

IDENTIFICATION OF CAUSES OF ARSENIC CONTAMINATION IN GROUNDWATER OF BANGLADESH

MOHAMMOD AKTARUL ISLAM CHOWDHURY



DEPARTMENT OF CIVIL ENGINEERING
BANGLADESH UNIVERSITY OF ENGINEERING AND
TECHNOLOGY
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IDENTIFICATION OF CAUSES OF ARSENIC CONTAMINATION IN GROUNDWATER OF BANGLADESH

by

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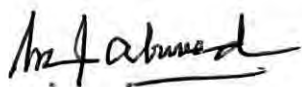
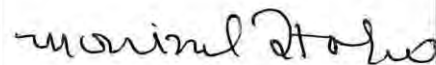
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degree of**

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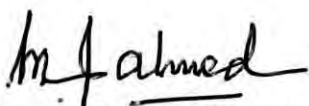
The thesis titled “**Identification of Causes of Arsenic Contamination in Groundwater of Bangladesh**” submitted by **Mohammad Aktarul Islam Chowdhury**, Roll No.: 001/04/1998 P, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **Doctor of Philosophy** on September 16, 2006

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Signature of the Candidate

***In the name of Allah, The Most Beneficent,
The Most Merciful***

DEDICATED

to

**My Father whom I lost during my Intermediate Study in
Dhaka College and Father in-law who passed away on
9th May'2006**

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ABSTRACT

Arsenic contamination of groundwater in shallow aquifers has become a severe water supply and health problem in many parts of Bangladesh. A national survey has identified 1.44 million tubewell contaminated with arsenic exceeding the Bangladesh drinking water standard of 0.05 mg/L and 38,420 cases of arsenicosis patient. In this study, groundwater, river water, suspended sediment of the river water, riverbed sediment, and floodplain sediment of three rivers (Jamuna, Padma and Meghna), and borehole sediment of alluvial plains of five arsenic affected districts of Bangladesh were collected and studied in an effort to identify sources of arsenic and mechanisms of its mobilization in the subsurface.

Arsenic content in river water, suspended sediment, riverbed sediment, and floodplain sediment of three rivers - Jamuna, Padma and Meghna was analyzed. Arsenic was found in suspended sediment at concentrations comparable to average arsenic content in soils in Bangladesh, but very little arsenic was found in the river water samples. The sediments were fractionated into sand, silt and clay fractions and the arsenic content in each of the fractions was determined. Highest concentration of arsenic was found in clay fraction of the sediment, followed by silt, with lowest concentration in sand. The arsenic content of fine-grained materials like clay is higher because they have higher surface area as well as adsorption sites per unit volume/weight. The beels and haors receive higher quantity of Arsenic as the clayey materials are deposited in these stagnant water bodies. It has been found that the districts with beel and haors and low-lying areas are severely affected by Arsenic contamination of groundwater.

An estimated 11,000 metric tons of arsenic is transported through Bangladesh each year from upstream with 2.4 billion tons sediment; a large fraction of this arsenic however is discharged in the Bay of Bengal with the sediment. The suspended sediment and river bed sediment may be an important source of arsenic in Bangladesh. Arsenic concentration in the floodplain sediments of three rivers - Jamuna, Padma and Meghna as well in the borehole sediments of alluvial plains of Sylhet, Chandpur, Munshiganj, Kushtia and Nawabganj were analyzed. Arsenic concentrations of these sediments have been found to be comparable to average arsenic contents in soils of Bangladesh.

Arsenic present in different chemical forms in the sediment samples from floodplain and alluvial plain were analyzed by sequential extraction method. Relatively small amount of Arsenic was found to be present as ionically bound and strongly adsorbed forms. Comparatively a larger amount of Arsenic was found to be associated with amorphous iron oxyhydroxides. However, there are variations in the chemical forms of Arsenic associated with sediment, depending on the geological history of the sediment. The Arsenic present in the sediments as ionically bound (IB), strongly adsorbed (SA), and associated with amorphous iron oxyhydroxides (AIO) accounts for significant quantities of total arsenic, which could be mobilized under reducing condition.

Arsenic and other relevant water quality parameters of groundwater samples were determined. Arsenic concentration was found to be positively correlated with ammonia, alkalinity and hardness of groundwater. This relationships support the process of Arsenic mobilization with the microbial breakdown of organic matters in the sub-soil environment. Arsenic was also found to be inversely correlated with oxidation-reduction potential (ORP) of groundwater.

The phase stability diagrams show that the eH-pH values of groundwater samples in the arsenic affected areas lie in the iron and arsenic soluble fields of the diagram. It indicates that arsenic and iron in the groundwater is likely to remain in soluble arsenite and ferrous form. The presence of soluble iron and arsenic (III) in fresh groundwater supports the findings. The presence of very low sulfate concentration found in the groundwater is also consistent with a reducing environment, and negates Arsenic mobilization as a result of oxidation of Arsenic bearing minerals.

Arsenic release from sediment was studied in the laboratory by simulating anaerobic reducing environment prevailing in aquifers in arsenic affected areas by introducing organic carbon in the form of glucose and molasses in closed reactors. Significant quantities of Arsenic were released in aqueous phase from sediment under anaerobic reducing condition at low Eh while no arsenic release was observed in control batch where enough oxygen was allowed to enter into the reactor to maintain aerobic condition. Arsenic was released from the sediments only when Eh values were lowered to less than zero. The study demonstrated that bacteria-mediated reducing state was a requirement for the release of arsenic from sediments.

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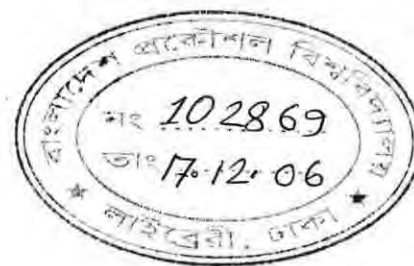
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Chapter 1

INTRODUCTION



1.1 BACKGROUND

Arsenic contamination of groundwater in many countries of the world has become a major problem in respect of water supply for drinking and irrigation purposes. An estimated 100 million people of the world are drinking water with arsenic in excess of WHO guideline value for drinking water and about 50% of them live in Bangladesh. Widespread Arsenic contamination of groundwater has become a major concern in Bangladesh where the water supply, particularly the rural water supply, is heavily dependent on groundwater extracted from shallow aquifers. Arsenic in groundwater of Bangladesh was first detected in the district of Nawabganj bordering the West-Bengal district of India in 1993 by Department of Public Health Engineering (DPHE). Since then higher levels of Arsenic (exceeding the WHO standard of 0.01 mg/L and Bangladesh standard of 0.05 mg/L) have been detected in many regions of the country by many of the initiatives like DPHE/British Geological Survey (BGS)/Mot Macdonalds Ltd (MML), Asia Arsenic Network (AAN) etc. (Ahmed et al. 1997; Khan et al., 1998; Talukdar et al., 1998; Safiullah et al., 1998; Ahmed, 1998; Tanabe et al., 1998; DPHE/BGS/MML, 1999; DPHE and BGS, 2000). According to a recent estimate of Bangladesh Arsenic Mitigation water Supply Project (BAMWSP), 27% of shallow hand-tube wells have Arsenic concentration exceeding 0.05 mg/L; in acute Arsenic problem areas more than 75% of shallow tube wells are contaminated with Arsenic. More than 38,000 Arsenicosis patient have so far been identified in Bangladesh (BAMWSP, 2005). Estimates of population exposed to Arsenic contamination vary from about 20 million to over 36 million (DPHE/BGS/MML, 1999). A more accurate estimation based on tubewell contamination shows that 29 million are exposed to arsenic in excess of Bangladesh Standard of 0.05 mg/L and 49 million people are exposed exceeding WHO Guideline value of 0.01 mg/L in Bangladesh (Ahmed, 2003). Thus arsenic contamination in groundwater has been regarded as the severe natural calamity in Bangladesh.

Oxidation of Sulphide minerals and release from Arsenic-rich Iron oxyhydroxides are the most commonly identified natural processes that may lead to widespread Arsenic contamination of groundwater. The geologic map of Bangladesh shows the presence of organic matter and peat in many locations. The swamp areas also produce a plenty of vegetation each year. Decomposition of these organic matter and nutrients in anaerobic condition would produce organic acids to produce an environment for the release of Arsenic by reduction process (Ali and Ahmed, 1998). Hydro-geological studies conducted so far did not reveal any evidence of widespread presence of Arsenic-bearing Sulfide minerals in Bangladesh. No studies have found empirical evidence to support oxidation hypothesis in absence of widespread arsenopyrite in Bangladesh. Hot spots in Bangladesh are not located in areas of high withdrawal of groundwater (Ahmed, 2003). In a recent study it was observed that Arsenic contaminated sediments are characterized by prominent ferruginous coatings around sand grains (Ahmed et al., 1998). BGS and MML (1999) considered reductive desorption and dissolution of Arsenic adsorbed onto Iron oxyhydroxides in recent sediments to be the most probable mechanism of Arsenic mobilization in groundwater. Based on the limited research conducted so far, Arsenic-rich Iron oxyhydroxides appear to be the major source of Arsenic in the groundwater, from which Arsenic is released as a result of dissolution and desorption. It has been suggested that reducing environment in the alluvial aquifer, primarily due to the presence of organic matter, promotes dissolution of Iron oxyhydroxides and consequent release of Arsenic (Ahmed, 2000). Also, use of phosphate fertilizer can potentially enhance release of Arsenic as a result of replacement of Arsenic by phosphate ions on the adsorption sites of Iron oxyhydroxides. However, there are considerable doubts and unanswered questions regarding the source of Arsenic and the mechanisms of its mobilization in the subsurface of Bangladesh. Presence of Arsenic has been detected in different regions of the country with varying hydro-geological characteristics. In some places, it has been found that although there is little variation in sediment-Arsenic concentration with depth, aqueous (i.e., groundwater) Arsenic concentration varies significantly with depth (Harvey, 2000). However, the mechanisms responsible for mobilization of Arsenic only at certain depths are not clear. Role of microbes, although to be very important in the mobilization of Arsenic, is still unclear.

Proper understanding of Arsenic source and its release mechanism can have important implications on the watershed management as well as on the development of remedial technologies. For example, over-extraction of groundwater may significantly influence the release of Arsenic from pyrite/arsenopyrite minerals by promoting its oxidation, while it may not have much influence in releasing Arsenic from Arsenic-rich Iron oxy-hydroxides. Success of some of the probable in-situ remedial technologies e.g., well aeration technology, also depend on the nature of the source of Arsenic in the subsurface. Also an important question that needs to be answered is whether Arsenic concentration in the still-unaffected shallow tube wells would increase with time. This is particularly important in view of the observed trend (DPHE/BGS/MML, 1999) that older tube wells are more likely to have higher Arsenic concentration. Sediment Arsenic concentrations in some deeper aquifers, with very little aqueous (i.e., groundwater) Arsenic concentration, have been found to be comparable to those found in the sediments of Arsenic affected shallow aquifers (Harvey, 2000). This certainly raises the question – whether the unaffected deeper aquifers could become contaminated with Arsenic in the future? This question is particularly important in view of the fact that deep-tube wells are being promoted as an alternative to Arsenic affected shallow-tube well water. Adequate knowledge of sources of Arsenic and mechanisms of its mobilization is essential for answering these important questions. The proposed intensive research on the causes of Arsenic contamination aimed at developing a better understanding of Arsenic source and its mobilization in the subsurface.

1.2 OBJECTIVES OF THE RESEARCH STUDY

The overall objective of the present research was to develop a better understanding of the causes of Arsenic contamination i.e. of the source of Arsenic, mechanism of its transportation and mobilization in the subsurface and release into groundwater of Bangladesh. Field and laboratory investigation was carried out to achieve the following specific objectives.

- (i) Determination of total Arsenic concentrations in suspended and river bed sediments and in water of major rivers in Bangladesh to understand the source of arsenic.
- (ii) Total arsenic in deposited sediments in floodplain and borehole sample from arsenic contaminated areas to understand the possible changes of arsenic content with time.
- (iii) Determination of arsenic in different forms associated with the sediment samples (e.g., ionically bound Arsenic, strongly adsorbed Arsenic, Arsenic co-precipitated with Iron oxyhydroxides) using *sequential extraction technique*.
- (iv) Detailed characterization of groundwater samples in order to understand the relationship of Arsenic with other water quality parameters and assess the geo-chemical environment in the subsurface vis a vis Arsenic mobilization.
- (v) Determination of seasonal fluctuations in water table or peizometric head (in the piezometers) and possible changes in groundwater composition (including variation in As concentration) with a view to assess its possible impact on Arsenic mobilization.
- (vi) Assessment of release of Arsenic in laboratory batch experiments with selected sediment samples under simulated anaerobic redox conditions prevailing in the aquifers in the arsenic affected areas.

1.3 SCOPE OF THE STUDY AND METHODOLOGY

1.3.1 Selection of the study area and sample collection

Based on available information on geology, hydrogeology, sedimentology and different types of other sites representing hydrogeologic characteristics, study areas were selected to collect surface water and groundwater samples, suspended sediments, river bed sediment, floodplain sediment and borehole sediment of alluvial plain in different Arsenic

affected areas considering the severity of prevailing Arsenic contamination in groundwater of Bangladesh. Borehole sediment samples were collected from bore holes drilled in Munshiganj, Chandpur, Sylhet, Kushtia and Chapainawabganj districts. Groundwater samples were collected from piezometers located in Chandpur, Sylhet, Kushtia and Chapainawabganj districts. Samples of surface water, suspended sediment water, river bed sediment from the depth (0-5 cm), core river bed sediment, core sediment from floodplain along the bank of the river during post-flood period in September-October of 2001 was collected from Bahadurabad, Jagannathganj, Bhuanpur and Aricha-Nagarbari along the Jamuna, Rajshahi-Kutibari, Pakshi, Aricha-Paturia, Mawa and Tongibari-Digirpar along the Padma and Sohagpur, Zia Fertilizer Factory at Ashuganj, Daudkandi, Chandpur and Heimchar along the Meghna. Also surface water and river bed sediment samples were collected during the pre-flood (April) period of 2001 from a few locations along these major rivers.

1.3.2 Experiment and Analysis

- Laboratory investigations were carried out to assess the quality of the groundwater and the bio-geochemical processes responsible for Arsenic mobilization. Detailed characterization of collected groundwater samples was done in order to assess the geochemical environment in the subsurface.
- Arsenic content in the sediment samples was determined after extraction of Arsenic from the sediments following standard procedure.
- Arsenic present in different forms (e.g., ionically bound Arsenic, strongly adsorbed Arsenic, Arsenic co-precipitated with Iron oxyhydroxides) in the sediment samples was determined using a *sequential extraction technique*.
- Laboratory batch experiments were conducted with selected sediment samples in order to assess release of Arsenic from sediment under anaerobic condition.

Detailed methodologies of each item of experimental works have been described in detail in the respective chapters.

1.4 IMPORTANT LIMITATIONS

- (i) There were some limitations with regard to sampling procedures. For example river bottom sediment could not be collected exactly from the middle way of the river. Floodplain sediment could not be collected from depths greater than 60 cm due to technical limitation.
- (ii) Borehole sediments were collected from bore-well of BWDB from where it was not possible to collect sediment from depths greater than 132 feet. Also due to the limitation of fund, excavation of deep borehole in the desired locations could not be done.
- (iii) Age of the sediments, though an important parameter, could not be determined by dating technique with the application of radiocarbon isotope technology. Determination of age of the sediments was beyond the scope of our study.
- (iv) Analysis of total organic carbon TOC, dissolved organic carbon DOC as well as total inorganic carbon content TIC and dissolved inorganic carbon DIC content in the aquifer sediment was vital to get the information about the causes of Arsenic contamination in groundwater; but TOC, DOC, TIC and DIC were not measured and analyzed in this study due to the lack of experimental facilities in the laboratory.
- (v) For the analysis of surface water as well as the suspended sediment, river bed sediment and the river flood plain sediments, samples were collected from three rivers Padma, Jamuna and Meghna. Samples could not be collected from the tributaries and distributaries of these rivers due to time and resource constraints.

1.5 ORGANISATION OF THE THESES

The content of this research work is organized in seven chapters.

The first Chapter includes the background and problem, objectives of the study, scope of the study and methodology, important limitations and organization of the thesis. Brief description of the study area and sample collection as well as the experiment and analysis is found here.

The second Chapter entitled 'Literature Review' presents a complete picture of Arsenic contamination in Bangladesh groundwater and a detailed review of the many of relevant works, factors and properties regarding the causes of Arsenic contamination in groundwater.

Arsenic in river water, suspended sediments and river bed sediments, and arsenic load in the river sediment is described in Chapter Three.

Arsenic in solid and aqueous phases in aquifers is discussed in Chapter Four. Total concentration of arsenic in both the floodplain sediment of the rivers and borehole sediment of alluvial plain are presented in this Chapter. Besides, arsenic present in different chemical forms in the sediment and its relationship with Arsenic mobilization are also presented and discussed in this Chapter.

The concentration of arsenic and other water quality parameters in the groundwater and the effects of these parameters on the mobilization of arsenic and its release mechanism from solid phase to aqueous phase are discussed in Chapter Five.

The Chapter Six presents the results of experiments carried out to assess the mobilization of Arsenic from sediments under anaerobic condition and its relevance to the arsenic release mechanism in the context of Bangladesh.

Conclusions including specific findings, recommendation for further works are presented in Chapter Seven.

Chapter - 2

LITERATURE REVIEW

2.1 SCOPE OF THE LITERATURE APPRAISAL

Problem being dealt with in the research is the causes of Arsenic contamination in groundwater of Bangladesh. Causes of Arsenic contamination in groundwater is related with natural or anthropogenic source(s) of Arsenic in subsurface from where Arsenic has been transported and deposited in the sediment aquifer for a long period such as thousands of years and subsequently these deposited Arsenic from solid sediment aquifer is being transported, mobilized and released in to liquid groundwater phase through various bio-geo-chemical processes such as oxidation, photo-chemical oxidation, precipitation, dissolution, adsorption-desorption, methylation, reduction, decoupling etc. mediated by oxidizing and reducing microbes as well as derived by redox driver and organic stimulus present in the bio-geo-chemical environment of the subsurface. In order to explain the causes of Arsenic contamination in groundwater, it is very vital to have clear understanding about Arsenic bearing mineral ores available in the surface, compounds and chemical forms of the Arsenic, properties of Arsenic and Arsenic compounds, acid-base chemistry of Arsenic, redox chemistry of Arsenic, speciation of Arsenic etc. as well as the extent and severity of Arsenic contamination prevailed in Bangladesh groundwater. Obviously this chapter presents a complete picture of Arsenic contamination in Bangladesh groundwater and a detailed review of the many of the such relevant phenomenon, factors and properties regarding the causes of Arsenic contamination in groundwater.

2.2 ARSENIC CONTAMINATION IN GROUNDWATER

Possibly Arsenic contamination in groundwater was first recorded as severe case in Taiwan after 1961 then reported as hazard in many other countries. The occurrences of Arsenic in drinking water drawn from a variety of groundwater environment has been reported in many places around the world particularly in Argentina (Nicolli et al, 1989; Smedley et al., 1998, 2001), Australia (Smith et al., 2003), Bangladesh (Karim, 2000; Nickson et al., 2000; Kinniburgh and Smedley, 2001; McArthur et. al., 2001; Ravenscroft

et al, 2001), Canada (Michel, 1990; Leger, 1991), Cambodia (Ahmed, 2003), Chile (Ahmed, 2003; Romero et al., 2003; Cacers et al., 1992), China (Inner Mongolia and Guizhou province) (Ahmed, 2003; Smedley et al., 2001), Hungary (Ahmed, 2003), India (West Bengal) (Bhattacharya et al., 1997; Acharyya et al., 1999, 2000), Iran (Mosaferi et al., 2003), Lao PDR (Ahmed, 2003), Mexico (Del Reza et al., 1990; Arminta et al., 1997), Mongolia (Ahmed, 2003), Nepal (Ahmed, 2003), Pakistan (Ahmed, 2003), Switzerland (Fabian et al., 2003), Taiwan (Kuo, 1968; Chen et al., 1996; Guo et al., 1997), Thailand (Ahmed, 2003), the USA (Matisoff et al., 1982; Welch et al., 1988, 2000; Robertson, 1989; Welch and Lico, 1998; Peters et al., 1999; Schreiber et al., 2000) and Vietnam (Berg et al., 2001). In west Bengal of India, the biggest Arsenic calamity of the world was identified in the decade of eighty where about 34 million people are "at risk" due to Arsenic in drinking water (Mandal et al, 1996).

High Arsenic in ground water in the young flood plains of the Bengal Delta (Bangladesh and West Bengal, Eastern India) has been shown to be a serious environmental issue in recent decades (PHED, 1993; Chatterjee et al., 1995; Bhattacharyya et al, 1997; CGWB, 1999; Nickson et al. 2000; BGS and DPHE, 2001; Smedley and Kinniburgh, 2002). The scale of the problem is grave and unprecedented exposing 36 million people to risk and covering a geographic area of $173 \times 10^3 \text{ km}^2$ (BGS and DPHE, 2001; RGNDWM, 2001). In terms of the population exposed, Arsenic problems in ground water from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. Concentrations in ground waters from the affected areas have a very large range from < 0.5 to $3200 \mu\text{g l}^{-1}$ (DPHE/BGS/MML, 1999; CGWB, 1999; BGS and DPHE, 2001). Some 27% of shallow ($< 150 \text{ m}$ deep) wells in Bangladesh while in some districts more than 90% of wells are affected. Up to around 30-35 million people in Bangladesh are estimated to be exposed to Arsenic in drinking water at concentrations above $50 \mu\text{g l}^{-1}$ (BGS and DPHE, 2001) and up to 6 million in West Bengal. Skin disorders including hyper/hypo pigmentation changes and kurtosis are the most common external manifestations, although skin cancer has also been identified. Around 5000 patients have been identified with Arsenic related health problems in West Bengal (including skin pigmentation changes) although some estimates put the number of patients with Arsenicosis at more than 200,000 (Smith et al., 2000). In groundwater of Bangladesh Arsenic was first detected in the district of Nawabgang bordering the West Bengal of India in 1993. Since then elevated levels of Arsenic (exceeding the WHO

guideline value of 0.01 mg/l and MCL in accordance with Bangladesh Water Quality Standard of 0.05 mg/l) have been identified and reported in many areas of Bangladesh (Ahmed et al. 1997; Khan et al., 1998; Talukdar et al., 1998; Safiullah et al., 1998; Ahmed, 1998; Tanabe et al., 1998). According to Dave (1997); about 23 million people are "at high risk" endangered by Arsenic in Bangladesh. Arsenic contamination of groundwater has been detected in 41 out of 61 administrative districts and an estimated 35 million people in Bangladesh are at risk of Arsenic toxicity (Khan et al., 1998). In accordance with survey findings of Dhaka Community Hospital (DCH) published in October 1997, 60 million people of 41 districts are "at risk of Arsenic contamination" as water of tube-wells of 41 districts showed Arsenic concentration above 0.05 mg/l (permissible limit of Arsenic in drinking water for Bangladesh). According to a study report published jointly by the School of Environmental Sciences of Jadabpur University of India and DCH, 50 million people of 29 districts of Bangladesh is at the risk of Arsenic poisoning. Field survey conducted from August 95 to February 2000 by School of Environmental Studies (SOES) and DCH shows that 100 million people of 54 districts of area 125,133 sq. km is at risk of Arsenic hazard where groundwater of 73.39% of tube wells contain Arsenic above 0.01 mg/l and 9.3 million people of 47 districts of area 112,407 sq. km is at risk of Arsenic poisoning where groundwater of 53.47% of tube wells contain above 0.05 mg/l. (SOES and DCH, 2000). All the facts, information and results obtained from the studies conducted by these organization have established the fact that the water in substantial number of tube-wells of Bangladesh is Arsenic contaminated in varying degrees and millions of people of Bangladesh are at risk of Arsenic poisoning. According to the reports of the national newspapers, a significant number of people are attacked by Arsenic lesions of which a few dies; severe social hazard emerges in the Arsenic affected areas; a large amounts of financial loss are being incurred (by the individual publics as well as by the Government) for Arsenic health hazard and setback of social structure. Skin lesions such as melanosis, gangrene, hyperkurtosis and hyper pigmentation in palms and soles and non-cirrhotic portal fibrosis are common Arsenical lesions among the population affected by Arsenic. In a later stage the patches might develop into cancer and foot will probably have to be amputated (Battacharya et al., 1997; Quadiruzzaman, 1996; Pontius et al., 1994). Characteristics skin lesions of Arsenic toxicity indicates high exposure of Arsenic which are distinctive in contrast to other clinical manifestations of Arsenic intoxication including weakness, conjunctiva congestion, edema, portal hypertension, bronchitis and hepatomegaly

(Tondel et al., 1999; Majumdar et al., 1992). An estimated 20 million people are exposed to the risk of Arsenic related ailment through drinking of Arsenic contaminated water (BGS and MML, 1999). It has been considered to be the most serious drinking water related Arsenic problem in the world in terms of population exposure. About 7,600 Arsenic affected patients have so far been identified in Arsenic affected areas. The Arsenic problem has emerged as a big environmental disaster and more than 50 million people are exposed to Arsenic above the Bangladesh drinking water standard (DPHE/BGS, 2000; DCH/SOES, 2000). However, all these investigations, studies and information signal Arsenic contamination in groundwater of Bangladesh as a looming "Disaster!".

The study conducted by British Geological Survey (BGS), Department of Public Health Engineering (DPHE) and Mott MacDonald Limited (MML) in two phases examined 3534 distributed water samples from 61 districts except 3 hilly districts (DPHE, BGS and MML, 1999; BGS and DPHE, 2001) with an average of 58 samples per district and 8 samples per upazila. The study showed that Arsenic concentration of 42% of all tube well samples exceeded 10 $\mu\text{g/l}$ and 25 % exceeded 50 $\mu\text{g/l}$. When only shallow tube wells are considered, 46% and 27% exceeded 10 $\mu\text{g/l}$ and 50 $\mu\text{g/l}$ respectively. In case of deep tube well (> 150m) samples, Arsenic content have only 5% exceeded 10 $\mu\text{g/l}$ and 1% exceeded 50 $\mu\text{g/l}$.

The most contaminated part of the country lies in the southern regions covering the greater districts Chandpur, Comilla, Noakhali, Munshiganj, Faridpur, Madaripur, Gopalganj, Shariatpur and Satkhira. Contamination has also been found in SW, part of NW, NE and North Central regions. There is large variability in the concentration ranges of Arsenic within an area. In certain areas the concentration ranges show normal distribution pattern, whereas in other areas bimodal or polymodal distribution patterns are shown. There are variations in concentration ranges even in village scales where areas of low and high Arsenic regions can occur as reported from Samta village of Sharsha thana of Jessore district (AAN, 1999).

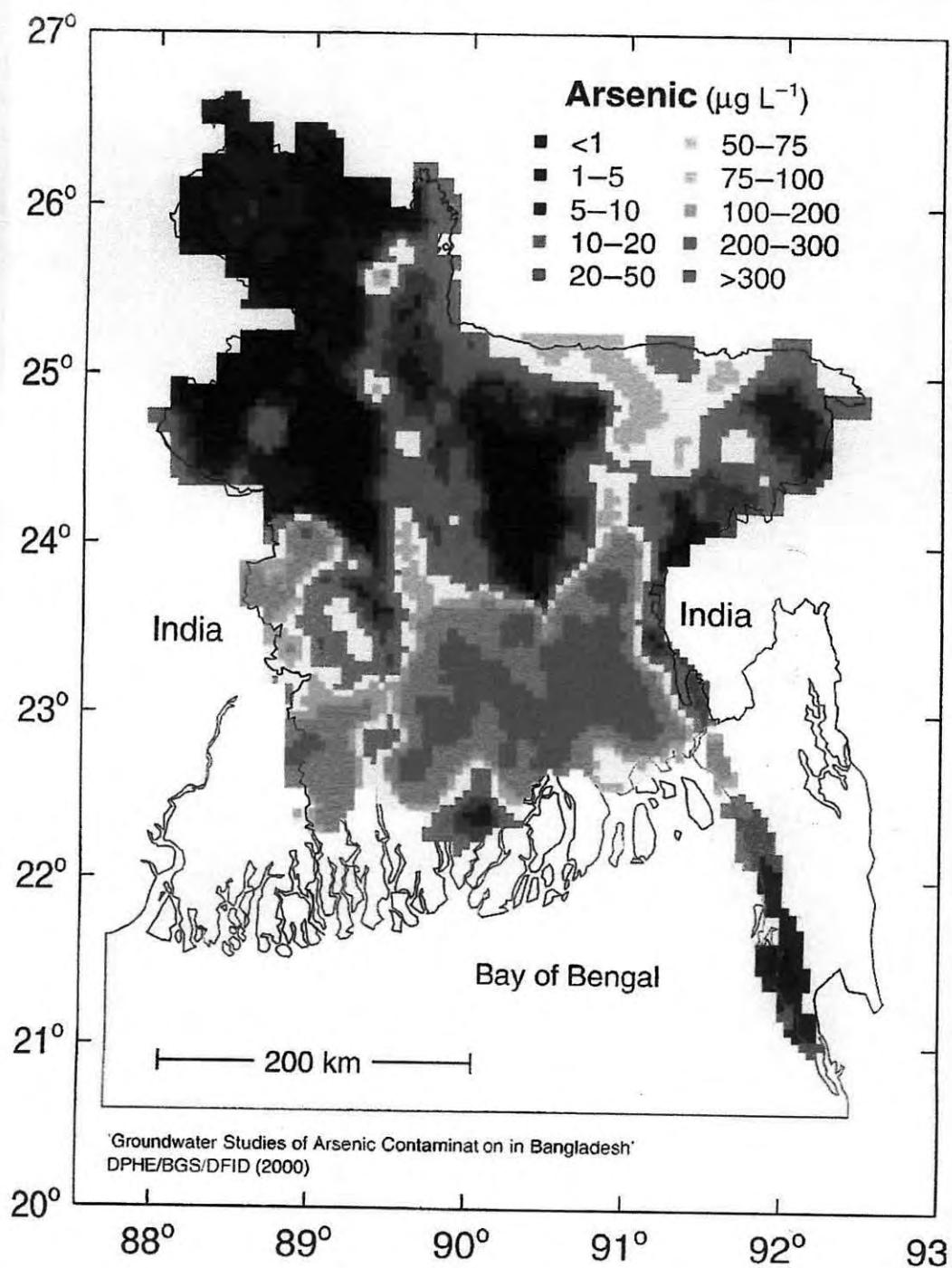


Fig. 2.1 Map showing geographical distribution of the levels of Arsenic concentration in tubewell water of Bangladesh (DPHE/BGS, 2000)

Groundwater studies for Arsenic contamination in Bangladesh carried out by DPHE and British Geological Survey funded by Department for International Development (DFID) of UK showed the geographical distribution of Arsenic contamination in groundwater of Bangladesh as shown in Fig 2.1.

The overall pattern of Arsenic shows a broad band with little contamination running along the north bank of the Padma in Rajshahi division; the southwest region of the country appears to show the greatest local variability but with the degree of contamination increasing from west to east, while the southeast region is the most uniformly contaminated.

The northeastern Sylhet region is contaminated in a highly irregular pattern; while along the coastal plain of Chittagong, there is significant contamination apparently reducing in intensity in the south of Chittagong City. The wells located on the Barind tract are mostly free of Arsenic. Alluvial sands in the upper part of the Padma floodplain and alluvial silt in the upper part of the Mahananda floodplain areas substantially free of Arsenic but highly contaminated in other areas.

The higher Arsenic contaminations are found at relatively shallow depths beneath the Padma and the Meghna flood plains in sands of early Holocene age. On the other hand, the Dupi Tila sands (which includes Madhupur and Barind Clay or Tracts) and other older strata are virtually devoid of Arsenic contamination (DFID, 1999). Very high concentrations can occur in a restricted area as found in Nawabgang Sadar of Chapai Nawabganj district, Charruppur of Iswardi of Pabna district, Gopalgang Sadar of Gopalgang district, Kachua, Hajigang and Faridgang of Chandpur district, Ramgang of Lakshmipur district, Begamgang of Noakhali district, Kushtia Sadar of Kushtia district, Sonargaon of Narayanganj district, Sreenagar of Munshiganj and Samta of Shariatpur of Jessore district etc. (AAN, 1997; DPHE/BGS, 2001). These types of occurrences can be termed as "hot spots". However overall-view of Arsenic contamination in groundwater of Bangladesh as the percentage of contaminated wells as per the upazilla wise combined results of National Screening Program 2002-2003 is shown in Fig 2.2.

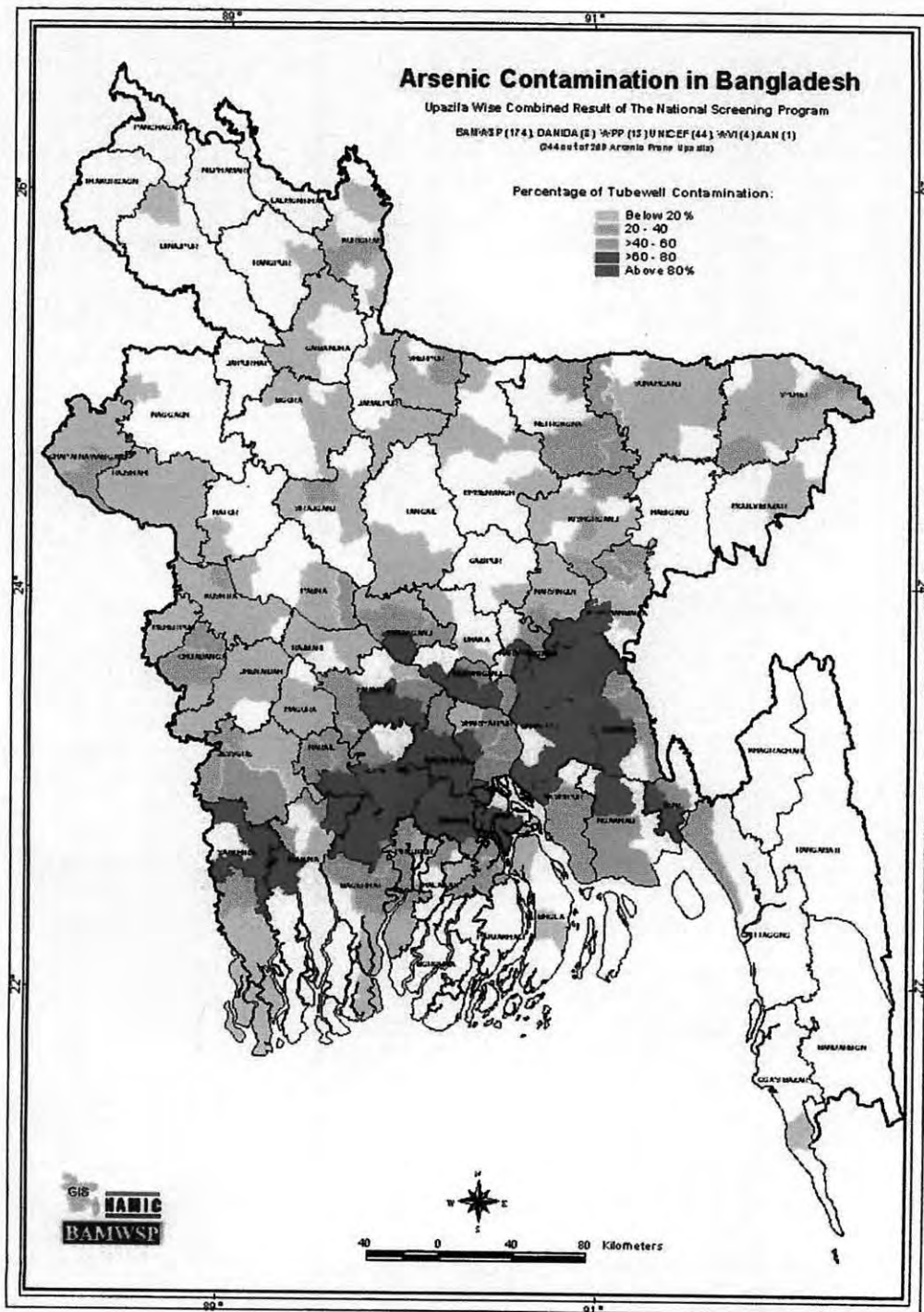


Fig. 2.2 : Map showing the intensity of contaminated tubewell (BAMWSP,2005)

2.3 SOURCES OF ARSENIC

Arsenic occurs widely in natural environments including air, soil, rock and minerals and water. More than one hundred Arsenic bearing minerals are available and the most common are arsenopyrite (FeAsS), realgar (AsS) and orpiment (As_2S_3). Other minerals containing Arsenic, as accessory component are also well known, such as pyrite and Iron-hydroxides. Bacterial and/or organic matters that affect the Arsenic cycle on earth's surface may be present (Bowell, 1994). Researchers worldwide accept that important sources of Arsenic in groundwater aquifers are Iron oxides and Sulfide minerals although oxides of Manganese and aluminium and clay minerals have also been cited as possible addition sources (Brannon and Patrick, 1987; Goldberg and Globig, 1988). Arsenic in drinking water can result from number of natural and anthropogenic processes (Smedley & Kinniburgh, 2002).

2.3.1 Natural sources of Arsenic

Arsenic bearing minerals are the primary natural sources of Arsenic. There are more than 245 such minerals, mostly ores containing Sulfide, along with copper, nickel, lead, cobalt and other metals, as well as some oxides. The most important ores of Arsenic are arsenopyrite or mispickel (FeAsS), realgar (As_4S_4), orpiment (As_2S_3), cludite, iollingite (FeAs_2), nicolite (NiAs), cobalt-glance (CoAsS), nickel-glance (NiAsS), smaltite (CoAs_2), and arsenolite (As_2O_3). Among these, arsenopyrite is probably the most common mineral. More than 99% of the total Arsenic in the environment is present in rocks (Mackenzie et. al., 1979). The Arsenic levels in soil derived from sedimentary rocks may attain a value of 20 to 30 ppm (Zou, 1980). The level of Arsenic in soils derived from granite is lower than those derived from basalt (Koyama, 1975). The average concentration of Arsenic in soils of the world is 7.2 ppm (Anonymous, 1978). Arsenic in natural environment occurs in soils at average concentration of about 5 to 6 mg/kg, but varies among geographic region (Peterson et. al., 1981). Leavander (1977) reported that soils close to or derived from Sulfide ore deposits may contain upto 8000 mg of As/kg. Amounts of Arsenic in earth's crust and shales are 1.5 and 13 ppm respectively (Iimura, 1981). Soils derived from shales and granites have been shown to contain elevated Arsenic concentration upto 250 mg/kg (Colbourn et al, 1975). Soils in

areas surrounding geothermal activities contain such a high As concentration that health of grazing animal is seriously affected (Grimmett, 1939; Grimmett and MacIntosh, 1939).

The source of Arsenic in groundwater is most often leaching of geological materials, input from geo-thermal sources, mining wastes and landfills either anthropogenically or naturally. Oxidation of Sulfide minerals and release from Arsenic-rich Iron oxyhydroxides are the most commonly identified natural processes that may lead to widespread Arsenic contamination of groundwater. A number of recent studies confirm that high Arsenic in Bangladesh groundwater has been mobilized by the reductive desorption and/or dissolution of Iron (and Manganese) oxyhydroxide where the organic matter play important role (Burgess et al, 2000; McArthur et al., 2001; Ravenscroft et al., 2001; Jacks et al., 2000; Shahnewaz et al., 2000, DPHE/BGS, 2000; AAN, 1999; Anwar et al., 2002). Acharyya et al. (2000) also supports Arsenic release under reducing conditions mediated by microbial reactions. DPHE/BGS study support the hypothesis that Iron oxides but not pyrite or arsenopyrite, are the main source of Arsenic in Bangladesh groundwater.

2.3.2 Anthropogenic sources of Arsenic

Arsenic may accumulate in soil by anthropogenic activities. The principal Arsenical compounds are herbicides, cotton desiccants, and wood preservatives and in 1990 their production rates were 8000, 12000, and 10000 tons Arsenic per year, respectively (Allaway, 1990). Arsenic may accumulate in soil from various anthropogenic activities through use of Arsenical pesticides, application of fertilizers and other agro-chemicals, irrigation and enhanced leaching beneath irrigated land, dust from the burning of fuels, fossil fuel burning, urban storm water pollution, disposal of industrial and animal wastes, mining activities and smelters, forestry, industrial activities & wastes, electric poles painted with Arsenic preservatives, etc. (Sandberg and Allen, 1975; Welch et al., 1988; Korte and Fernando, 1991}. Uncontrolled anthropogenic activities such as smelting of metal ores, use of Arsenical pesticides and plant/wood preservative agents may release Arsenic directly to the groundwater environment (Bhattacharyya et al., 1995). Anthropogenic sources may account for isolated cases of Arsenic contamination, but it is

clear from available information that such sources can't account for the extent of occurrence of Arsenic contamination in Bangladesh (BGS and MML, 1999; NRECA, 1997).

2.4 ARSENIC IN SEDIMENT

Arsenic not rare in the geo-soil environment; is found in all sediments, typically at total concentrations from a few mg/kg up to about 10 to 15 mg/kg normally less than 30 mg/kg in most uncontaminated rocks and soil the global average concentration of Arsenic probably ranges from 2-5 mg/kg based on the type of the sediment, although concentration of Arsenic in unconsolidated sediment, typically varying from 3-10 mg/kg depending upon texture and mineralogy, does not usually differs from those in their indurate equivalents, with mud and clay having higher concentrations than sands and carbonates. Arsenic occurs in soils all over the world at an average concentration of about 5 to 6 mg/l (Bhumbla and Keefer, 1994), but mean Arsenic contents in soils as high as 20 ppm in Italy, 14 ppm in Mexico, 11.2 ppm in China, and 11 ppm in Japan have been reported (Yan-Chu, 1994). Arsenic concentration in the sediment from Lapampa, Argentina ranged from 3 to 18 mg/kg, sediment from Hubhot Basin of Inner Mongolia of China contains 3 to 29 mg/kg of Arsenic (BGS and DPHE, 2001).

In Bangladesh, As concentration varies from 0.6 to 50 mg/kg in alluvial sand (Azcu and Nrigu, 1995), 1.0 to 6 mg/kg in alluvial mud/clay (Kinniburg and Smedley, 2001); from 2-10 mg/kg in the alluvial sediments (Bose and Sharma, 2002); and from 2.7 to 14.7 mg/kg in alluvial sediment (Kinniburg and Smedley, 2001). Arsenic concentrations in Bangladesh soils as high as 51 mg/kg in Faridpur and 83 mg/kg in Comilla have been reported (Ullah, 1998). In Bangladesh, sediments appear to be typical young alluvial sediment; the average concentration of Arsenic in alluvial sand and mud/clay have been reported to be 2.9 mg/kg and 6.5 mg/kg respectively in Bangladesh while the Arsenic content in the sediment of three specific study areas Nawabgang, Faridpur and Lakshmipur varied from 0.4 to 10.3 mg/kg with the averages of 5.9, 3.4 and 3.2 mg/kg in Nawabgang, Faridpur and Lakshmipur respectively (DPHE/BGS, 2001).

The geo-chemical analysis of the core samples demonstrate that silty sand, clayey silt and peat soils, that are generally enriched in organic content, oxide phases of Fe and Mn and Fe Sulfide, contains very high concentration of Arsenic while the Arsenic content is very low in sand. Arsenic content in sediments was found to be 28.32 mg/kg in clayey silt at 5-7 feet, 54.19 mg/kg in peat soil at 20-22 feet, 1.39 mg/kg in coarse sand at 40-42 feet, and 4.06 mg/kg in sand at 120-122 feet depth in Kolora, Satkhira district (Anwar et al., 2002).

Datta and Subramanian (1997) reported that Arsenic concentrations in sediments ranged from 1.2 mg/kg to 5.9 mg/kg in the mighty rivers Ganges (Padma), Brahmaputra (Jamuna) and Meghna varying from 1.2-2.6 mg/kg averaging 2 mg/kg in the river Ganges, from 1.4-5.9 mg/kg averaging 2.8 mg/kg in the river Brahmaputra, from 1.3-5.6 mg/kg averaging 3.5 mg/kg in the river Meghna.

Groundwater from all peat, coal in swamp and marshy lands is severely contaminated by Arsenic. The surface peat layers contain significantly higher Arsenic concentrations than do deeper peat. Arsenic contaminated aquifers at Laxmipur and Chandpur areas of the Meghna estuary are located within the same depth zones of enormous pockets of biogenic gas. Thus Arsenic contaminated aquifers are genetically related to the back swamp, lagoon environment of deposition.

In shallower aquifer depth from 1 m to 20 m, Arsenic content in the sediment decrease with the increase of depth (Kinniburgh and Smedley, 2001). High Arsenic concentrations in shallow aquifer may be associated with:

- areas with low recharge, either because of low rainfall, high evaporation or high runoff;
- silts and fine sands within alluvial floodplains and delta areas leading to low groundwater flow rates;
- relatively low hydraulic conductivity (0.4 to 43 m/d), high porosity (0.2 to 0.3);
- areas where flushing takes 50-200 ka per pore volume even during last glacial maximum
- areas with low gradients at present time leading to flushing times exceeding 200 ka.

On the other hand, in relatively higher aquifer depth from 25 m to 40 m Arsenic concentration decreases also with increase of depth. According to the BGS study (Kinniburgh and Smedley, 2001), low Arsenic concentrations in deep aquifers may be associated with:

- Coarse sands at the base of the incised channels possibly stacked channel in fluvial areas of the delta region;
- relatively high conductivity (61 to 95 m/d), medium porosity (0.1 to 0.15);
- relatively rapid flushing, some 2-10 ka per pore volume;
- sediments greater than 10 ka old.

2.5 ARSENIC CHEMISTRY

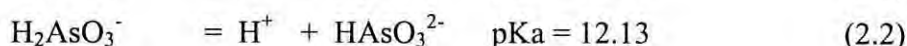
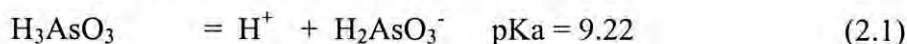
The occurrence and origin of Arsenic as well as attenuation and mobilization of Arsenic in groundwater depends on several chemical factors such as adsorption-desorption, as well as precipitation-dissolution of unstable Arsenic minerals, subsurface redox condition, grain size of aquifer materials, ion-exchange capacity of the aquifer, mineralogical chemistry of the aquifers, organic contents, bio-chemical characteristics and activities of the aquifers (Forest and Griffin, 1977; Robertson, 1989; Lin and Puls, 2000). Arsenic can be adsorbed onto Al-OH groups as the constituents on the edges of mineral particles; As(V) can be preferentially adsorbed over As(III) on illitic and kaolinitic clays (Manning and Goldberg, 1977).

