegetable Samples

				Edible Part	
				Leaf (mg/kg)	
Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Inner Part	Outer Part
svf 10	Cabbage	0.88	0.4	1.6	0.38
svf 11	Cabbage	1.36	0.56	0.62	0.49

Table B17: As Concentrations of Different Parts of Sonargaon vegetable Samples

				Leaf (mg/kg)		
Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Inner Part	Outer Part	Edible Part(mg/kg)
svf 12	Cauliflower	1.24	0.34	2.50	0.66	0.35

Table B18: Arsenic Concentrations (mg/kg) of different layers of Noakhali vegetable Field Samples

Field ID	Source of water and As con(ppb)	Vegetable Type	1st layer (0-75mm)	2nd layer (75-50mm)	3rd layer (150-00mm)	4th layer (300-50mm)
nvf 1	Pond (< 1 ppb)	Datashak	4.68	4.91	4.81	4.77
nvf 2	Tube Well (159ppb)	Datashak	2.26	1.93	2.52	3.64
nvf 3	Pond (28.29 ppb)	Arum	4.40	2.67	3.26	3.75
nvf 4	TubeWell(472.45ppb)	Arum	1.99	2.26	5.27	5.8

Table B19: As Concentrations of Different Parts of Noakhali vegetable Samples

			Edible Part	
Field ID	Vegetable Type	Root (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)
nvf 1	Datashak	0.76	1.61	0.18
nvf 2	Datashak	0.44	0.34	0.46
nvf 3	Arum	1.48	0.85	0.98
nvf 4	Arum	1.05	0.7	0.73

Table B20: Arsenic Concentrations (mg/kg) of different layers of Srinagar, Munshigonj Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Srinagar, Munshiganj. 2nd Sampling (22/06/2002)	mrf 1	25.91	11.36	6.12	5.53
	mrf 2	36.45	47.60	14.82	8.74
	mrf 3	10.99	11.21	8.62	6.51
	mrf 4	36.26	45.00	20.31	12.32
	mrf 6	24.87	25.62	10.83	6.02
	mrf 7	12.75	11.93	7.43	5.98
	mrf 8	13.12	14.30	7.45	5.16
	mrf 9	19.43	22.19	18.74	18.04

Table B21: Arsenic Concentrations of different layers of Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Srinagar, Munshiganj.	mrf 1	13.28	9.03	8.03	7.73
	mrf 2	21.93	16.71	9.20	8.57
	mrf 4	22.27	23.31	9.40	8.56
3rd Sampling (26/11/2002)	mrf 6	9.74	13.16	8.83	7.58
	mrf 9	12.47	12.67	7.50	6.91

Table B22: Arsenic Concentrations (mg/kg) of different layers of Paddy Field Samples

Location and Date	Paddy Field ID	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
Sonargaon, Narayanganj. 2nd Sampling (18/12/2002)	srf 1	8.59	9.5	3.28	3.62
	srf 2	13.16	3.97	3.68	2.80
	srf 3	3.51	3.48	2.79	2.72
	srf 4	5.64	3.22	3.82	4.37
	srf 6	9.63	20.52	6.46	9.59
	srf 12	36.55	3.51	3.81	3.22

Table B23: Arsenic Concentrations (mg/kg) of different layers of Srinagar, Munshigonj Vegetable Field Samples (2nd Sampling)

Field ID	Vegetable Type	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
mvf 1	Potato	7.42	8.04	8.06	9.08
mvf 2	Potato	6.82	8.21	8.58	10.04
mvf 3	Potato	5.17	4.95	4.56	3.28
mvf 5	Potato	6.2	6.16	5.78	5.64
mvf 6	Potato	5.42	6.09	5.96	4.98

Table B24: Arsenic Concentrations (mg/kg) of different layers of Sonargaon vegetable Field Samples(2nd Sampling)