2.5.1 Acid-Base Chemistry of Arsenic

Apart from the elementary Arsenic with oxidation state of 0, Arsenic is stable in the oxidation states of +5, +3 and -3 (Table 2.1), but generally found in water only in the trivalent and pentavalent states. The oxides of both Arsenic (III) and Arsenic (V) are soluble in water. The dissolution implies direct reaction with the water, hydration, where the oxides behave like non-metals and exhibit acidic character.

Arsenic (III) forms arsenious acid also called arsonic acid. Arsenic (V) forms the Arsenic acid, also called arsinic acid. The two acids dissociate to form respectively arsenite and arsenate ions as shown in the following reactions.

Dissociation of Arsenious Acid:



Dissociation of Arsenic Acid:

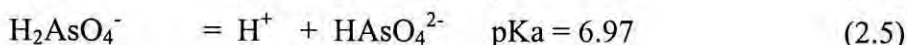
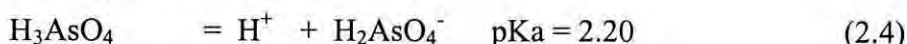


Table 2.1: Arsenic species and their environmental importance in water

Compounds	Example	Environmental Significance/ Dominant pH region
Arsine Oxidation state: -3	As^{3-}	Minor importance [Most toxic As species]
Elemental Arsenic Oxidation state: 0	As	Minor importance [Least toxic As species]
Trivalent Arsenic Oxidation state: +3	As(III)	Dominant under anaerobic condition [10 times more toxic than As(V)]
Arsenite, Inorganic	H_3AsO_3 $\text{H}_2\text{AsO}_3^{1-}$ HAsO_3^{2-} AsO_3^{3-}	pH = 0 – 9 pH = 10 – 12 pH = 13 pH = 14 Important
Methylated As(III) MMAs(III) DMAs(III) TMAs(III) Organo-As(III)	$\text{CH}_3\text{As(III)O}_2^{2-}$ $(\text{CH}_3)_2\text{As(III)O}^{1-}$ $(\text{CH}_3)_3\text{As(III)}$	Minor importance [Less toxic than inorganic As(III)]
Pentavalent Arsenic Oxidation state: +5	As(V)	Dominant under aerobic condition [10 times less toxic than As(III)]
Arsenate, Inorganic	H_3AsO_4 $\text{H}_2\text{AsO}_4^{1-}$ HAsO_4^{2-} AsO_4^{3-}	pH = 0 – 2 pH = 3 – 6 pH = 7 – 11 pH = 12 – 14 Important
Methylated As(V) MMAs(V) DMAs(V) TMAs(V) Organo-As(V)	$\text{CH}_3\text{As(V)O}_3^{2-}$ $(\text{CH}_3)_2\text{As(V)O}_2^{1-}$ $(\text{CH}_3)_3\text{As(V)O}$	Minor importance [Less toxic than inorganic As(V)]

Figure 2.3 shows the predominance diagram of Arsenic species as a function of pH. From Figure 2.3 it is seen that Arsenic acid is stronger than arsenious acid. Within the range of natural waters (particularly groundwater), where pH is usually between 6 and 9, the trivalent inorganic Arsenic is found as non-dissociated arsenious acid (H_3AsO_3); while the pentavalent Arsenic is primarily found as the ionized di-hydrogen arsenate (H_2AsO_4^-) and mono-hydrogen arsenate (HAsO_4^{2-}). The relatively more mobile monomethylated and dimethylated forms are observed in ocean and lake waters, but seldom in groundwater.

The trivalent Arsenic is more difficult to remove from the water than the pentavalent (Kartinen and Martin, 1995). Probably this ionization of Arsenic (V) is also important for the fate of Arsenic in the human body. The reduced toxicity of the Arsenic (V) may be, to a large extent, due to its ionization, which enables easier control of its intracellular transportation (Dahi, 1997).

2.5.2 Redox Chemistry of Arsenic

Arsenic is a redox sensitive element. Arsenate [As(V)] and Arsenite [As(III)] are common oxidation states of Arsenic in water. The mobility of Arsenic is controlled, in large part, by oxidation-reduction (redox) transformations. The valence in which Arsenic exists is related to both pH and the oxidation-reduction (or redox) potentials, Eh . The hypothetical electron activity at equilibrium, pE , is used interchangeably with Eh .

These parameters are related by $pE = (F/2.3 RT) Eh$, where T is the absolute temperature, and F and R are the Faraday and Gas constants, respectively. Thus at 25°C , $2.3RT/F = 0.059 \text{ V}$ and $pE = Eh/0.059$. The equation linking Arsenic speciation to pH and pE are readily available, but Eh versus pH diagrams (Figure 2.4), which indicate the predominant soluble species and relevant solids, are the most concise way of presenting this information.

The Eh -pH diagram for Arsenic (total concentration 10^{-5} mol/L) in a system including oxygen, H_2O and sulfur (total concentration 10^{-3} mol/L) is shown in Fig. 2.4. The diagram represents equilibrium conditions of Arsenic under various redox potentials. Well-aerated surface waters would tend to induce high Eh values, therefore, any Arsenic present should be in the arsenate [As(V)] form. Mildly reducing conditions, such as can be found in

groundwater, should produce arsenite [As(III)]. By calculating the pH and Eh of water, it is possible to determine which species is prevalent.

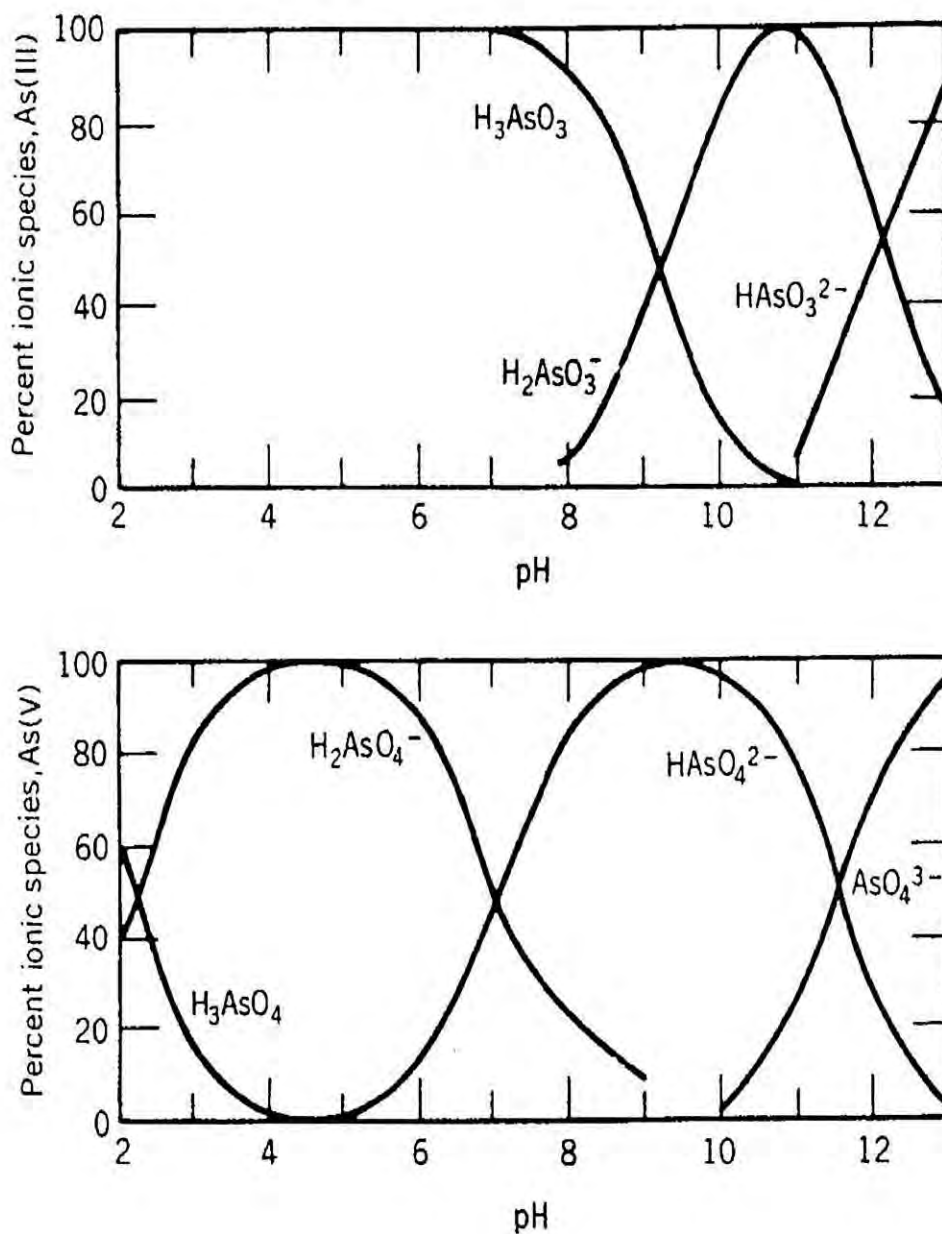


Fig. 2.3: Predominance diagram of As(III) and As(V) as a function of pH (Montgomery, 1985)

These parameters are related by $pE = (F/2.3 RT) Eh$, where T is the absolute temperature, and F and R are the Faraday and Gas constants, respectively. Thus at $25^\circ C$, $2.3RT/F =$

0.059 V and $pE = Eh/0.059$. The equation linking Arsenic speciation to pH and pE are readily available, but Eh versus pH diagrams (Figure 2.4), which indicate the predominant soluble species and relevant solids, are the most concise way of presenting this information.

The Eh - pH diagram for Arsenic (total concentration 10^{-5} mol/L) in a system including oxygen, H_2O and sulfur (total concentration 10^{-3} mol/L) is shown in Fig. 2.4. The diagram represents equilibrium conditions of Arsenic under various redox potentials. Well-aerated surface waters would tend to induce high Eh values, therefore, any Arsenic present should be in the arsenate [As(V)] form. Mildly reducing conditions, such as can be found in groundwater, should produce arsenite [As(III)]. By calculating the pH and Eh of water, it is possible to determine which species is prevalent.

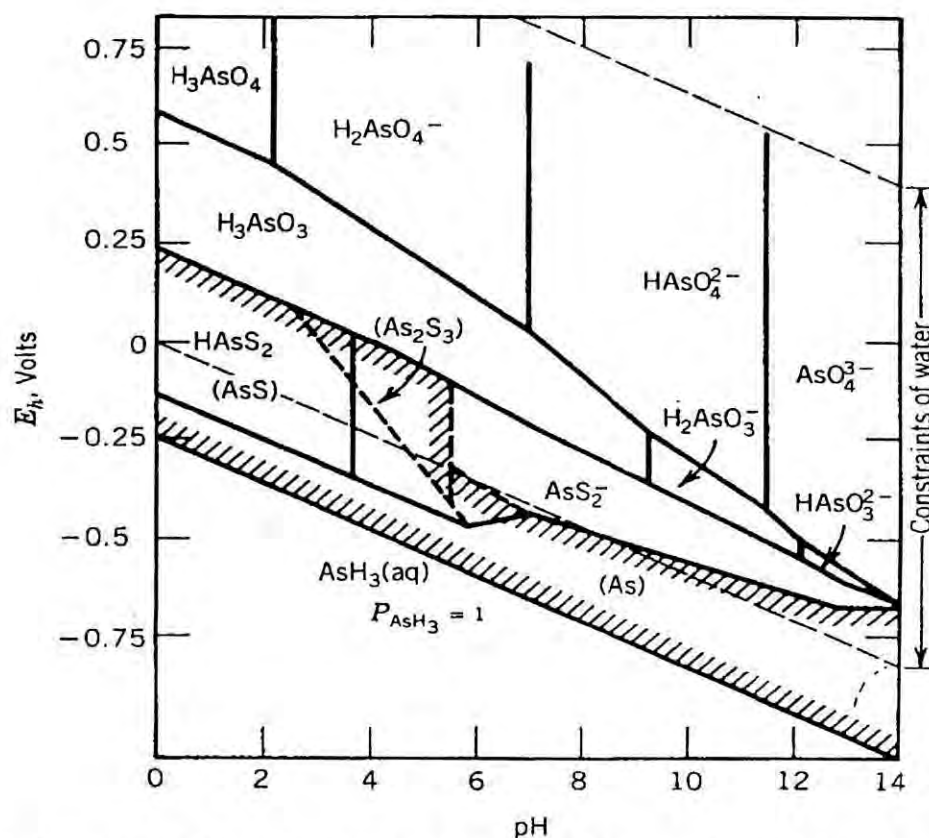


Fig. 2.4: The Eh - pH diagram for As at $25^\circ C$ and 1 atm with total Arsenic 10^{-5} M and total sulfur 10^{-3} M. Solid species are enclosed in parenthesis in cross-hatched area, which indicates solubility less than $10^{-5.3}$ M (Montgomery, 1985)

2.5.3 Oxidation Reactions of Arsenic

Arsenate is dominant in oxygenated water while arsenite is dominant in non-oxygenated water. Although thermodynamics can provide an accurate prediction of possible changes in a given non-equilibrium conditions, they give no insight to the rate at which those changes will occur. While As(III) and As(V) acid-base reactions can be assumed to occur instantaneously, changes between oxidation states require indeterminate time periods in natural waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, yet the transformation takes days, weeks or months depending on the specific conditions. The reduction of As(V) to As(III) is similarly kinetically constrained. This is the reason why As(V) can be found in some anoxic waters (Dahi, 1997). This process is however also known to be facilitated through catalysis and require bacterial mediation. Oxidation of As(III) to As(V) occurs on the clay surfaces, provided de-sorption of As from the clays is higher for As(III) than As(V) (Manning and Goldberg, 1997).

Adsorption-desorption of Arsenic onto Iron oxide surfaces are important controlling reactions in the subsurface because Iron oxides are widespread in the hydro-geologic environment as coatings on other solids, and because arsenate adsorbs strongly to Iron oxide surfaces in acidic and near-neutral pH conditions. Desorption of arsenate is favored at higher (i.e., alkaline) pH values. The pH dependence of arsenate adsorption-desorption appears to be related to the change in net charge on Iron-oxide surface with pH.

The net charge on Iron oxide surface changes from positive to negative as pH increases above the "zero-point-of-charge" (pH at which net surface charge is zero). The "zero-point-of-charge" is about 7.7 for goethite (crystalline Iron oxide) and about 8.0 for ferrihydrite (amorphous Iron oxide). Thus as pH increases above about 8, the net negative surface charge on Iron oxides can repel the negatively charged ions such as arsenate. Compared to arsenate, arsenite is less strongly adsorbed by Iron oxides. Arsenate and arsenite adsorption-desorption reactions onto other common surfaces are less well characterized.

In Bangladesh Arsenic-rich Iron oxyhydroxides present in aquifer materials appear to be the primary source of Arsenic in groundwater. In the subsurface environment, adsorption-desorption of Arsenic onto Iron oxyhydroxides is an important mechanism controlling its mobility. As noted earlier, presence of ligands, which may compete with Arsenic for adsorption sites on Iron oxyhydroxides, e.g., phosphate, silicate and sulfate can also influence the mobility of Arsenic in the subsurface, if present in large enough concentrations. Besides oxyanions of molybdenum, selenium and vanadium can also compete with Arsenic for adsorption sites.

As a result of pH dependence of Arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of Arsenic. Similarly, redox reactions can control aqueous Arsenic concentration by their effect on Arsenic speciation and hence on adsorption-desorption reactions. For example reduction of arsenate to arsenite can promote Arsenic mobility because arsenite is less strongly adsorbed than arsenate. It should be noted that in nature bacteria often mediate oxidation-reduction reactions.

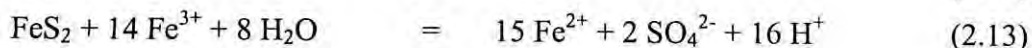
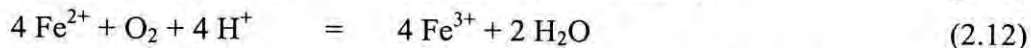
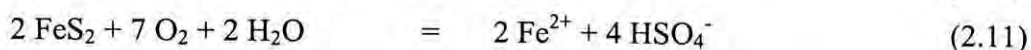
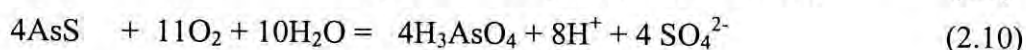
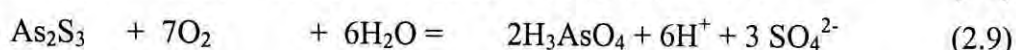
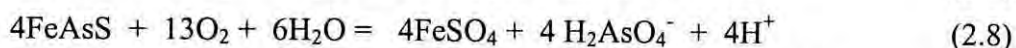
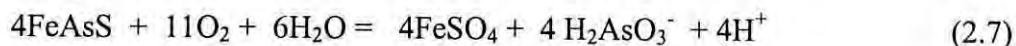
Finally, structural changes in solid phases at the atomic level can also affect Arsenic adsorption-desorption (USGS, 1999). For example, conversion of amorphous ferrihydrite to crystalline goethite may occur gradually over time (Dzombak and Morel, 1990) and this can be accompanied by a decrease in adsorption site density. This reduction in site density may result in desorption of adsorbed Arsenic. Structural changes in other solid phases may also affect Arsenic mobility (USGS, 1999).

2.5.4 Precipitation and Dissolution of Arsenic

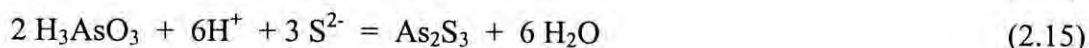
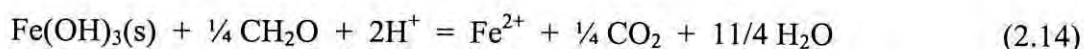
Precipitation-dissolution reactions are important mechanisms controlling mobility of Arsenic in the subsurface. Arsenic contained within solid phases, either as a primary structural component of Arsenic bearing minerals (e.g., arsenopyrite) or an impurity in any of a variety of solid phases (e.g., pyrite), is released to groundwater when these solid phases dissolve. Similarly, Arsenic is removed from groundwater when solid phases containing Arsenic precipitate from aqueous phase. As an example, because Arsenic often co precipitates with Iron oxide, Iron oxides may act as an Arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater (USGS, 1999). Besides, solid phase dissolution will contribute not only Arsenic contained within that phase, but

also any Arsenic adsorbed to the solid-phase surface. In Bangladesh, reductive dissolution Iron oxyhydroxides and consequent release of adsorbed Arsenic could be an important mechanism of Arsenic mobilization in the subsurface.

Oxidative dissolution reactions (Bhumba and Keefer, 1994) of arsenopyrite (FeAsS) (Eq. 2.7-2.8), Orpiment (As₂S₃), (Eq. 2.9) and Reagler (AsS) (Eq. 2.10) are shown below. Oxidative dissolution of pyrite (FeS₂) is shown in Eq. 2.11-2.13 (Chowdhury et al., 1998).



The interplay of redox reactions and solid phase precipitation and dissolution may be particularly important with regard to aqueous Arsenic and solid-phase Iron oxides and Sulfide minerals (USGS, 1999). High concentrations of Arsenic often are associated with Iron oxides and Sulfide minerals. Iron oxides frequently dissolve under reducing conditions (e.g., in the presence of organic matter, as shown in Eq. 2.14), but often precipitate under oxidizing conditions. Sulfide minerals generally are unstable under oxidizing conditions, but may precipitate under reducing conditions (e.g., precipitation of As₂S₃, as shown in Eq. 2.15). Thus, as a result of redox sensitive nature of Iron oxides and Sulfide minerals, transfer of large amounts of Arsenic between these solid phases and neighboring water may result from redox-facilitated precipitation and dissolution reactions (USGS, 1999).



2.6 RELEASE MECHANISM AND MOBILIZATION OF ARSENIC INTO GROUNDWATER

Mobilization of Arsenic in groundwater is mainly governed by low temperature geochemical processes that involves leaching of naturally occurring ores, As-bearing rocks and sediments (Cullen and Reimer, 1989; Korte and Fernando, 1991; Nriagu, 1994; Rude, 1996; Peters et al., 1999) as well as accumulation of Arsenic in soil and ground subsurface by microbiological reduction processes especially under anoxic conditions and may also be due to anthropogenic input or human activities (Bowell et al., 1994; Azcue et al., 1995; Mariner et al., 1997; Chakraborti et al., 1998; Ashley and Lottermoser, 1999; Madhvan and Subramanian, 2000; Stuben et al., 2001; Cumming et al., 2002; Stuben et al., 2003).

Mobilization of Arsenic in natural groundwater occurred in a range of geochemical environments can be divided into (i) aquifers under reducing conditions, (ii) aquifers under oxidizing high pH (>8) conditions, (iii) areas of Sulfide liberalization (especially in mining areas) and (iv) geothermal areas. In regions with oxidizing groundwater, potentially useful indicators of Arsenic problems include high pH values >8, and high alkalinities >500 mg/l. On the other hand, in regions with reducing groundwater, useful indicators are the significant occurrence of As, Fe, Mn, HCO₃ and NH₄ at higher concentrations and often significant amount of phosphorus concentration and typically low concentration of dissolved oxygen, NO₃-N, PO₄, Cu, Ni, Zn, Pb, Co and Se in addition to the relatively very low concentration of SO₄ showing negative correlation with Arsenic.

Arsenic release from Iron oxides can be achieved by desorption under aerobic conditions or by desorption and dissolution under anaerobic condition as follows.

- (a) In aerobic oxidizing condition, precipitation/desorption of Arsenic particularly As (V) from Iron oxides by oxidative reactions is known to be strongly pH dependent (Pierce and Moore, 1982; Dzombak and Morel, 1990); competition with other ions such as phosphate (Hiemstra and vanRiemsdijk, 1999) and possibly bicarbonate HCO₃ can also reduce the sorption of As (V). Conditions of high groundwater pH are commonly (though not exclusively) found in the Quaternary

sedimentary and volcanic aquifers of arid and semi-arid regions like Central Argentina, Northern Chile, North-central Mexico and parts of South-western USA (Smedley et al., 2001) where groundwater are dominantly enriched with Na-HCO₃ & recharge is low and where evaporation becomes important as an additional control on increasing concentration in groundwater from aquifer (Welch and Lico, 1998; Leavy et al., 1999). Arsenic pollution by oxidation of Arsenical pyrite is a mechanism valid for oxic environment where oxic conditions invade a previously anoxic environment, for example, one hosting Sulfide ore such as occurs in northwestern Wisconsin (Schreiber et. al., 2000), where a commercially prospective Sulfide ore-body, up to 3 m thick, is exposed to oxic conditions in domestic borehole hand-tube-wells. Oxidation of the ore results in pollution of groundwater by high concentrations of Arsenic up to 15000 µg/l, sulfate < 618 mg/l, Iron <160 mg/l and acidity with pH of 2.1 (Schreiber et. al., 2000).

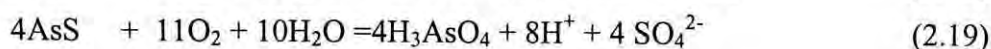
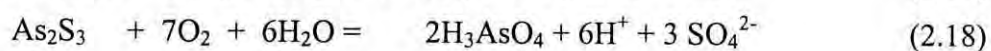
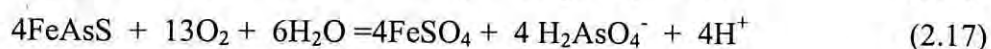
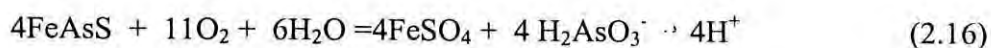
- (b) Under anaerobic reducing condition, Arsenic release and mobilization is believed to be largely linked to reduction of As (V) on Iron oxides to As (III) with resultant desorption, as well as the reductive dissolution of the oxides themselves and the processes such as aging and restructuring of the Iron oxides during sediment diagenesis (Kinniburgh and Smedley^{1,2}, 2001). The generation of strongly reducing condition appears to have had a large impact on Arsenic chemistry of groundwater in the quaternary aquifer of Australia, Bengal delta of Bangladesh and West Bengal of India, China including Inner Mongolia, Taiwan, Vietnam, Hungary and Rumania as well as parts of the Western USA (Smedley et al., 2001). Besides, with the solid/solution ratios found in the aquifer, even a small shift in the sorption isotherm can have a large impact on the concentration of Arsenic found in the groundwater; such shifts may occur due to a reduction of surface area of the oxide or to a change in surface structure and may possibly be related to the development of reducing condition as well as to the changes in the oxidation state of the Arsenic. Where Arsenic pollution occurs in most subsurface and most anoxic environment reduction of FeOOH would serve in most instances.

Three major available hypotheses developed by three schools of thoughts in the present and last decades are in prevalence pertaining to the release and mobilization of Arsenic in groundwater of the Bengal delta to explain Arsenic contamination in the Bengal basin including Bangladesh as mentioned below:

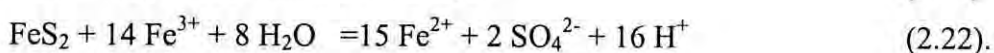
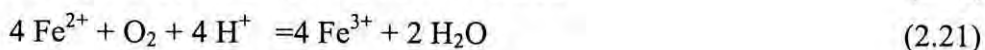
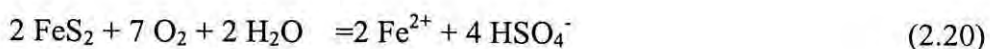
- (i) The first school of thought believes that oxidation of Arsenic-bearing pyrite minerals such as pyrite (FeS_2)/arsenopyrite (FeAsS) in the alluvial sediments due to excessive withdrawal of groundwater allowing substantial portion of air entry is responsible for Arsenic release and mobilization in groundwater regarded as Oxidation Theory (Mallick and Rajagopal, 1995; Mandal et. al., 1998, Bose and Sharma, 2002). According to Acharyya (1997), the excessive withdrawal of groundwater induces oxidation of aquifer material. Due to heavy ground water withdrawal by pumping and fluctuation of water table from pre-monsoon to post-monsoon, the underground aquifer of bore holes is aerated by the entry of oxygenated groundwater and the pyrite decomposes and Arsenic is entered into groundwater (by the leaching of acid released by decomposition of pyrite);
- (ii) The second school of thought (proposed by Bagla and Kaiser, 1996) believes that the high concentration of phosphate sourced from over application of fertilizer to surface soils has desorbed and displaced Arsenic from the aquifer mineral surface of pyrite into solution by competitive exchange of anions known as Phosphate Hypothesis (Acharya et. al., 2000; Bose and Sharma, 2002);
- (iii) Third school of thought believes that naturally occurring adsorbed Arsenic in grain coating of Iron oxyhydroxide (FeOOH) and in Manganese oxyhydroxide (MnOOH) is released into groundwater when the Arsenic contaminated oxyhydroxide reduced on dissolution as anaerobic (anoxic) condition develop during sediment burial (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001; Bose and Sharma, 2002) termed as Oxyhydroxide Theory.

2.6.1 Pyrite Oxidation

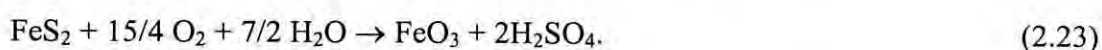
According to the pyrite oxidation hypothesis, Arsenic is released to groundwater due to oxidation of pyrite/arsenopyrite contained as pocket deposits in the aquifer sands. This oxidation is initiated by the entry of air into the aquifer due to lowering of water table as a result of large-scale groundwater abstraction for irrigation. The known affinity of pyrite to accommodate Arsenic (Han and Fyfe, 2000; Shuvaeva et al., 2000; Lumsdon et al., 2001) and the detection of Arsenic-rich pyrite in aquifer sediment have been invoked by several researchers (Das et al., 1996; Nickson et al., 2000; McArthur et al., 2001) to support the idea that Arsenic is released into groundwater from Sulfide ores such as pyrite, arsenopyrite, orpiment, realgar etc. mostly pyrite which were oxidized primarily due to water-level draw down as a consequence of intensive irrigation and groundwater exploitation by human activities where precipitation-(oxidative) dissolution reactions are important mechanisms controlling Arsenic release mechanism and mobility of Arsenic in the subsurface. Arsenic contained within solid phases, either as a primary structural component of Arsenic bearing minerals (e.g., pyrite/arsenopyrite/orpiment/realgar etc.) or an impurity in any of a variety of solid phases (e.g., pyrite), is released to groundwater when these solid phases dissolve. Besides, solid phase dissolution will contribute not only Arsenic contained within that phase, but also any Arsenic adsorbed to the solid-phase surface. Relevant oxidative dissolution reactions of arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS) (Bhumba and Keefer, 1994) are given according to the equations (Eq. 2.16-2.19).



Oxidative dissolution reactions of pyrite (FeS_2) decomposition (Chowdhury et al., 1998) are cited in accordance with the chemical equations (Eq. 2.20-2.22).



In pyrite decomposition $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions formed act as catalyst for the further decomposition of pyrite. If the source of Arsenic in Arsenic-rich pyrite in the Arsenic affected areas of Bengal basin (nine districts of West Bengal, and 61 districts of Bangladesh) then the questions arise how Arsenic came into the underground sediment and how Arsenic was released from pyrite? The experimental findings of the bore-hole sediment may give the explanation - in the Ganges basin there is deposition of weathered base metals; due to reducing condition of the Delta, available Iron and sulfur combined to form FeS_2 (by authogenic formation) and Arsenic from Arsenic-rich base metals entrapped in the crystal or replaced sulfur in pyrite. Then question comes why and how pyrite decomposed and released Arsenic? Subsequent answer is – although Iron pyrite is not soluble in water, it can be decomposed to ferrous sulfate, ferric sulfate and sulfuric acid when exposed to air or in water containing dissolved oxygen; in the nine Arsenic affected districts of west Bengal, millions of cubic meters of groundwater are withdrawn by large diameter water production tube-wells from shallow and deep aquifers for agricultural irrigation and in most cases such tube wells are not properly sealed with cement and concrete; as a result, there is the probability of flowing of air to the aquifer (Mallick and Rajgopal, 1996). Further the upper delta plain is mostly under unconfined conditions except near the southern fringe and there is a fluctuation of the water table from wet season to dry season that is increasing every year. Thus groundwater is aerated and complex chemical process of pyrite oxidation is happened involving 15 or more steps of reaction resulting in overall reaction commonly written as:



As Arsenic concentrations in pyrite generally range from 0.02% to 0.5% and may as large as 6.5% (Kolker et. al., 1998), the above reaction can release a significant amount of Arsenic to the aqueous phase.

Choudhury *et al.* (1998) reported the presence of Arsenic-rich pyrite in a number of Arsenic affected districts in West Bengal, India and concluded that due to heavy withdrawal of groundwater, aquifer was aerated and oxygen entering into the aquifer oxidized pyrites rich in Arsenic and acid released in the oxidation process leached out the Arsenic in soluble form in groundwater. In dry season, ground water table becomes deeper by agricultural irrigation declining water table; due to lowering of water table

aerobic environment appears in the deeper sediment where organic matters can be decomposed easily by aerobic bacteria. Such changes in the sediment by stratification allow the favorable condition for some of the aerobic bacteria to grow. Groundwater of many tube wells of Samta village in Bangladesh contain significant amount of nitrogen (AAN, RGAG and NIPSOM, 1999) which is oxidized to nitrite and then soon to nitrate by available aerobic bacteria under oxic condition (Akai et al, 2001) according to the chemical reactions given below.



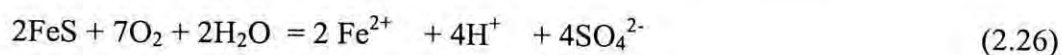
Overall situation of Sylhet basin and upper flood plain of Meghna may be compared with Arsenic contamination of Bardhaman, Maldah, Murshidabad, Nadia, 24-Pargana (north) and 24-Pargana (south), six districts of West Bengal India where analysis of bore-hole sediment showed Arsenic-rich Iron pyrite FeS_2 in sediment layers (Das et al., 1997). Since Iron pyrite FeS_2 is not soluble in water, the question obviously arise how Arsenic from pyrite enters in the groundwater. Insoluble pyrite decomposes when exposed to air or in aerated air; a probable explanation may be that the changes of geo-chemical environment due to high withdrawal of groundwater might have resulted in decomposition of pyrites to ferrous sulfate, ferric sulfate and sulfuric acid and thus Arsenic in pyrite become available. Such kind of mobilization of Arsenic in the groundwater of the Western USA may be, in part, a result of changes in the geo-chemical environment due to agricultural irrigation; in the deeper subsurface, elevated Arsenic concentration are associated with compaction caused by groundwater withdrawal (Welch et al., 1988). It is also stated that due to heavy groundwater withdrawal, the underground aquifer is aerated and oxygen causes degradation/decomposition of Arsenic-rich sources (Das et al., 1997).

Although a few experts and geologist cited the oxidation of Sulfide as the cause of Arsenic release and mobilization of Arsenic in the sediment aquifers of Bengal Delta including Bangladesh (Chowdhury et. al, 1997) resulting from excessive and alleged irrigation by over-abstraction of groundwater and consequent dewatering of the aquifer like the oxidation of Sulfide minerals of which pyrite is the most common particularly in

the sediments of mining areas, being the dominant controlling factor on mobilization of Arsenic, it gets very little authenticity.

Pyrite oxidation can be rejected as a mechanism of Arsenic pollution for the reasons as follows:

(a) The sediment contains too little Arsenical pyrite; measured sulfur concentrations in aquifer sediments contain both pyrite and organic sulfur but allow upper limits to be placed on pyrite abundance of 0.3% (Nickson et al.), 0.02% (AAN, 1999), 0.1% (McArther, et al., 2001), and 0.06% (DPHE, 1999). Arsenic to be released by partial oxidation of Arsenical pyrite in Bangladesh groundwater in anoxic condition would have an Iron/sulfate molar ratio of 0.5 from the stoichiometry of the reaction:



In reality, Iron and sulfate are mutually exclusive in solution occurring Arsenic concentration $> 50 \mu\text{g/l}$ and sulfate concentration $< 30 \text{ mg/l}$. If oxidation were complete and FeOOH would be produced rather Fe^{2+} would form by partial oxidation, the Arsenic would be sorbed to this FeOOH (Mock and Wai, 1994, Savage et al. 2000). Arsenic pollution is not common in hand-dug well (Chakraborti, 2001) which are shallowest and most exposed to atmospheric oxygen, consequently groundwater in intermediate shallow depth contaminated by Arsenic may not be derived from pyrite by oxidation.

(b) In Bangladesh, there is no apparent relationship between Arsenic occurrences and irrigation withdrawal, neither is there a correlation between lowering of water table with groundwater fluctuation and occurrence of Arsenic. The hydrograph of highly contaminated Chandpur do not show any declining pattern. At the same time groundwater underneath Dhaka city is Arsenic safe despite continuous decline in water level. It is therefore evident that decline in water level is not the cause of Arsenic as mentioned in the pyrite oxidation hypothesis. Thus there is no support for pyrite oxidation hypothesis in which pyrite oxidation in the zone of water table fluctuation is assumed to release Arsenic and ultimately to be responsible for the groundwater Arsenic problem. Also there is no evidence to support the proposition that Arsenic contamination in groundwater is caused by the recent seasonal draw down of the water table due to a recent increase in irrigation

abstraction (Kinniburgh and Smedley¹, 2001). Similarly, the hot spots in Bangladesh are not located in areas of high withdrawal of groundwater for irrigation.

(c) Even geological studies (Umitsu, 1987; Bose and Sharma, 2002) in the affected region of Bangladesh show no evidence of a discrete set of Arsenic-rich Sulfide mineral deposition either on surface or subsurface in the affected regions. Furthermore, mobilization of Arsenic from Arsenic-bearing Sulfide minerals will require oxidation of these minerals, which is unlikely in the relatively oxygen-poor subsurface environment of Bangladesh (Von, 1999).

Hence, the hypothesis of Arsenic release by oxidation of top layer of soil is not being considered as main mechanism of groundwater contamination in Bangladesh.

2.6.2 Competitive Adsorption of Phosphate and Arsenic

The most likely competitive anions in the groundwater of Bangladesh are phosphate, bicarbonate, silicate and dissolved organic matter. The increasing use of phosphate fertilizer in Bangladesh for the last two/three decades developed an assumption (Acharya et al., 1999; 2000) that Arsenic contamination in Bangladesh groundwater may result, at least in part, from the displacement of FeOOH on sorbed Arsenic as a result of competitive anion exchange by phosphate leached from soil. Phosphates hypothesis can be reviewed and rejected by the following arguments:

- (a) Although phosphate fertilizer such as triple super phosphate (TSP) and muriate of potash. (MOP) are widely used in Bangladesh, the amount of use are not so high in comparison to international standard. Generally TSP of 40, 110, 70 & 50 kg/hactre and MOP of 10, 50, 25 & 15 kg/hactre are used for the cultivation of HYVT aus (irrigated), HYVT aman (Irrigated), HYV bore and HYVT aman (rainfed) which are quite below the use in the USA, Japan, China, Taiwan etc. There are extensive areas where groundwater is essentially free of both Arsenic and phosphorous in spite of the intensive irrigation and probably highest application of fertilizer. This argument rejects any link between phosphate fertilizer and Arsenic.

- (b) Another argument in favor of the rejection of Arsenic-phosphate link concerns the fact that water contain the bicarbonate concentration of at least 200 mg/l before phosphorous, Arsenic or Iron, are found in significant amount (Mcarther et. al, 2001). Waters (aquifer) containing lowest carbonate, are the youngest and least evolved, also they would contain most phosphorous (and so Arsenic) supplied from surface application of fertilizer. Phosphorous in groundwater cannot contribute much to Arsenic contamination is shown by the experimental desorption by phosphate of Arsenic sorbed to mineral surfaces with the P/As mole partition ratios of around 500 for desorption of Arsenic by phosphate (Manning and Goldberg, 1997); with this ratio, no more than 2 $\mu\text{g/l}$ of Arsenic would be desorbrd by a phosphorous concentration in groundwater of 5 $\mu\text{g/l}$., the permissible limit of Bangladesh water standard in groundwater.
- (c) Other argument for rejection of Arsenic-phosphate link is that phosphate fertilizer contains uranium so that this element can be used as a tracer for fertilizer phosphate. In Bangladesh groundwater concentration of uranium is mostly low being usually < 2 $\mu\text{g/l}$; where uranium is found in high concentration being slightly > 2 $\mu\text{g/l}$, phosphate concentration is very low to zero BGS and DPHE, 2001). The distribution of uranium is therefore de-coupled from the phosphorous distribution probably because of fertilizer phosphorous is taken up by plants (as intended) on infiltration, whilst fertilizer uranium, which is mobile in the oxic environment, moves downwards to the water table and contaminate some of the wells. Furthermore, uranium is found in wells greater than 41 m deep while phosphorous concentration increase with depth in both Faridpur and Lakshmipur (DPHE and BGS, 2000). These arguments further reinforce that phosphorous/phosphate from fertilizer has no significant role in causing Arsenic contamination in Bangladesh groundwater.
- (d) Moreover, the idea that fertilizer phosphate has caused or exacerbated the Arsenic problem, may have arisen because of groundwater in Bengal Basin including Bangladesh have high concentration of phosphorous 5 mg/l (Frisbie et al., 1999; DPHE, 2000); these high concentration of phosphorous arises from release of phosphorous sorbed to FeOOH during Iron reduction in minor quantity but from

microbial degradation of organic matter both peat and human waste in major quantity (McArther et al., 2001).

- (e) Furthermore, migration of phosphate due to surface-application of fertilizers to the aquifers is considered unlikely, at least to the deeper aquifers, considering the low mobility of phosphate in soil. Hence, it is unlikely that quantities of phosphate required for explaining the substantial subsurface Arsenic mobilization in the affected region can reach the deep aquifer (Bose and Sharma, 2002) .
- (f) Besides, Arsenic adsorbed on FeOOH as a result of competitive anion exchange by phosphate (ONeill, 1990) leached from soils treated with fertilizers (Acharyya et al., 2000) can not explain the regional Arsenic contamination of groundwater, it possibly has the relevance on a local scale which might be true for the probable negligible effect of phosphate anion derived from agrochemicals used in the agricultural activities in the paddy field of Bangladesh on Arsenic contamination of ground water.

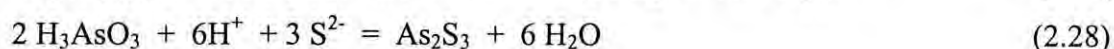
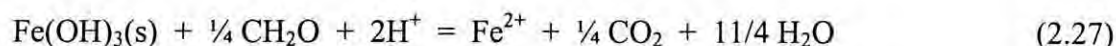
Thus all of these literary arguments break the link between agricultural phosphate/phosphorous fertilizer and Arsenic contamination.

2.6.3 Reduction of Oxy-hydroxides (Reduction Hypothesis)

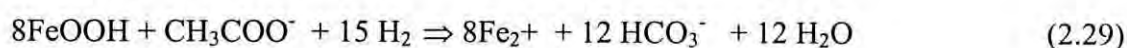
In Bangladesh Arsenic-rich Iron oxyhydroxides present in aquifer materials appear to be the dominant factor to release Arsenic into groundwater and to cause mobilization of Arsenic in the ground subsurface under reducing condition. In the subsurface environment, adsorption-desorption of Arsenic onto Iron oxyhydroxides is an important mechanism controlling its release into groundwater and mobility in the subsurface. Reduction of arsenate to arsenite can promote Arsenic release into groundwater and its mobility in the subsurface because arsenite is less strongly adsorbed than arsenate (Ali and Ahmed, 2003).

High concentrations of Arsenic often are associated with Iron oxides and Sulfide minerals. Iron oxides frequently dissolve under reducing conditions (e.g., in the presence of organic matter, as shown in Eq. 98), but often precipitate under oxidizing conditions.

Sulfide minerals generally are unstable under oxidizing conditions, but may precipitate under reducing conditions (e.g., precipitation of As_2S_3 , as shown in Eq. 99). Thus, as a result of redox sensitive nature of Iron oxides and Sulfide minerals, transfer of large amounts of Arsenic between these solid phases and neighboring water may result from redox-facilitated precipitation and dissolution reactions (USGS, 1999) under reducing condition.



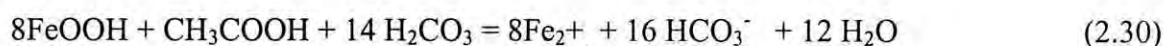
In Bangladesh, reductive dissolution of Iron oxyhydroxides and consequent release of adsorbed Arsenic could be an important mechanism of Arsenic mobilization in the subsurface. Consequently reductive dissolution of Fe(II) oxy-hydroxides has been considered as a major cause of Arsenic in aquatic systems in Bangladesh (Nickson et al., 2000; Kinniburgh and Smedley, 2001; Mcarther et al., 2001; Ravenscroft et al., 2001). The release of Arsenic from arseniferous Fe-oxyhydroxides by the reducing groundwater is most common for the sediment where rapid consumption of O_2 by the microbial metabolism of organic matter produces a strongly reducing environment of the aquatic system (Lovely, 1997; Banefield et al., 1998; Chapelle, 2000; Lovely and Anderson, 2000). This process releases As, HCO_3^- and Fe^{2+} into solution according to the equation:



Obviously strong reducing condition is the most notable feature of the tube-well groundwater of Bangladesh. The strong redox control has given rise due to the characteristic set of water quality features showing reducing environment including high concentration of other redox-sensitive species Fe, Mn, and $\text{NH}_4\text{-N}$ as well as As, and typically low concentration of dissolved oxygen, $\text{NO}_3\text{-N}$, PO_4 , Cu, Ni, Zn, Pb, Co and Se in addition to the relatively high concentration of bicarbonate HCO_3^- and low concentration of sulfate SO_4 showing negative correlation with Arsenic. High Arsenic concentration in groundwater is often associated with high Iron concentration but the positive correlation of Arsenic with Iron is far from perfect and is not sufficiently good to be generally useful for predicting groundwater Arsenic concentration due to high

concentration of Arsenic with low concentration of Iron to some extent. Rochette et. al. (1998) demonstrated with XANES spectroscopy that reducing conditions can lead to the sorption by conversion of As (V) to As (III) in the solid phase of Arsenic minerals. Preliminary results based on XANES also indicate a change in solid-state speciation of the As in Bangladesh sediments in going from oxidizing to reducing conditions (Foster et. al., 2000). Thus strong sorption of As (V) and As (III) by Iron oxides suggests that relevant water quality characteristics play an important role in creating the high concentration of Arsenic in groundwater under reducing condition.

Reduction of FeOOH has been invoked to explain the presence of Arsenic in anoxic ground (Gulens et al., 1997; Matisoff et al., 1982; Korte, 1991, Korte and Fernando, 1991; Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001;). Reduction of FeOOH is a microbial process that is driven by microbial metabolism of organic matter, particularly acetate, vinegar, molasses, glucose (Nealson, 1997; Lovley, 1997; Banfield et al., 1998; Chapelle, 2000; Lovley and Anderson, 2000, Farhana et al; 2004) according to the following equation and is accompanied by microbial reduction of arsenate to arsenite (Dowdle et al., 1996; Ahmann et al., 1997, Stolz and Oremland, 1999; Zobrist et al., 2000;).



Such reduction of FeOOH is common and intense in the groundwater aquifer of Bangladesh shown by high concentration of dissolved Iron vis-à-vis 24.8 mg/l (DPHE, 1999), 29.2 mg/l (Nickson et al., 2000), 80 mg/l (Safiullah, 1998) etc. that is accompanied by reduction of As (V) to As (III) is shown by the fact that dissolved Arsenic is present overwhelmingly as arsenite (Gavrieli et al., 2000). The presence of the significant amounts of arsenate in Bangladesh groundwater and the relevant findings (DPHE, 2000) is an artifact of the storage of Iron-rich water (Cherry et al., 1979; Borho and Wilderer, 1997; Hall et al., 1999; Volke and Merkel, 1999). The spatial distribution of phosphorus in well water shows the modest correlation between Arsenic and phosphorus concentration; such similarity of distribution points to a common diagenetic origin for both Arsenic and phosphate; both of Arsenic and phosphate anions that sorb strongly to Iron oxyhydroxides and their joint release reduction of FeOOH probably contribute to their similar geographic distribution.

An invocation of FeOOH reduction to explain Arsenic contamination needs to argue why there is seldom a good relation in groundwater between the concentration of Arsenic and Iron or between Iron and bicarbonate. The co-variance between Iron and carbonate may be poor because bicarbonate is produced by reduction of nitrate and sulfate and weathering reactions driven by methanogenic CO₂, not by reduction alone. Poor correlation of Arsenic with Iron may arise because of resorption (partial, as arsenite sorbs less well than arsenate) of Arsenic onto fresh FeOOH exposed by dissolution, or because the As/FeOOH ratio may vary from place to place, for example in response to differing amounts of FeOOH on mineral surfaces and differing mineral abundances. Finally poor correlation between Iron and other constituents may result from the sampling protocol used in survey.

In Bengal delta FeOOH reduction and ammonium production possibly derived by the biodegradation of peat that releases short-chain carboxylic acids and methylated amines (Bergman et al., 1999). As Arsenic concentration is strongly dependent on depth, these short-chain organic molecules have not succeeded in migrating far, in a vertical sense from their peat source. In most areas of Bangladesh Arsenic contamination in groundwater aquifer occurs at a depth near to 10 m, must define the maximum depth to which recharging water carries dissolved oxygen that will prevent redox processes except oxic degradation. By recharged water passing through shallow peat layers and spreading through the aquifer sands, small organic molecules are necessary to drive FeOOH reduction and Arsenic release in the aquifer where water is captured by the wells with short screens placed at the top of the aquifer. The depth of penetration by organic matter and Arsenic will be governed by vertical permeability distribution and by the depth of wells in a region. But the modern peats are typically underlain by impermeable clays and so older peats may also be so underlain, thereby restricting downward migration of organic moieties, later channel may cut through peat deposits as rivers alter course and so provide pathways through channel sands for dissolved organic material to move downward. Rahman and Rahman (1998) collected sediment samples from different Arsenic-prone areas, lying mostly in lower Gangetic plain and found Arsenic-rich Iron oxide coatings of varying thickness on sand grains. They concluded that adsorption of Arsenic on Iron oxide might have occurred during transportation of sand and Arsenic bearing mineral grains by flowing water in open channel. British Geological Survey (BGS) and Mott MacDonald Limited (MML), (1999) considered the reductive desorption

and dissolution of Arsenic adsorbed onto Iron oxyhydroxides in recent sediments to be the most probable mechanism of Arsenic mobilization in groundwater. Moreover, mineralogical examination suggested that the small amount of pyrite present in the sediments had been precipitated since burial. Bhattacharya, et al., (1999) stated that during groundwater development, flow of reducing groundwater through the aquifers resulted in the dissociation of ferric hydroxide and released bulk of the Arsenic due to the reduction dissolution of ferric oxyhydroxides. All of these statements are in favor of the reduction hypothesis of Arsenic contamination.

Negative relationship between As and SO_4 in shallow aquifers from specific study areas Nawabgang, Lakshmipur and Faridpur of DPHE/BGS also ensure that groundwater have also undergone sulfate reduction generating sufficiently reducing condition to facilitate the release of Arsenic into solution. Mobilization of As has therefore apparently been under highly reducing condition, rather than by widespread oxidation of Sulfide minerals. Enriched sulfur-isotope compositions of the dissolved SO_4 in a limited number of groundwater samples from Lakshmipur also suggest the possibility of representing residual sulfur after biogenetic reduction of SO_4 to Sulfide. High SO_4 concentration in groundwater from Lakshmipur appears to be derived from residual seawater rather than from pyrite oxidation.

A possible reason for the pattern of Arsenic contamination by reduction hypothesis is the location of palaeo-channels. The lack of organic material in the clean, coarse sands that comprise the channel fill inhibits the evolution of sufficiently strong reducing condition for reduction of Iron (III) and subsequent release of Arsenic into groundwater. Another important explanation involves urban pollution, the influx of nitrate over the main settlement areas acts as an oxidizing agent which causes Iron to precipitate out of solution, Arsenic is then rapidly sorbed onto the surface of these particles (FeOOH) and is depleted in water (Burren, 2000).

Thus a number of recent studies confirm that high Arsenic in Bangladesh groundwater has been released and mobilized into groundwater by the reductive desorption and/or dissolution of Iron (and Manganese) oxyhydroxide where the organic matter play important role (Burgess et al, 2000; McArthur et al., 2001; Ravenscroft et al., 2001; Jacks et al., 2000; Shahnewaz et al., 2000, DPHE/BGS, 2000; AAN, 1999; Anwar et al., 2002).

2.7 ROLE OF BACTERIA IN ARSENIC RELEASE MECHANISM

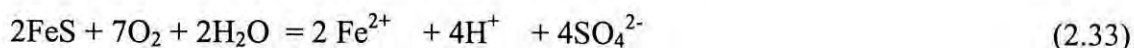
The microbes include bacteria, fungi, algae can make physical and chemical changes in the environment. Bacteria in soil and sediment of Arsenic contaminated sites possess Arsenic detoxification pathways and this pathway may function in aerobic as well as anaerobic environments contributing to apparent non-equilibrium conditions where As (III) has been occurred in waters of oxic surface.

2.7.1 Aerobic Oxidizing Bacteria

In dry season due to lowering of water table by agricultural irrigation, aerobic environment appears in the deeper sediment where organic matters can be decomposed easily by aerobic bacteria. Such changes in the sediment by stratification allow the favorable condition for some of the aerobic bacteria to grow. Groundwater of many tube wells of Samta village in Bangladesh contain significant amount of nitrogen (AAN, RGAG and NIPSOM, 1999) which is oxidized to nitrite and then soon to nitrate by available aerobic bacteria under oxic condition (Akai et al, 2001) according to the chemical reactions given below.



Exposure of sediments to oxygen provides conditions suitable for aerobic bacteria e.g. chemolithotrophic bacteria to oxidize the Sulfides, releasing Iron and any Arsenic associated with the Sulfides in a manner similar to acid mine drainage AMD. Arsenic is released by partial oxidation of Arsenical pyrite in Bangladesh groundwater in oxic condition the according to the reaction:



The results obtained from the study at two hot spots of Arsenic contamination in Bangladesh viz., Nawabgang (24.7°N 88.2°E) and Lakshmipur (22.6°N 90.5°E) indicate that Arsenic is released from the sediments in the groundwater by the acid formation – an activity principally played by oxidizing bacteria (Khan, et al., 2001). The aerobic bacteria

Thiobacillus ferrooxidans, *Thiobacillus thiooxidans*, and *Leptospirillum ferrooxidans* can increase reaction rates for Sulfide mineral oxidation by five orders of magnitude with abiotic reaction rates (Schrenk et al., 1998). *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* increase the oxidation rate indirectly by catalyzing the reaction between dissolved oxygen and Fe (II) to form Fe (III). Microbial oxidation of Arsenic Sulfide minerals such as orpiment, realgar and arsenopyrite proceeded most typically by means of a microbial or surface catalysis activated by arsenite-oxidizing bacteria (Ferguson and Gavis, 1992; Cherry et al., 1979), releases Arsenic (III) into the aqueous phase.

2.7.2 Anaerobic Reducing Bacteria

Different type of metal reducing bacteria such as Iron and Manganese reducing bacteria are responsible to create mobilization and release of Arsenic into groundwater from different Arsenic bearing bounds. Metal reducing bacteria breathe metals such as Iron to get energy from their food i.e. available nutrients in the same way that human breathes oxygen to break down food; the bacteria breathe by passing electrons onto metals which changes the characteristics of the metals by metal reduction. A number of arsenate-reducing bacteria have been isolated from Arsenic-rich soils and sediments using anaerobic minimal media on the basis of their ability to respire arsenate where As (V) serves as the sole terminal electron acceptor in the biological oxidation of organic matter. Jones et al., (2000) reported that in an un-enriched (by Arsenic) soil community arsenate reduction commenced largely after microbial growth had ceased. Reduction of As (V) to As (III) in anoxic environments is thought to occur primarily by dissimilatory reduction where microorganisms utilize As (V) as a terminal electron acceptor for anaerobic respiration. To date, dissimilatory arsenate reduction has been characterized in at least seven bacteria such as *Sulfurospirillum barnesii*, *Sulfurospirillum arsenophilum*, *Bacillus Arsenicoselenatis*, *Bacillus selenitireducens*, *Desulfotomaculum auripigmentum*, *Chrysiogenes arsenatis* and *Desulfomicrobium*, which represent genera scattered throughout the bacterial domain. In addition, dissimilatory reduction of As(V) has been observed in two hyperthermophylic archaea such as *Pyrobaculum arsenaticum* and *Pyrobaculum aerophilum*. Specific biotic arsenate reduction by arsenate-reducer a facultative anaerobe *Bacterium arsenireducens* (Green, 1917), arsenate respiring bacteria microaerophile *Sulfurospirillum barnesii* (Laverman et al., 1995; Stolz et al., 1999), *Sulfurospirillum arsenophilum* and *Sulfurospirillum barnesii* belonging to the ϵ -

subdivision of the Proteobacteria, *Desulfomicrobium* and *Desulfovibrio* of δ -subdivision of the Proteobacteria from an Arsenic contaminated reed bed in Bendigo of Australia (Macy et al., 2000), gram-positive spore forming arsenate reducer and sulfate reducer *Desulfotomaculum auripigmentum* (Newman et al., 1997), spore forming bacteria *Desulfutobacterium frappieri* and *Desulfutobacterium hafniense* (Niggemyer et al., 2001), *Chrysiogenes arsenatis* (Macy et al., 1996), Microbe *Thermus* (Gihring and Banfield, 2001; Kieft et al., 1999), a hyperthermophilic archaeon *Pyrobaculum arsenaticum*, (Huber et al., 2000). *Pyrobaculum aerophilum* (Volkl et al., 1993) have been documented. Respiratory reduction of Fe (III) to Fe (II) accounted for Arsenic mobilization; such ability to couple reduction of Fe (III) with growth is broadly distributed. Landa et al. (1991) established causality between dissimilatory Iron reduction and trace element mobility that demonstrated that Arsenic could be mobilized by the activity of Iron-reducing bacteria (Cummings et al., 1999). Both as (V) and As (III) bind hydrous ferrous oxide HFO strongly (Manning et al., 1998), and reducing conditions lead to Arsenic and Iron co-mobilization (Rochette et al., 1998). Respiratory Fe (III)-reducing bacteria could mobilize Fe-bound Arsenic by reduction of Fe (III); *Shewanella* alga reduced Fe (III) in well defined crystalline ferric arsenate (scorodite) as well as in complex, poorly defined Arsenic contaminated subsurface sediments showing the concomitant solubilization of Arsenic from both of the matrices (Cumming et al., 1999). SO_4^{2-} reducing bacteria can promote deposition of As (III) as Sulfide minerals via their production of Sulfides (Goldhaber and Kaplan, 1974). Newman et al. (1997) provided evidence that sulfate reducing bacteria *Desulfotomaculum auripigmentum* can precipitate orpiment As_2S_3 .

The study conducted by BUET and MIT revealed that Arsenic release is triggered by introduction of food for the bacteria in the aquifer. The presence of methane in water indicates that organic matter is being utilized in the aquifer by anaerobic bacteria. Akai et al. (2001) suggested bacterial reductive dissolution of Arsenic based on the culture experiments using sediments from Bangladesh and lakes Sagata and Mitarase, Japan. Arsenic elution from sediments apparently occurred after rapid dropping of eH values, which were caused by enhanced bacterial activity due to added nutrients, glucose and polypepton. The reducing condition that favors Arsenic release is caused by anaerobic condition in the aquifer.

2.8 RELEVANT STUDIES ON CAUSES OF ARSENIC CONTAMINATION IN GROUNDWATER

A few but not a lot of relevant studies on occurrence and sources of Arsenic contamination in groundwater were carried out in Australia, Bengal Delta (Bangladesh and India), China (Inner Mongolia), Taiwan, the USA, and Vietnam where the cases of natural contamination of groundwater with Arsenic under reducing environment have been documented (Smith et al., 2001, 2003; Tseng et al., 1968; Welch et al., 1988; Nicolli et al., 1969; Luo et al., 1999; Berg et al., 2001; Gurzau and Gurzau, 2001; Kinniburgh and Smedley^{1,2}, 2001).

2.8.1 Studies in Bangladesh

Bangladesh, suffered with the biggest Arsenic calamity of the world and being the hot talk of the worldwide Arsenic hazard is giving continuous efforts to handle the Arsenic problem with the assistance of international agencies and donors like World Bank/IDA/IMF/UNDP, UNICEF, ADB, DFID, US Aid, AusAid, JICA etc.

2.8.1.1 DPHE/DFID/BGS Studies

Groundwater Studies for Arsenic Contamination in Bangladesh carried out during 1998-2000 is such an initiative by Department of Public Health Engineering (DPHE) of Bangladesh Government funded by Department of International development (DFID) of UK and technically assisted by British Geological Survey (BGS), UK. National Hydro-chemical Survey (NHS) as well as detailed survey on specific study areas Lakshmipur (near Chandpur), Chapainawabgang and Faridpur (near to Faridpur) was conducted under DPHE/DFID/BGS study.

A survey of 3534 tube-well water from entire Bangladesh excluding the Chittagong Hill Tracts under NHS showed that water from 25% tube-wells exceeded the Bangladesh standard of Arsenic in drinking water 50 µg/l, 9% exceeded 200 µg/l, 5% exceeded 300 µg/l, .8% exceeded 500 µg/l and 0.1% exceeded 1000 µg/l while water from 27% shallow tube wells (whose depth less than 150 m) exceeded the Bangladesh standard of Arsenic in drinking water 50 ug/l & 47% exceeded WHO guideline value of 10µg/l and water from

only 1% of deep tube wells (whose depth greater than 150 m) exceeded 50 $\mu\text{g/l}$ & 5% exceeded 10 $\mu\text{g/l}$ respectively. Arsenic concentrations range between $< 0.25 \mu\text{g/l}$ and 1600 $\mu\text{g/l}$ with the overall median values of 6 $\mu\text{g/l}$ and 1 $\mu\text{g/l}$ in shallow and deep groundwater aquifers. Wells deeper than 150-200 m show a sharp reduction in their average Arsenic concentration and in the percentage of wells that exceed both of the WHO guideline value and the Bangladesh standard Table 2.2. High Arsenic concentrations are almost entirely restricted to groundwater from shallow aquifers of depth < 150 m composed of Holocene alluvial and deltaic sediment.

Table 2.2: Average Concentration of Arsenic in Wells as a Function of Depth

DEPTH INTERVAL (METER)	NUMBER OF WELLS	PERCENTAGE OF WELLS	AVERAGE ARSENIC CONCENTRATION ($\mu\text{g/l}$)	PERCENTAGE OF WELLS WITH CONC $>$ 50 ($\mu\text{g/l}$)
<15	287	8	58	25
15-30	1180	33	76	31
30-60	1258	36	56	26
60-90	317	9	33	21
90-150	165	5	45	35
150-200	32	1	7	1
>200	295	8	3	1
All	3534	100	55	25

The most important properties of groundwater of specific study areas of Lakshmipur, Chapainawabgang and Faridpur is their predominantly reducing condition which is demonstrated by low redox potential showing the lowest eH value (down to -105 mV) in shallow aquifers, negligible concentration of dissolved oxygen, higher concentration of Iron >1 mg/l and Manganese >0.5 mg/l in numerous samples investigated, low or non detectable concentration of $\text{NO}_3\text{-N}$ but higher concentration of $\text{NH}_4\text{-N} > 1$ mg/l in most samples, very low concentration of $\text{SO}_4 \leq 1$ mg/l, typical concentration of dissolved organic carbon in the range of 1-3 mg/l, pH values from 6.5-7.6, high HCO_3 concentration up to 1140 mg/l, alkalinity ranged from 199 mg/l to 826 mg/l as CaCO_3 , electrical conductivity less than 1000 $\mu\text{S/cm}$, high concentration of dissolved phosphate

frequently exceeding 1 mg/l and the characteristic trace element composition of low content in the groundwater of specific study areas Nawabgang, Lakshmipur and Faridpur.

The presence of reducing condition in the groundwater aquifer of the specific study areas appears to have a strong control in the release mechanism and mobilization of Arsenic in the ground subsurface. Ground waters from Chapainawabgang have low eH values ranging from 341 mV to -102 mV (in shallow aquifer) showing reducing condition; in both shallow and deep aquifers of Lakshmipur, reducing conditions are demonstrated by the low eH values showing the lowest eH value (down to -105 mV) in shallow aquifers. Other evidence of the reducing environment is high concentration of $\text{NH}_4\text{-N}$ typically in excess of 1 mg/l and very low concentration of SO_4 particularly very low (< 1 mg/l) at a depth of 10-30 m, and typical concentration of dissolved organic carbon DOC in the range of 1 to 3 mg/l. Reducing condition is also proved by negligible concentration of dissolved oxygen supporting the presence of high concentration of $\text{Fe} > 1$ mg/l with median value 12 mg/l reaching up to 25 mg/l. Another notable feature of the groundwater is the high concentration of dissolved phosphate frequently exceeding 1 mg/l. Bangladesh groundwater has the characteristic trace element composition that reflects the reducing property.

2.8.1.2 SAMTA Case Study on Arsenic Contamination of Groundwater in Bangladesh by AAN AND RGAG

SAMTA case study on Arsenic Contamination of Groundwater in Bangladesh was carried out by the Asia Arsenic Network (AAN), Research Group for Applied Geology (RGAG) and Miyazaki University Research Group for Arsenic Contamination in Groundwater (MURGACG) at the village of SAMTA under Sharsha Upazilla of Jessore district during 1996 to 2000 to reveal the mechanism of Arsenic contamination.

Samta study revealed that the pyrite especially framboidal pyrite, precursor minerals of the framboidal pyrite, Iron oxides and hydroxides found in the sediment contain Arsenic; wood flakes, organic matter and carbonate present in the sediment may also be the source of Arsenic. Arsenic might have come from the upstream and then was deposited in the sediments where strongly reducing environment has been created.

Arsenic eluted from pyrite in the upper muddy layer in the oxidation state and Arsenic release from Iron hydroxide/oxyhydroxide in the upper sandy layer in the reduction state are considered to be the major processes for Arsenic elution and release from sediment to groundwater. The changes of oxidation-reduction states in underground phases are generally affected by the changes in groundwater level. In the upper half of the muddy layer, the oxidation-reduction states change repeatedly with seasons, which suggests that Arsenic is eluted from Iron hydroxide/oxyhydroxide (which produced instantaneously by the oxidation of pyrite previously) under the reduction state and from pyrite under the oxidation state. When piezometric head is lower in dry season, the water in muddy layers, which normally moves slowly, is squeezed out, thus creating a condition in which Arsenic can move into the shallow first aquifer easily. Thus there is a possibility that Arsenic can be released into groundwater of Samta occurring under both of the reduction and oxidizing state.

According to water quality measurement of the wells used by the villagers, all the oxidation-reduction potential values were negative which speculated that Arsenic and Iron hydroxide/oxyhydroxides are apt to be separated by reduction process under anaerobic condition in the upper sandy layer. Very low concentration of SO_4 in groundwater mostly less than 2 mg/l ensure the reducing condition of Arsenic release. Iron (Fe^{2+}) varying from 3.9 mg/l to 10.5 mg/l had the strongest positive correlation with Arsenic concentration in the shallow aquifer supports the reducing state of Arsenic mobilization in Samta village. On the other hand, by observing the soil samples under electronic microscope, pyrite rich with Arsenic was identified in the upper muddy layer and the Arsenic may have been eluted from pyrite under the oxidizing state.

2.8.1.3 Study on Source Detection of Arsenic Contamination by BWDB and Others

Processing and Flood Forecasting Circle of Bangladesh Water Development Board conducted the study with the technical assistance of Geology Department of Dhaka University in 1999. Sedimentological studies were performed using grain size distribution followed by lithofacial sequence and petrographic microscopic analysis.

Lithofacial sequence analysis identified four distinct lithofacies classified as clay, silty clay, sandy clay and sand, it is evident that facies occur as two distinct lithofacies associations: (a) dominantly sandy channel-fill association and (b) fine grained over bank

association. Litho-logs from boreholes at Nawabganj signify that the Quaternary aquifers are characterized by fining-upward sequence inter-calated by channel-fill and over-bank deposits with frequent channel migration (Figure 2.5).

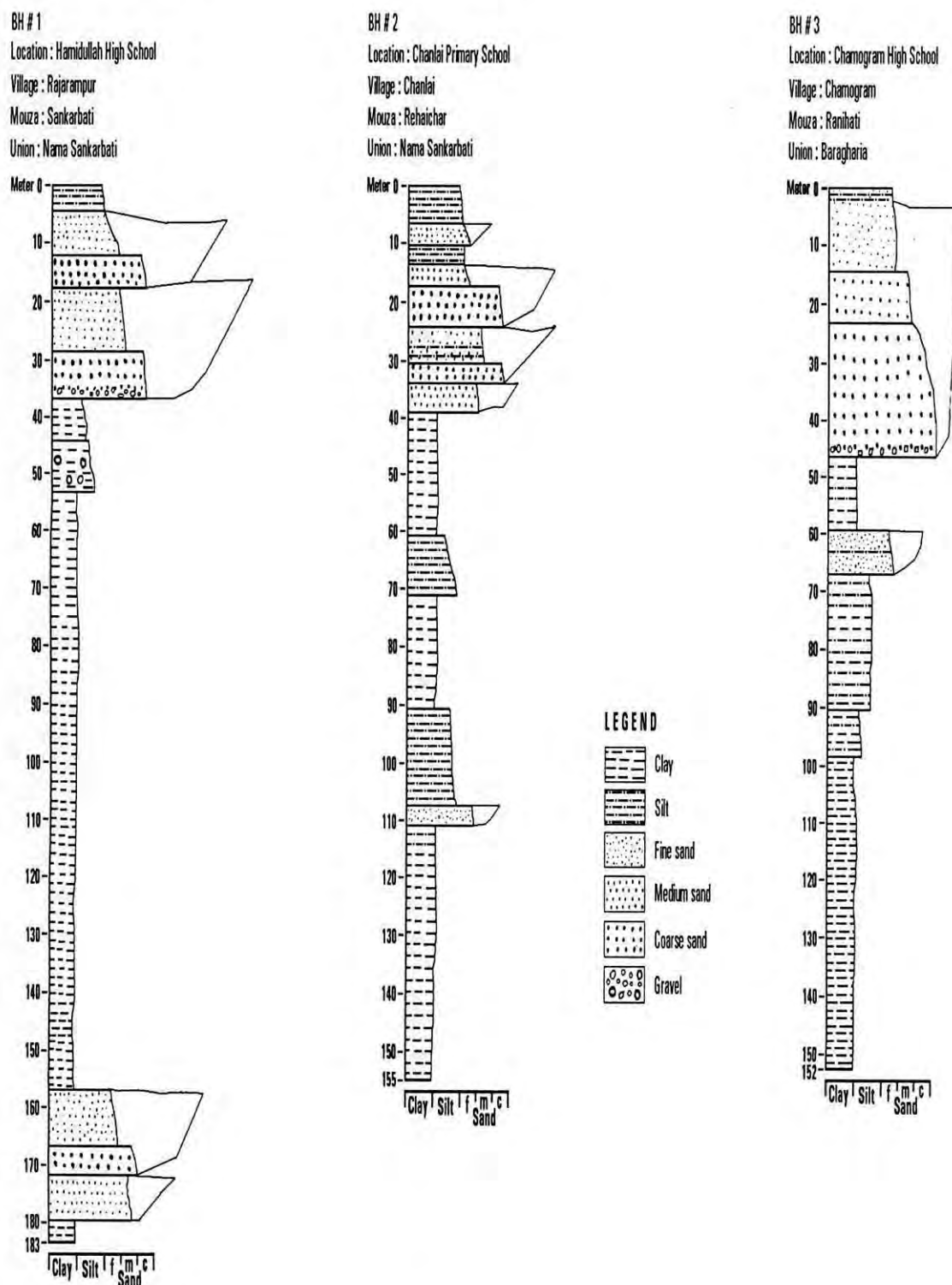


Figure 2.5 : Columnar section of thick layer of calcareous clay/ carbonate mud in vertical lithofacies profile of the Nawabganj area.

Petrographic Microscopic Analysis reveals that the sands are typically consists of quartz, feldspar and lithic grains as a major components in many samples, mica forms a fourth major component (Khan et al., 1998; Rahman and Hossain, 1999); several minor minerals such as titanium oxides, Iron oxides, pyrite, phosphate minerals (apatite), copper, silver, gold were identified by scanning electron microscopic analysis (Perrin, 1998). A characteristic feature of the detrital grains including quartz and feldspar is the pronounced development of the surface coating in most of the samples; the coatings are deep brown to black in colour, generally thin but often thick to very thick as well as partial and discontinuous (Khan et al., 1998). The coating on quartz grain is considered to be ferruginous in composition i.e. Iron oxide/hydroxide/oxyhydroxides but mainly of FeOOH and MnOOH (Alam, 1999; Rahman and Hossain, 1999, Ahmed 2003, and Khan, 2003). Iron- rich oxyhydroxides present in aquifer materials and sediments appear to be the major source of Arsenic in groundwater of Bangladesh (Nickson, 1997), which is also supported by Nickson et al. (1998). Microprobe analysis of sediment discovered small crystals of Iron Sulfide, analysis of one pyrite showed to contain Arsenic, the plate taken of pyrite crystal clearly showed that Arsenic either occur as diagenetic framboidal clusters of crystals or as secondary diagenetic pyrite coatings on clay grains (Nickson, 1997). Diagenetic pyrite acts as a sink for Arsenic explaining the decrease of Arsenic concentration in deeper wells.; the existence of diagenetic pyrite is a convincing argument for the reducing condition of the aquifer.

Meanwhile in Dhaka University, a team of geologist observed that the contaminated sediments were characterized by prominent ferruginous coating around the sand grains (Ahmed et al., 1998). They revealed that fine coatings on sand grains and in the silty and clay fractions of sediments are rich in Arsenic. Their mineralogical and sedimentological studies concluded that the Arsenic adsorbed on the ferruginous coatings on the sand grains is the most likely source of Arsenic and the main contributor for Arsenic release.

2.8.2 Studies outside Bangladesh

2.8.2.1 Australia

In the Holocene barrier of the Stuarts Point coastal sandy aquifer in the northern New South Wales of Australia, Arsenic (V) is present due to either dissolution of Al-

hydroxides and release of absorbed As (V) (Ferguson and Gavis, 1972) or concurrently via pH-influenced desorption of Arsenic enriched Fe-oxides (Owen-Joyce, 1984; Robertson, 1989). Arsenic present in circum-neutral groundwater is associated to some extent with reductive dissolution of FeOOH, with the highest Arsenic concentration being present over low values of DOs and reduced environment with oxidation-reduction potential values from 0 to -200 mV (Smith et al, 2000). The SO_4^{2-} concentration is affected by several processes such as oxidation of FeS_2 present in the acid sulfate soils, dissolution of CaSO_4 , and the flux from the marine aerosols and precipitation; the low concentration of SO_4^{2-} compared with the other coastal aquifers of the eastern Australia (Jankowski and Beck, 2000) is attributed to the redox reactions and the formation of S^{2-} . At the aquifer depth 24-26 m, As (III) ranging up to 212 $\mu\text{g/l}$ dominates with water being slightly alkaline with pH up to 7.46, elevated in HCO_3^- up to 216 mg/l, and depleted in Fe^{2+} (down to 100 $\mu\text{g/l}$), Fe^{3+} (down to 30 $\mu\text{g/l}$), S^{2-} (down to 3 $\mu\text{g/l}$) and SO_4^{2-} (down to 6.5 mg/l) under reducing condition with oxidation-reduction potential eH going down up to -166 mV. The high concentration of Arsenic in correlation with high pH and HCO_3^- suggests that HCO_3^- competition with HAsO_4^{2-} is reducing the possible extent of As sorption on Fe and Mn-oxyhydroxides in water (Smedley et al., 1998). Application of PO_4 -rich fertilizer as well as the PO_4 derived from organic matter and its decay can enhance the mobility of Arsenic in groundwater system in Stuarts Point coast of Australia (Hongshao and Stanforth, 2001).

2.8.2.2 India (West Bengal)

Around 6.97 million people in West Bengal are at risk of Arsenic hazard from drinking water with greater than 50 $\mu\text{g/l}$, Indian permissible value for Arsenic concentration in groundwater (Chakraborti et. al., 2003). About 38.4% of the area and 44.4% of the population of West Bengal, appear to be affected by Arsenic poisoning exceeding 10 $\mu\text{g/l}$, MCL of Arsenic in groundwater recommended by WHO (Stuben et.al., 2003). The Arsenic content in groundwater of west Bengal varies from 0.5 to 135.9 $\mu\text{g/l}$ (Nag et al., 1996), up to 3.7 mg/l with an average concentration of 0.2 mg/l (Mandal et. al., 1996), from 0.06 to 3.7 mg/l (Mazumdar, 1997), from 0.2 to 2 mg/l (Mazumder et al., 1997), from 0.01 to > 0.5 mg/l ((Chowdhury et al., 1997), up to 2.3 mg/l (Das et al., 1997), from 0.05 mg/l to 3.7 mg/l with an average of 0.2 mg/l (Stuben et.al., 2003), and up to 38 mg/l (Chakraborti et. al., 2003). An abundance of solid organic matters deposited with the

sediment has resulted in the development of highly reducing aquifer condition and dominance of Arsenic As (III).

Although the specific source Arsenic in Ganges basin of India is not yet identified; likely sources of Arsenic in the Ganges delta include:

- the Damodar valley Gondwana coal seams in Rajmahal (Acharyya et al., 2000);
- the Arsenic mineral lollingite and pyrite occurred sporadically in association with pegmatites in the mica-belt of Bihar (Bhattacharya, 1972);
- pyrite bearing shale from Proterozoic Vindhyan range - Amjhore mine (Das, 1977);
- the gold belt of the Son Valley of Bihar (Mishra et. al., 1996);
- the isolated outcrops of Sulfide in the Darjeeling Himalayas (Acharyya et al., 2000);
- Weathered as-rich base metals deposits in Ganges basin in the Darjeeling Himalayas
- the outcrops in the upper reaches of the Ganges river systems (Acharyya et al., 2000).

2.8.2.3 China

Arsenic has been found at high concentration (in excess of the Chinese national standard of 50 µg/l) in groundwater from Inner Mongolia as well as Xinjinag and Shanxi Provinces (Wang, 1984; Wang and Huang, 1994; Niu et al., 1997; Smedley et al., 2001). In Inner Mongolia, concentrations of As in excess of 50 µg/l have been identified in groundwater from aquifers in the BaMen region and the Tumet Plain, which includes the Huhhot Basin (Luo et al., 1997; Ma et al., 1999). Hubhot basin are associated with strongly reducing conditions, evidence by high concentrations of dissolved Fe (up to 4.5 mg/l), Mn (up to 1.3 mg/l), NH₄-N (up to 1.3 mg/l), HCO₃ (up to 1150 mg/l), NO₃-N (up to 34.3 mg/l), dissolved phosphate (up to 3.1 mg/l) and DOC, dominance of As (III) over As (v) and relatively low concentrations of SO₄ (being < 0.2 mg/l). The latter suggests that condition is sufficiently reducing for some SO₄ reduction to have occurred. The concentration of dissolved SO₄ are much lower in aerobic groundwater of the central part

of the basin which suggests that SO_4 reduction has been an important process indicative to the strongly reducing condition of the groundwater aquifer where Arsenic mobilization has been occurred.

2.8.2.4 Taiwan

Arsenic problems in groundwater in Taiwan were first recognized during the 1960s (e.g. Tseng et al., 1968) and chronic As-related health problems have been well documented by several workers since then (e.g. Chen et al., 1985). High As concentrations in groundwater have been recognized in both the southwest (Tseng et al., 1968) and northwest (Hsu et al., 1997) of the island. In the southwest, the high As concentrations are found in groundwater from deep artesian wells (mostly 100-280 m) abstracted from sediments, which include fine sands, muds and black shale (Tseng et al., 1968; Kuo, 1968;). Groundwater abstracted from the northeast of Taiwan are also artesian, but of shallower depth (Lo et al., 1977; Hsu et al., 1997). In each area, the groundwater are likely to be strongly reducing, a hypothesis supported by the observation that the As is present largely as As (III) (Chen et al., 1994).

2.8.2.5 The USA

Many areas have been identified in the USA with As problems in groundwater. Most of the worst affected and best-documented cases occur in the southwestern states Nevada, California, Arizona. However, within the last decade, aquifers in Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin have been found with concentrations of As exceeding 10 $\mu\text{g/l}$ and smaller areas of high As groundwater have been found in many other States (Welch et al., 2000). Welch and Lico (1998) reported high As concentrations, often exceeding 100 $\mu\text{g/l}$ but with extremes up to 2600 $\mu\text{g/l}$, in shallow groundwater from the southern Carson Desert. These are largely present under reducing conditions, having low dissolved- O_2 concentrations and high concentrations of dissolved organic C, Mn and Fe. The groundwater also has associated high pH (>8) and high concentrations of P (locally >4 mg/l) and U (>100 $\mu\text{g/l}$; Welch and Lico, 1998).

2.8.2.6 Vietnam

The groundwater aquifers of the large deltas of the Mekong and Red rivers are now widely exploited for drinking water with Arsenic hazard; aquifers exploited are of both Holocene and Pleistocene age. Results from Hanoi (Wegelin et al., 2000; Berg et al.,

2001) indicate that there is a significant As problem in shallow tube wells in the city, particularly in the south. Concentrations in the range 1-3050 $\mu\text{g/l}$ (average 159 $\mu\text{g/l}$) were reported by Berg et al. (2001). Wegelin et al. (2000), mentioned that there is significant Arsenic problem in shallow tube-well water in Hanoi City, particularly in the south; also there appears to be a seasonal variation in Arsenic concentration with significantly higher values during rainy season. In this delta region, groundwater exists in strongly reducing environment with high concentration of Iron, Manganese and ammonium.

2.9 SUMMERY

From literature review it is evident that significant amount of Arsenic is present in groundwater, subsurface sediment and river sediments of Bangladesh. There are three available hypothesis via-a-vis Oxidation hypothesis, Phosphate theory and Reduction hypothesis about how does Arsenic release from solid aquifer material to aqueous phase in Bangladesh subsurface. But neither pyrite oxidation nor competitive exchange of fertilizer phosphate for sorbed Arsenic, can give satisfactory explanation of the cause Arsenic contamination in groundwater of entire Bangladesh. Indeed, pyrite in Bangladesh aquifers is a sink for Arsenic but not the source of Arsenic. In the literature of Arsenic contamination, reduction of FeOOH and release of sorbed Arsenic from aquifer materials received greater attention as a phenomenon for Arsenic pollution of aquifers because groundwaters in contaminated areas of Bangladesh in recently deposited sediments are anoxic due to the presence of abundant organic matters and peat.

The groundwater from the special study area of DPHE/DFID/BGS were almost universally reducing with characteristically high concentration of Iron, Manganese and ammonium as well as Arsenic and low concentration of nitrate, sulfate, dissolved oxygen, copper and selenium. Negative co-relation of Arsenic concentration with sulfate ion, according to many researchers, negates the oxidation of pyrites as a source of Arsenic contamination in Bangladesh.

Chapter 3

ARSENIC IN RIVER WATER AND SEDIMENTS

3.1 INTRODUCTION

Bangladesh being located in the downstream of the mighty rivers, the Ganges and the Brahmaputra, works as a retention basin of excess water carried by the river system for final discharge in the Bay of Bengal. The Ganga-Padma and Brahmaputra-Jamuna river systems drain a huge area of land outside the territory of Bangladesh. There are some direct and indirect references of occurrence of Arsenic and Arsenic related minerals in the upstream of the rivers carrying water and sediments in Bangladesh (DPHE, BGS and MML, 1999). The river systems in Bangladesh carry 2.4 billion tons of sediments, a part of which is deposited in the floodplains each year (Khan, 1994). The comparison between deeply flooded areas in Bangladesh and the areas having more than 10 and 50 percent of the tubewells producing Arsenic more than 0.05 mg/l showed that the deeply flooded areas are mainly Arsenic problem areas of Bangladesh (Ahmed, 2000). The reducing soil environment in the deeply flooded areas appears to be conducive to the release of Arsenic from sediment. The tubewells sunk in shallow aquifers in the Ganges and Meghna floodplains except in coastal areas are the worst affected; in the coastal areas, water supply is mainly based on manually operated deep tubewells as the water available in the shallow aquifer is saline. In Bangladesh, deep tubewells at depths greater than 500 ft have been found to be largely free from Arsenic contamination (DPHE and BGS, 2000). Arsenic contamination of flooded areas of both sides of the Jamuna is very low probably because of the dynamic nature of the river at a relatively higher energy level and deposition of sandy soil of low Arsenic content on the floodplain. Annual floods usually submerge most of the Arsenic contaminated areas; where the soil is characterized by paludal deposit of clay, silt and peat and alluvial deposit of silt and silty clay. The growth of vegetation in nutrient rich floodplains enriches the fine-grained soils and inorganic debris. The anaerobic condition in soils in deeply flooded wetlands is characterized by a gray to blackish color and the release of methane gas. The available dissolved oxygen in infiltrated floodwater is exhausted in the topsoil rich in bio-decomposable organic matters. Pore water devoid of dissolved oxygen produces a reducing environment suitable for dissolution of both Fe and As. Mok and Wai (1994) reported that under reducing

conditions, Arsenic mobilization was controlled by dissolution of hydrous iron oxyhydroxides. DPHE, BGS and MML (1999) mentioned that there was a direct relationship between the degree of reduction in groundwater and As concentration. The reducing environment in the floodplain is produced by anaerobic conditions in fine-grained sediments rich in organic matters. The reducing environment in recently deposited sediments in floodplains appears to be the main cause of Arsenic dissolution from soil to groundwater in Bangladesh. The old sediments and oxidized reddish soils in Bangladesh do not release Arsenic, rather they adsorb Arsenic from water.

In this study, Arsenic concentrations in the suspended sediments carried by river flow and flood water, river bed sediment, and sediment deposited in the floodplains of the major rivers of Bangladesh were collected to assess the quantity of incoming Arsenic from upstream sources and its role in Arsenic contamination of groundwater in Bangladesh.

3.2 MATERIALS AND METHODS

3.2.1 Study Area

In this study, Arsenic concentrations in water and sediment samples of three major rivers – Padma, Meghna and Jamuna were assessed. River water samples, suspended sediment samples, river bed sediment samples were collected at different locations along these rivers for analysis in the laboratory.

Majority of samples were collected during the post-flood period (September-October) of 2001. Along the Padma river, samples (i.e., river water, suspended, and riverbed sediments) were collected from five different locations. These locations were (from upstream to downstream): (i) Rajshahi-Kutibari, (ii) Pakshi, (iii) Aricha-Paturia, (iv) Mawa, and (v) Tongibari-Digirpar. Along the Meghna river, samples were collected from: (i) Sohagpur, (ii) Zia Fertilizer Factory at Ashuganj, (iii) Daudkandi, (iv) Chandpur, and (v) Heimchar. Along the Jamuna river, samples were collected from 4 locations: (i) Bahadurabad, (ii) Jagannathganj, (iii) Bhuanpur, and (iv) Aricha-Nagarbari. Figure 3.1 shows sampling locations along the major rivers.

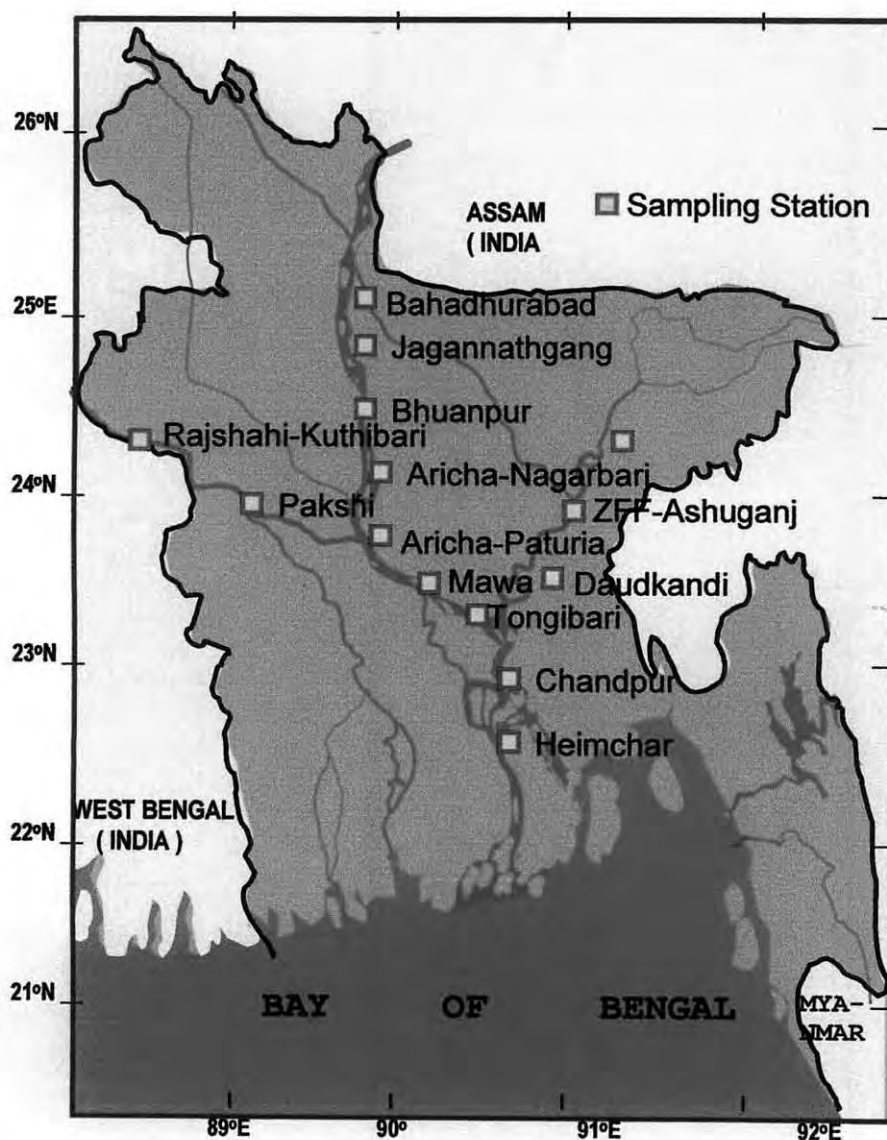


Fig. 3.1: Sampling locations along the major rivers

Besides, during the pre-flood (April) period of 2001, river water and riverbed sediment samples were also collected from a few locations along these major rivers. Along Jamuna, river water and riverbed sediment samples were collected from Bhuanpur and Sirajganj (close to middle of the river); along Padma samples were collected from Bheramara, Pakshi (side and the middle of the river); and along Meghna from Gazaria, Daudkandi (on side and middle of the river).

3.2.2 Collection of Sample

3.2.2.1 Collection of river water samples

River water samples were collected from the Padma, Meghna and Jamuna rivers at two different times – April 2001 (pre-flood period) and September-October 2001 (post flood period). During April 2001, river water samples were collected from 6 locations, two from each river (as noted in Section 3.2.1). During September-October 2001, river water samples were collected from 4 locations along Jamuna and 5 locations each from the Padma and Meghna rivers. The sampling locations are listed in Section 3.2.1.

River water samples were collected from each sampling location away from the bank and close to the mid-width of the river. An engine boat was used for the sampling operation. Water samples were collected from a depth of 30-35 cm below water surface. Water samples were collected in pre-washed 500 ml plastic bottles. For analysis of dissolved Arsenic, the collected water samples were filtered in the field and were immediately acidified with nitric acid (1 ml HNO₃ per liter of water). A total of 14 river water samples were collected during September-October 2001, 4 from Jamuna, 5 from Padma and 5 from Meghna.

3.2.2.2 Collection of sediment samples

Suspended Sediments

For the analysis of Arsenic attached to suspended sediment (SS), samples were collected from 6 locations (2 from each river) during April 2001, and from 14 locations during the post-flood period of September-October 2001. Suspended sediments were collected using an engine boat with a sediment sampler.

Riverbed Sediment

During the pre-flood period of April 2001, riverbed sediments were collected from 6 location (2 from each river, shown in Section 3.2.1) using a grab sampler.

Riverbed sediments (RBS) were collected during the post-flood period of September-October 2001 from each of the 14 selected locations (Section 3.2.1). The top portion (0-5 cm) of the riverbed sediment was collected using a grab sampler. Besides, core riverbed

sediment samples were collected using PVC pipe samplers of 5 cm (2 inch) diameter and 30 to 60 cm in height. One core sample was collected from each sampling location.

3.2.3 Analysis of Samples

3.2.3.1 Analysis of water samples

Collected river water samples were settled for about two months. The settled water samples were filtered and tested for Arsenic with Atomic Absorption Spectrophotometer (Shimadzu, AA6800) attached with a graphite furnace (GF-AAS). The detection limit for this system was 1 µg/l.

3.2.3.2 Analysis of sediment samples

Suspended Sediment

The suspended sediment samples were analyzed for total Arsenic after digestion with aqua-regia (see digestion process below). Extracted Arsenic was determined by GF-AAS (Shimadzu, AA6800).

Riverbed Sediment

As noted earlier, two types of samples were collected from the riverbeds of the rivers: grab samples (0-5 cm) and core samples. Before analysis, each core sample (about 20 to 25 cm in depth) was divided into two segments, the top segment consisting of the top 10 cm and the bottom segment consisting of the rest of the core. Here, these two segments are referred to as "riverbed core: top" and "riverbed core: bottom", respectively. Total Arsenic concentrations in the riverbed sediment (0-5 cm), "riverbed core: top", and "riverbed core: bottom" sediments were determined after digestion with aqua-regia (see digestion process below). Besides, these three types of riverbed sediments were fractionated into sand, silt and clay fractions (following the procedure described below) and total Arsenic contents of each fraction was extracted after digestion with aqua-regia determined by GF-AAS (Shimadzu, AA6800).