Field ID	Vegetable Type	1st layer (0-75mm)	2nd layer (75-150mm)	3rd layer (150-300mm)	4th layer (300-450mm)
svf 6	Tomato	2.23	2.25	2.62	2.87
svf 7	Tomato	4.12	3.26	4.86	6.15
svf 8	Datashak	4.58	4.79	3.69	4.02
svf 9	Datashak	3.56	4.22	4.3	4.83
svf 11	Cabbage	5.1	6.82	5.67	5.89

APPENDIX-C

(Wilcoxon Rank Test)

Table C1: Comparison of arsenic concentrations of different parts of paddy plants of the three sites by rank test

Samples	Comparison	Comment
Grain	Srinagar vs Sonargaon	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	Concentrations of two sites are equal/identical
Husk	Srinagar vs Sonargaon	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	Concentrations of two sites are equal/identical
Stem	Srinagar vs Sonargaon	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	Concentrations of two sites are equal/identical
Leaf	Srinagar vs Sonargaon	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	Concentrations of two sites are equal/identical
Root	Srinagar vs Sonargaon	Concentrations of two sites are equal/identical
	Srinagar vs Dinajpur	Concentrations of two sites are equal/identical
	Sonargaon vs Dinajpur	Concentration in Sonargaon is higher

Table C2: Wilcoxon Rank Test

smaller sample size = 9, larger sample size =9

W	P	W
100	0.111	71
101	0.095	70
102	0.081	69
103	0.068	68
104	0.057	67
105	0.047	66
106	0.039	65
107	0.031	64
108	0.025	63
109	0.02	62
110	0.016	61
111	0.012	60
112	0.009	59

smaller sample size = 9, larger sample size =10

W	P	W
106	0.106	74
107	0.091	73
108	0.078	72
109	0.067	71
110	0.056	70
111	0.047	69
112	0.039	68
113	0.033	67
114	0.027	66
115	0.022	65
116	0.017	64
117	0.014	63
118	0.011	62
119	0.009	61

W= Sum of combined ranking

Source : Adapted from C.kraft and C. van Eeden, A Nonparametric Introduction to Statistics, Macmillan, New York, 1968.

APPENDIX-D
(The *t*-Distribution)

Table D1: The *t*-Distribution

d.f.	$t_{0.1}$	$t_{0.05}$	$t_{0.025}$	$t_{0.01}$	$t_{0.05}$	d.f.
1	3.078	6.314	12.706	31.821	63.657	1
2	1.886	2.92	4.303	6.965	9.925	2
3	1.638	2.353	3.182	4.541	5.841	3
4	1.533	2.132	2.776	3.747	4.604	4
5	1.476	2.015	2.571	3.365	4.032	5
6	1.44	1.94	2.447	3.143	3.707	6
7	1.415	1.895	2.365	2.998	3.499	7
8	1.397	1.86	2.306	2.896	3.355	8
9	1.383	1.833	2.262	2.821	3.25	9
10	1.372	1.812	2.228	2.764	3.169	10
11	1.363	1.796	2.201	2.718	3.106	11
12	1.356	1.782	2.179	2.681	3.055	12
13	1.35	1.771	2.16	2.65	3.012	13
14	1.345	1.761	2.145	2.624	2.977	14
15	1.341	1.753	2.131	2.602	2.947	15
16	1.337	1.746	2.12	2.583	2.921	16
17	1.333	1.74	2.11	2.567	2.898	17
18	1.33	1.734	2.101	2.552	2.878	18
19	1.328	1.729	2.093	2.539	2.861	19
20	1.325	1.725	2.086	2.528	2.845	20
21	1.323	1.721	2.08	2.518	2.831	21
22	1.321	1.717	2.074	2.508	2.819	22
23	1.319	1.714	2.069	2.5	2.807	23
24	1.318	1.711	2.064	2.492	2.797	24
25	1.316	1.708	2.06	2.485	2.787	25
26	1.315	1.706	2.056	2.479	2.779	26
27	1.314	1.703	2.052	2.473	2.771	27
28	1.313	1.701	2.048	2.467	2.763	28
29	1.311	1.699	2.045	2.462	2.756	29
inf.	1.282	1.645	1.96	2.326	2.576	inf.