Fractionation of Riverbed Sediments in Sand, Silt and Clay

Three types of riverbed sediments [i.e., riverbed sediment (0-5 cm); riverbed core: top and riverbed core: bottom] were divided into sand, silt and clay fractions following the procedure described in Peck and Hanson (1998). The procedure is described below:

- Settling of total sediment was achieved in a large plastic container of about 80 liter by allowing the river water and sediment for at least one week. A significant amount (at least 20 gram) of settled sediment was separated and kept for extracting total Arsenic. The remaining river water was used for separating sand, silt and clay fraction of the sediment.
- Settling of sand was achieved in a large cylinder or glass jar or plastic container (of at least 2 liter) by stirring collected river water sample and keeping it at least for 1 minute to settle. Sand would be settled within one minute; the supernatant was transferred into another (second) jar or cylinder.
- Settling of silt was carried out in the second jar by stirring supernatant water and keeping it at least for 10 minute to settle. All silt would be settled within one hour and the supernatant containing the clay fractions was transferred into a third jar or cylinder.
- The clay was settled by keeping the supernatant in the third jar for several days until the clay particles flocculate and settle down.

3.3 RESULTS AND DISCUSSION

3.3.1 Arsenic Concentration in River Water

In April 2001 (pre-flood period), water samples were collected from 8 locations (see Section 3.2.1) in the 3 major rivers. Arsenic concentrations of all these river water samples were below the detection limit of 1 $\mu\text{g/l}$. Table 3.1. shows Arsenic concentrations of river water samples collected during the post-flood period of September-October 2001. It shows that Arsenic concentrations of water of the Jamuna, Padma and Meghna rivers are extremely low, mostly below the detection limit of 1 $\mu\text{g/l}$. Among the 14 samples, only 2 had As concentration above 1 $\mu\text{g/l}$; Arsenic concentration of 2.3 $\mu\text{g/l}$ and 1.4 mg/l were detected in the Meghna river water at Heimchar and Chandpur, respectively.

Table 3.1: Arsenic concentrations in river water samples in post-flood period of 2001

River	Location	Arsenic Concentration ($\mu\text{g/l}$)
Jamuna	Bahadurabad	< 1 $\mu\text{g/l}$
	Jagannathgang	< 1 $\mu\text{g/l}$
	Bhuanpur	< 1 $\mu\text{g/l}$
	Aricha-Nagarbari	< 1 $\mu\text{g/l}$
Padma	Rajshahi (Kutibari)	< 1 $\mu\text{g/l}$
	Pakshi	< 1 $\mu\text{g/l}$
	Aricha-Paturia	< 1 $\mu\text{g/l}$
	Mawa	< 1 $\mu\text{g/l}$
	Tongibari-Digirpar	< 1 $\mu\text{g/l}$
Meghna	Sohagpur	< 1 $\mu\text{g/l}$
	Zia Fertilizer Factory	< 1 $\mu\text{g/l}$
	Daudkandi	< 1 $\mu\text{g/l}$
	Chandpur	1.4
	Heimchar	2.3

3.3.2 Arsenic Concentration in Sediment Samples

3.3.2.1 Arsenic Concentration in Sediments during Pre-flood Period

No suspended sediment could be collected from the rivers during the pre-flood period (April) of 2001. Only riverbed sediments (0-5 cm) were collected from 7 locations using grab samplers during the pre-flood period of 2001. Table 3.2 shows As concentrations of riverbed sediments during the pre-flood period, which shows that As concentration in the riverbed sediment samples varied from 2.67 to 3.26 mg/kg in Jamuna, 1.02 to 3.16 mg/kg in Padma, and 1.08 to 3.38 mg/kg in Meghna. It appears that in Jamuna river at Bhuapur-Sirajganj, As concentration in riverbed sediments is higher on the Bhuapur side. Similar, for Padma, As concentration in riverbed sediments is much higher on Bheramara side as compared to the Pakshi side; for Meghna, As in riverbed sediments is much higher on the Daudkandi side as compared to the Gajaria side.

Table 3.2: Arsenic concentrations of riverbed sediments during pre-flood period (April 2001)

River	Sampling Location	As Concentration (mg/kg)
Jamuna (Bhuapur-Sirajganj)	Bhuapur	3.53
	Sirajganj (close of middle-river)	2.67
Padma (Bheramara-Pakshi)	Bheramara	3.16
	Pakshi	1.02
	Mid-river	1.11
Meghna (Daudkandi-Gajaria)	Gajaria	1.08
	Daudkandi	3.38
	Mid-river	3.34

3.3.2.2 Arsenic Concentration in Sediments during Post-flood Period

Total Arsenic Contents of SS and Riverbed Sediments:

Table 3.3 shows As concentrations of suspended sediment (SS) and river bed sediments at the sampling locations along the Jamuna, Padma and Meghna rivers during the post-flood period. It shows that As contents of SS of the three rivers do not vary significantly. Arsenic concentrations in SS from Jamuna rivers varied from 4.07 mg/kg (at Jagannathganj) to 5.09 mg/kg (at Aricha-Nagarbari); that from Padma river varied from 4.32 mg/kg (at Kutibari) to 5.47 mg/kg (at Tongibari-Digirpar). In case of Meghna river As concentrations varied from 4.16 mg/kg (at Heimchar) to 4.99 mg/kg (at Chandpur). Highest As content of 5.47 mg/kg was measured in the SS of Padma river at Tongibari-Digirpar, just before the junction point of Padma with Meghna; while the lowest concentrations was measured in the SS of Jamuna river at Jagannathganj.

Arsenic concentrations of riverbed sediments (0-5cm) in September-October 2001 have been found to be higher than those collected in April 2001 (Table 3.2). At any particular location, As contents of riverbed sediments have been found to be lower than those of the SS. Table 3.3 shows that the As contents of the riverbed sediment (0-5 cm), riverbed core-top and riverbed core-bottom sediments differ to some extent, with no clear trend of higher or lower As in a particular segment of bed sediment. Highest As concentration of 4.74 mg/kg in the riverbed sediment (0-5 cm) was measured in the sample from Meghna river at Daudkandi, and the lowest concentration of 2.65 mg/kg was measured in the river bed sample from Jamuna river at Jagannathganj.

Table 3.3: Arsenic concentrations in suspended sediment and river bed sediments of Padma, Meghna and Jamuna rivers during post-flood period

River	Location	Arsenic Content, mg/kg			
		Suspended Sediment (SS)	Riverbed (0-5 cm)	Riverbed core: top	Riverbed core: bottom
Jamuna	Bahadurabad	4.87	4.41	3.20	3.29
	Jagannathganj	4.07	2.65	2.87	3.54
	Bhuanpur	4.34	4.17	4.19	3.72
	Aricha-Nagarbari	5.09	3.05	2.92	2.68
Padma	Rajshahi (Kutibari)	4.32	3.65	3.78	3.13
	Pakshi	4.32	3.40	2.46	5.81
	Aricha -Paturia	4.34	3.30	3.37	3.20
	Mawa	4.69	3.91	2.71	4.64
	Tongibari-Digirpar	5.47	3.01	2.88	4.68
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	--	4.31	5.84	3.53
	Zia Fertilizer Factory	--	4.73	5.08	2.04
	Daudkandi	--	4.74	3.31	3.87
	Chandpur	4.99	3.24	3.80	4.23
	Heimchar	4.16	3.29	3.33	4.27

Arsenic Concentrations of Sand, Silt and Clay Fractions of Riverbed Sediments:

Table 3.4 shows As concentrations in sand fractions of riverbed sediments (0-5 cm, riverbed core-top and riverbed core-bottom). Highest (2.98 mg/kg) and lowest (1.00 mg/kg) As contents in the sand fractions of riverbed sediment (0-5cm) were both found in Meghna river at Heimchar and at Zia Fertilizer Factory respectively. Arsenic content in sand fraction of riverbed core-top sediments ranged from 1.00 mg/kg at Kutibari of Padma river to 1.88 mg/kg at Bhuapur of Jamuna river. Arsenic contents of riverbed core-bottom sediments ranged from 1.10 mg/kg at Bahadurabad of Jamuna river to 2.47 mg/kg at Aricha-Paturia of Padma river. In general, As contents of sand fractions of riverbed (0-5 cm) sediments were found to be relatively higher than those in the riverbed core – top and bottom sediments.

Arsenic content of silt fractions of river bed sediments was also extracted and measured in the laboratory. Table 3.5 shows As concentrations in silt fractions of riverbed sediments (0-5 cm, riverbed core-top and riverbed core-bottom). The As contents of silt fractions varied from 1.86 to 3.78 mg/kg in riverbed sediment (0-5 cm), from 2.32 to 3.68 mg/kg in riverbed core-top sediment, and from 2.63 to 3.88 mg/kg in riverbed core-bottom sediment. With some exceptions, As contents of silt fractions of riverbed (0-5 cm)

sediments were found to be relatively higher than those in the riverbed core – top and bottom sediments. A comparison of Table 3.4 and Table 3.5 reveals that As contents of sand and silt fractions at all the 14 sampling locations are significantly higher than those in the sand fractions.

Table 3.4: Arsenic contents in sand fractions of riverbed sediments

River	Location	Arsenic Content, mg/kg		
		Riverbed (0-5 cm)	Riverbed core: top	Riverbed core: bottom
Jamuna	Bahadurabad	2.51	1.85	1.10
	Jagannathgang	2.52	1.83	1.25
	Bhuanpur	Sand absent	1.88	1.25
	Aricha-Nagarbari	1.51	1.08	1.37
Padma	Rajshahi (Kutibari)	Sand absent	1.00	1.41
	Pakshi	Sand absent	1.77	Sand absent
	Aricha –Paturia	2.67	1.81	2.47
	Mawa	2.63	Sand absent	1.60
	Tongibari-Digirpar	2.07	1.72	2.22
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	2.65	1.61	1.58
	Zia Fertilizer Factory	1.00	1.30	1.54
	Daudkandi	2.45	1.27	2.38
	Chandpur	2.24	1.39	2.43
	Heimchar	2.98	1.13	2.40

Table 3.6 shows As concentrations in clay fractions of riverbed sediments (0-5 cm, riverbed core-top and riverbed core-bottom). It shows that the As contents of clay fractions varied from 3.87 to 6.28 mg/kg in riverbed sediment (0-5 cm), from 4.59 to 6.64 mg/kg in riverbed core-top sediments and from 4.58 to 5.85 mg/kg in riverbed core-bottom sediment. Unlike sand and silt, As contents of clay fractions of riverbed core sediments (top and bottom) have been found to be higher than those in the riverbed sediments (0-5 cm). A comparison of Table 3.4 through 3.6 shows that As contents of clay fractions at all the 14 sampling locations are much higher than those in the sand and clay fractions. For example, As contents of sand, silt and clay fractions of riverbed sediments (0-5 cm) from Jamuna river at Bahadurabad were found to be 2.51, 3.11 and 4.38 mg/kg respectively. Similarly, As contents of sand, silt and clay fractions riverbed sediments (0-5 cm) from Padma river at Mawa were 2.63, 2.84 and 6.28 mg/kg, respectively.

Table 3.5: Arsenic contents in silt fractions of riverbed sediments

River	Location	Arsenic Content, mg/kg		
		Riverbed (0-5 cm)	Riverbed core: top	Riverbed core: bottom
Jamuna	Bahadurabad	3.11	2.53	Silt absent
	Jagannathgang	3.14	2.73	3.67
	Bhuanpur	3.31	2.32	3.11
	Aricha-Nagarbari	Silt absent	2.34	3.22
Padma	Rajshahi (Kutibari)	2.86	2.40	3.88
	Pakshi	3.57	2.96	Silt absent
	Aricha -Paturia	3.61	3.27	2.82
	Mawa	2.84	Silt absent	3.08
	Tongibari-Digirpar	2.86	2.56	3.02
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	3.94	3.68	3.13
	Zia Fertilizer Factory	1.86	2.38	2.63
	Daudkandi	3.78	2.89	3.39
	Chandpur	2.51	3.25	3.48
	Heimchar	3.40	3.59	3.23

Table 3.6: Arsenic contents in clay fractions of riverbed sediments

River	Location	Arsenic Content, mg/kg		
		Riverbed (0-5 cm)	Riverbed core: top	Riverbed core: bottom
Jamuna	Bahadurabad	4.38	Clay absent	Clay absent
	Jagannathgang	3.87	4.97	5.449
	Bhuanpur	4.37	6.46	Clay absent
	Aricha-Nagarbari	4.11	Clay absent	5.26
Padma	Rajshahi (Kutibari)	4.94	Clay absent	5.02
	Pakshi	4.03	5.45	4.86
	Aricha-Paturia	4.83	Clay absent	5.42
	Mawa	6.28	4.93	5.07
	Tongibari-Digirpar	6.18	4.59	4.58
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	4.58	4.61	5.85
	Zia Fertilizer Factory	Clay absent	Clay absent	4.99
	Daudkandi	Clay absent	5.72	5.15
	Chandpur	Clay absent	6.64	5.28
	Heimchar	Clay absent	Clay absent	Clay absent

Figure 3.2 shows As concentrations in sand, silt and clay fractions of riverbed sediments (0-5cm) from different locations of Jamuna, Padma and Meghna rivers.

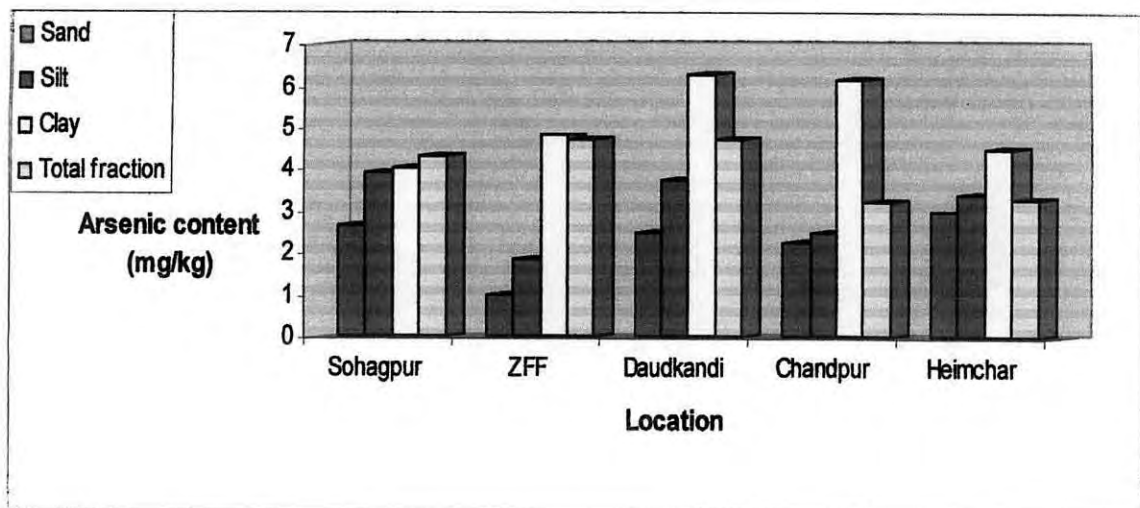
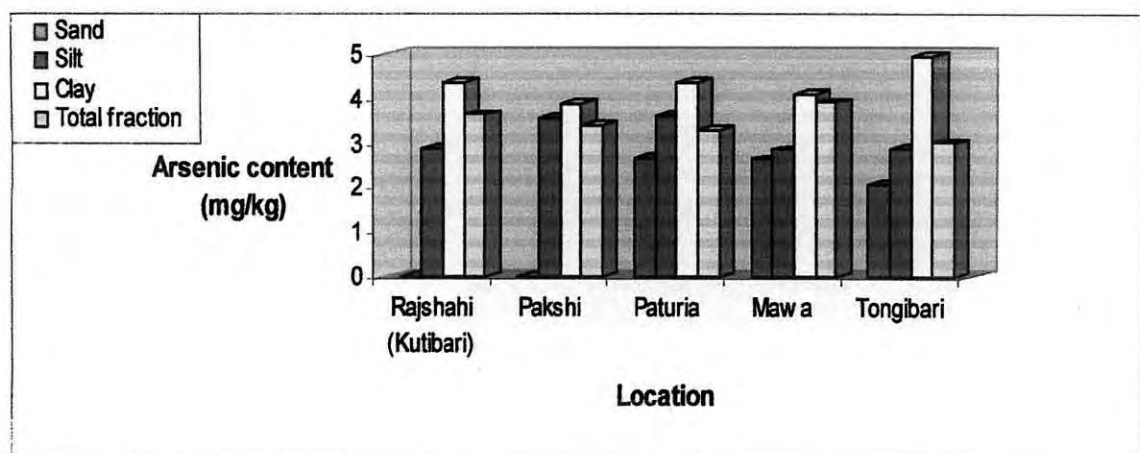
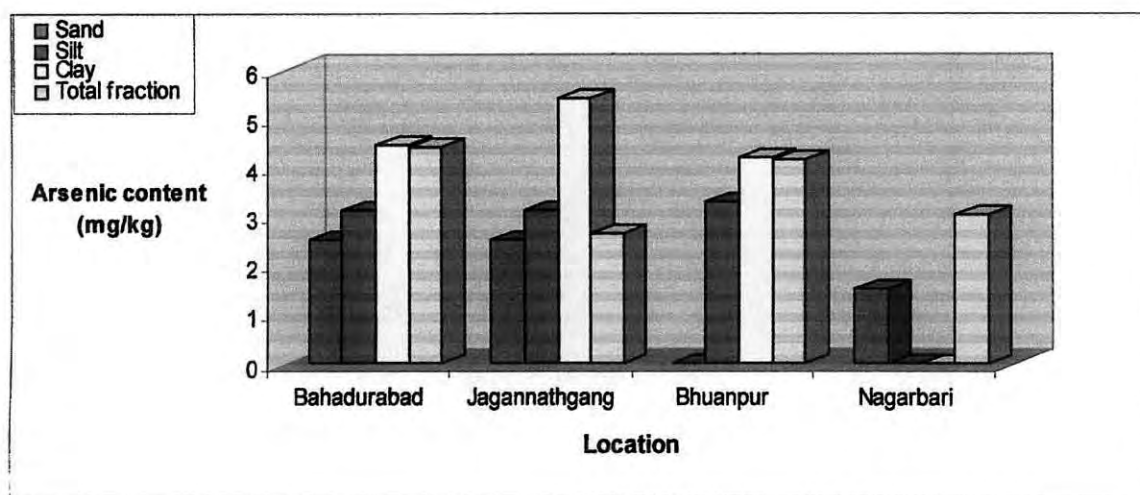


Fig. 3.2: Arsenic contents in sand, silt and clay fractions of the riverbed sediments (0-5 cm) of Jamuna, Padma and Meghna rivers

3.3.2.3 Ratio of Arsenic Concentrations in Sediment and Surface Water

Arsenic concentrations in suspended sediment and river bed sediment are very high as compared to Arsenic content of surface water. The ratios of Arsenic concentration in suspended and river bed sediments to surface water are presented in Table 3.7. Ratio of Arsenic concentration between suspended sediment and surface water varied from 19 to 55×10^3 while the ratio of Arsenic content in river bed sediment to surface water ranged from 15 to 48×10^3 .

Table 3.7: Ratio of Arsenic contents of river sediment to surface water

River	Location	Ratio of concentrations of As in sediment to As in Water, [(mg/kg)/(mg/l)] $\times 10^3$	
		Suspended Sediment	Riverbed (0-5 cm)
Jamuna	Bahadurabad	49	45
	Jagannathgang	41	27
	Bhuanpur	44	42
	Aricha-Nagarbari	51	31
Padma	Rajshahi (Kutibari)	44	37
	Pakshi	44	34
	Aricha-Paturia	44	33
	Mawa	47	40
	Tongibari-Digirpar	55	31
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	-	44
	Zia Fertilizer Factory	-	48
	Daudkandi	-	48
	Chandpur	36	24
	Heimchar	19	15

3.3.2.4 Weight Fractions of Sand, Silt and Clay River Sediment

The river sediments are fractionated into sand, silt and clay as described in section 3.2.3.2. Table 3.8 shows the weight fraction of sand, silt and clay in the riverbed sediments (0-5 cm) of the rivers. It shows that sand fraction varied from 20% to 38% with an average value of 27%, silt fraction varied from 11% to 53% with 46% as average value and clay fraction varied from 15% to 49% with an average value of 27%. On average 6% weight loss was observed, which was added to clay fraction. It is assumed that the material lost during experimentation is the colloidal fraction of the soil, which did not settle during the observed time of sedimentation. The lost fraction actually belongs to clay and the lost

Arsenic is obviously tied to these colloidal fractions. Hence, all the computations were made by including lost fractions of soil and Arsenic into clay.

Table 3.8: Weight fractions of sand, silt and clay in riverbed sediments

River	Location	Sand (%)	Silt (%)	Clay (%)
Jamuna	Bahadurabad	20	41	39
	Jagannathgang	38	40	22
	Bhuanpur	Sand absent	52	48
	Aricha-Nagarbari	Sand absent	Clay absent	100
Padma	Rajshahi (Kutibari)	Sand absent	53	47
	Pakshi	Sand absent	51	49
	Aricha -Paturia	26	52	22
	Mawa	24	47	29
	Tongibari-Digirpar	23	48	29
Meghna	Sohagpur (10 km u/s of Bhairab Bridge)	25	44	31
	Zia Fertilizer Factory	22	30	48
	Daudkandi	34	45	21
	Chandpur	36	49	15
	Heimchar	29	46	25

3.3.2.5 Arsenic Load in River Sediment

Arsenic is transported through the rivers Jamuna, Padma and Meghna as dissolved load with water and as sediment associated load. The dissolved Arsenic is transported into the Bay of Bengal but part of the Arsenic associated with sediment is deposited in Bangladesh. An estimation of the Arsenic load carried by the river system can be calculated from available information on suspended sediment load carried by this river system. The sediment loads transported by the rivers Jamuna, Padma and Meghna integrated over the year were estimated as 499, 890 and 1003 million tons respectively (FAP 24, 1996 b). On the basis of these figures, Arsenic carried with the sediment of rivers Jamuna, Padma and Meghna can be estimated as 3,054 , 4,121 and 4,584 tons respectively.

The study confirms that Arsenic is carried from upstream by the rivers Jamuna, Padma, and Meghna with sediment. Bangladesh has been formed by the deposition of sediment carried by these three rivers and Arsenic is being deposited in the downstream in the floodplains of Bangladesh for thousands of years. The estimated quantity of Arsenic carried within Bangladesh by these rivers with 2.4 billion tons of sediment (Khan, 1994)

is 11,000 tons per year considering on average 4.58 mg/kg of Arsenic in the suspended sediment of the rivers. However, a major fraction of this Arsenic is discharged into the Bay of Bengal with the sediment.

3.4 SUMMARY

In this study, river water and riverbed sediment samples were collected during the post-flood period (September-October 2001) from 14 locations along three major rivers of the country, 4 from the Jamuna River and 5 each from the Padma and the Meghna rivers. Besides floodplain samples were collected from 6 locations, two from the floodplain of each river. In addition, river water and riverbed sediment samples were collected from limited number of locations along these rivers during the pre-flood period (April 2001).

Arsenic concentrations of the river water samples have been found to be very low, especially for samples collected during pre-flood period. Even for river water samples collected during post-flood period, highest measured As concentration in river water was only 2.3 $\mu\text{g/l}$. The Arsenic content of river water in most of the cases was found below detection level of 1 $\mu\text{g/l}$.

Suspended solids collected during the post-flood period from the major rivers have been found to contain significant amount of As. Arsenic concentrations in the suspended solids varied from 4.07 mg/kg at Jagannathganj of Jamuna river to 5.47 mg/kg at Tongibari-Digirpar of Padma river. Arsenic concentrations of the riverbed sediments (0-5cm) collected during post-flood period have been found to be higher than those collected during the pre-flood period. Arsenic content of river bed sediment was comparatively lower than that of the suspended sediments collected along the rivers.. Arsenic concentrations of the riverbed sediments (0-5cm) varied from 2.65 to 4.74 mg/kg.

Analysis of As concentrations in fractions of the riverbed sediments showed that clay fraction contained highest concentrations of As, followed by silt and sand. Arsenic concentration in sand fraction of riverbed sediments (0-5cm) varied from 1.00 to 2.98 mg/kg, in silt fraction 1.86 to 3.94 mg/kg, and in clay fraction from 3.87 to 6.28 mg/kg. Total Arsenic in floodplain sediments varied from 3.54 to 5.81 mg/kg.

The As concentrations in riverbed and floodplain sediments are comparable to those reported for aquifer sediments. For example, DPHE and BGS (2001) reported average concentration of As in alluvial sand and mud/clay to be 2.9 mg/kg and 6.5 mg/kg, respectively in Bangladesh. Kinniburg and Smedly (2001) reported that As concentration in sediments of Chapainawabgang and Lakshmipur varied from 0.4 mg/kg to 10.3 mg/kg with an average of 5.9 and 3.2 mg/kg, respectively. Arsenic content in Bangladesh sediment typically ranges from 0.4 to 10 mg/kg. Thus, like the older aquifer sediments, the more recent riverbed and floodplain sediments could also be an important source of Arsenic in the aquifer.

The As content of fine-grained materials like clay is higher because they have higher surface area as well as adsorption sites per unit volume/weight. On the other hand, coarse-grained materials like sand have relatively smaller surface area as well as adsorption sites per unit volume/weight. Therefore, the beels and haors receive higher quantity of As the clayey materials are deposited in these stagnant water bodies. Chandpur, Madaripur, Munshiganj, Gopalganj, Lakshmipur, Noakhali, Bagerhat, Shariatpur, Comilla, Faridpur, Satkhira and Meherpur districts have numerous beels and haors with stagnant water bodies, and these districts are also very severely affected by As contamination of groundwater.

The estimated quantity of Arsenic carried within Bangladesh by the rivers with 2.4 billion tons of sediment is 11,000 tons per year considering on average 4.58 mg/kg of Arsenic in the suspended sediment of the rivers, a major fraction of which is discharged in the Bay of Bengal with the sediment.

Chapter 4

ARSENIC IN AQUEOUS AQUIFER - GROUNDWATER

4.1 INTRODUCTION

The presence of high concentrations of As in groundwater is generally not dependent on the concentration of As in soils. Sediment As concentrations in some deeper aquifers, with very little aqueous (i.e., groundwater) As concentration, have been found to be comparable to those found in the sediments of As affected shallow aquifers (Harvey, 2000). This certainly raises the question – whether the unaffected deeper aquifers could become contaminated with Arsenic in the future? From this point of view, As concentration in the sediment aquifer is of prime importance and obviously essential for proper understanding of the source of As and mechanism of its mobilization into the water phase. Also an important question that needs to be answered is whether As concentration in the still-unaffected shallow tubewells would increase with time. This is particularly important in view of the observed trend (DPHE/BGS/MML, 1999) that older tubewells are more likely to have higher As concentration. Proper understanding of the water quality parameters as well as correlation of As with other water quality parameters is essential for answering these important questions.

In this study, groundwater samples collected from 16 well located in 4 different districts of Bangladesh have been analyzed for a wide range of water quality parameters, including As. This chapter presents the results of these analyses and assesses the relationships between As and other water quality parameters to better understand the processes leading to As mobilization in the subsurface.

4.2 MATERIALS AND METHODS

4.2.1 Study Area

In this study, groundwater samples were collected from existing tubewells in Sylhet, Chandpur, Kushtia and Nawabganj districts from which borehole sediment samples were collected. In each district, groundwater samples were collected from 4 tubewells located in close vicinity of the area, where the borehole was constructed.

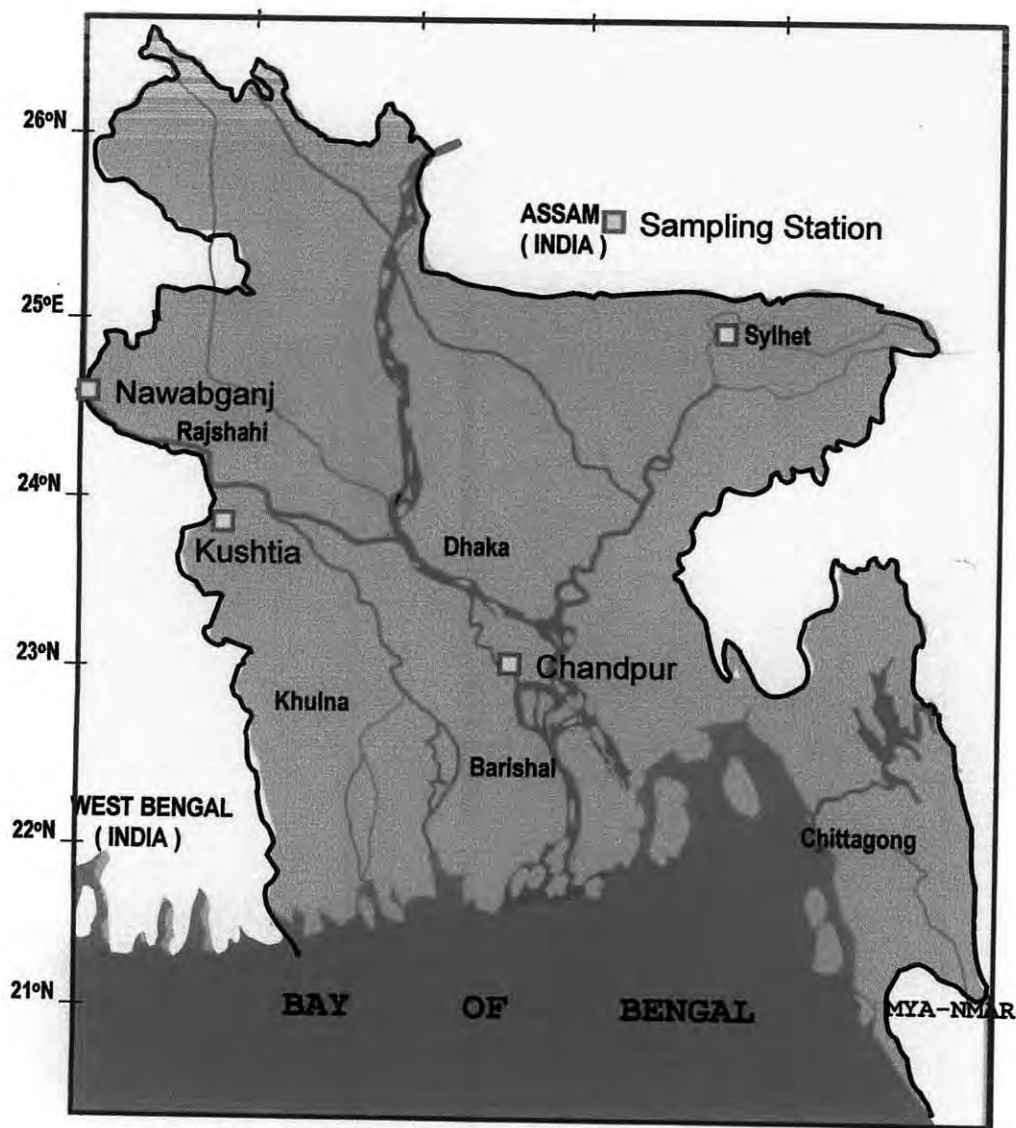


Fig. 4.1: The location of groundwater sampling points on Bangladesh map

4.2.2 Collection of samples

Groundwater samples were collected from 4 tubewells in each of the 4 districts (Sylhet, Chandpur, Kushtia and Nawabganj). From each tubewell groundwater samples were collected at 3 different times: August 2001 (during rainy season), December 2001 (during winter season), and April 2002 (during summer). During each sampling, groundwater samples were collected, after pumping the tubewell for a few minutes (to purge the standing water in the well pipe), in two pre-washed 1 L plastic bottles. One of the bottles was acidified (with 1 mL conc. Nitric acid per 500 mL of water) in the field for subsequent analysis of metals ions in the laboratory. Depths of the 16 tubewells sampled

in this study are shown in Table 4.1. During collection of water samples, depth of water level in the well pipe was measured.

Table 4.1: List of sampling wells with depth from ground surface

Well No.	Depth (ft)	Well No.	Depth (ft)
1(S-4)	205	9(N-1)	100
2(S-3)	205	10(C-4)	90
3(S-2)	195	11(N-2)	85
4(S-1)	170	12(C-1)	80
5(K-1)	130	13(C-2)	80
6(K-2)	130	14(N-3)	75
7(K-4)	130	15(C-3)	70
8(K-3)	110	16(N-4)	38

4.2.3 Analysis of groundwater samples

Groundwater samples were analyzed for a wide range of parameters. pH and eH were determined in the field during sampling while pH, electrical conductivity (EC), total dissolved solids (TDS), chloride, alkalinity, hardness, nitrate, phosphate, ammonia, sulfate, sulfide, CO₂, As, Fe, Mn, Pb etc. were measured in the laboratory. Detailed characterization of groundwater samples collected from piezometers was carried out in order to assess the geo-chemical environment in the subsurface.

The pH value of water samples was measured with a pH meter (Hach) attached with a glass electrode, conductivity with a conductivity meter (CMD8500 WPA), and eH with an eH meter. Chloride was measured using AgNO₃ titration method. Ammonia, nitrate, and phosphate concentrations were determined with a spectrophotometer (Hach, DR4000U). Ammonia was measured using the Nessler method, nitrate by the cadmium reduction method and phosphate by the molybdenum blue method. Sulfate and sulfide concentrations in groundwater were also determined with a spectrophotometer (Hach, DR4000U) by the SulfaVer-4 method (equivalent to USEPA method 375.4) and methylene blue method (equivalent to USEPA method 367.2), respectively. Carbon-dioxide was determined by titration with standard NaOH solution, alkalinity by titration with standard H₂SO₄, and hardness by EDTA titration method, all following the Standard Methods (APHA, AWWA and WEF, 2000). Arsenic, Mn, and lead concentrations were measured with GF-AAS (Shimadzu, AA6800). Iron concentration was measured with Flame-AAS (Shimadzu, AA6800).

4.3 RESULTS AND DISCUSSION

4.3.1 Arsenic Concentration in ground water

Table 4.2. shows the Arsenic concentration of groundwater in the piezometers, measured in the month of August , December in 2001 and April, 2002. Most GW samples contain high content of As varying from 0.012 mg/l to 1.030 mg/l.

Table 4.2: Arsenic concentration in groundwater in the month of August and December, 2001 and April, 2002

Well No	Depth		Arsenic in mg/l measured by AAS		
	Feet	Meter	Rainy Season (August '01)	Winter Season (December '01)	Summer Season (April '02)
1(S-4)	205	62.5	0.093	0.137	0.162
2(S-3)	205	62.5	0.101	0.106	0.141
3(S-2)	195	59.44	0.095	0.101	0.145
4(S-1)	170	51.82	0.103	0.155	0.067
5(K-1)	130	39.62	0.021	0.020	0.019
6(K-2)	130	39.62	0.162	0.150	0.134
7(K-4)	130	39.62	0.506	0.393	0.423
8(K-3)	110	33.53	0.623	0.423	0.322
9(N-1)	100	30.48	1.030	1.016	0.706
10(C-4)	90	27.4	0.187	0.152	0.183
11(N-2)	85	25.91	0.978	0.764	0.881
12(C-1)	80	24.39	0.185	0.148	0.182
13(C-2)	80	24.39	0.174	0.150	0.136
14(N-3)	75	22.86	0.650	0.668	0.774
15(C-3)	70	21.34	0.157	0.084	0.073
16(N-4)	38	11.25	0.039	0.021	0.033

4.3.2 Variation of Groundwater As Concentration with Other Water Quality and Aquifer Parameters

4.3.2.1 Variation of As concentration with sampling time

Figure 4.2 shows variation of As concentration in the tubewells as a function of sampling time. It shows that As concentrations in tubewells do not follow any particular trend with sampling time (i.e., with season of the year).

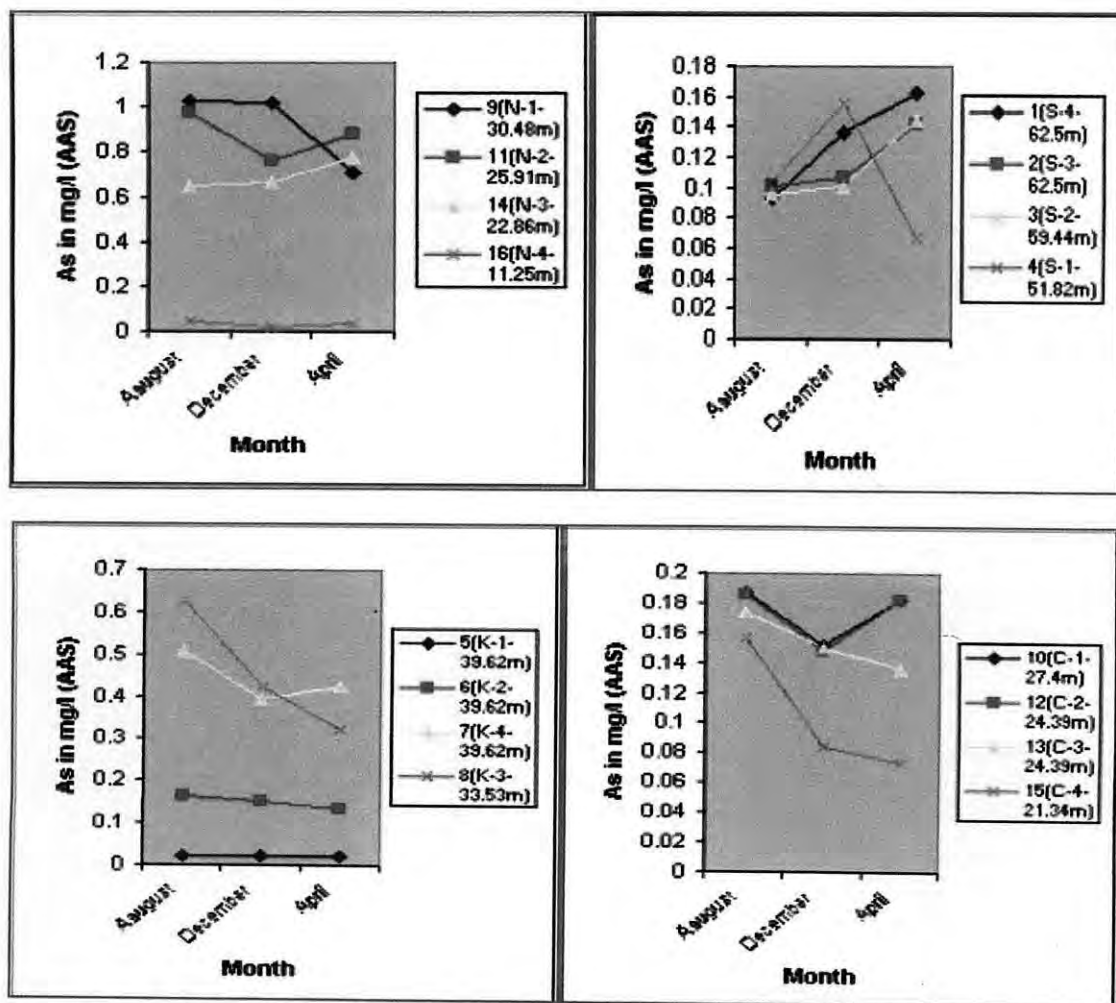


Fig. 4.2: Variation of As concentration in the tubewells as a function of sampling time (Well # K from Kushtia, S from Sylhet, N from Nawabganj, and C from Chandpur)

For example, among the 4 wells sampled in Nawabganj district, 3 had relatively high As concentrations. Among these 3, As concentrations in 2 increased in April 2002 (summer), compared to concentrations in August 2001 (rainy season), but that in one well decreased significantly in April 2002. Among the 4 wells in Sylhet, As concentrations in 3 increased while one decreased in April 2002, compared to concentrations in August 2001.

Water level in tubewells was measured by water level meters as shown in Fig. A-19 of appendix. Fig 4.3 shows variation of water level in the well as a function of sampling time. It shows that, as expected, depth of water level from ground level increased i.e. water level decreased as the dry season progressed. The trend of variation of water level with sampling time was more or less similar for the wells in each district. In Kushtia and Nawabganj, depths of water levels from ground were lowest in the month of August

2001, and water level decreased significantly in December 2001, and then continued to decrease up to the last sampling time of April 2002. In Kushtia, water level from ground surface in the 4 wells varied from 2.6 to 3.5 m in August 2001, 5.72 to 6.05 m in December 2001, and from 8.1 to 8.8 m in April 2002. In Sylhet and Chandpur, water levels were close to ground level in August 2001, decreased in December 2001, and then increased to some extent in April 2002, possibly due to early rains in these two districts. In Sylhet, water level from ground surface in the 4 wells varied from 2.77 to 3.05 m in August 2001, 3.84 to 4.12 m in December 2001, and from 3.8 to 3.96 m in April 2002.

Figure 4.4 shows As concentration as a function of depth of water level for one tubewell in each of the four districts. It shows no particular trend of As concentration in water with water level. For the wells in Kushtia and Chandpur, As concentration decreased with increasing depth of water level. On the other hand, for the two wells in Nawabganj and Sylhet, As concentration increased with increasing depth of water level. Similar results i.e., no particular trend of As concentration with well depth was also observed for the other 12 wells in these 4 districts.

4.3.2.2 Variation of Arsenic Concentration with pH, EC, TDS, Chloride, CO₂

The variation of As concentrations in the tubewell water with pH is shown in Fig. 4.5 (including Fig A-2 of Appendix). It shows no particular trend of As concentration with pH of water. In fact, such variations are not expected. Both the oxidation and reduction reactions that may mobilize As from sediments may release or consume protons (as discussed in Chapter 2), but since concentrations of As in groundwater are typically low (compared to concentrations of major anions and cations), these reactions are not at all likely to control pH of groundwater. Other processes, e.g., dissolution of minerals (e.g., calcite, dolomite, etc.) are likely to control pH of groundwater. The pH values of the 16 tubewells varied from 5.6 to 7.5, a range typical of groundwater in Bangladesh.

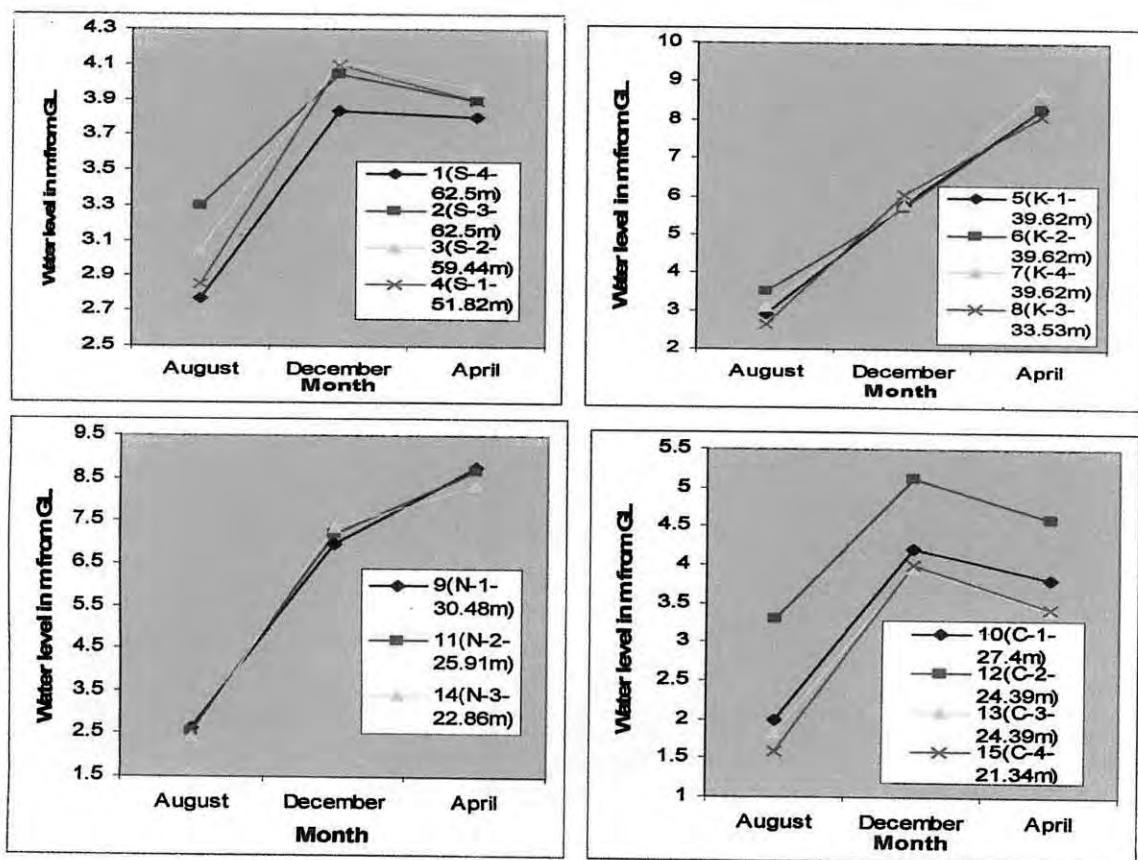


Fig. 4.3: Variation of water level in the tubewells with sampling time

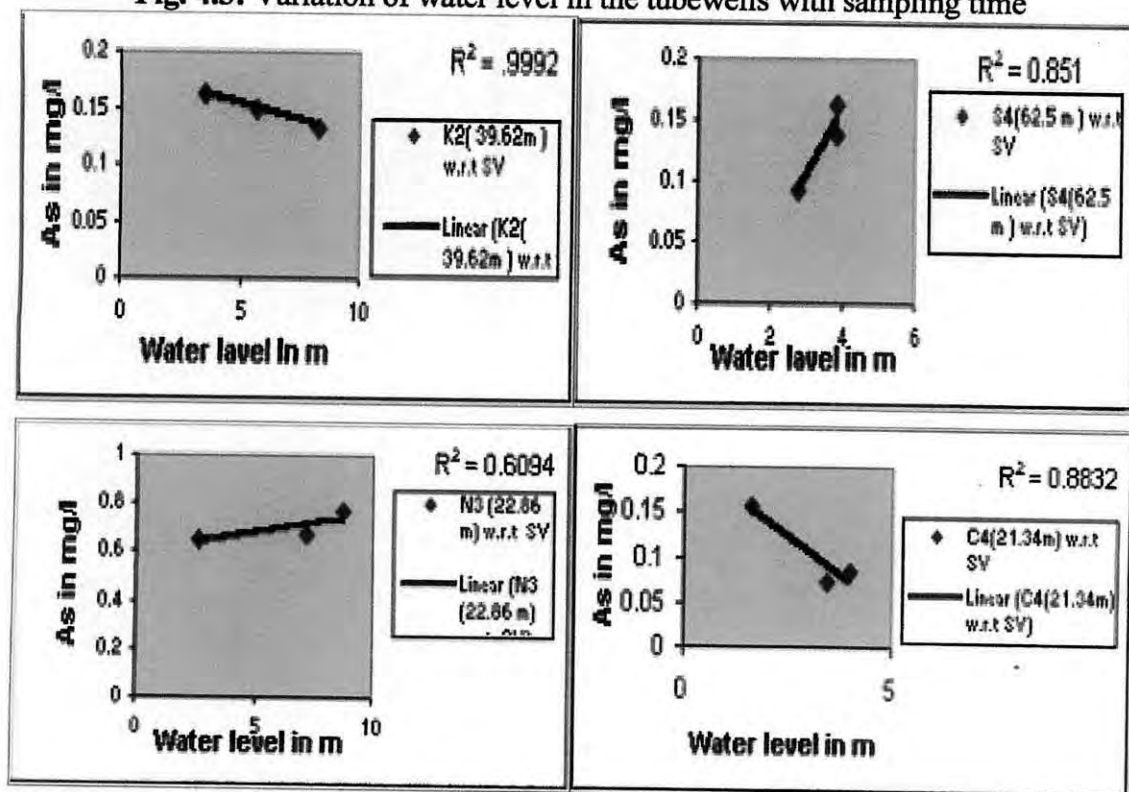


Fig. 4.4: Variation of As concentration in one well from each district with water level in the wells (Well # K2 from Kushtia, S4 from Sylhet, N3 from Nawabganj, and C4 from Chandpur)

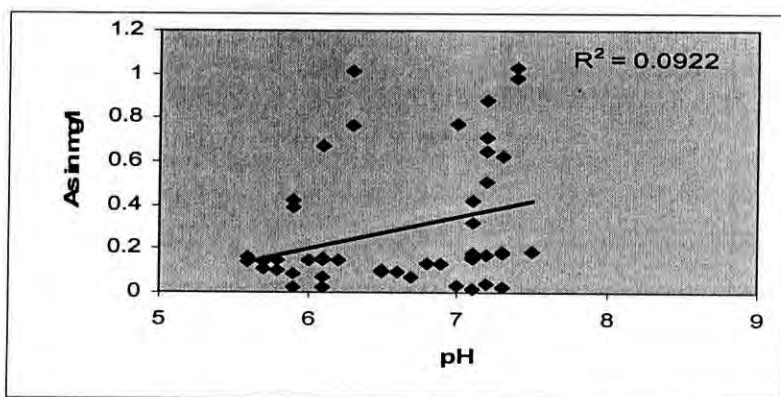


Fig. 4.5: Correlation between As and pH

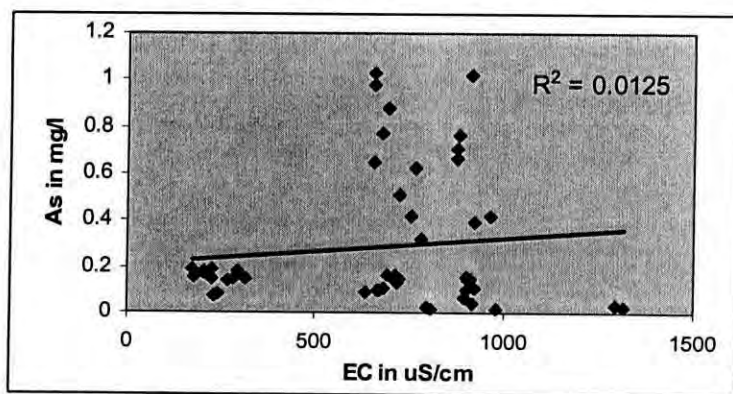


Fig. 4.6: Correlation between Electric Conductivity and As

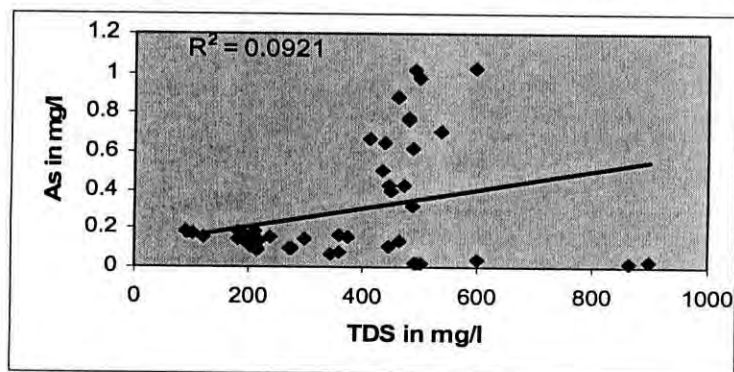


Fig. 4.7: Variation of As concentration with TDS

Figures 4.6 and 4.7 (including Fig. A-4 and Fig. A-5 of Appendix) show variation of As concentration with EC and TDS, respectively. The EC and TDS concentrations are typically found to be proportional; as a result variation of As concentrations with EC and TDS are almost identical. No clear trend of variation of As concentration with EC or TDS could be seen from Figs. 4.6 and 4.7. Among the wells in 4 districts, EC varied from 172 to 920 $\mu\text{S}/\text{cm}$ in August 2001, from 226 to 1315 $\mu\text{S}/\text{cm}$ in December 2001 and 206 to

1295 $\mu\text{S}/\text{cm}$ in April 2002. The TDS concentrations varied from 90 to 600 mg/l in August 2001, 181 to 866 mg/l in December 2001, and 183 to 898 mg/l in April 2002.

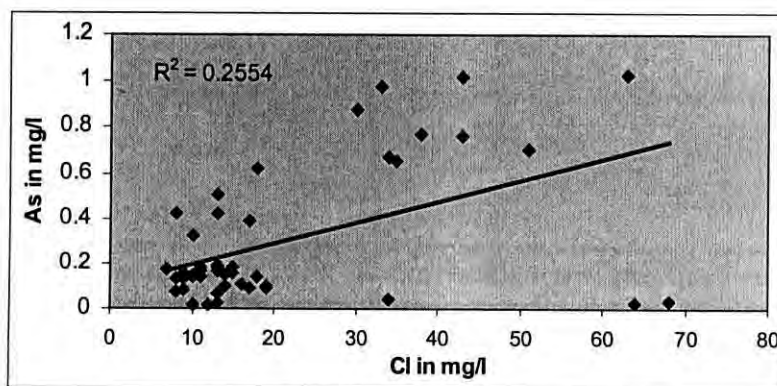


Fig. 4.8: Correlation between As and chloride

Figure 4.8 (including Fig. A-8 of Appendix) shows the correlation between As concentration and chloride concentration in groundwater. Chloride concentration in the tubewell water samples varied from 7 mg/l in Chandpur in August to 68 mg/l in Nawabganj in April. Figure 4.8 appears to show a positive trend of increasing As concentration as chloride concentration increases. When the data points were plotted district-wise (shown in Fig. A-8 of Appendix), a positive trend (as observed in Fig. 4.8) was found for the districts of Kushtia and Chandpur, while a negative trend (i.e., decreasing As concentration with increasing chloride concentration) was observed for Sylhet and Nawabganj. This is not surprising because variation in chloride concentration is not likely to be governed by the geochemical processes resulting in mobilization of As.

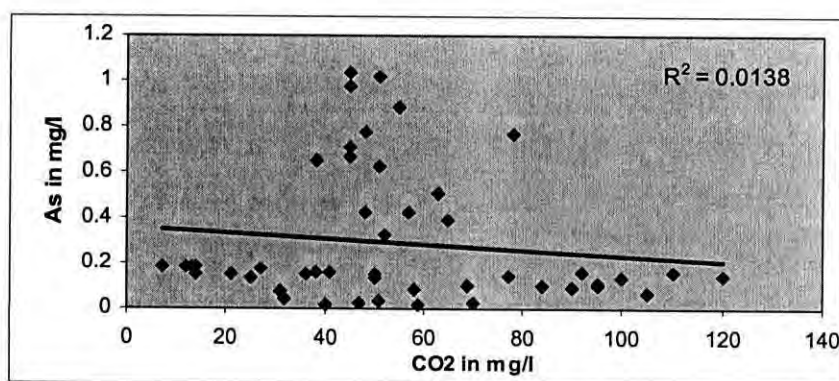


Fig. 4.9: Correlation between As and carbon dioxide

Carbon dioxide concentration in the tubewell water samples ranged from 7mg/l to 90 mg/l during August, from 14 mg/l to 110 mg/l in December and from 13 mg/l to 120 mg/l

in April. In all seasons, highest carbon dioxide was measured in Sylhet and the lowest in Chandpur district. Figure 4.9 (including Fig. A-10 of Appendix) shows variation of As concentration with CO₂ in the study areas. As expected, no definite trend of As and CO₂ concentrations is observed from Fig. 4.9.

4.3.2.3 Variatin of Arsenic Concentration with Phosphate

Figure 4.10 (including Fig. A-12 of Appendix) shows variation of As concentration with phosphate concentration in groundwater; which shows no definite trend of variation. Higher phosphate concentration in groundwater is often thought to promote mobilization of As due to high affinity of phosphate for adsorption onto iron hydroxides. Thus, phosphate may promote desorption of As from Fe-oxyhydroxides and As concentration in groundwater may increase. While the combined data from all 4 districts did not show any significant correlation between As and PO₄, some weak correlation is observed when the data are plotted district wise (Fig. 4.11). As shown in Fig. 4.11, groundwater samples from Chandpur and Nawabganj districts show a somewhat positive correlation between As and PO₄ concentrations, while a somewhat negative correlation is observed for Kushita.

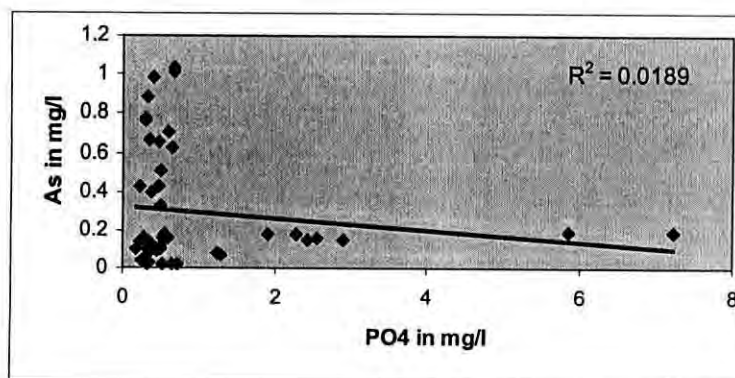


Fig. 4.10: Relationship between As and phosphate concentrations

The Samta case study (AAN, 1999) showed that the correlation of As concentration with phosphate is negative; when As concentration is high, PO₄ ion is often absent. DPHE/BGS (2000) study showed that phosphate concentration is quite variable in Bangladesh groundwater, ranging between <0.1 mg/l and 19 mg/l in the shallow groundwater and between <0.1 mg/l and 6.1 mg/l in the deep groundwater with the median concentration of 0.29 mg/l and 0.33 mg/l, respectively. However, the generally

poor correlation between As and phosphate in the groundwater as per DPHE/BGS study and this study and the presence of high phosphate concentration in deep groundwater aquifers in many of the cases as per BGS/DPHE study, which have low Arsenic concentration indicate that the geo-chemical processes are complex and that a number of factors are involved in As mobilization in the groundwater.

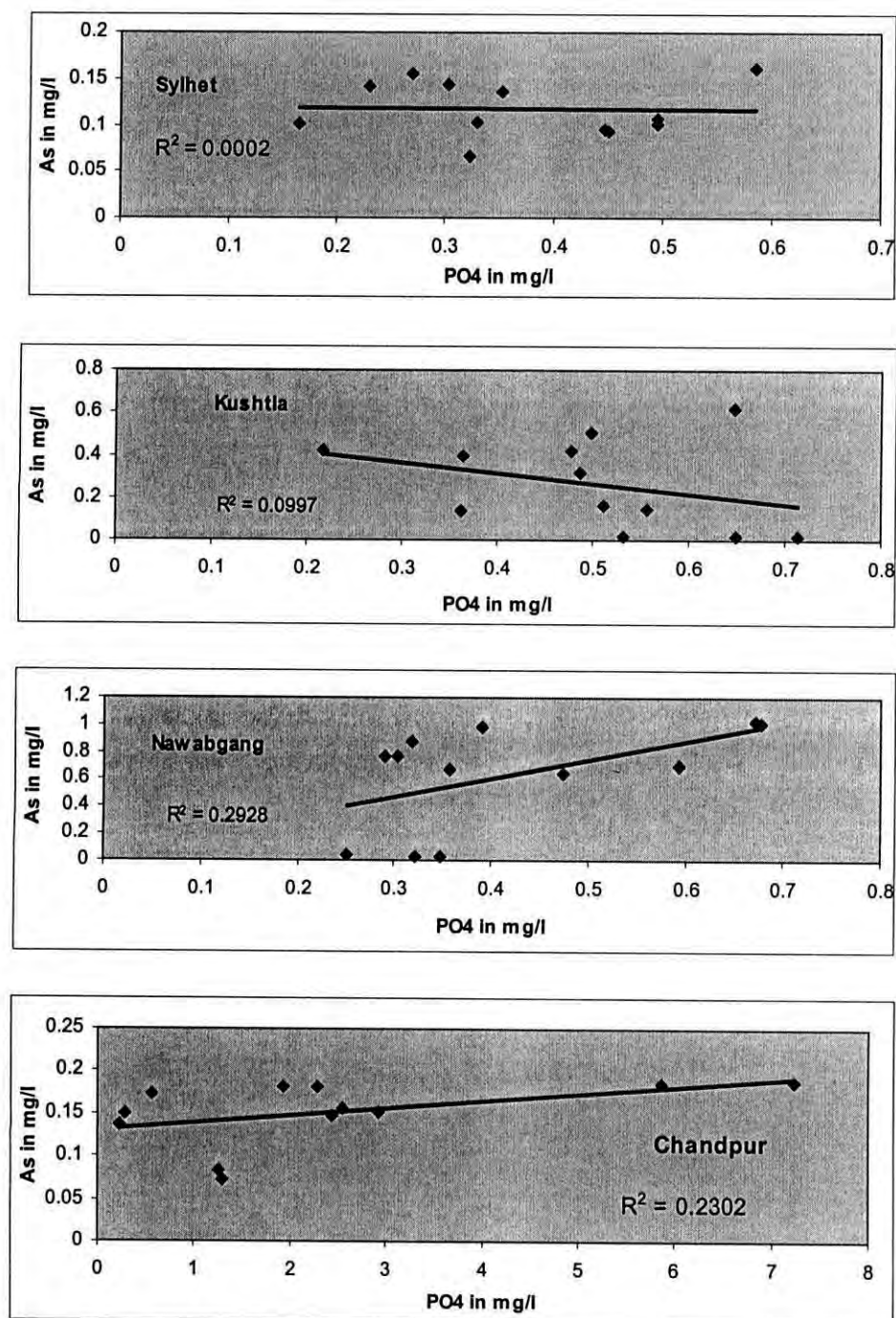


Fig. 4.11: Correlation between As and phosphate concentrations in four districts

4.3.2.4 Variation of Arsenic Concentration with Nitrate

Nitrate content varied from 0.1 mg/l in August to 1.4 mg/l in April, always remaining below 10 mg/l, which is the permissible limit of nitrate according to the Bangladesh Water Quality Standard. High nitrate concentrations in groundwater may indicate an oxidizing environment because nitrate can act as an electron acceptor and may promote oxidation (e.g., of Fe^{2+} into Fe^{3+}) in the absence of oxygen. Since oxidizing environment in the aquifer is likely to cause a reduction of As concentration (because dissolved As will get adsorbed onto oxidized iron hydroxides), one may expect lower As concentration in the presence of high nitrate. However, nitrate concentration in Bangladesh groundwater is typically low, as found in the well monitored in this study as well. Figure 4.12 (including Fig. A- 13 of Appendix) shows the relationship between As and nitrate concentrations, which show absolutely no trend of variation.

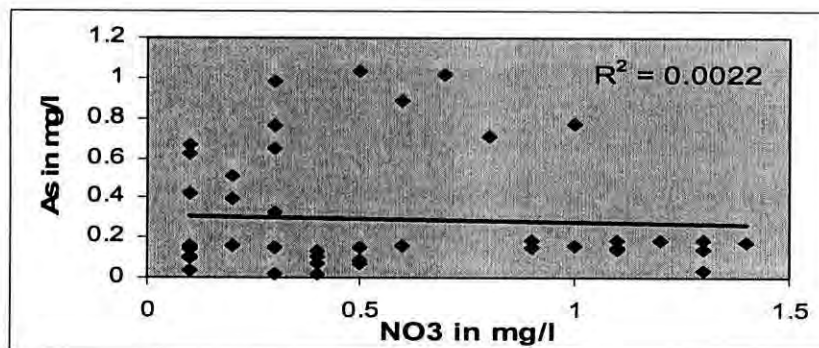


Fig. 4.12: Relationship between As and nitrate concentrations in groundwater

4.3.2.5 Variation of Arsenic Concentration with Hardness and Alkalinity

In Sylhet and Chandpur districts of eastern Bangladesh, hardness of groundwater was found to be below 200 mg/l, the lower limit of the drinking water standard of Bangladesh for hardness. On the other hand, hardness in wells of Kushtia and Nawabganj of western Bangladesh was within 200-500 mg/l, within the limits of national drinking water standard. In Sylhet hardness values ranged from 40 April to 90 mg/l as CaCO_3 in December; in Chandpur, hardness ranged from 102 (in August) to 152 mg/l as CaCO_3 (in December). In Kushtia, hardness varied from 216 (in April) to 346 mg/l as CaCO_3 (in August); in Nawabganj, hardness varied from 222 (in August) to 304 mg/l as CaCO_3 (in December).

A number of studies (e.g., Harvey et al., 2002) have found a positive correlation between dissolved As and Ca^{2+} concentrations in groundwater. The positive correlation between As and Ca^{2+} is explained by oxidation of organic matter, which produces CO_2 and CO_2 in turn induces calcite dissolution (resulting in high Ca^{2+} concentration in groundwater). Since Ca^{2+} typically accounts for major portion of total hardness in Bangladesh groundwater, a positive correlation between As and hardness concentrations would provide support for this “reduction hypothesis” of As mobilization. Figure 4.13 (including Fig. A-6 of Appendix) shows the relationship between As concentration and hardness in the well waters. A rather weak but positive correlation can be detected from Fig. 4.13. Thus, although the correlation is weak, results presented in Fig. 4.13 appear to support the “reduction hypothesis” of As mobilization.

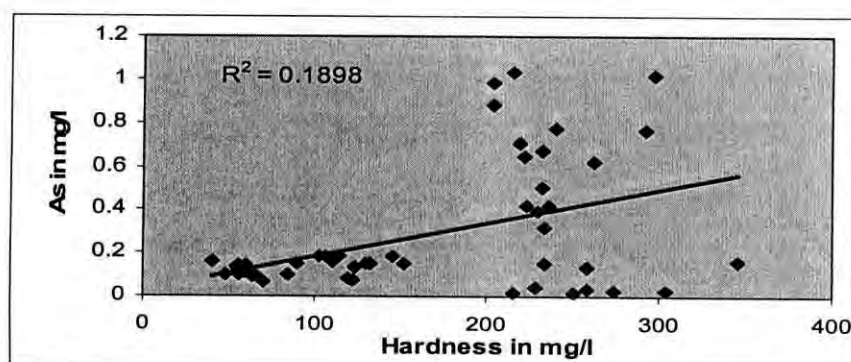


Fig. 4.13: Correlation between As concentration and Hardness

Alkalinity among the well water varied over a wide range, from 86 to 745 mg/l. Since pH of most water samples are within neutral range, bicarbonate ions account for most of the alkalinity. Alkalinity in groundwater of Chandpur ranged from 86 (in April) to 172 mg/l as CaCO_3 (in August). In Sylhet, alkalinity ranged from 200 to 218 mg/l as CaCO_3 ; in Kushtia, from 419 to 488 mg/l as CaCO_3 ; in Nawabganj, from 330 to 745 mg/l as CaCO_3 .

Harvey et al., (2002) have found As concentration to increase along with concentrations of DIC (dissolved inorganic carbon). This is explained by the oxidation of DOC (Dissolved Organic Carbon, i.e., dissolved organic matter), which produces DIC, e.g., bicarbonate (HCO_3^-). Thus, a positive correlation between As and alkalinity is indicative of the oxidation of organic matter. Figure 4.14 (including Fig. A- 7 of Appendix) shows the relationship between As concentration and alkalinity, which shows a weak positive

correlation between As and alkalinity. Thus, the correlation between As and alkalinity also appears to support the “reduction hypothesis” of As mobilization.

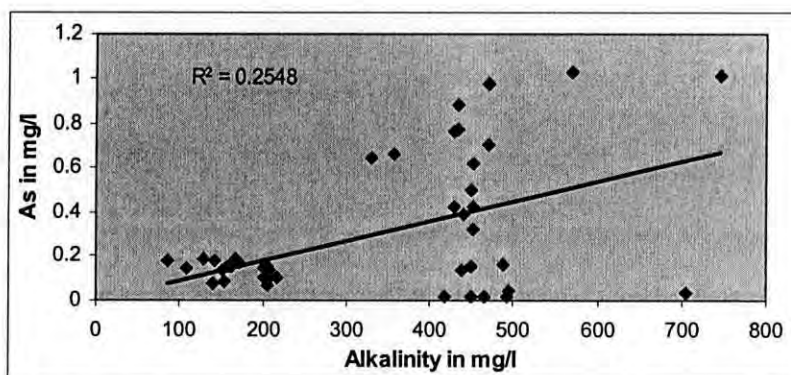


Fig. 4.14: Correlation between As and Alkalinity

4.3.2.6 Variation of Arsenic Concentration with Ammonia

Ammonia concentration in well waters ranged from 0.5646 mg/l to 71.375 mg/l. However, except for 3 values, the rest of ammonia concentration were below 20 mg/l. Figure 4.15 (including Fig. A- 14 of Appendix) shows relationship between As and ammonia concentrations. Here, the 3 high ammonia concentrations dictated much of the correlation and does not represent the actual scenario. Hence relationship between As and ammonia concentrations were plotted district-wise as shown in Fig. 4.16.

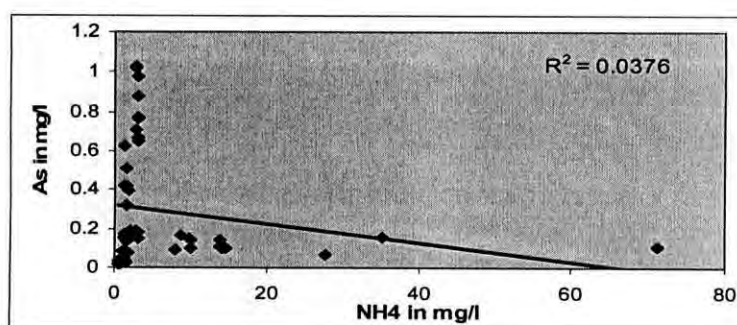


Fig. 4.15: Correlation between arsenic and ammonium

Except for Sylhet, Fig. 4.16 shows relatively moderate to strong correlation between As and ammonia concentrations. A number of other studies have also found positive correlation between As and ammonia concentrations. This is explained by the decomposition of organic matter, which produces ammonia. Thus, results from this study appear to support As mobilization through oxidation of organic matter under reducing condition.

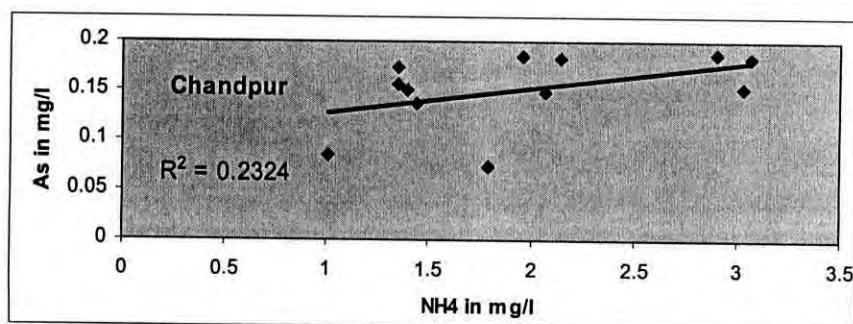
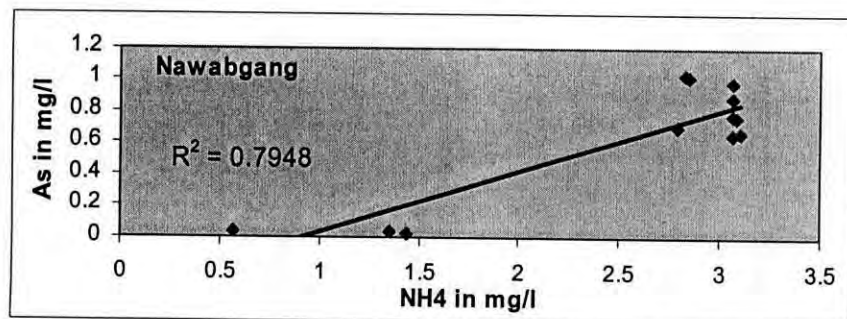
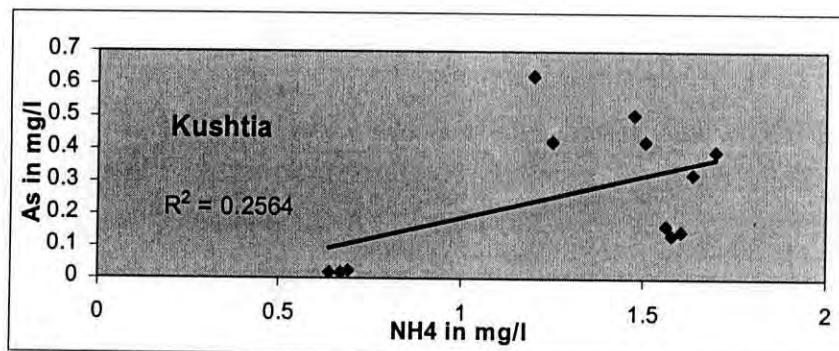
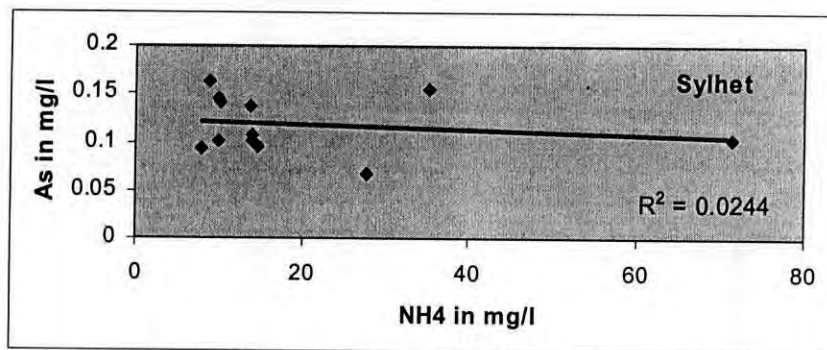


Fig. 4.16: Correlation between As and ammonium in four districts

4.3.2.7 Variation of Arsenic Concentration with Redox Potential (eH)

Redox potential (eH) provides an indication of the oxidizing or reducing condition in an aqueous system. Higher redox potential values indicate oxidizing environment, while lower redox potentials indicate reducing environment. Figure 4.17 (including Fig. A- 3 of Appendix) shows variation of As concentration with redox potential for all water samples from all wells monitored in this study. The measured redox potential (eH) varied from -6 to -99 mV, indicating reducing environment. Similar results were also observed in BGS and DPHE (2001) study which showed that almost all samples investigated have low redox potential in both shallow and deep aquifers showing the lowest eH value of -105 mV in shallow aquifers.

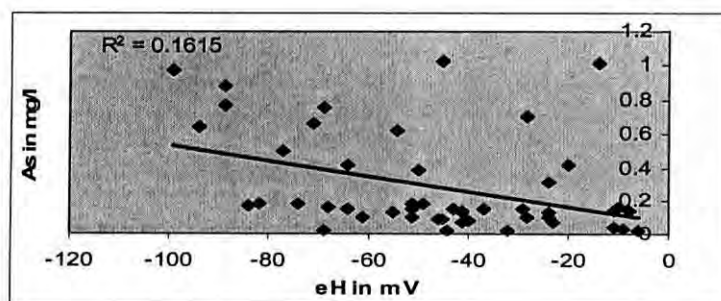


Fig. 4.17: Variation of As with eH in the piezometers

Although there are significant variations, a trend is apparent from Fig. 4.17, which is that As concentration in groundwater increases as the condition becomes more and more reducing. Figure 4.18 shows variation of As concentration with eH separately for groundwater samples collected in August 2001, December 2001, and April 2002. The same general trend, that is increasing As concentration with increasingly reducing environment is also apparent from this figure.

The increase of dissolved As concentration with decreasing eH value is consistent with the “reduction hypothesis” of arsenic mobilization. The reducing environment is thought to be created due to oxidation of organic matter, accompanied by reductive dissolution of iron-oxyhydroxides. Arsenic associated with iron oxyhydroxides is mobilized / released due to its dissolution (from Fe^{3+} solids into dissolved Fe^{2+}). Thus, results from this study appear to support the “reduction hypothesis” for mobilization of As.

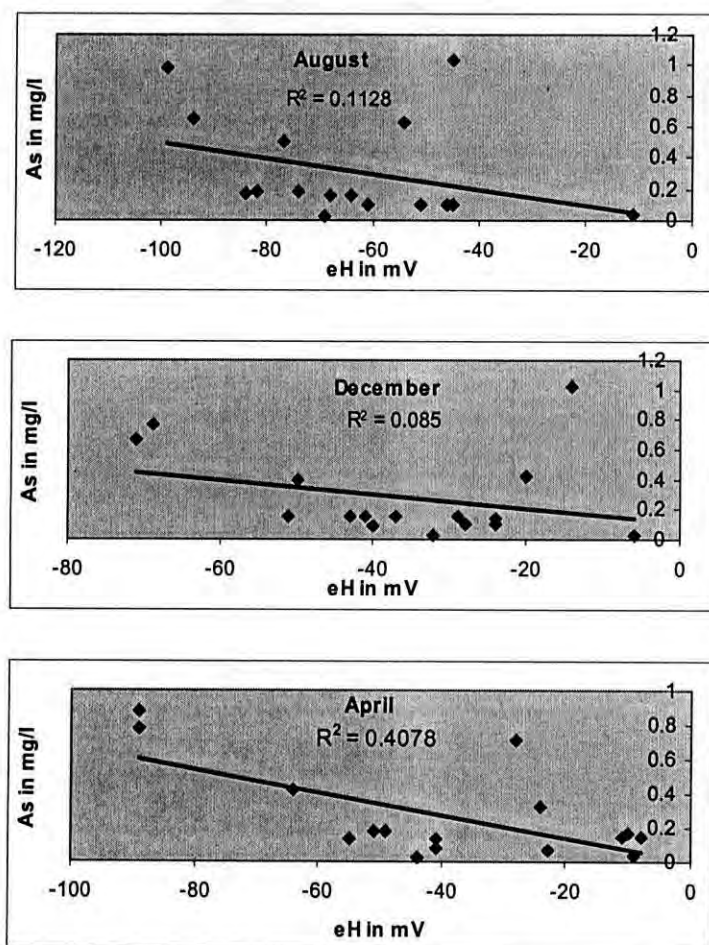


Fig. 4.18: Variation of As concentration with eH at different sampling times

4.3.2.8 Variation of As Concentration with Sulfide and Sulfate

Sulfide concentrations of the tubewells monitored in this study varied from 1 to 10 $\mu\text{g/l}$ in August, 1 to 17 $\mu\text{g/l}$ in December, and 3 to 22 $\mu\text{g/l}$ in April. Figure 4.19 (including Fig. A- 9 of Appendix) shows relationship between As and sulfide concentrations. It does not show any apparent correlation between As and sulfide concentrations.

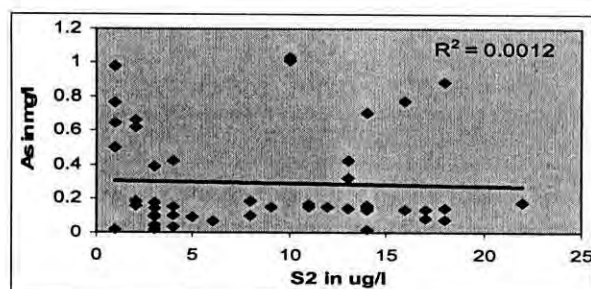


Fig. 4.19: Relationship between As and sulfide

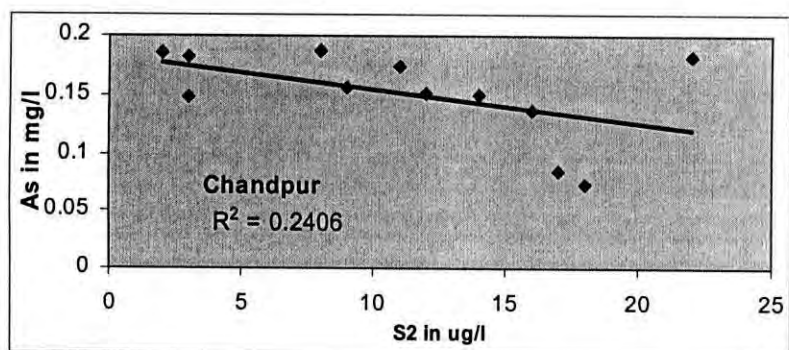
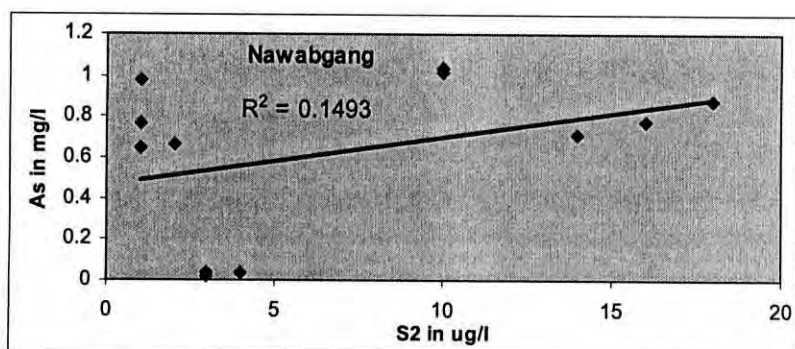
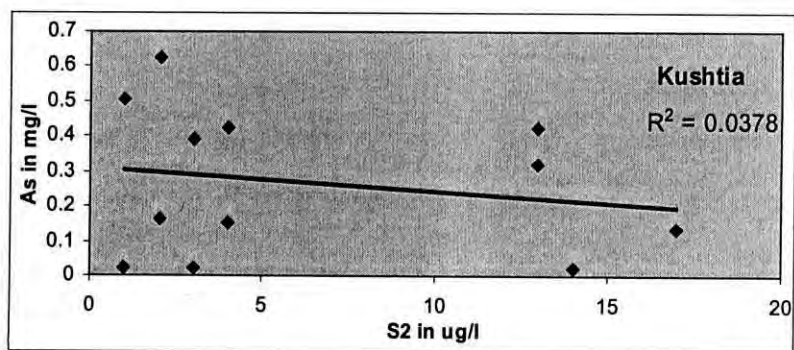
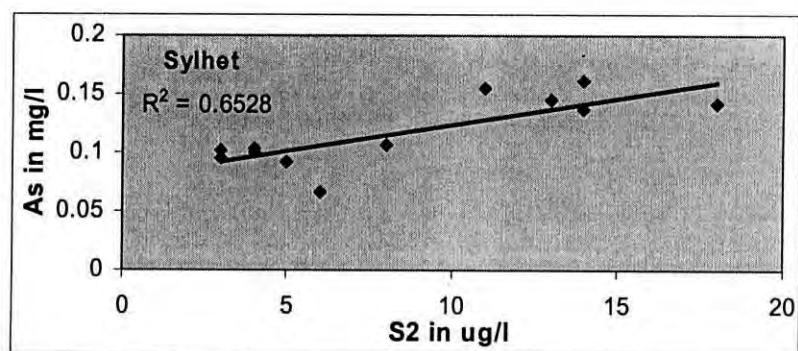


Fig. 4.20: Correlation between arsenic and sulphide in 4 districts

Figure 4.20 shows relationship between As and sulfide concentrations in the 4 districts. It shows strong positive correlation between As and sulfide in Sylhet and a relatively weak positive correlation in Nawabganj district. But, negative correlation was observed between As and sulfide concentrations in Chandpur and Kushtia. In general, higher sulfide concentrations indicate a reducing condition, which might promote oxidation of organic matter and concurrent dissolution of iron oxyhydroxides. However, other processes may also control sulfide concentrations in groundwater and hence the lack of strong correlation between As and sulfide is not surprising.

Sulfate concentrations in the groundwater samples varied 0.1 mg/l to 0.9 mg/l, except one tubewell in Sylhet and another in Nawabganj, which had relatively high sulfate concentrations. Figure 4.21 (including Fig. A - 11 of Appendix) shows correlation between As and sulfate concentrations. No strong correlation between As and sulfate was found in the observed data.

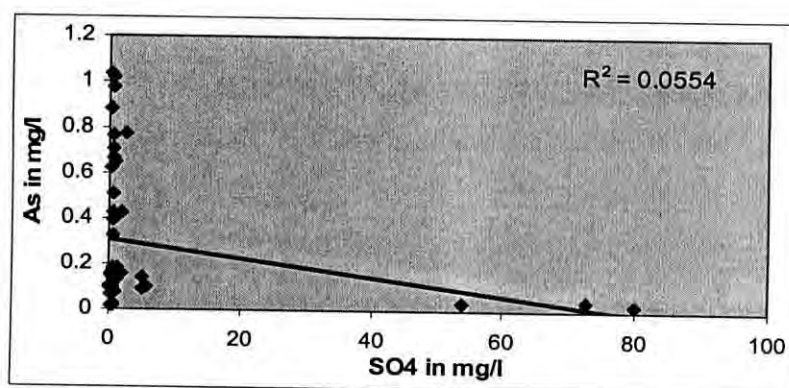


Fig. 4.21: Correlation between arsenic and sulfate concentrations

4.3.2.9 Arsenic Versus Iron Concentration

Iron concentration in the tubewells monitored in this study varied from 5.07 mg/l to 21.7 mg/l. The Samta case study (AAN, 1999) found iron concentration to vary from 3.9 mg/l to 10.5 mg/l; for shallow aquifer iron (Fe^{2+}) had the strongest correlation with As concentration; for deep aquifer both As and Fe concentrations were low. The DPHE/BGS study found iron concentration in the Bangladesh groundwater to range between < 0.004 mg/l to 61 mg/l, with the median values of 1.4 mg/l and 0.2 mg/l in the shallow and deep groundwater aquifer respectively. Iron concentration is high in most of the groundwater in Bangladesh as a result of the predominantly reducing condition in the aquifer,

especially in the southern Bangladesh (south of the Ganges-Padma) and in the northeastern Bangladesh (Sylhet basin). The proportions of wells with high iron concentrations are particularly high in the Jamuna valley with majority of wells exceeding 10 mg/l Fe. The median concentration of Fe in As contaminated (with > 50 ug/l As) shallow groundwater aquifer area is 4 mg/l. Lowest Fe concentrations are found in the groundwater from the Dupi Tila aquifers of the Barind and Madhupur Tracts, older deep aquifers of the Barisal region and the Tista Fan, north-western part of Bangladesh.

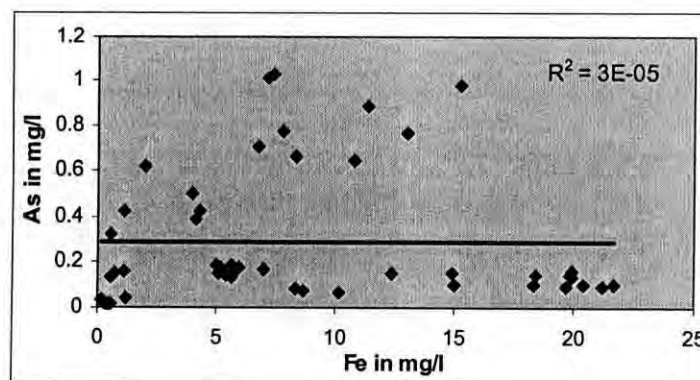


Fig. 4.22: Relationship between As and iron concentrations in groundwater

Figure 4.22 (including Fig. A-15 of Appendix) shows relationship between As and Fe concentrations in groundwater of all the wells monitored in this study. Although, no particular trend could be seen from this figure, when the data points were plotted separately for each district (Fig. 4.23), some trends became apparent. For Kushtia and Nawabganj, the As concentrations have been found to be relatively strongly correlated with Fe concentrations; in Sylhet, the correlation was relatively poor. However, in Chandpur negative correlation, though poor, could be seen. Overall, the results from this study are in agreement with the observations in other large scale studies (e.g., BGS and DPHE, 2001) that there is a weak but statistically significant correlation between As and Fe concentrations.

The positive correlation between Fe and As supports the reduction hypothesis, whereby oxidation of organic matter in the aquifer is accompanied by reduction of As-rich iron hydroxide solids, resulting in increase of both As and Fe concentrations in groundwater.

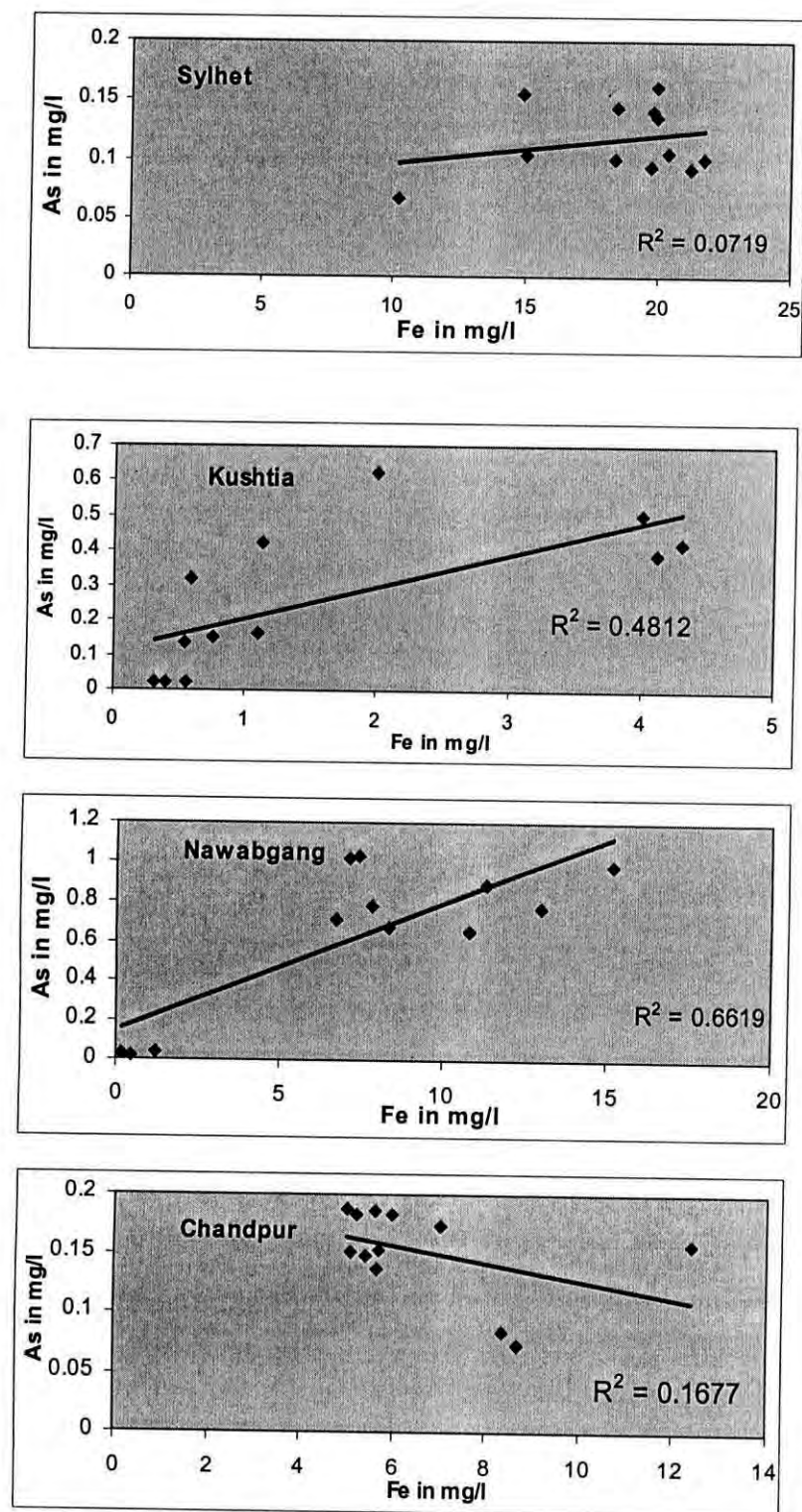


Fig. 4.23: Correlation between As and Fe concentrations in 4 districts

Figure 4.24 shows the Eh and pH values recorded in this study in the phase stability (Eh-pH) diagram of iron and arsenic. It shown that soluble Fe^{2+} and H_3AsO_3 are predominant

forms of iron and As in eH-pH range found for the groundwater samples in this study. These forms of As and iron are soluble in water.

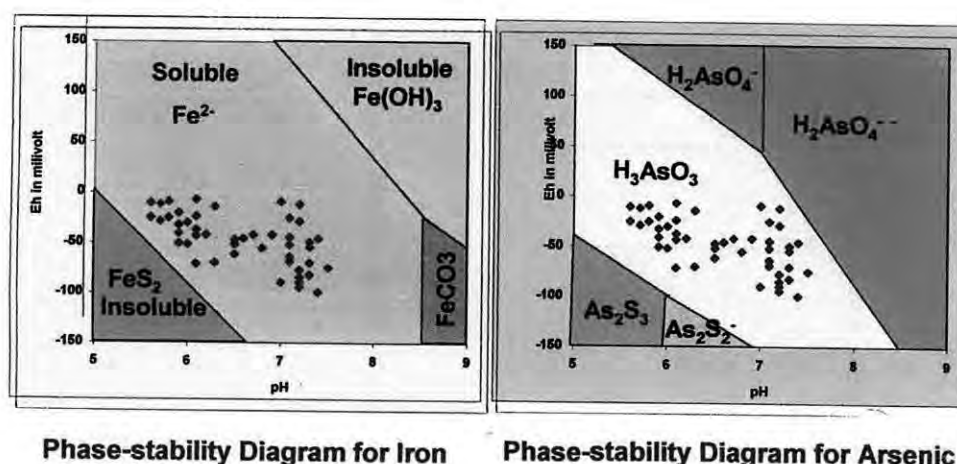


Fig. 4.24: Eh and pH values of groundwater in phase stability diagram of Fe and As.

4.3.2.10 Variation of Arsenic Concentration with Manganese and Lead

Manganese (Mn) concentrations in the tubewell water samples varied from 0.1828 mg/l in Chandpur to 2.3184 mg/l in Kushtia in August; from 0.1164 mg/l in Chandpur to 1.8656 mg/l in Kushtia in December; and from 0.098 mg/l in Chandpur to 1.709 mg/l in Kushtia in April. Manganese concentration in 50% of the wells exceeded the WHO guideline value for Mn 0.4 mg/l. Figure 4.25 (including Fig. A- 16 of Appendix) shows a positive correlation between As and Mn concentrations in groundwater. However, no such correlation has been found in the BGS-DPHE study, which covered a much larger data set. Some studies have shown that in the Ganges-Delta floodplain, Mn concentration is high and As concentration is low. They have attributed this to a situation where the redox condition in the aquifer is low enough for reductive dissolution of Mn(IV) solids, but not low enough for reductive dissolution of Fe(III) solids. The data obtained in this study is not large enough to test such a hypothesis.

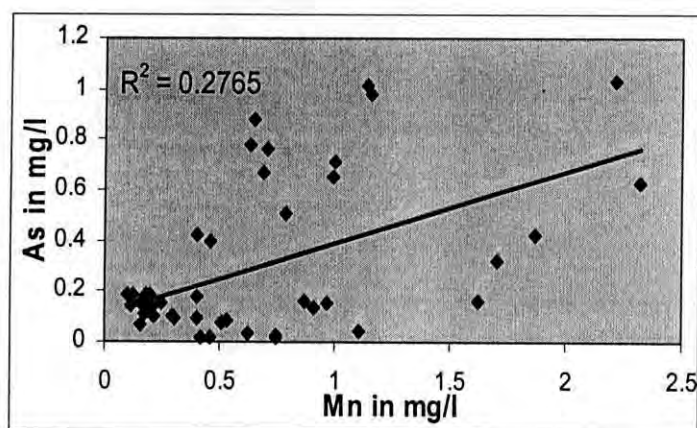


Fig. 4.25: Relation between As and Mn concentrations

Lead concentrations in the groundwater samples were relatively low. In August, lead concentration varied from 0.0032 mg/l in Chandpur to 0.0351 mg/l in Nawabganj; in December from 0.0054 mg/l in Chandpur to 0.0182 mg/l in Nawabganj and in April from 0.005 mg/l in Sylhet to 0.031mg/l in Nawabganj. Figure 4.26 (including Fig. A- 17 of Appendix) shows relationship between As and Pb concentrations. As expected, not particular trend could be detected from this figure.

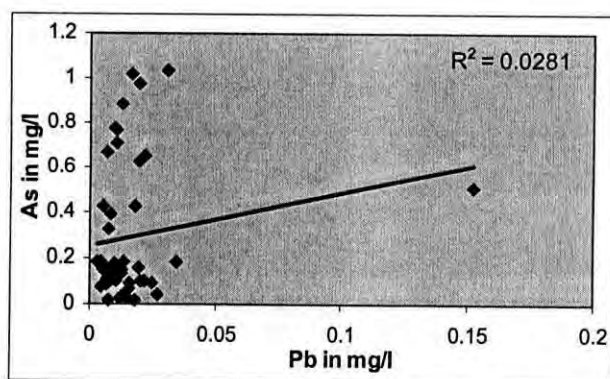


Fig. 4.26: Relationship between As and Pb concentrations in groundwater

4.4 SUMMARY

Characteristics of groundwater samples collected from 16 wells in 4 different districts provide some indication of the possible processes responsible for mobilization of As in the subsurface. The strongest indication comes from the negative correlation between As and eH values (i.e., increasing As concentration with decreasing redox potential). This

indicates that reducing environment promotes mobilization of As in the subsurface. Under reducing environment, organic matter (i.e., organic carbon, DOC) gets oxidized with concurrent reductive dissolution of iron oxyhydroxides. This process releases the As associated with iron oxyhydroxides (e.g., in adsorbed form) into the aqueous phase. Additional support for this process of As mobilization comes from the positive correlation of As concentration with ammonia, alkalinity (i.e., HCO_3^- or DIC), and hardness (actually Ca^{2+}), values. Oxidation of organic matter carbon produces CO_2 , DIC (e.g., in the form of HCO_3^-) and ammonia. Carbon-di-oxide induces dissolution of calcite resulting in higher Ca^{2+} and hence higher hardness in groundwater. Very low sulfate concentration found in the groundwater samples is also consistent with a reducing environment, and negates As mobilization as a result of oxidation of As bearing minerals.

Chapter 5

ARSENIC IN AQUIFER SOLIDS

5.1 INTRODUCTION

The primary source of Arsenic (As) in the natural environment is As bearing minerals, mostly ores containing sulfide along with copper, nickel, lead, cobalt and other metals. Arsenic in soils is mainly derived from its parent rock materials. Weathering of rocks converts As-rich metal sulfides to As trioxides, which eventually finds its way into surface water, groundwater and sediments. Arsenic in sediments mainly comes from suspended solids that acquire their As from flowing rivers water. Arsenic in suspended solids and sediments was found to be about 2000 times higher than that in river water indicating that the suspended solids were a good scavenging agent and the sediments a sink for Arsenic (Mok and Wai, 1994).

Arsenic occurs in soils all over the world at an average concentration of about 5 to 6 mg/l (Bhumbla and Keefer, 1994). The average concentrations of Arsenic in alluvial sand and mud/clay have been reported to be 2.9 mg/kg and 6.5 mg/kg respectively in Bangladesh (BGS and DPHE, 2001). Arsenic concentrations in soils as high as 51 mg/kg in Faridpur and 83 mg/kg in Comilla have been reported (Ullah, 1998).

5.2 MATERIALS AND METHODS

5.2.1 Study Area

In this study, sediment samples were collected from drilling one boreholes in each of the 5 As affected districts of Munshiganj, Chandpur, Sylhet, Kushtia and Nawabganj (Fig. 5.1). The locations of boreholes are shown in Table 5.1. The borehole samples from Chandpur, Sylhet, Kushtia and Nawabganj districts were collected from the Hydrology division of the Bangladesh Water Development Board (BWDB); BWDB constructed the boreholes in these districts as part of its routine annual program. Boreholes were constructed with a rig and sediment samples were collected continuously at the interval of five feet. Borehole sample from the Munshiganj district was collected from BUET-MIT

joint research project. Boring works for sediment collection in Munshiganj is shown in Fig. A-19 of appendix. From each borehole in the 5 districts, sediment samples from two different depths (as shown in Table 5.1) were collected.

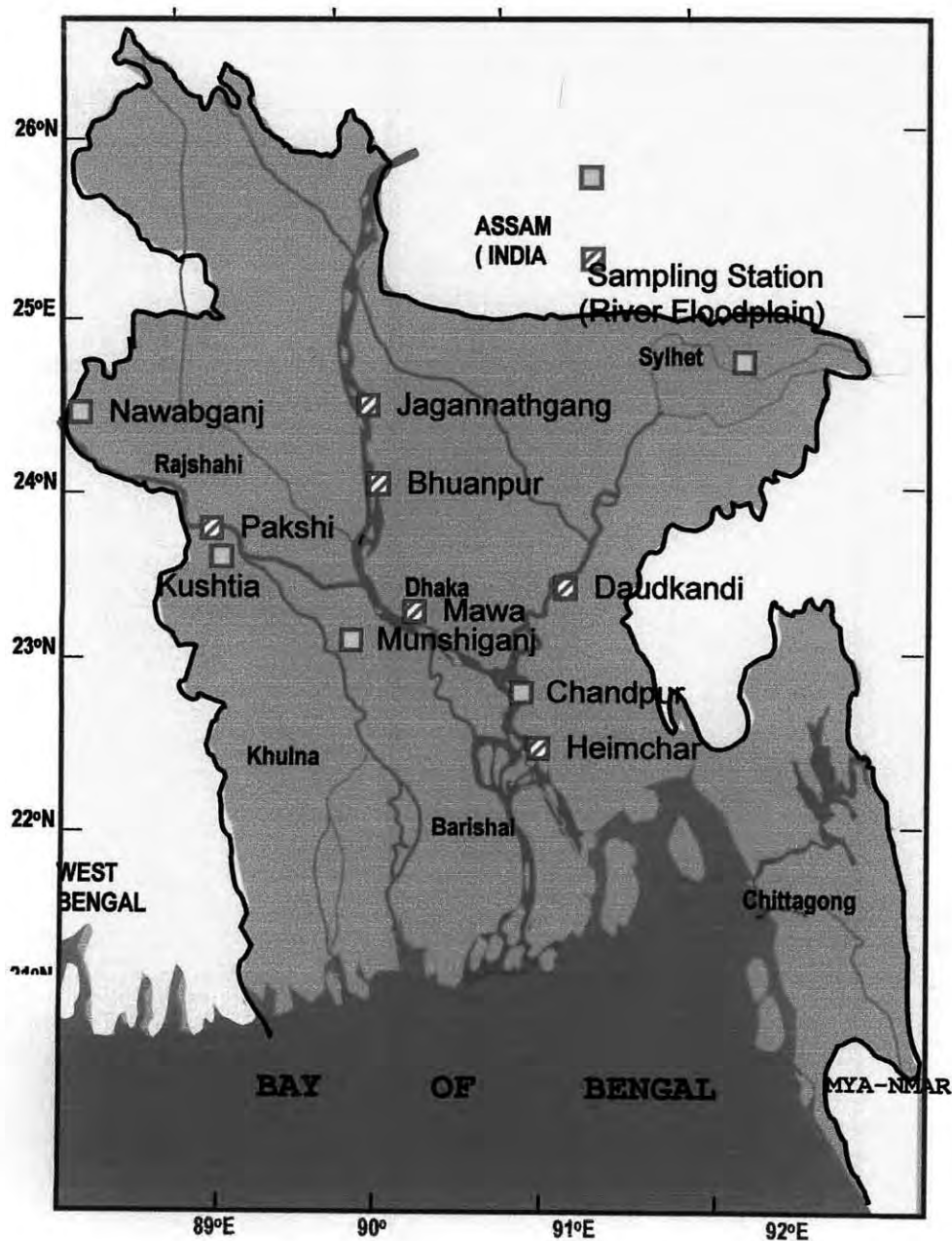


Fig. 5.1: Map of Bangladesh showing the locations from where sediment samples were collected

Table 5.1: Locations of boreholes in 5 districts

Sl. No.	District	Upazila/ town	Borehole location	Depths of sediment samples (ft)
1	Munshiganj	Sreenagar	Bejgaon, by the side of Dhaka-Khulna Highway near to Mawa Ferryghat	94-96 110-112
2	Chandpur	Kachua	Uzanee Madrasha Compound of Uzanee village near to Dhaka-Chandpur Road	33-34 53-54
3	Sylhet	Kanaighat	Near Parbatpur Primary School by the side of Sylhet-Kanaighat Road	90-91 130-132
4	Kushtia	Kushtia town	Courtpara, near Kushtia Government College	50-52 90-92
5	Nawabganj	Nawabganj town	Rajarampur Primary School yard located at West Rajarampur	50-52 80-82

5.2.2 Collection of samples

5.2.2.1 Collection of Borehole Sediment Samples

As noted earlier, sediments samples were collected from the boreholes constructed in each of the 5 districts (Munshiganj, Sylhet, Chandpur, Kushita and Nawabganj). One borehole was constructed in each of these districts and sediment samples from two different depth intervals were collected from each borehole (as shown in Table 5.1). Except for Munshiganj, where the borehole was constructed as part of the BUET-MIT joint research project, the boreholes were constructed and the sediments were supplied by the BWDB.

5.2.2.2 Collection of Floodplain Sediment

Sediment core samples were also collected from the floodplains of these rivers during post-flood period (September-October 2001). Two core samples were collected from each river floodplain, at locations about 10 to 15 m from the riverbank. These core samples were also collected using PVC samplers of 5 cm (2 inch) in diameter and 30 to 60 cm in length. Along Padma, floodplain core samples were collected from Ishardi-Pakshi and

Mawa; along Meghna, floodplain core samples were collected from Daudkandi and Heimchar; along Jamuna, floodplain core samples were collected from Jagannathgang and Bhupur.

5.2.3 Analysis of samples

Ten borehole samples (two from each of the 5 districts) as well as each of the 6 floodplain sediment samples were analyzed for total As after digestion with aqua-regia. Arsenic concentration was determined by GF-AAS (Shimadzu, AA6800). Besides, the borehole sediment samples as well as floodplain sediment samples were subjected to sequential extraction for determining the quantities of Arsenic existing in different forms (e.g., ionically bound, strongly adsorbed, associated with iron oxyhydroxides) in the sediment.

5.2.3.1 Extraction of Arsenic from sediment samples

For determination of aqua-regia extractable As, the sediment samples were taken in an aluminum bowl and kept in an oven at 110⁰ C for 24 hours. After drying for 24 hours, the samples were grinded in a grinder. The grinded soil samples were digested with aqua-regia for extraction of metal ions. For digestion, 2.5 ml concentrated nitric acid and 7.5 ml concentrated hydrochloric acid were added to 5 gm grinded oven dried soil sample taken in a 500 ml volumetric flask. The sample was kept overnight in the flask and then it was heated to boiling for two hours. Afterwards deionized water was added up to the 500 ml graduation mark. The contents of the flask were stirred for 5 minutes, then cooled and finally filtered using a filter paper (0.45 micron). The filtrate was stored in a plastic bottle for analysis of Arsenic using an AAS attached with a graphite furnace (Shimadzu, Japan AA6800). The detection limit of Arsenic in this system was 1 µg/l.

5.2.3.2 Sequential Extraction Procedure for Sediments

The floodplain sediments were subjected to sequential extraction for determining the quantities of As existing in different forms (e.g., ionically bound, strongly adsorbed, associated with iron oxyhydroxides) in the sediment. Based on the available methods for sequential extraction and considering availability and limitation of laboratory facilities the following method shown in Table 5.2 was selected for sequential extraction.

Table 5.2. Sequential extraction techniques considered for this study

Step	Extractant	Target Phase	Possible Mechanism
Mg	1 M MgCl_2 , pH 8, 2 hrs, 25°C ; * 2 repetitions + 1 water wash	Ionicly (weakly) bound Arsenic (IB)	Anion exchange of Cl^- for As; possible Mg-As complexes
PO_4	1 M NaH_2PO_4 , pH 5, 16 & 24 hrs, 25°C ; * 1 repetition of each time duration + 1 water wash	Strongly adsorbed Arsenic (SA)	Anion exchange of PO_4 for AsO_4 and AsO_3
HCl	1 N HCl, 1 hr, 25°C ; * 1 repetition + 1 water wash	Arsenic co-precipitated with acid volatile sulfides, carbonates, manganese oxides and very amorphous iron oxyhydroxides i.e., acid volatile sulfide bound (AVS)	Proton dissolution; Fe-Cl complexation
Oxalate	0.2M Oxalate/ Oxalic acid, pH 3, 2 hrs, 25°C , in dark; * 1 repetition + 1 water wash	Arsenic co-precipitated with amorphous iron oxyhydroxides (AIO)	Ligand-promoted dissolution
HNO_3	16N HNO_3 , 2 hrs, 25°C ; * 2 repetitions + 1 water wash	Arsenic co-precipitated with pyrite and amorphous crystalline sulfides (PCA)	Oxidation of crystalline Sulfide
Aqua Regia	33% conc. HNO_3 +67% HCl	Orpiment and remaining recalcitrant As minerals bound (MB)	Stronger oxidation of Sulfides and organic matters.

As noted earlier, only the floodplain sediments were subjected to sequential extraction. For sequential extraction, 5 gm wet sediment sample (from previously collected floodplain core sediments) was put in 15 ml centrifuge tube and 10 ml of extractant (as shown Table 5.2.) was added to the wet sample in the tube. The centrifuge tube was tightly closed. The centrifuge tube with sample and extractant was tumble shaken for two hours. They were then centrifuged at 2500 rpm for about 5 minutes to settle colloids at the bottom. The tubes were then taken out from the centrifuge and the supernatant was

separated by decanting. The supernatant liquid was filtered through micro filter (0.45 μm) and the filtrate was acidified with 5% HCl and stored for As analysis. For repeat extraction, the same amount of extractant was added to the residue in the centrifuge tube and the same procedure was repeated. For wash step, same amount (10 ml) of deionized water was added to the residue in the centrifuge tube and the same procedure was repeated. Extraction was continued with each extraction fluid in succession as shown in Table 5.2. After extraction, the fluids were tested for As by GF-AAS (Shimadzu, AA6800).

5.3 RESULTS AND DISCUSSION

5.3.1. Arsenic Concentration in the Sediments

5.3.1.1 *Arsenic Concentration in the Borehole Sediments of Alluvial Plain*

Table 5.3 shows As concentrations in the borehole sediment samples from 5 districts. Arsenic content in the sediments varied from 1.82 mg/kg to 3.9 mg/kg, with average As concentrations of 2.67, 2.47, 3.56, 2.55 and 3.35 mg/kg in Sylhet, Munshiganj, Kushtia, Nawabganj and Chandpur respectively. These values are within the typical range of As contents in the sediments. In each borehole, two sediment samples were collected from two different depths. For the borehole samples from Munshiganj and Kushtia, As concentrations were higher in the sediments of higher depth, whereas for the other three districts As concentrations were higher in sediments from shallower depths. BGS and DPHE (2001) reported As contents of 21 sediments samples from Nawabganj, Lakshmipur and Kushtia districts to vary from 0.4 to 10.3 mg/kg. with averages of 5.9, 3.4 and 3.2 mg/kg, respectively. Higher concentrations of As in the upper layers of soils have also been reported in Samta village in Jessore district (Kubota, 1998) and in Rajshahi Areas (DPHE, BGS and MML, 1999). Samta case study conducted by AAN showed the average As concentration in the upper muddy layer ranged from 6.97 to 19.42 mg/kg, with an average of about 11 mg/kg; whereas in the upper sandy layer As varied from 0.7 to 3.62 mg/kg, with an average of about 1 mg/kg (AAN, RGAG and NIPSOM, 1999).

Table 5.3 : Arsenic concentration in borehole sediment samples

District	Depth of Sediment layer (ft)	As concentration (mg/kg)	Avg. As concentration (mg/kg)
Sylhet	130-132	1.82	2.674
	90-91	3.53	
Munshiganj	110-112	2.79	2.473
	94-96	2.16	
Kushtia	90-92	3.55	3.355
	50-52	3.16	
Nawabganj	80-82	2.02	2.55
	50-52	3.08	
Chandpur	53-54	2.80	3.35
	33-34	3.90	

5.3.1.2 Arsenic Concentrations in Floodplain Sediments

The floodplain sediment samples were analyzed for total (aqua-regia extractable) As and were also subjected to sequential extraction in order to determine the quantities of different forms for As (e.g., ironically bound, weakly adsorbed) associated with the sediments. Table 5.4 shows the total concentration of As in the floodplain sediments collected from 6 locations, 2 from floodplains of each river. Total Arsenic concentration in the floodplain sediments varied from 3.54 to 5.81 mg/kg while Arsenic content in suspended sediment of the rivers varied from 4.07 to 5.47 mg/kg and Arsenic content in river bed sediment of the rivers varied from 2.65 to 4.74 mg/kg.

Table 5.4: Arsenic concentrations of floodplain sediments

River	Sampling Location	As Concentration (mg/kg)
Jamuna	Bhuapur	3.72
	Jagannathganj	3.54
Padma	Mawa	4.64
	Pakshi	5.81
Meghna	Heimchar	4.27
	Daudkandi	3.87

5.3.2 Arsenic present in different forms associated with sediments

Figure 5.2 and 5.3 shows the results of sequential extraction experiment of the river floodplain sediment samples of Jamuna, Padma and Meghna and the bore hole sediment samples of alluvial plain of Sylhet, Chandpur, Nawabganj, Kushtia and Munshiganj where As (in percentage) present in different forms in the floodplain samples are presented. It shows that a significant portion of As in the floodplain sediments are associated with pyrite and amorphous crystalline sulfides (PCA). Arsenic associated with amorphous iron oxyhydroxides (AIO) and acid volatile sulfides (AVS) also account for significant portion of As in the sediments. Ionically bound As constitutes a small portion of total As in the sediments. Arsenic associated with pyrite and amorphous crystalline sulfides (PCA) and acid volatile sulfides (AVS) are likely to be mobilized under oxidizing condition, a situation that is likely to prevail during the dry season. On the other hand, As associated with amorphous iron oxyhydroxides (AIO), ionically bound (IB) and strongly adsorbed (SA) Arsenic are likely to be mobilized under reducing condition, a situation that is likely to prevail during the wet season.

Variation of Arsenic content in different reducing forms in percentage associated with AIO, SA and IB in aggregate and independently froms upstream (u/s) to downstream (d/s) of the rivers Jamuna, Padma and Meghna are presented in Tables 5.5 . Highest amount of Arsenic in these forms was found in Padma and the lowest in Jamuna. Arsenic in these forms is likely to be released from solid phase to aqueous phase under reducing condition

Table 5.5: Variation of Arsenic associated with AIO, SA and IB from u/s to d/s of rivers

Location	Jagannathganj (Jamuna)	Bhuanpur (Jamuna)	Mawa (Padma)	Heimchar (Meghna)
% of As in the forms AIO	24	19	31	30
% of As in the form SA	14	6	14	12
% of As in the form IB	1	3	3	1
Total As (%) in AIO, SA, and IB	39	28	48	43

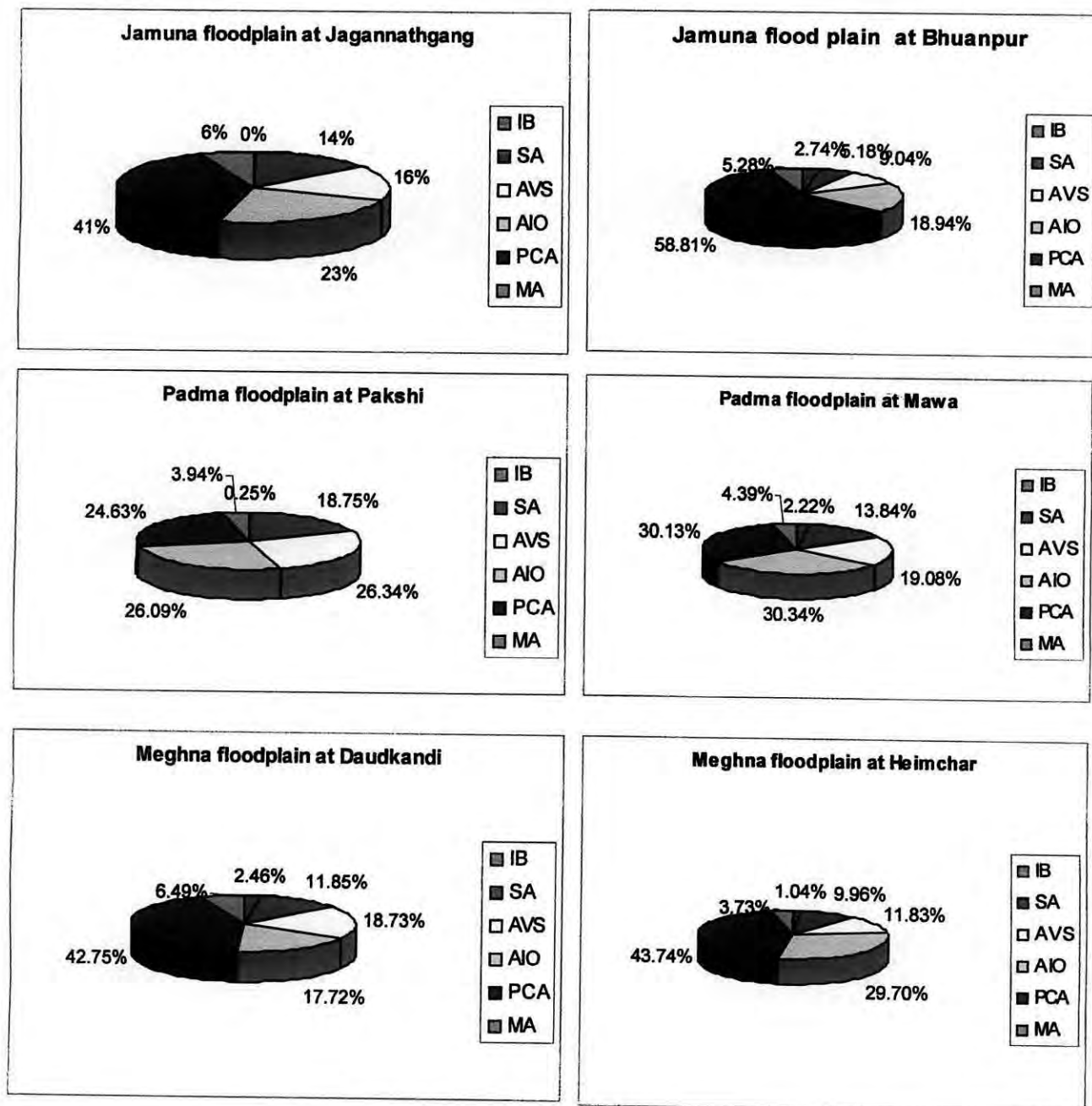


Fig. 5.2: Different forms of As present in the floodplain sediments expressed as a percentage of total As present in the sediments

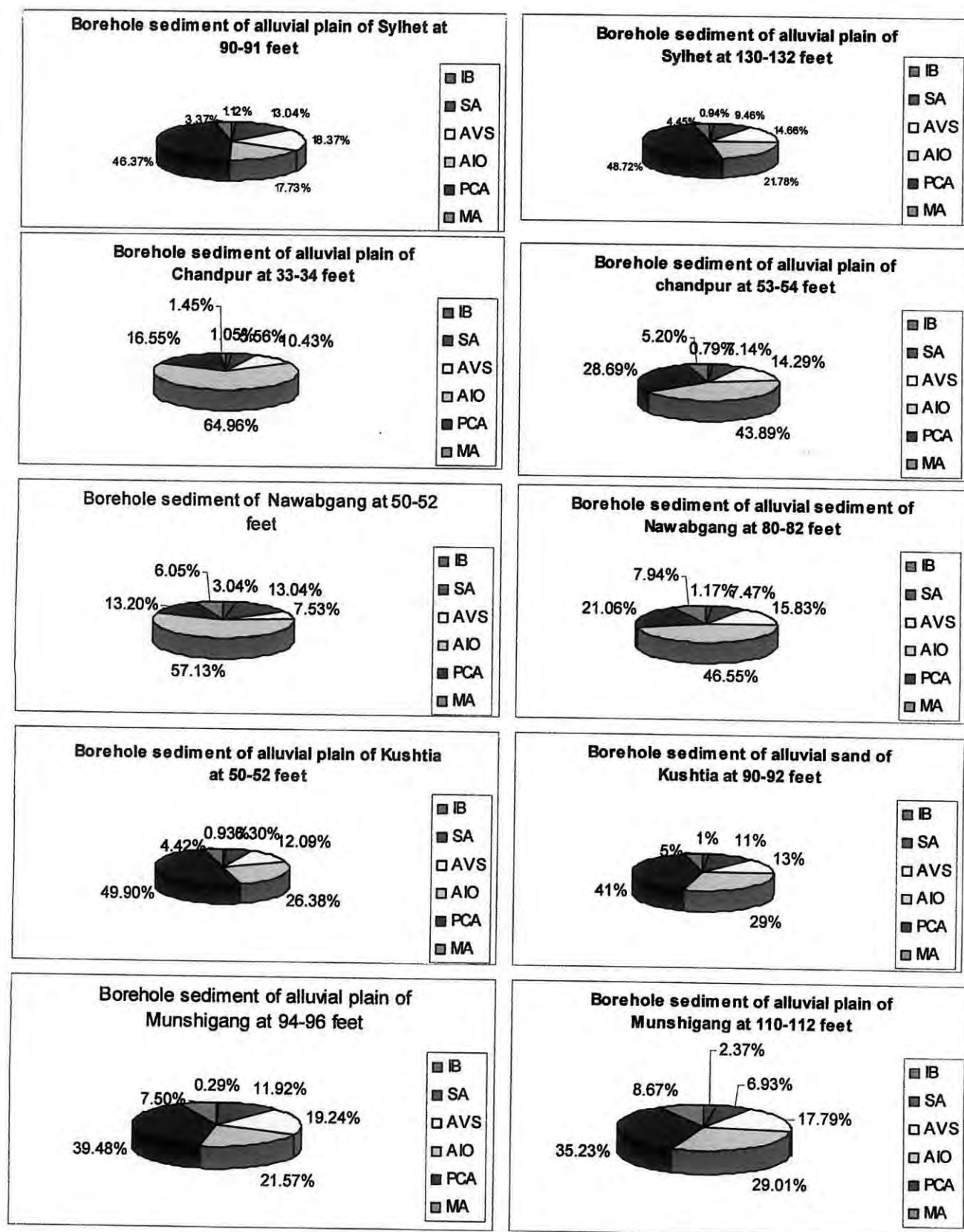


Fig. 5.3: Arsenic present in different forms in the alluvial plain sediments as determined from the sequential extraction experiments

5.4 SUMMARY

Arsenic associated with pyrite and amorphous crystalline sulfides (PCA) and acid volatile sulfides (AVS) are likely to be mobilized under oxidizing condition. This oxidizing condition may be created in the top soil strata due to excessive fluctuation of water level between dry and wet seasons. Consequently cyclical oxidation can release As from sediments into the aqueous phase. Arsenic associated with amorphous iron oxyhydroxides (AIO), ionically bound (IB) and strongly adsorbed (SA) Arsenic are likely to be mobilized under reducing condition. Presence of decomposing organic matters in soils consume available dissolved oxygen in water and creates reducing condition for the dissolution of iron and Arsenic.

This experiments shows that Arsenic present in soils in both strongly and weakly bound forms. The total amount of Arsenic present in AIO, IB and SA forms is in the range of 28 to 48 percent in sediments collected from different locations. The remaining Arsenic in PCA, AVS and MA forms are strongly bound and comparatively higher in proportion as compared to relatively weakly bound forms of Arsenic in sediment. Since Arsenic in soils is very high as compared to pore water, release of a small fraction of Arsenic from solid to liquid phase can cause a significant increase in Arsenic content of pore water.

Chapter 6

RELEASE OF ARSENIC FROM AQUIFER MATERIAL

6.1 INTRODUCTION

Arsenic is a commonly occurring and widely distributed toxic metalloid in natural ecosystems of environment. The major starting point for introduction of Arsenic into the environment is mispickel or arsenopyrite, the most common Arsenic containing mineral. Constituent mineral species in the alluvial deposits being the most probable sources of Arsenic, the environmental conditions of the soil have a greater influence on Arsenic release and mobility than the total concentration in soils. In nature, Arsenic-containing minerals undergo oxidation and releases Arsenic into water. Rapid oxidation of Arsenic-containing minerals is also facilitated when geological materials from a reduced environment are brought to the surface of the earth during mining. Arsenic can also be released into the groundwater in the subsurface environment from the overburden material and from coal too. Arsenic is released into groundwater from solid phase of Arsenic containing minerals deposited in the subsurface through different mechanism activated by microbes under oxidizing or reducing environment.

Arsenic release in groundwater in the reduced environment created by anaerobic condition is a well known hypothesis. Lack of oxygen and low redox condition in tubewell water support anaerobic microbial activity in the aquifer in the arsenic contaminated areas. Reviewing the available hypothesis on Arsenic release mechanism and water quality results, batch experiment was designed to observe the release of Arsenic in anaerobic condition. In this experiment microbial activity was stimulated by adding molasses and glucose in a soil-water system in a closed environment avoiding contact with air (oxygen). A similar sample preserved in aerobic condition was used a control.

6.2 MATERIALS AND METHODS

Batch experiment was conducted to observe Arsenic release mechanism from sediment in anaerobic condition created by microbial oxidation of organic matter (i.e., glucose or molasses). Also experiment in the blank medium with distilled water was done under aerobic condition.

Anaerobic Batch Experiment

Sediment and nutrient such as molasses and glucose (food for bacteria) mixed with batch fluid were put in one-liter capacity plastic containers. The plastic container used as reactors had a round thick plastic cover easily fitted in the mouth of the container. Two smaller holes fitted with plastic tubes were made on the thick plastic cover of the container. One tube is used to supply nitrogen gas from gas cylinder and another to expel out oxygen (air) from the container in order to attain anaerobic condition inside the container. Also a medium size hole was made on thick plastic cover through which an ORP meter and a pH meter can be inserted inside the container to determine eH and pH of mixed batch solution. Three openings of the plastic container remained tightly closed in such an away that no air can enter into the container. The round plastic cover is tightly fitted with the container making the attachment completely airtight.

A total of 50 gm sediment was taken in each plastic container for batch experiment from previously collected sediment from river bottom, river floodplain and alluvial sediment from boreholes in arsenic affected areas. The sediment samples collected from different parts of Bangladesh were preserved in plastic tubes in air-tight condition. A batch fluid was prepared in the laboratory with the addition of small quantity of anaerobic sewage in arsenic free distilled water. The sediment is soaked in the container by adding 750 ml batch fluid and about 5-7 gm of molasses/10 gm of glucose from stock solution. The molasses/glucose is the food for anaerobic bacteria present in batch water. Oxidation-reduction potential (eH) and pH of fluid in the batch reactor was measured at the time of collection of fluid sample for Arsenic analysis. A 10 ml sample was collected from the reactor by plastic syringe for arsenic analysis. eH and pH, and Arsenic content of the sample from batch reactor were determined at the end of 4th, 8th, 12th, 15th, 18th, 22nd, 26th

and 30th day. The content of the batch reactor was thoroughly mixed one day before the date of sampling for arsenic.

6.3 RESULTS AND DISCUSSION

Batch experiment was performed with the floodplain sediment of Jamuna, Padma and Meghna and borehole sediment Sylhet, Chandpur, Munshigang, Nawabganj and Kushtia in molasses and glucose medium under anaerobic condition in batch fluid and also under aerobic condition in blank medium with distilled water.

Experiment with batch fluid under anaerobic condition was performed and the results for Arsenic release and corresponding eH and pH both in molasses and glucose media under anaerobic condition was observed and recorded at the end of days 4, 8, 12, 15, 19, 22, 26 & 30. Also experiment in the blank medium with distilled water was done under aerobic condition and the results was noted at the end of days 4, 8, 12, 15, 19, 22, 26 and 30.

Reduction of Arsenic in anoxic environments is thought to occur primarily by dissimilatory reduction where microbial bacteria utilize As(V) as a terminal electron acceptor for anaerobic respiration. To date, dissimilatory arsenate reduction has been characterized in at least seven bacteria such as *Sulfurospirillum barnesii*, *Sulfurospirillum arsenophilum*, *Bacillus arsenicoselenatis*, *Bacillus selenitireducens*, *Desulfotomaculum auripigmentum*, *Chrysiogenes arsenatis* and *Desulfomicrobium* which represent genera scattered throughout the bacterial domain. In addition, dissimilatory reduction of Arsenic has been observed in two hyperthermophylic archaea such as *Pyrobaculum arsenaticum* and *Pyrobaculum aerophilum*. Specific biotic arsenate reduction by arsenate-reducer a facultative anaerobe *Bacterium arsenireducens* (Green, 1917), arsenate respiring bacteria microaerophile *Sulfurospirillum barnesii* (Laverman et al., 1995; Stolz et al., 1999), *Sulfurospirillum arsenophilum* and *Sulfurospirillum barnesii* belonging to the ϵ -subdivision of the Proteobacteria, *Desulfomicrobium* and *Desulfovibrio* of δ -subdivision of the Proteobacteria (Macy et al., 2000), gram-positive spore forming arsenate reducer and sulfate reducer *Desulfotomaculum auripigmentum* (Newman et al., 1997), spore

forming bacteria *Desulfutobacterium frappieri* and *Desulfutobacterium hafniense* (Niggemyer et al., 2001), *Chrysiogenes arsenatis* (Macy et al., 1996), Microbe *Thermus* (Gihring and Banfield, 2001; Kieft et al., 1999), a hyperthermophilic archaeon *Pyrobaculum arsenaticum*, (Huber et al., 2000). *Pyrobaculum aerophilum* (Volkl et al., 1993) have been documented.

Table 6.1: Summary for anaerobic Arsenic release experiment

Location	Total As in mg/kg	Highest Arsenic Release and corresponding eH in Molasses Medium				Highest Arsenic Release and corresponding eH in Glucose medium				Comment
		As in mg/kg	eH in mV	Day	% of Total As	As in mg/kg	eH in mV	Day	% of Total As	
Jagannathganj (Jamuna)	3.54	0.3	-222	30	8.47	0.156	-82	30	4.4	1.92
Bhuanpur (Jamuna)	3.72	0.3	-220	30	8.59	0.175	-108	30	4.7	1.83
Pakshi (Padma)	5.81	0.29	-268	30	4.96	0.02	-185	30	0.34	14.4
Mawaghat (Padma)	4.64	0.39	-304	30	8.41	0.15	-127	30	3.23	2.6
Daudkandi (Meghna)	3.87	0.10	-181	30	2.69	0.071	-107	30	1.83	1.47
Heimchar(Meghna)	4.27	0.13	-141	30	3.14	0.11	-85	30	2.58	1.22
Sylhet (90-91')	3.53	0.18	-143	30	5.05	0.09	-129	30	2.55	1.98
Sylhet (130-131')	1.82	0.17	-160	30	9.12	0.09	-61	30	4.94	1.84
Chandpur (33-34')	3.9	0.18	-182	30	4.62	0.12	-130	26	3.08	1.5
Chandpur (53-54')	2.8	0.20	-112	30	6.96	0.122	-48	26	4.36	1.58
Nawabganj (50-51')	3.08	0.4	-330	30	12.99	0.02	-154	30	0.65	20
Nawabganj (80-82')	2.02	0.35	-394	30	17.48	0.08	-171	30	3.97	4.41
Kushtia (50-52')	3.16	0.32	-389	30	10.13	0.12	-87	22	3.78	2.67
Kushtia (90-92')	3.55	0.15	-112	30	4.17	0.068	-64	26	1.92	2.18
Munshiganj (94-96')	2.155	0.09	-122	30	4.32	0.054	-43	22	2.5	1.72
Munshiganj (110-112')	2.79	0.16	-151	30	5.56	0.07	-78	22	2.51	2.21

During 30 day of the anaerobic test, 2.7% to 17.5% of the total arsenic were released in molasses medium for floodplain sediment (from 2.7 to 8.6%) and borehole sediment (from 4.2 to 17.5%). In the glucose medium, about 0.3 to 4.9% of the total arsenic were released from sediment for floodplain sediment (from 0.3 to 4.7%) and borehole sediment (from 0.65 to 4.94%). Arsenic release in molasses medium was 1.22 to 20 times higher than that in glucose medium. Major findings of anaerobic tests are presented in Table 6.1.

6.3.1 Role of pH and eH

6.3.1.1 Variation of pH

Figure 6.1 shows the remarkable variations of pH by the microbial activity under anaerobic condition with respect to time. Initial pH of 7.5 before sampling lowers as soon as the microbial action starts under anaerobic condition. Lowering of pH values continued up to a value of 3.67 in the bore hole sediment of Munshiganj at a depth of 94-96 feet and 4.37 in the sediment of floodplain of the Padma river at Pakshi (Ishwardi) by 4th day in molasses medium and to 3.54 in the sediment of floodplain of the Meghna at Heimchar and 5 in the sediment of floodplain of the Padma at Pakshi (Ishwardi) by 12th or 8th or 12th day in glucose medium. Besides, lowest pH attained a value in the range of 4-5 in case of the floodplain sediment of the Padma River and the bore hole sediment of Nawabganj. Then pH increased gradually with the increase in microbial activity under anaerobic condition from 8th day in molasses medium and from 12th to 15th day in glucose medium but remained below 7 except in the case of the floodplain sediment of the Padma at Pakshi and the bore hole sediment of Nawabganj. In the floodplain sediment of the Padma highest pH value of 7.91 and 7.6 in molasses medium and 7.48 in glucose medium was attained in 30th day. In the borehole sediment of Nawabganj the highest pH value of 7.64 and 7.87 in molasses medium and of 7.28 in glucose medium was attained in 30th day. Thus it is evident that rate of change of pH is much higher in molasses medium than that of glucose medium both in case of increase and decrease of pH by microbial action under anaerobic condition. In the control batch of blank medium under aerobic condition generally pH increases and remains above 7 except the cases of the sediment of floodplain of the Meghna at Daudkandi and the borehole sediment of the Surma basin at Sylhet and Nawabganj at a depth of 50-52 feet where pH decreases.

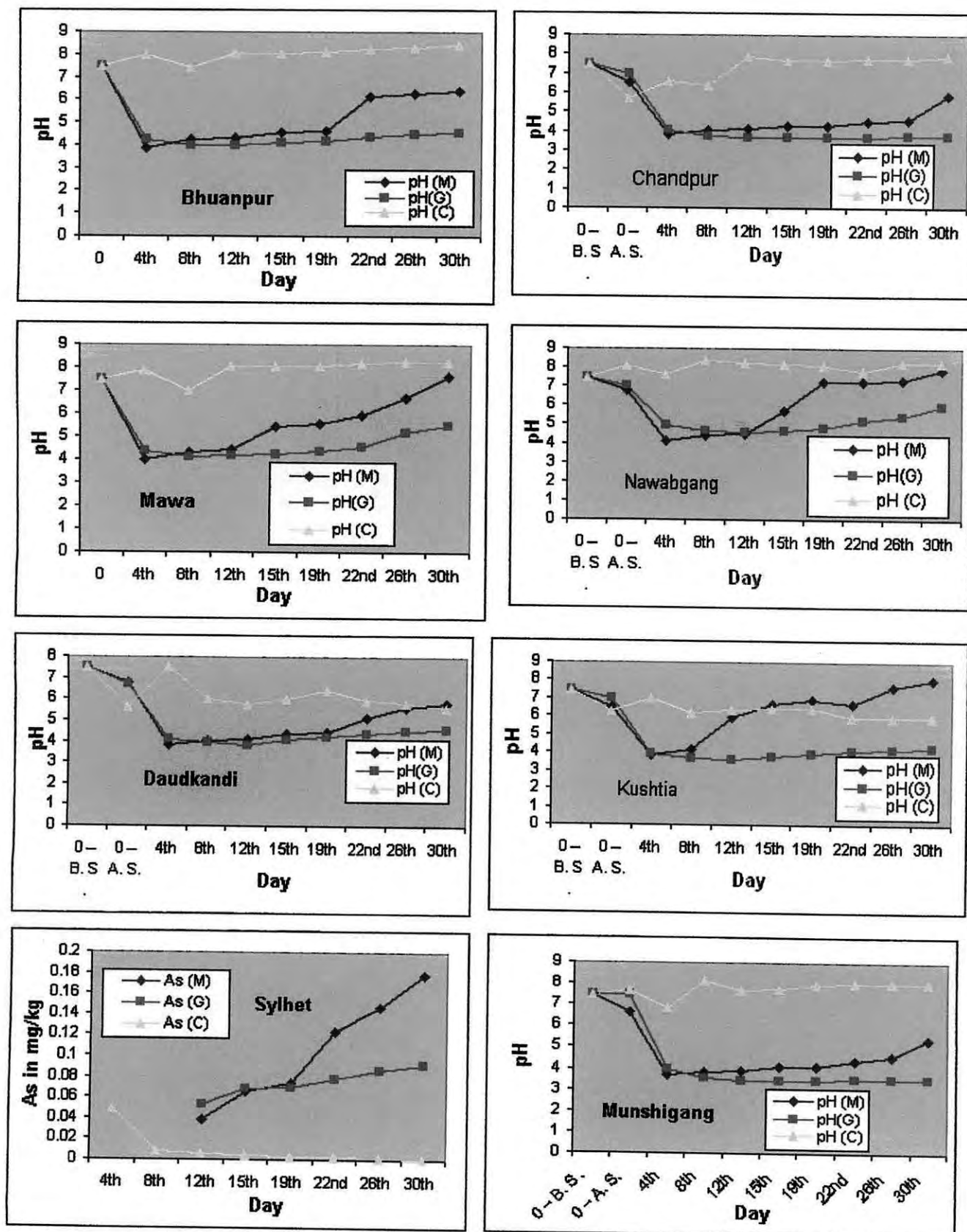


Fig 6.1 : Variation of pH with time in the sediments of different locations

6.3.1.2 Variation of eH

The eH values at first increased to some extent in sediment samples upto 4th to 8th day in both molasses and glucose media as shown Fig 6.2 . Then eH values went down with the increase in anaerobic condition; eH value lowered to -112 and -394 by 30th day in the borehole sediment of Chandpur at a depth 53-54 feet and Nawbganj at a depth 80-82 feet respectively in case of molasses medium while to -43 by 22nd day and -185 by 30th day in the borehole sediment of Munshiganj at a depth of 94-96 feet and in the sediment of floodplain of the Padma at Pakshi in case of glucose medium. In case of both of the molasses and glucose medium, Arsenic was released only when eH values were lowered to less than zero showing that Arsenic was dissolved into water when reducing condition was achieved; that means reducing condition is a requirement for release of Arsenic. In the experiment conducted under aerobic condition in blank medium with distilled water without nutrients, Arsenic release was not observed or stopped with time where eH values were greater than zero. In blank medium highest values of eH was raised to 463 by 22nd day in the borehole sediment of Surma basin at Sylhet at a depth of 90-91 feet and to 285 by 30th day in the borehole sediment of Nawabganj at a depth of 80-82 feet.

6.3.1.3 Correlation between pH and eH

The correlation between eH and pH is presented side by side for both of the molasses and glucose medium in Fig. 6.3 to Fig. 6.10. It is observed that:

- pH increases with decrease of eH .
- A correlation coefficient > 0.7 (from 0.7023 to 0.9355) in the molasses medium shows very good correlation between pH and eH.
- A correlation coefficient < 0.3 (in the glucose medium except 0.4345 for the deposited sediment of Padma river) shows poor correlation.

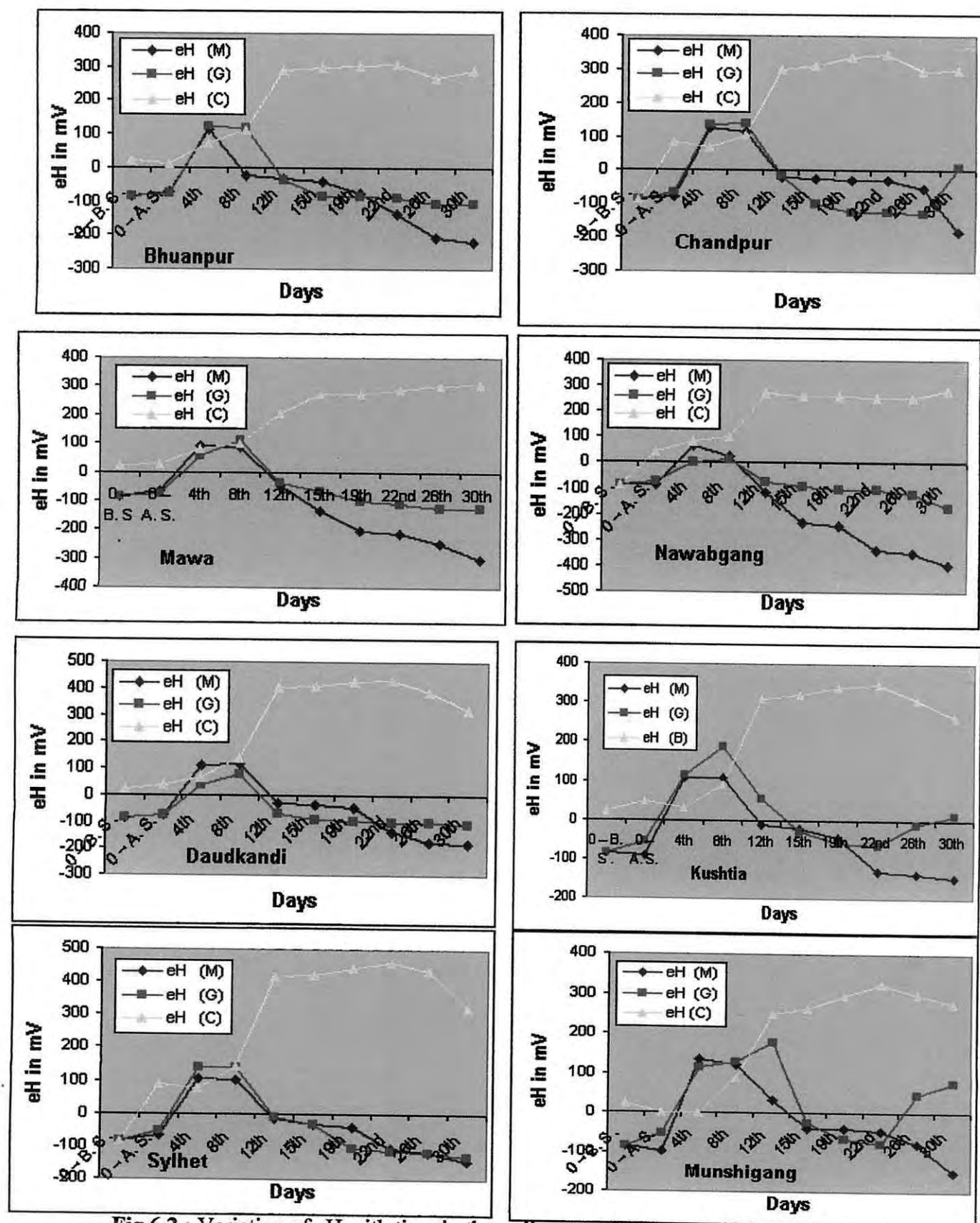


Fig 6.2 : Variation of eH with time in the sediments of different locations

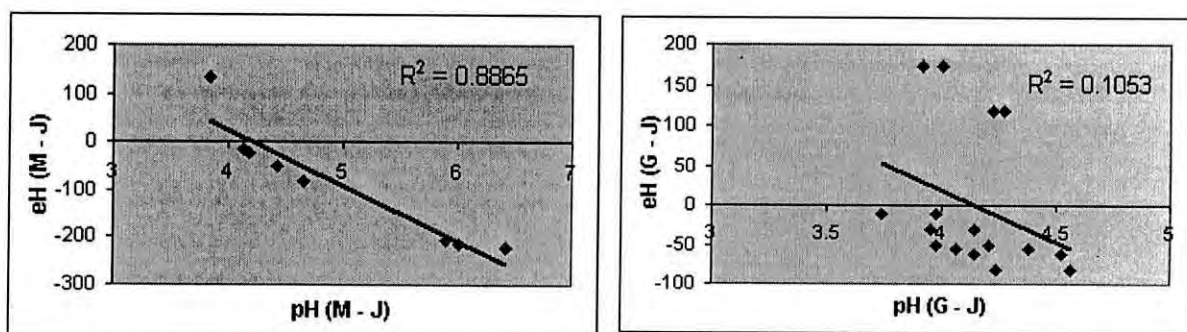


Fig. 6.3: eH vs pH during arsenic release for the sediment of floodplain of river Jamuna

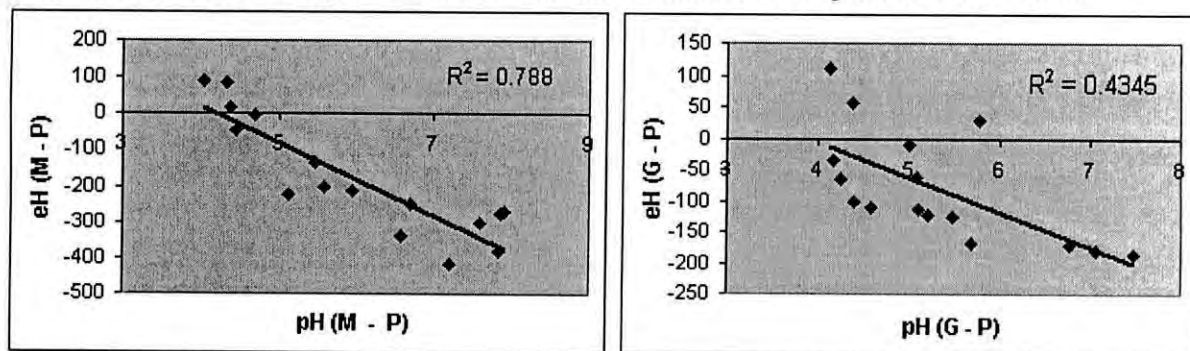


Fig. 6.4: eH vs pH during arsenic release for the sediment of floodplain of river Padma

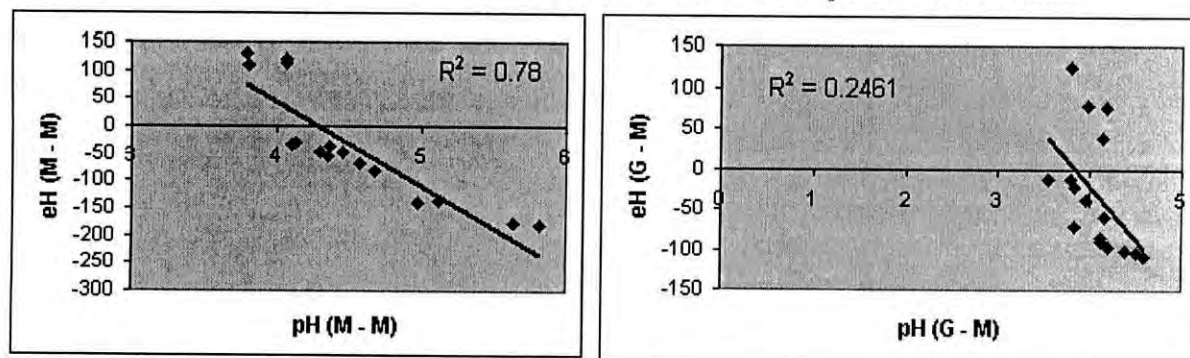


Fig. 6.5: eH vs pH during arsenic release for the sediment of floodplain of river Meghna

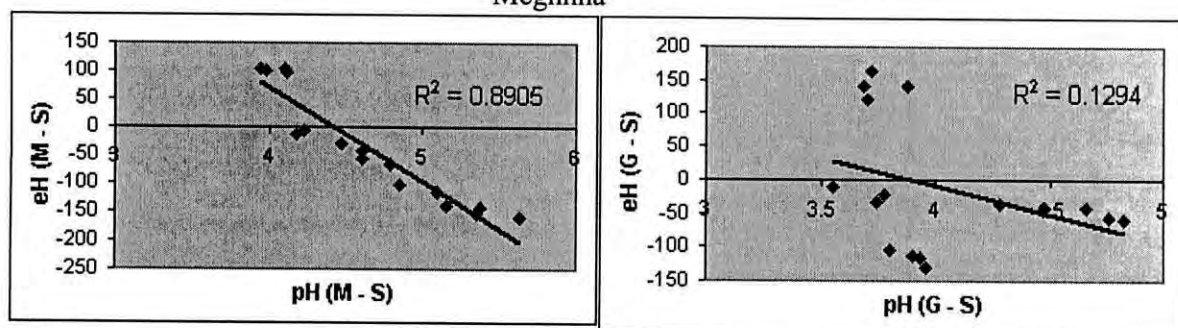


Fig. 6.6: eH vs pH during arsenic release for the borehole sediment of alluvial plain of Sylhet

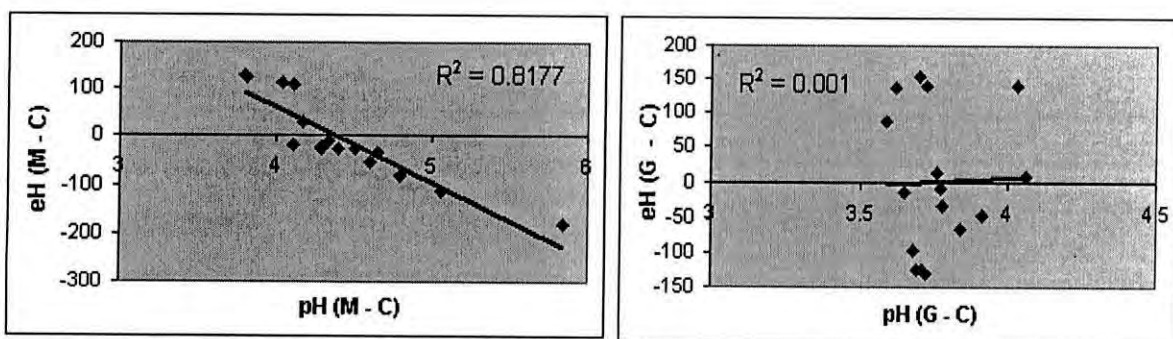


Fig. 6.7: eH vs pH during arsenic release for borehole sediment of alluvial plain of Chandpur

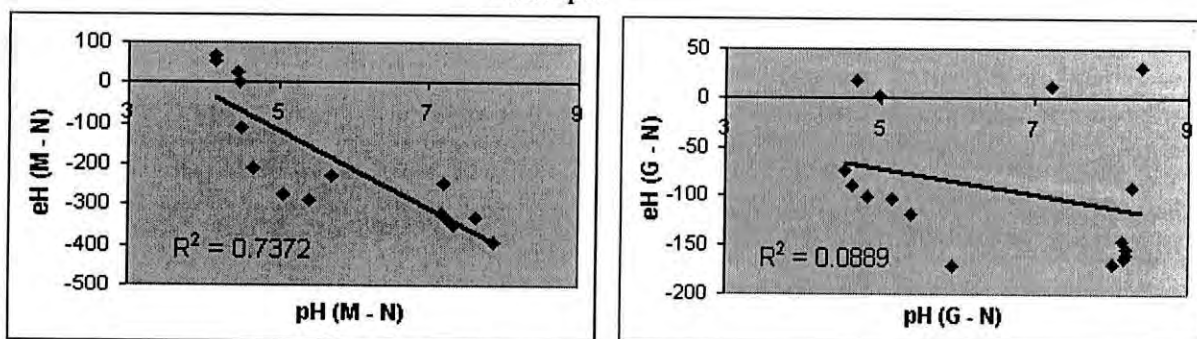


Fig. 6.8: eH vs pH during arsenic release for borehole sediment of alluvial plain of Nawabganj

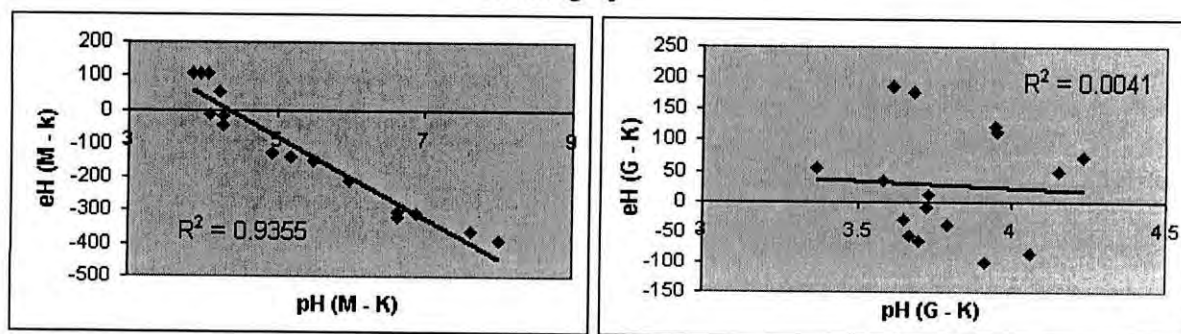


Fig. 6.9: eH vs pH during arsenic release for borehole sediment of alluvial plain of Kushtia

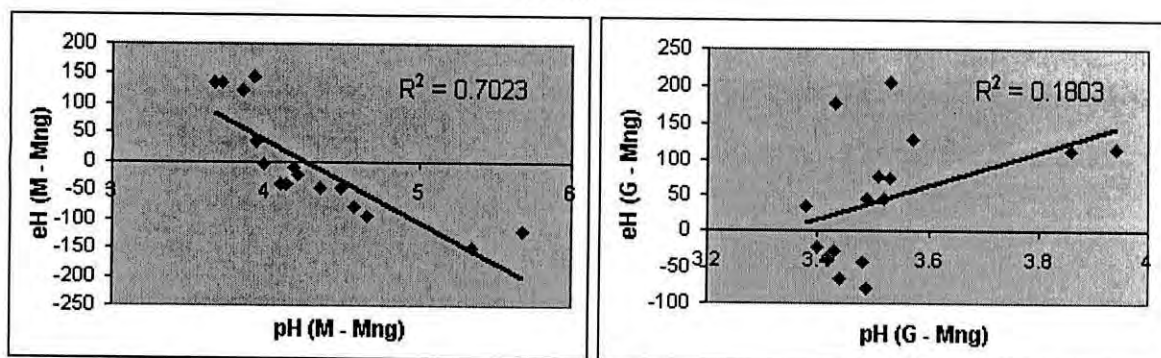


Fig. 6.10: eH vs pH during arsenic release for borehole sediment of alluvial plain of Munshiganj

6.3.2 Observation of Arsenic Release

Table 6.1 showing summary of Arsenic release in anaerobic condition reveals that total amount of Arsenic release in molasses medium varying from 0.093 mg/kg in the borehole sediment of Munshiganj at a depth of 94-96 feet to 0.4 mg/kg in the borehole sediment of Nawabganj at a depth of 50-52 feet was always higher than that in glucose medium varying from 0.02 mg/kg in borehole sediment of Nawabganj at a depth of 50-52 feet to 0.02 mg/kg in floodplain sediment of the Padma at Ishwardi. It was also observed that about 2.7% (in Meghna floodplain sediment at Daudkandi) to 17.5% (in the borehole sediment of Nawabganj at a depth of 80-82 feet) of total Arsenic were released (as the highest Arsenic release) at the end of 30th day in molasses medium, whereas about 0.34% (in Padma floodplain sediment at Pakshi) to 4.9% (in the borehole sediment of Sylhet at a depth of 130-131 feet) of total Arsenic were released (as the highest Arsenic release) at the end of 30th day in glucose medium in 10 out of 16 cases.

The ratio of total Arsenic release in molasses medium to glucose medium varied from 1.22 to 4.41 with the exception in Padma floodplain sediment at Ishwardi and the borehole sediment of Nawabganj at a depth of 50-51 feet where the ratios are exceptionally high being 14.4 and 20. Arsenic release in molasses medium is always higher than in glucose medium.

In blank medium of control batch measured Arsenic content remained constant and sometimes decreased with the days. It means no Arsenic is released from solid phase to water medium, rather the initial dissolved Arsenic present in the liquid phase is oxidized and subsequently adsorbed in bottom sediment of the control batch. A few representative cases of variation of Arsenic releases with respect to time under different situation are depicted in Fig 6.11 (including Fig. A-18 of appendix). Also initial arsenic concentration in the sediment of each cases are marked in the diagram through a horizontal line.

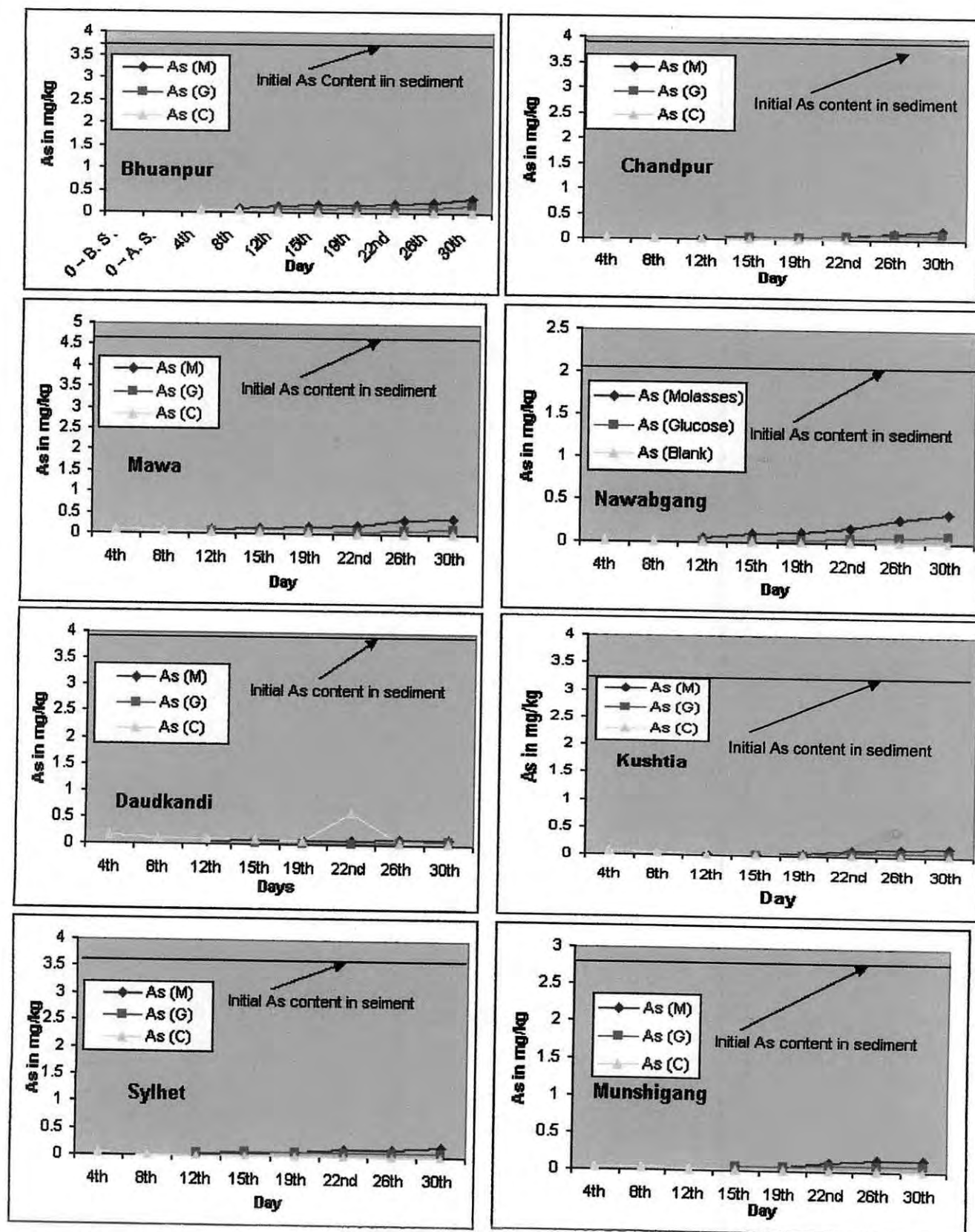


Fig. 6.11: Arsenic release w.r.t. time in the sediments of different locations.

6.3.2.1 Arsenic release by molasses

The rate of release of arsenic increases with the decreasing rate of eH in molasses medium. Arsenic release rate in molasses medium was faster than glucose medium. The correlation coefficient between As and eH was found > 0.5 in molasses medium except in case of the deposited sediment from the floodplain of Padma. Trend of arsenic release with respect to time in molasses medium is shown in Fig 6.12 and 6.13.

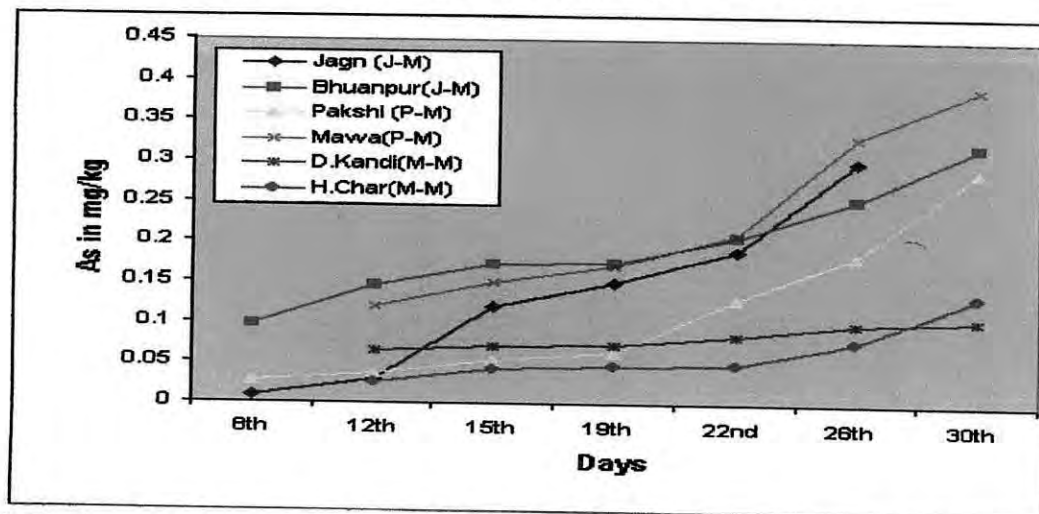


Fig 6.12: Arsenic release in molasses medium w.r.t. time for the deposited sediment of floodplain of Jamuna, Padma and Meghna

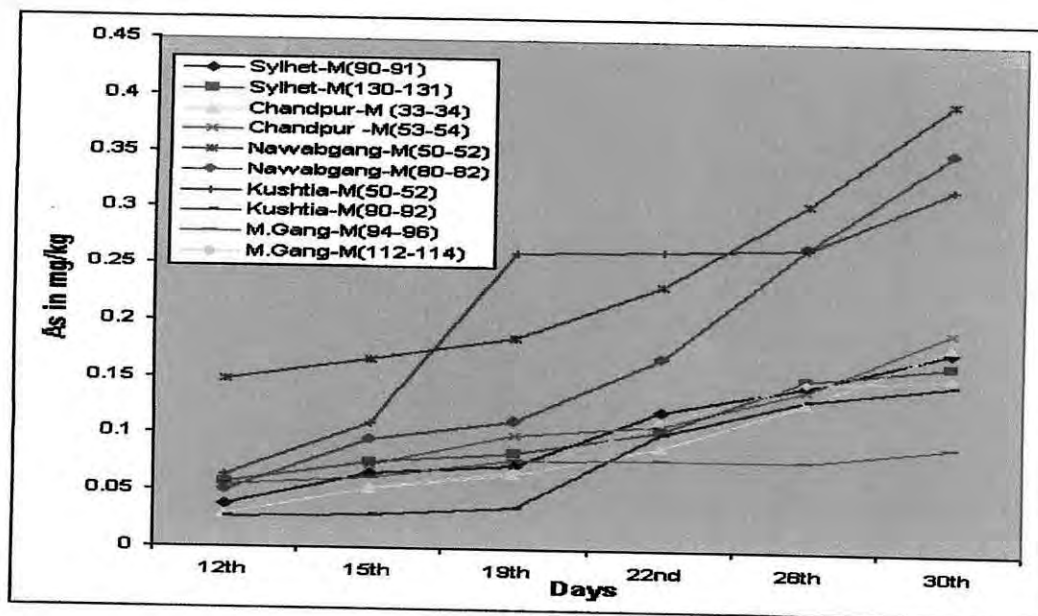


Fig 6.13: Arsenic release in molasses medium w.r.t. time for the borehole sediment of alluvial plain of Sylhet, Chandpur, Kushtia, Nawabganj and Munshiganj

6.3.2.2 Arsenic release by glucose

In glucose medium, arsenic release from sediment followed the same trend of release with time but at a slower rate as compared to molasses. The trend of arsenic release with respect to time in glucose medium is presented in Fig 6.14 and 6.15.

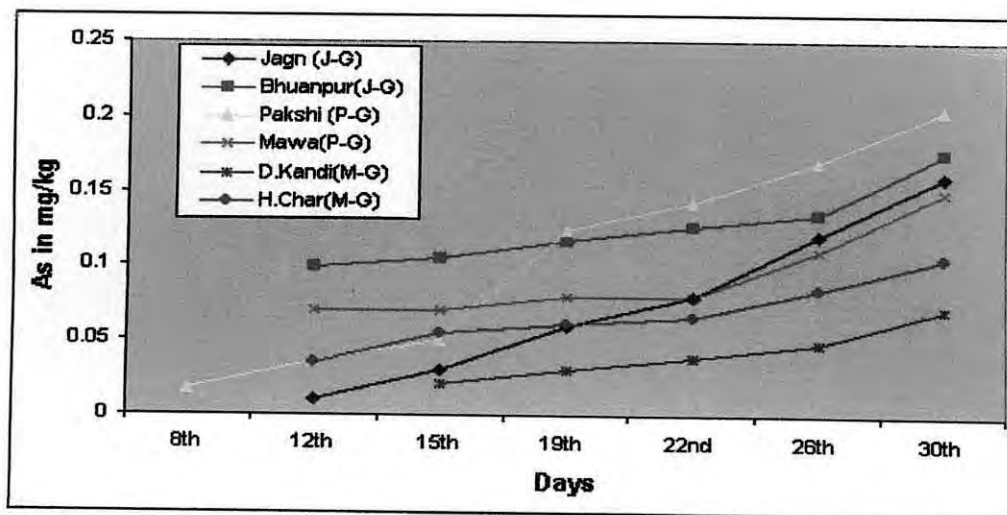


Fig 6.14: Arsenic release in glucose medium w.r.t. time for the deposited sediment of floodplain of Jamuna, Padma and Meghna

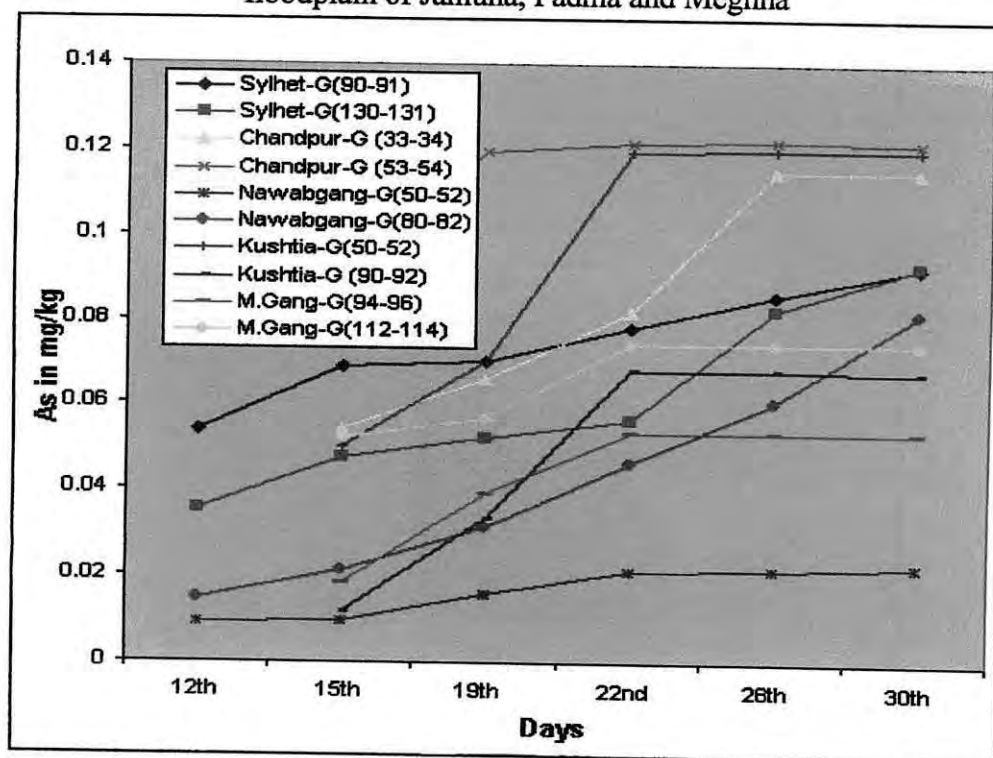


Fig 6.15: Arsenic release in glucose medium w.r.t. time for the borehole sediment of alluvial plain of Sylhet, Chandpur, Kushtia, Nawabganj and Munshiganj

6.3.3 Relationship between Arsenic and eH

It was observed that Arsenic was released only when eH values is lowered to < 0 showing that arsenic was dissolved into water when reducing condition was achieved; that means reducing condition is a requirement for the release of arsenic. As release is inversely proportional with eH in anaerobic medium of molasses and glucose; Arsenic release rate in molasses medium (in three cases out of 16 cases) is faster than glucose medium (correlation coefficient varying up to 0.8606 in the borehole sediment of Sylhet) than glucose medium (correlation confident varying up to 0.6878 in the borehole sediment of Kushtia) as shown in Fig. 6.16 to Fig. 6.24. The correlation between eH and Arsenic release is relatively good in case of molasses medium as compared to glucose medium. In glucose medium, Arsenic release was not significant or delayed in the initial stage of incubation. Within the limits of eH changes studied in batch experiments, Arsenic release varied with reducing state; high reducing state ensured more Arsenic release that is, higher the negative value of eH, higher the amount of Arsenic released from the sediment specially in the case of molasses medium. In molasses medium, amount of Arsenic release reached to value higher than 0.3 mg/kg at the end of 30th day under anaerobic condition in a few cases; probably Arsenic release would be continued if the batch experiment were continued. In the control batch of blank medium, eH values were always greater than zero i.e., no reducing state was observed; also measured Arsenic concentration was decreasing with time; that means no new Arsenic release was observed in the control batch of blank medium under aerobic condition in the presence of oxygen, rather Arsenic appeared to have been adsorbed on sediment. Correlation between arsenic release and eH in both of the molasses and glucose medium is explained in Fig 6.16 to 6.24.

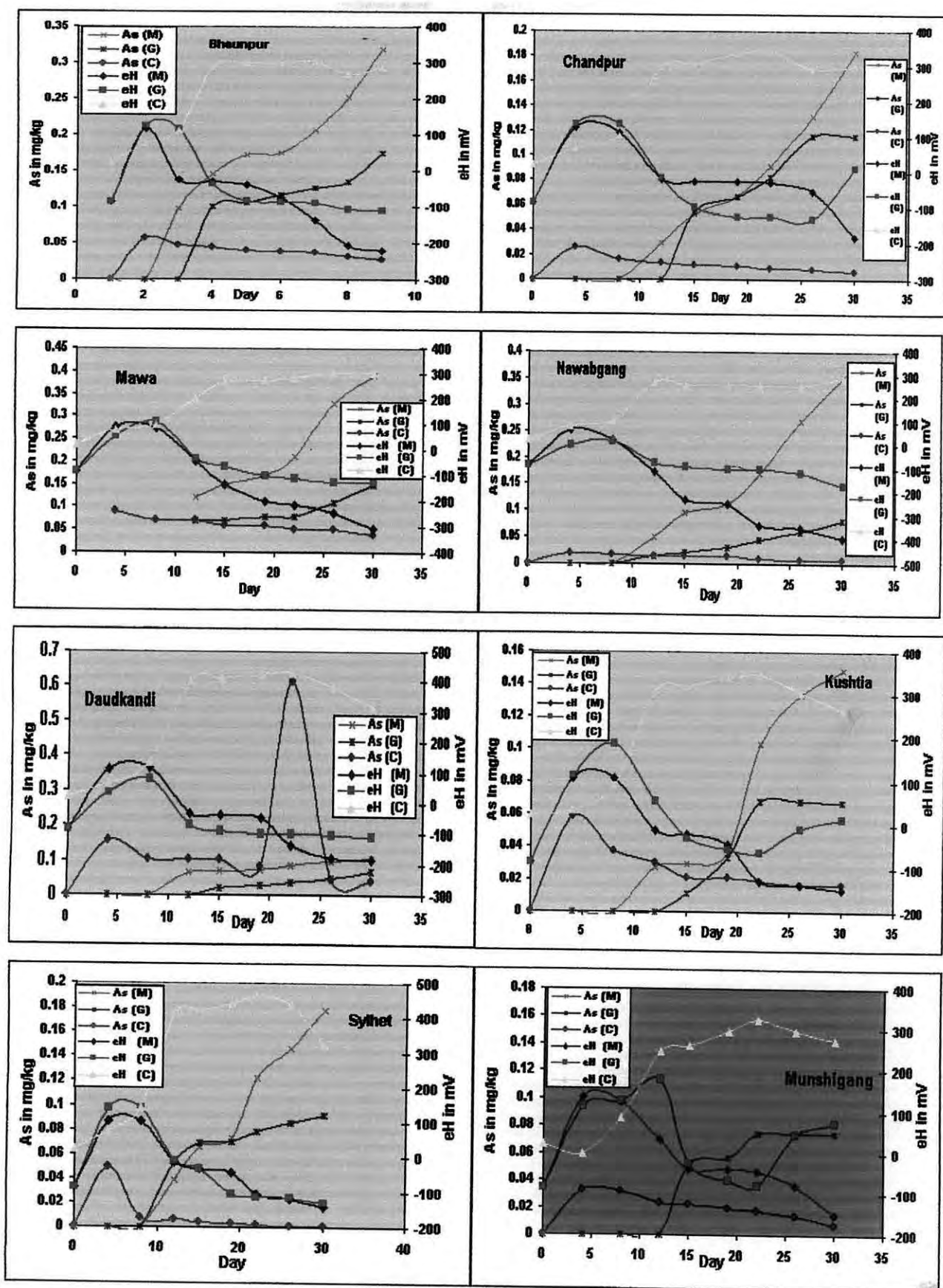


Fig 6.16 : Arsenic release and eH with time in the sediments of different locations.

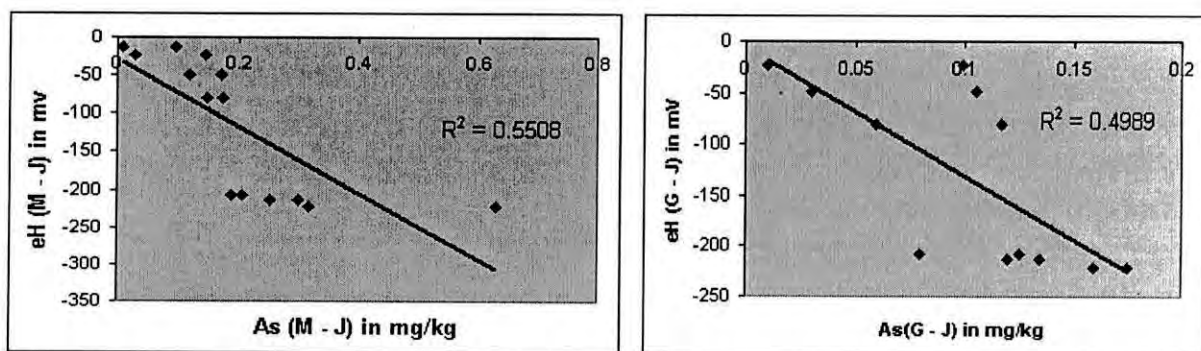


Fig. 6.17: Arsenic release vs eH in the deposited sediment of floodplain of Jamuna

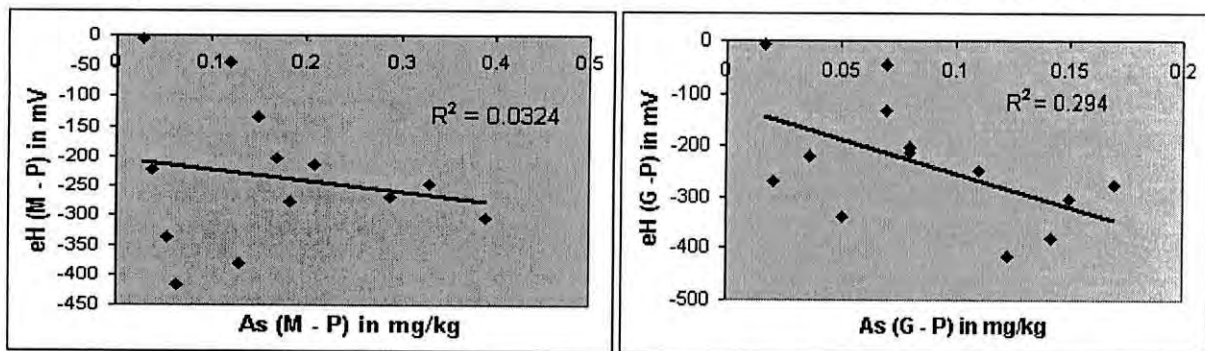


Fig. 6.18: Arsenic release vs eH in the deposited sediment of floodplain of Padma

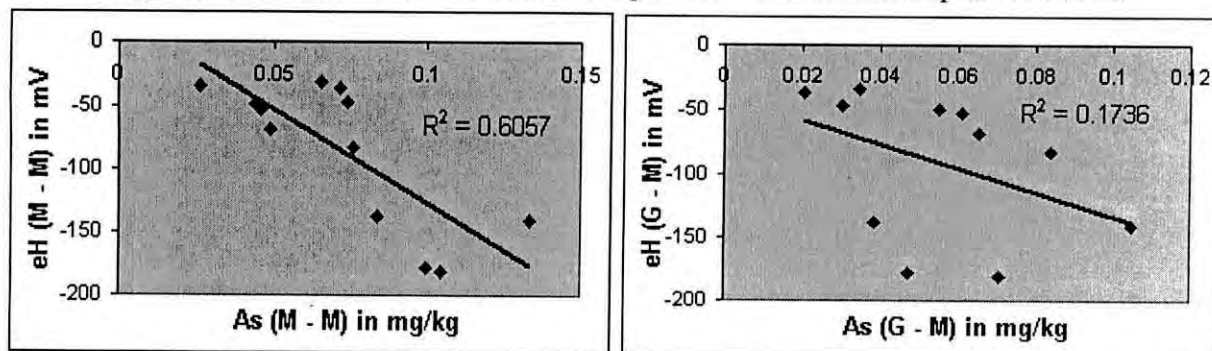


Fig. 6.19: Arsenic release vs eH in the deposited sediment of floodplain of Meghna

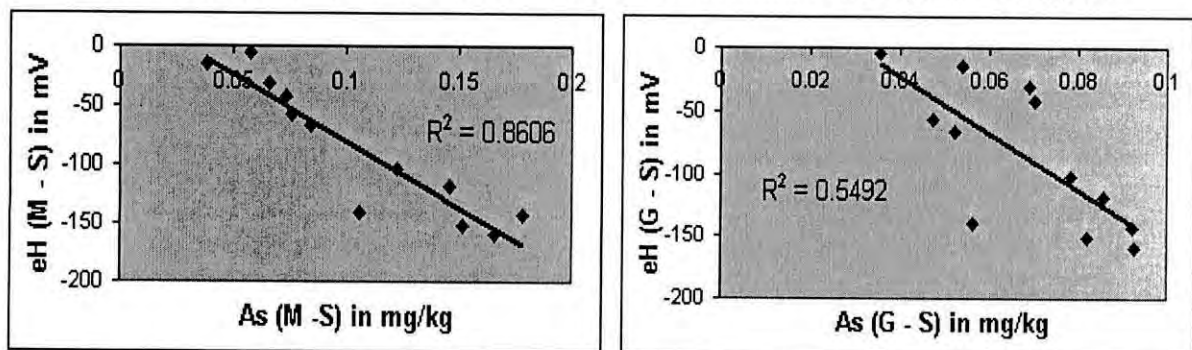


Fig. 6.20: Arsenic release vs eH in the borehole sediment of alluvial plain of Sylhet

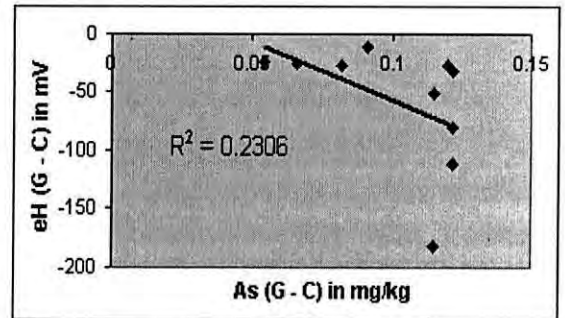
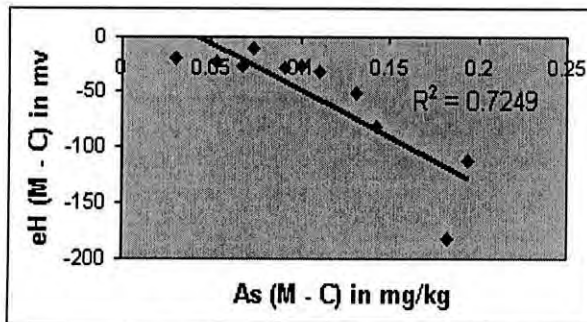


Fig. 6.21: Arsenic release vs eH in borehole sediment of alluvial plain of Chandpur

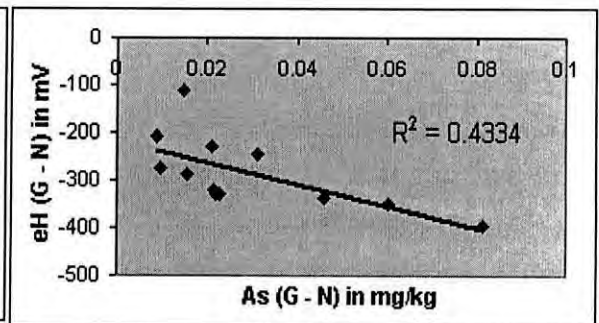
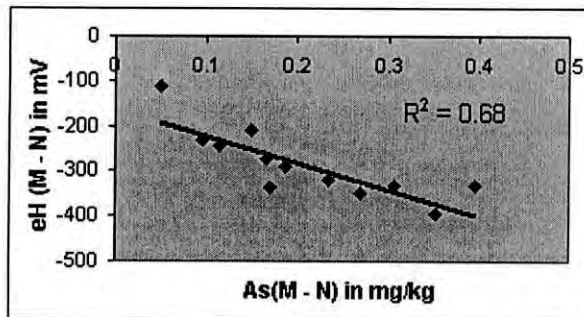


Fig. 6.22: Arsenic release vs eH in the borehole sediment of alluvial plain of Nawabganj

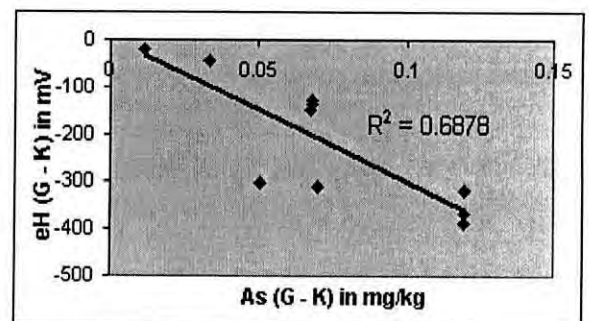
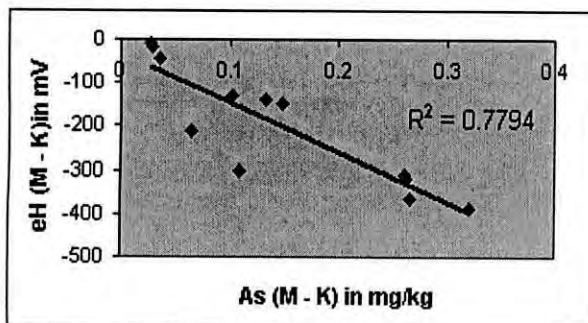


Fig. 6.23: Arsenic release vs eH in borehole sediment of alluvial plain of Kushtia

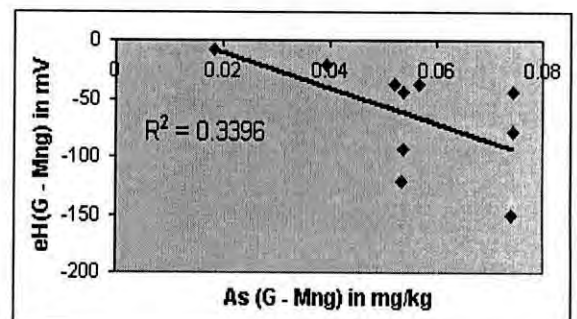
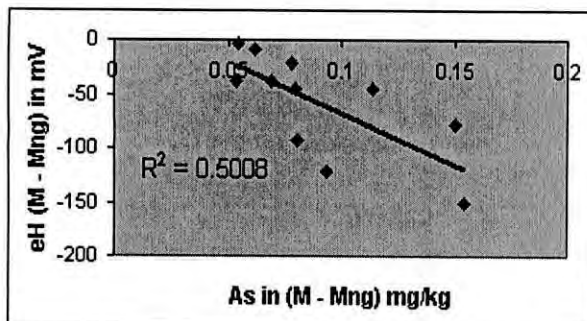


Fig. 6.24: Arsenic release vs eH in the borehole sediment of alluvial plain of Munshiganj

6.3.4 Relationship between Arsenic Release and the Arsenic Present in Different Reducible Forms in the Sediment

Figure 6.25 to 6.28 (including Fig. A-1 of Appendix) shows the correlation between Arsenic release and Arsenic present in different forms in the floodplain and borehole sediments. Figure 6.25 indicates the positive correlation between Arsenic release under anaerobic condition in molasses medium and total concentration of arsenic available in three relatively easily mobilized forms – AIO (amorphous iron oxide bound), SA (strongly adsorbed) and IB (ionically bound); meaning that higher the Arsenic content in the easily mobilized forms, the higher the Arsenic release. A stronger positive correlation was observed between Arsenic release and the amount of Arsenic present as AIO, which is quickly mobilized as iron solids dissolve under reducing condition. However, relatively poor correlation was observed between Arsenic release and Arsenic present in the sediments as SA and IB forms (see Figs. 6.27 and 6.28). Thus, Arsenic associated with amorphous iron oxyhydroxides appear to be dominant mobilized form of Arsenic.

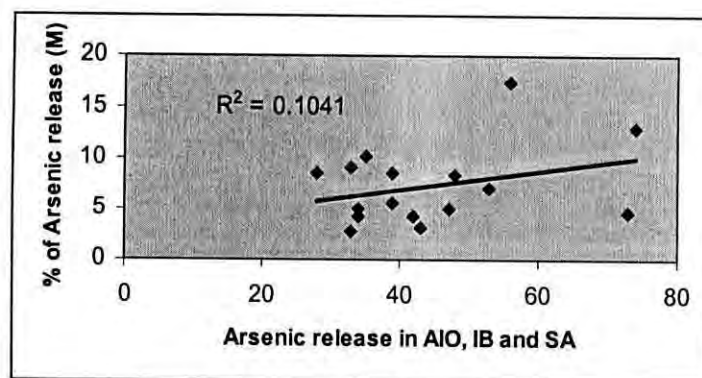


Fig. 6.25: As release in molasses medium versus % of As in AIO, IB and SA of sediment

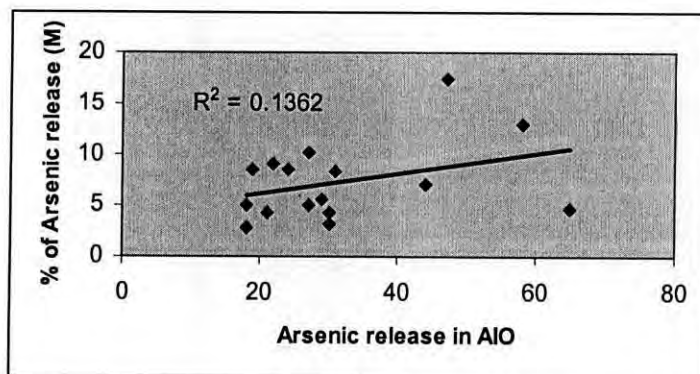


Fig. 6.26: As release in molasses medium versus % of As in AIO of sediment

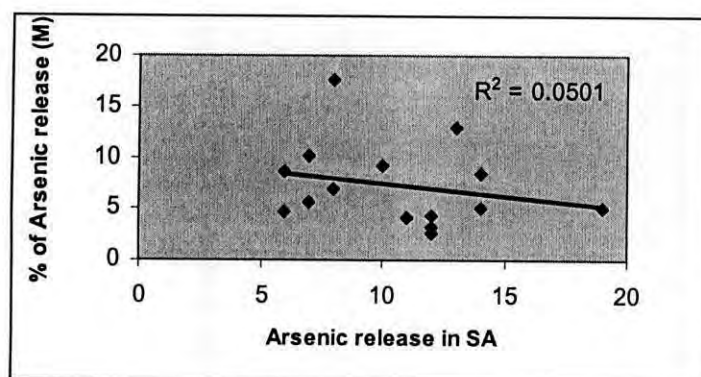


Fig. 6.27: As release in molasses medium versus % of As in SA of sediment

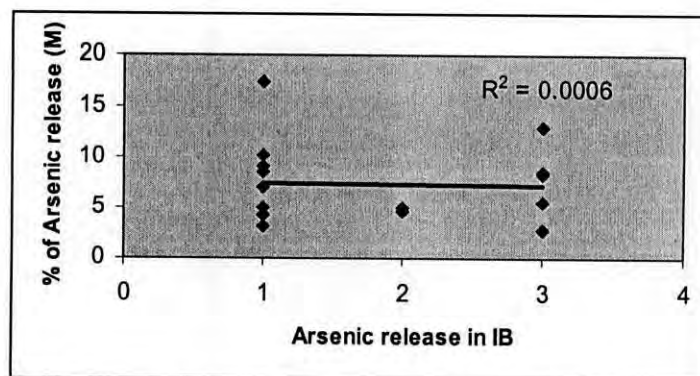


Fig. 6.28: As release in molasses medium versus % of As in IB of sediment

6.4 REVIEW OF PREVIOUS STUDIES

Batch culture experiments using sediments from Bangladesh carried out by Akai et al.(2000) using glucose and polypepton as nutrient for bacterial growth showed no clear relationship between pH and Arsenic but significant relationship between eH and Arsenic was observed showing changes due to microbial activity; eH values went down and Arsenic was released after few days with the addition of nutrients. Arsenic was released only when eH value was less than or about to zero i.e., Arsenic was released and dissolved into water when reductive condition was achieved. Without nutrient, no Arsenic was released; growth of bacteria was very slow when nutrients are not added. Metal reducing bacteria such as Iron bacteria played a vital role in release of Arsenic from solid phase to water under anaerobic condition with the addition of proper nutrients. The presence of Iron reducing bacteria and Iron hydroxide precipitates indicate that they may occur around interface between anoxic and oxic regions with high concentration of Iron. Extremely high $\text{NH}_4\text{-N}$ (which is more reduced than N_2) in groundwater in Bangladesh are attributed to the direct input of nutrient e.g., ammonium containing anthropogenic materials or decomposition of organic matter in reducing groundwater. Waste and excreta may contribute $\text{NH}_4\text{-N}$ contents. Thus, reducing environment in the alluvial aquifer of the subsurface, primarily due to the presence of organic matter such as acetate, organic acids, alkenes like methane, alcoholic compounds like molasses, glucose, polypeptone etc. promotes dissolution of Iron oxyhydroxides and release of Arsenic into groundwater; introduction of organic waste into aquifer may also promote reducing environment. Thus, these laboratory experiments suggested bacterial reductive dissolution of Arsenic showing Arsenic elution from sediments apparently occurred after rapid dropping of eH values, which were caused by enhanced bacterial activity due to added nutrients, glucose and polypepton, which further confirm Arsenic release from sediments in reducing conditions.

Relevant study entitled 'Investigation of Arsenic release from sediment minerals to water phase' conducted by Con et al (2003) suggested that the release of As under anaerobic reduction of organic matters in aquifers is closely related to the MnO_2 content in the alluvial sediment, the reduction of Fe (III) to Fe (II) and the quantity of FeS formed. When MnO_2 level in the sediment is higher, the reduction of Fe (III) to Fe (II) and release

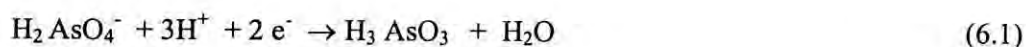
of As are inhibited. Weathering processes are the potential sources for the release of Arsenic from Arsenic-rich minerals to water phases while Arsenic is trapped in alluvial sediment layers, which is again released to water phases during anaerobic disintegration. In the reducing zone at low redox potential, insoluble ferric Iron minerals are partially reduced to soluble ferrous Iron; similarly Manganese is partially reduced to manganous state. Consequently reduction and subsequent dissolution of oxides of Iron, Manganese and other minerals that contribute to sorption and retention of Arsenic can provide an explanation of the mechanism of Arsenic release and contamination of groundwater.

The study conducted by BUET and MIT revealed that As release is triggered by introduction of food for the bacteria in the aquifer. The presence of methane in water indicates that organic matter is being utilized in the aquifer by anaerobic bacteria. The reducing condition that favors Arsenic release is caused by anaerobic condition in the aquifer (Ahmed, 2003).

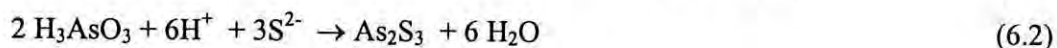
A number of arsenate-reducing bacteria have been isolated from As-rich soils and sediments using anaerobic minimal media where As (V) serves as the sole terminal electron acceptor in the biological oxidation of organic matter. Jones et al., (2000) reported that in an un-enriched (by Arsenic) soil community arsenate reduction commenced largely after microbial growth had ceased. Microorganisms possess a variety of mechanism for reducing arsenate As (V) and oxidizing arsenite As (III) in anoxic environment occurred primarily by dissimilatory reduction where As (V) used as a terminal electron acceptor for anaerobic respiration.

Respiratory reduction of Fe (III) to Fe (II) accounted for Arsenic mobilization while ability to couple reduction of Fe (III) with growth is broadly distributed. Landa et al. (1991) established causality between dissimilatory Iron reduction and trace element mobility demonstrating Arsenic mobilization by Iron-reducing bacteria (Cummings et al., 1999). Both As (V) and As (III) bind hydrous ferrous oxide HFO strongly (Manning et al., 1998), and reducing conditions lead to Arsenic and Iron co-mobilization (Rochette et al., 1998). Respiratory Fe (III)-reducing bacteria could mobilize Fe-bound Arsenic by reduction of Fe (III).

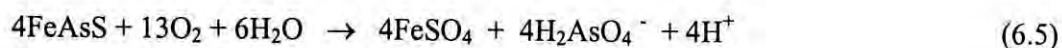
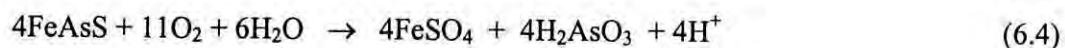
Arsenic can be mobilized from soil by sulfate reducing bacteria where Arsenic will dominate in pore water as As (III). SO_4^{2-} bacteria can promote deposition of As (III) as Sulfide minerals via their production of Sulfides (Goldhaber and Kaplan, 1974). The reduction process converts precipitated and adsorbed As (V) into more soluble Arsenic (III) as follows:



Also Arsenic derived from weathering of Arsenic-rich base metal Sulfides may accumulate in Iron oxyhydroxides because of its affinity for the latter. Further reduction of As (III) in the presence of Sulfides will immobilize Arsenic in soils with the formation of Arsenic Sulfide precipitates as shown in equation (5.2) & (5.3).



Microbial oxidation of Arsenic bearing Sulfide minerals such as orpiment, realgar and arsenopyrite proceeded most typically by means of a microbial or surface catalysis (Ferguson and Gavis, 1992; Cherry et al., 1979), releases Arsenic (III) into the aqueous phase. A few arsenite oxidizing bacteria such as hitherto belonging to heterotrophs appear to engage the microbial activity as a detoxification measure. Oxidation of Arsenic bearing Sulfide minerals (arsenopyrite FeAsS and pyrite FeS_2) as well as realger(AsS) and orpiment (As_2S_3) in aquifer can release Arsenic in ground water (Yan-chu, 1994). In presence of oxygen, arsenopyrite FeAsS oxidizes by oxidizing bacteria as follows:



6.5 SUMMARY

This study revealed that the release of Arsenic from sediment phase to water phase and subsequent solubility of Arsenic in water is usually controlled by redox conditions, pH, biological activity of the metal reducing bacteria and the amount of available organic carbon to stimulate microbial activity of surviving microorganisms to the sediments.

Initially the pH values decreased and then increased after few days of incubation in anaerobic condition. The variation of pH is coherent with the variation of pH in anaerobic decomposition of organic matters. In the initial phase, pH is decreased due to formation of organic acids and soon the pH is increased in the alkali fermentation phase leading to breakdown of organics. Variation of pH was markedly observed in molasses medium compared to glucose, both in cases of increase and decrease of pH by microbial action under anaerobic condition. Arsenic in sediment is relatively stable at neutral pH and exhibits mobility both at higher and lower pH values. At lower pH values, metal oxyhydroxides (e.g., iron hydroxides) solubilize from the sediments with concurrent release of Arsenic species. At high pH levels, the increased hydroxide concentrations cause displacement/desorption of Arsenic species from their binding sites.

Arsenic release is inversely correlated with eH in anaerobic medium produced by both molasses and glucose; Arsenic release rate in molasses medium was faster than glucose medium. The correlation between arsenic and eH is good in most cases specially in cases of arsenic release induced by molasses. Arsenic release constantly increased with the reduction of eH, even at lowest eH observed. Arsenic in aqueous phase can be reduced at very low eH in extremely reduced condition through formation of insoluble sulfides of arsenic. The overall performance of molasses in producing anaerobic condition and arsenic release is better as compared to glucose. It may be due to the fact that glucose is a pure material and a good source of organic carbon only, while molasses contain organic carbon as well as other organic and inorganic nutrient which help balanced growth of microorganism. It was observed that Arsenic release from sediment increased with increasing concentration of Arsenic associated with amorphous iron oxyhydroxides (AIO) in the sediments.

Arsenic was released only when eH values were lowered to less than zero indicating that Arsenic was dissolved into water when reducing condition was achieved; that means reducing condition is a requirement for release of Arsenic. In the laboratory batch experiments, anaerobic condition prevailing in the sub-surface aquifers in arsenic contaminated areas were reproduced to simulate arsenic release. Generally different types of metal reducing bacteria are responsible to create mobilization and release of arsenic, iron and manganese into groundwater from aquifer materials. The reducing condition at low eH value converts Arsenic into a more mobile As (III) form, whereas at high Eh value, As (V) is the major Arsenic species.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 INTRODUCTION

This chapter summarizes the major findings as well as conclusions of the present study. Recommendations for further research works have also been made to find out more about the causes of Arsenic contamination in groundwater of Bangladesh and entire Bengal Delta.

7.2 CNCLUSIONS

7.2.1 Source and Concentration of Arsenic

- a. Arsenic concentrations of water samples from the rivers Jamuna, Padma, and Meghna were found to be very low, and most of the samples showed a concentration below detection level. The highest measured Arsenic concentration in river water was only 2.3 $\mu\text{g/l}$ in a sample collected during post-flood period. The extremely low amount of Arsenic in river water in Bangladesh is consistent with the characteristic quality of surface water.
- b. Suspended solids collected from the rivers Jamuna, Padma, and Meghna during post flood period were found to be contain significant amount of Arsenic varying from 4.07 mg/kg to 5.47 mg/kg. The concentration of arsenic in river sediment is similar to that of soil and does not vary significantly from river to river.
- c. Analysis of Arsenic concentrations in fractions of the riverbed sediments showed that clay fraction contained highest concentrations of Arsenic, followed by silt and sand. The Arsenic content of fine-grained materials like clay is higher because they have

higher surface area as well as adsorption sites per unit volume/weight. On the other hand, coarse-grained materials like sand have relatively smaller surface area as well as adsorption sites per unit volume/weight.

- d. Arsenic concentrations of the riverbed sediments collected during post-flood period have been found to be higher than those collected during the pre-flood period, but were somewhat lower than those of the suspended sediments. This small variation is assumed to be due variation in proportion of sand, silt and clay fractions in different types of sediment.
- e. This study confirms that Arsenic is carried from upstream by the rivers Jamuna, Padma, and Meghna with sediment, not with water. Bangladesh has been formed by the deposition of sediment carried by these three rivers and arsenic is being deposited in the downstream in the floodplains of Bangladesh for thousand of years. The estimated quantity of arsenic carried within Bangladesh by these rivers with 2.4 billion tons of sediment is 11,000 tons per year. However, a major fraction of this arsenic is discharged in the Bay of Bengal with the sediment.
- f. The beels and haors receive higher quantity of Arsenic as the clayey materials are deposited in these stagnant water bodies. Sandspur, Madaripur, Munshiganj, Gopalganj, Lakshmipur, Noakhali, Bagerhat, Shariatpur, Comilla, Faridpur, Satkhira and Meherpur districts have numerous beels and haors with stagnant water bodies, and these districts are also very severely affected by As contamination of groundwater.

7.2.2 Arsenic-Sediment Bonding

- a. Arsenic has been found to be associated with sediment in ionically weak bound, strongly adsorbed, acid volatile sulfide bound, amorphous iron oxyhydroxides, to strongly bound pyrite and amorphous crystalline sulfide and Arsenic mineral forms, as determined by sequential extraction technique. Relatively small amount of Arsenic was found both in weakly ionic bound and strongly Arsenic bound forms. Larger

amount of Arsenic was found in moderately bound forms in sediments. However there are variations in the forms of arsenic associated with sediment type depending on the geological history of the sediment.

- b. Arsenic associated with amorphous iron oxyhydroxides (AIO), ionically bound (IB) and strongly adsorbed (SA) arsenic can be mobilized under reducing condition that prevail in the sediment plains in Bangladesh. The reducing environment converts iron from insoluble ferric form into soluble ferrous form. Similarly, manganese is also dissolved in water in reducing environment in the aquifer. Dissolution of iron and manganese also releases arsenic bound to them into water. The presence of high concentrations of iron, manganese and arsenic in groundwater in Bangladesh is an indication of reductive dissolution.
- c. Cyclical oxidation and reduction could release Arsenic from sediments into the aqueous phase. Because some Arsenic in the sediments associated with pyrite and amorphous crystalline sulfides (PCA) and acid volatile sulfides (AVS) are likely to be mobilized under oxidizing condition which prevail in the sediment plains during the dry season. This hypothesis received minimum attention because of no correlation between arsenic and sulfur in groundwater and arsenic and water level fluctuations in Bangladesh.

7.2.3 Characterization of Groundwater

- a. The groundwater in arsenic affected areas was found to be completely devoid of oxygen and of negative eH value (lower than zero) indicating the prevalence of strong reducing condition in the aquifer. The dissolved oxygen present in water is used for initial oxidation of organic matters present in the soil leaving no oxygen for maintenance of oxic condition in the aquifers. The remaining organic matters stimulate anaerobic condition in the sub-soil environment.
- b. Arsenic was found positively correlated with ammonia, alkalinity and hardness in groundwater. This relationships support the process of Arsenic mobilization with the

microbial breakdown of organic matters in the sub-soil environment. Oxidation of organic matter carbon produces CO₂, DIC (e.g., in the form of HCO₃⁻) and ammonia. Carbon dioxide induces dissolution of calcite resulting in higher Ca²⁺ and hence higher hardness in groundwater.

- c. Very low sulfate concentration found in the groundwater samples is also consistent with a reducing environment, and negates Arsenic mobilization as a result of oxidation of Arsenic bearing minerals.
- d. The phase stability (eH-pH) diagrams shows that all the groundwater samples in the arsenic affected areas lie in the iron and arsenic soluble fields. It indicates that arsenic and iron in the groundwater is likely to remain in soluble arsenite and ferrous form. The presence of soluble iron and arsenic (III) in fresh ground water support the findings.
- e. Inverse correlation between Arsenic and eH values (i.e., increasing Arsenic concentration with decreasing redox potential) strongly indicates that reducing environment promotes mobilization of Arsenic in the subsurface. Under reducing environment, organic matter (i.e., organic carbon, DOC) gets oxidized with concurrent reductive dissolution of iron oxyhydroxides. This process releases the Arsenic associated with iron oxyhydroxides (e.g., in adsorbed form) into the aqueous phase.

7.2.4 Experimental Verification

- a. Arsenic release from sediment was achieved in the laboratory by simulating anaerobic condition prevailing in aquifers in arsenic affected areas by introducing organic carbon in the form of glucose and molasses in a closed reactor. No arsenic release was observed in control batch where enough oxygen was allowed to enter into the reactor to maintain the system aerobic throughout the period of experiment. It proves that anaerobic and low redox conditions stimulate the release of arsenic from sediments.

- b. Arsenic was released only when eH values lowered to less than zero in simulated experiments in the laboratory. It indicates that arsenic was dissolved into water when significant reduction condition was achieved by added organic stimulants like molasses and glucose. It also indicates that bacteria mediated reducing state under anaerobic condition is a requirement for the release of arsenic.
- c. Arsenic release rate in molasses medium was faster than that of glucose medium and the total arsenic release in glucose medium is lower or delayed in comparison to molasses medium. This observation may be attributed to the reason that pure glucose provides only organic carbon but molasses introduces enough micronutrient along with organic carbon for balanced growth of microorganisms in the reactor.

7.3 RECOMMENDATION AND SCOPE OF FURTHER RESEARCH

- a. Significant amount of arsenic in sediment was found associated with sulfide minerals, which can go into solution in water by oxidation of these minerals. Although oxidation hypothesis is not supported by secondary evidences, the hypothesis should be experimentally verified by simulation of oxidizing condition in sediment. This can be done by simulating artificial fluctuations of water level in a column of sediment in the laboratory.
- b. The change of Arsenic concentration with time (seasons, years and decades), regions (highly, moderately, low and non-contaminated areas), and depth (shallow, intermediate and deep aquifers), should be observed and analyzed for better understanding of the nature of arsenic contamination. To determine the mobility of Arsenic and other relevant parameters with depth, piezometers in different depths may be installed at a number of strategic locations and water quality be tested on a regular basis.
- c. Although arsenic content in sediment was similar to that of average concentration in soil, very high concentration of arsenic is found in irrigated land and peat deposits.

The fate of arsenic affected by human activity and natural biological system is needed to be studied in the context of arsenic contamination of groundwater.

- d. Natural isotope variation and artificial tracer study should be conducted to estimate the mobility of arsenic in the aquifer. The pathways and time-scales for Arsenic movement to tubewells (for both hand-pumps, irrigation pumps and deep tube-wells) should be established using a contaminant transport model backed up by field tracer tests and piezometer monitoring.
- e. The ages of groundwater and sediments are the important scientific aspects of the Arsenic problem; systematic studies using a variety of dating techniques utilizing isotope technology should be conducted for determining the ages of sediments.
- f. Since the detailed knowledge about the suspended sediment carried out by upstream river flow as well as the bed sediment of the rivers and floodplain of the rivers with respect to the causes of Arsenic contamination in groundwater is of prime importance for applying proper mitigation options and remedial measures against Arsenic contamination, continuous collection of sediments from rivers at a fixed time interval, during and after flood at the predetermined locations should be conducted from the Indian borders to the estuary of the rivers.
- g. In order to observe the release mechanism of Arsenic, batch experiments under anaerobic condition in presence of the anaerobic microorganisms should be conducted for sediments of alluvial plain, crop-land, floodplain and borehole sediments at different depth in selected locations from both Arsenic contaminated/non-contaminated areas.
- h. To investigate the form of Arsenic in sediments, more sequential fractions should be done for borehole sediments of alluvial plain, crop-land sediments and borehole sediments at selected locations from both of the Arsenic contaminated/ non-contaminated areas. The results will provide the forms of arsenic remaining with sediments after dissolution in anaerobic environment.

- i. Policy makers of Bangladesh Government should give due consideration to the sources and causes of Arsenic contamination of groundwater in Bangladesh in developing long-term strategic planning for safe water supply for both domestic purposes and for irrigation.
- j. With the proper understanding of the causes of arsenic contamination, low cost as well as environment friendly remedial measures of arsenic contamination should be developed.
- k. Regional cooperation and international linkages should be developed to carry out more research on sources and causes of arsenic contamination in groundwater and for development of appropriate remedial measures.

Priority Actions

The following priority actions should be taken for the mitigation of arsenic contamination in groundwater of Bangladesh:

- a. Detailed investigation on sediment characteristics of subsurface specially with regard to the presence of arsenic sulphides, organic carbon etc.
- b. Detailed study on water quality parameters to assess the release mechanism of arsenic from solid to aqueous phase.
- c. Study on water level fluctuation to investigate the oxidation hypothesis.
- d. Continuous assessment of river water, suspended sediment and river-bed sediment quality of the rivers flowing through the arsenic affected areas.
- e. Low cost and environment friendly biological remedial measures instead of chemical processes should be given due consideration to tackle the arsenic problem in Bangladesh.

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APPENDIX

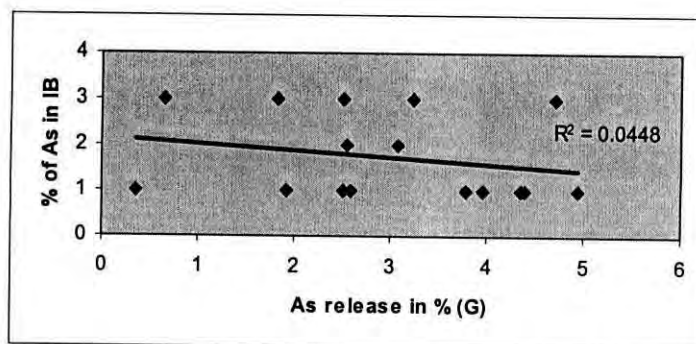
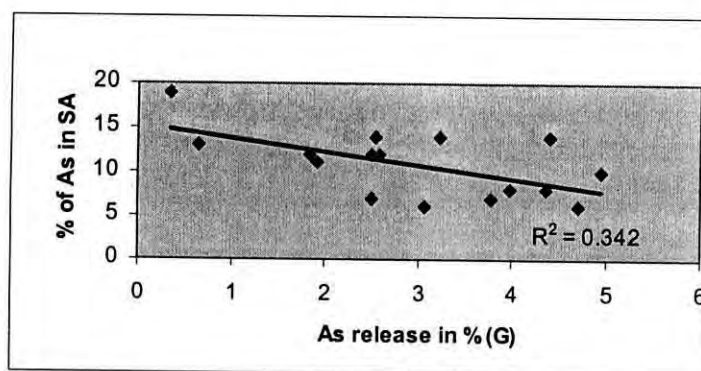
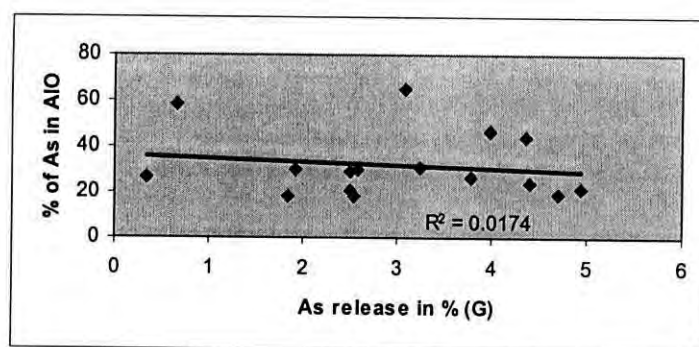
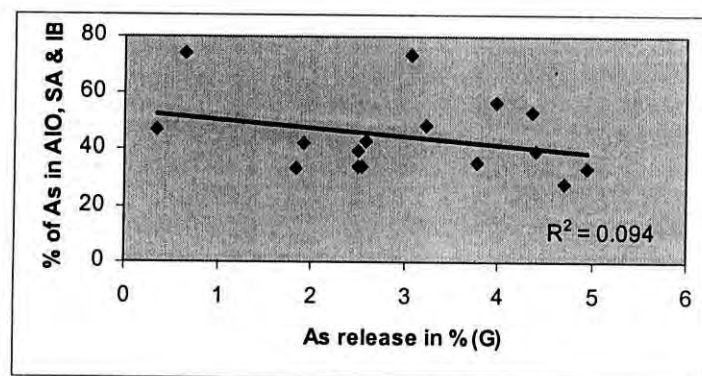


Fig. A-1: Arsenic in reducible forms of sediment versus arsenic release in glucose medium

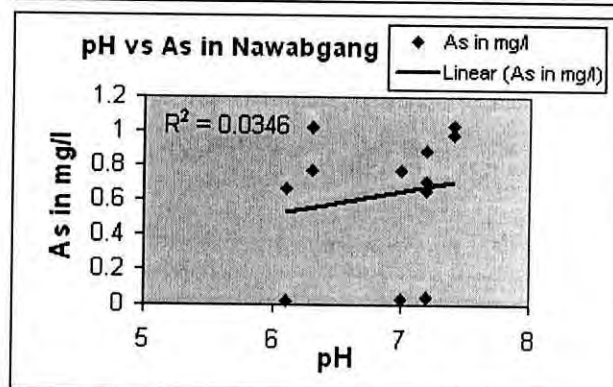
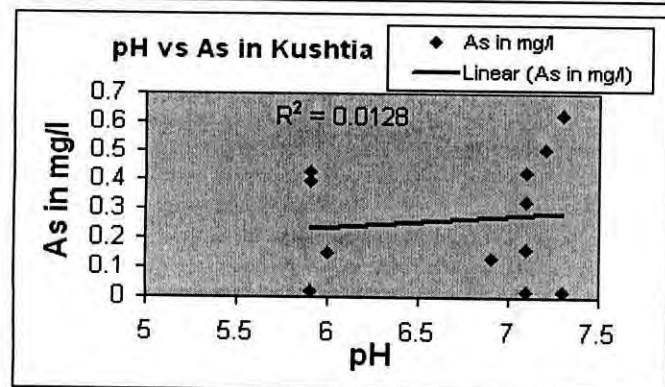
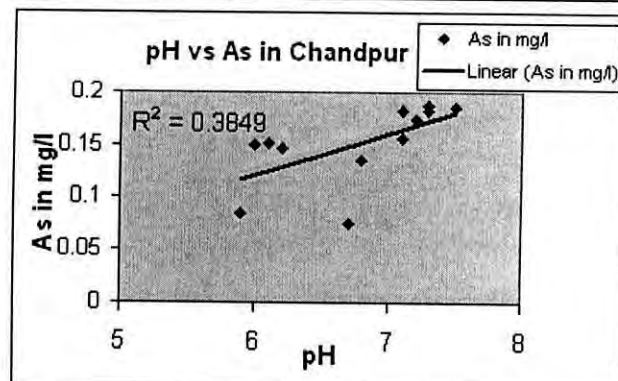
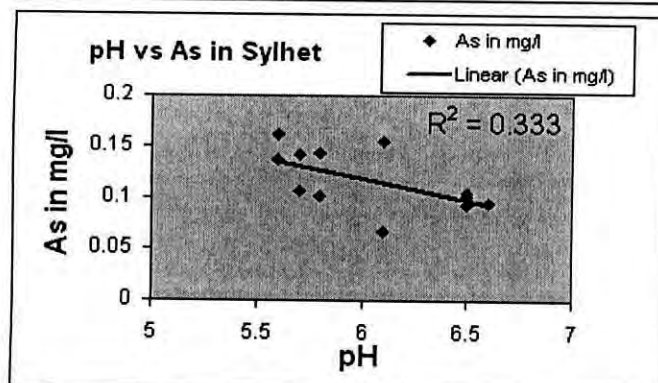
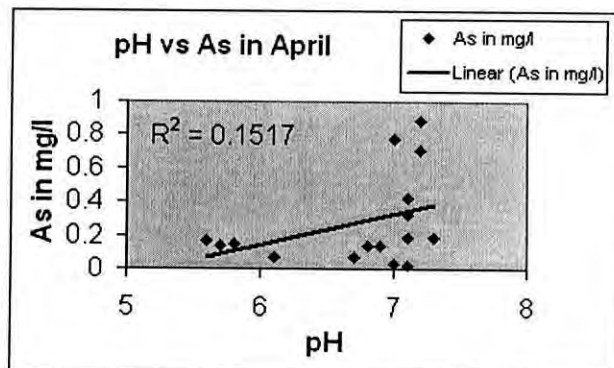
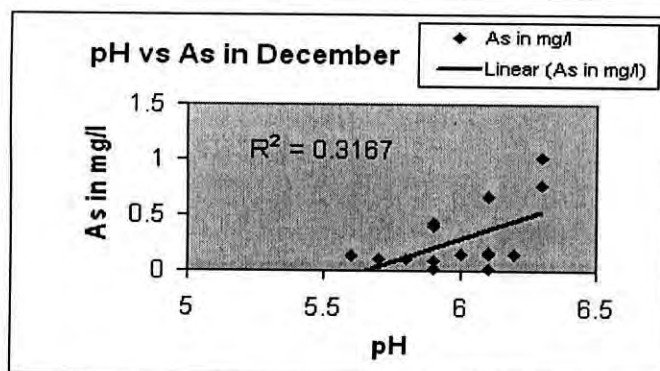
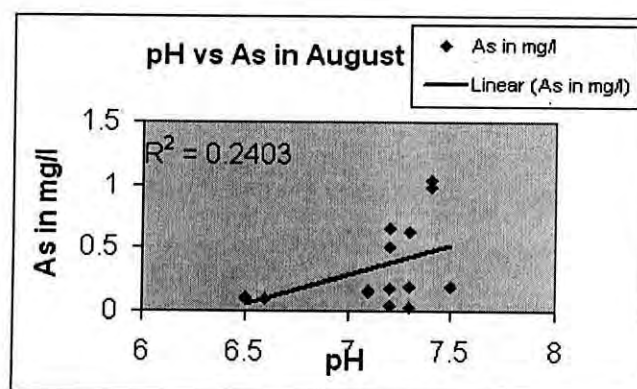


Fig A-2: Additional correlation between Arsenic and pH in the Study area.

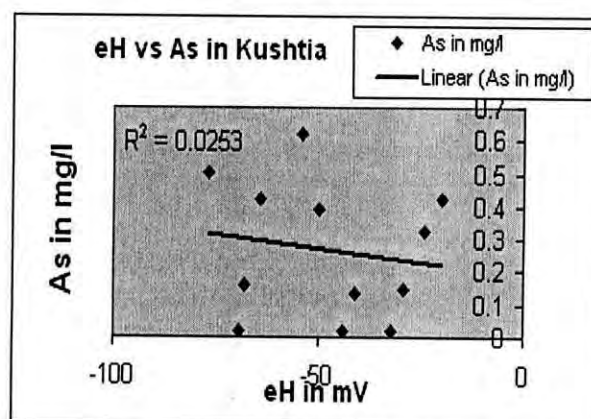
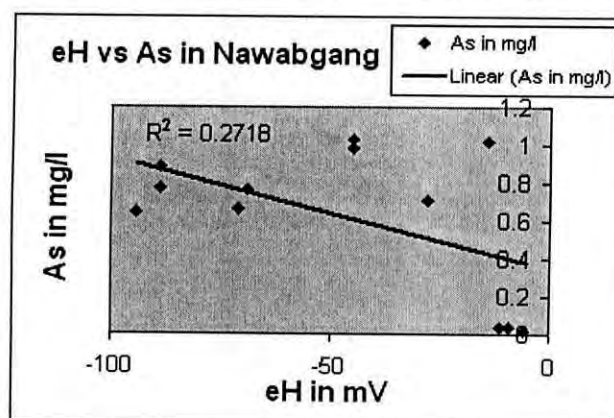
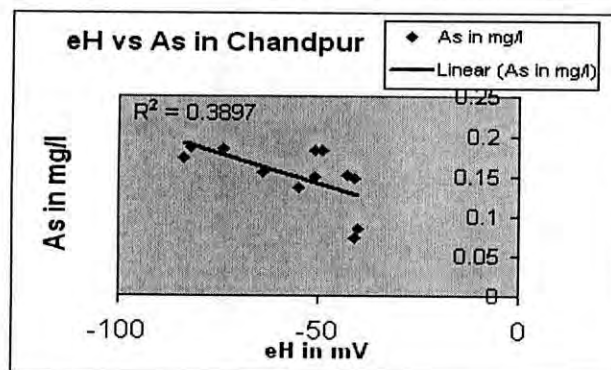
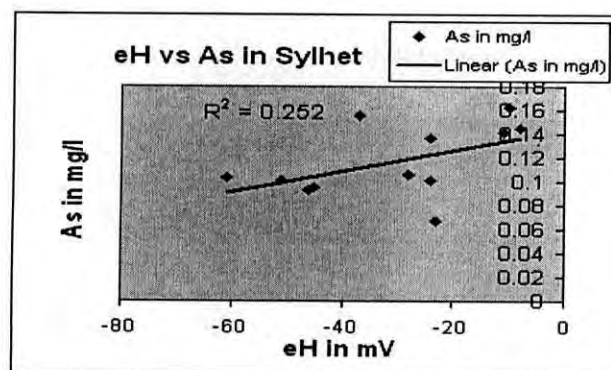


Fig A-3: Additional correlation between eH and arsenic in study areas

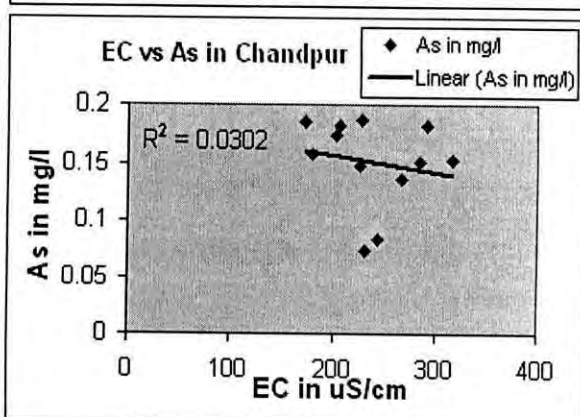
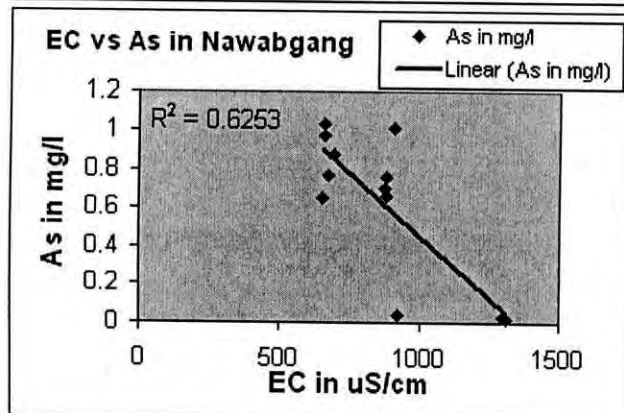
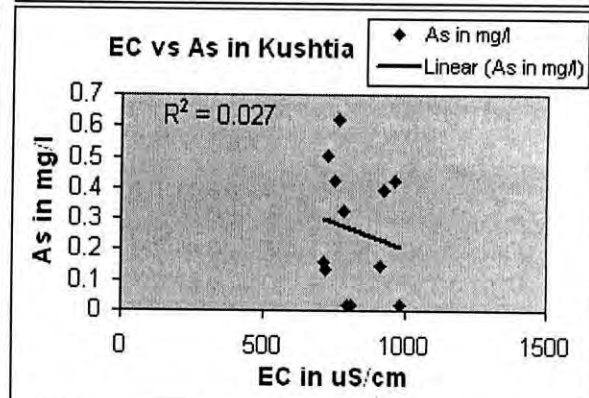
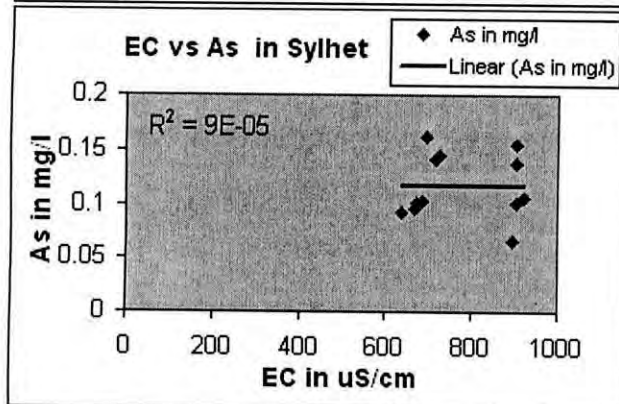
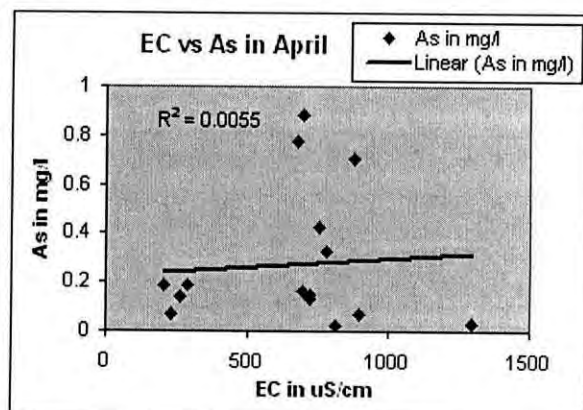
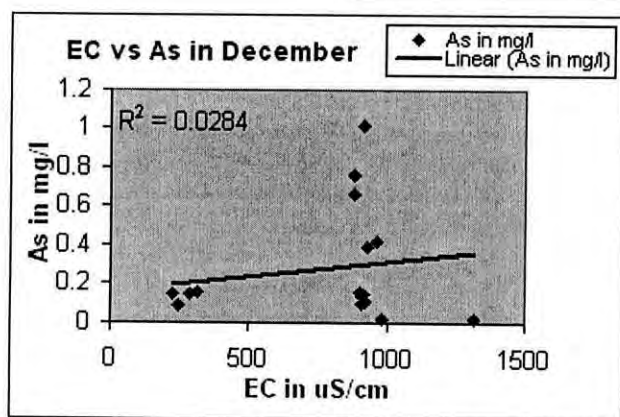
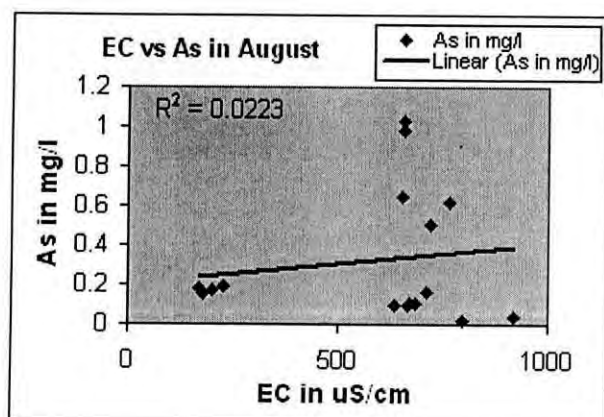


Fig A-4 : Additional correlation between electric conductivity and arsenic in the study areas

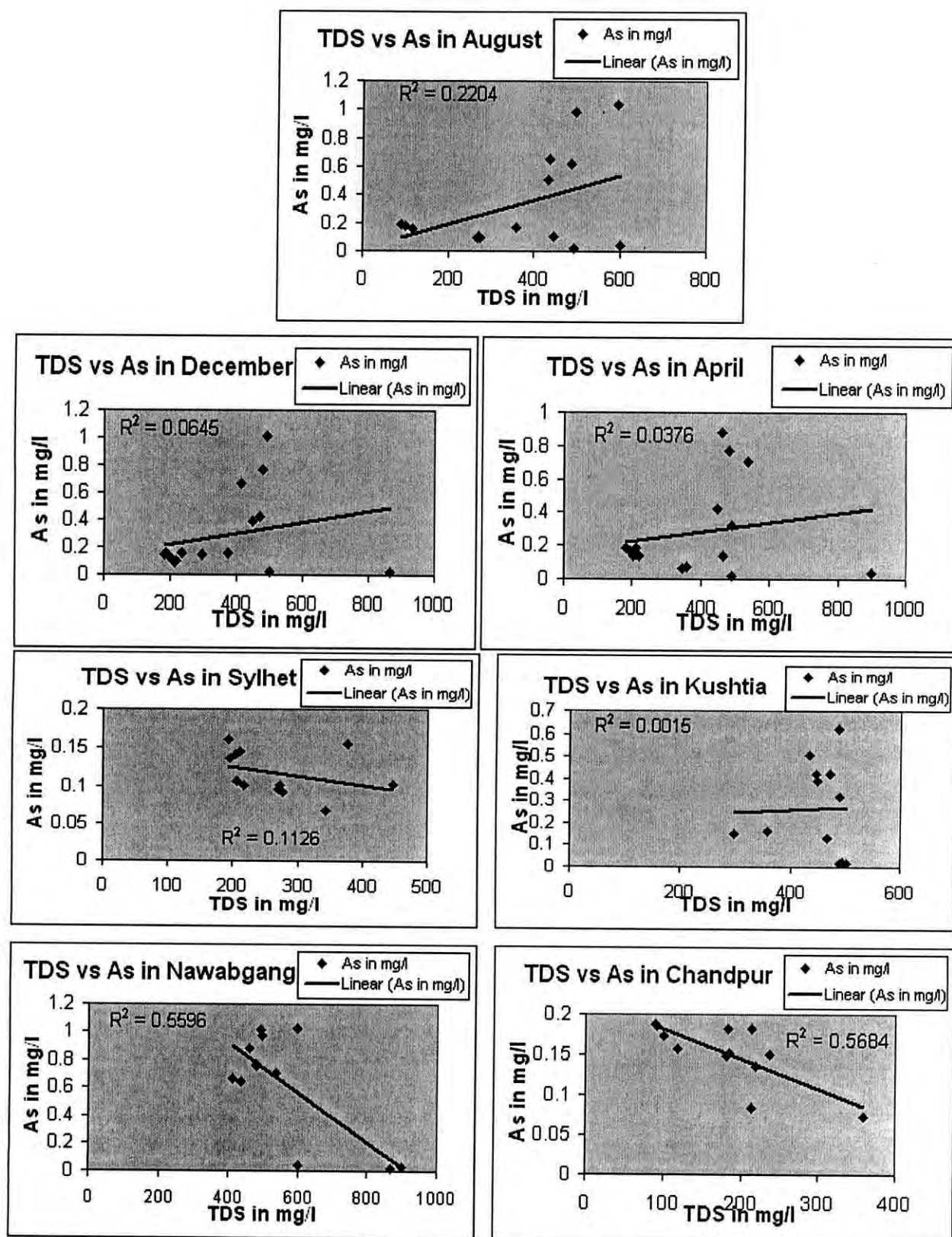


Fig A-5: Additional correlation between TDS and arsenic in the study area

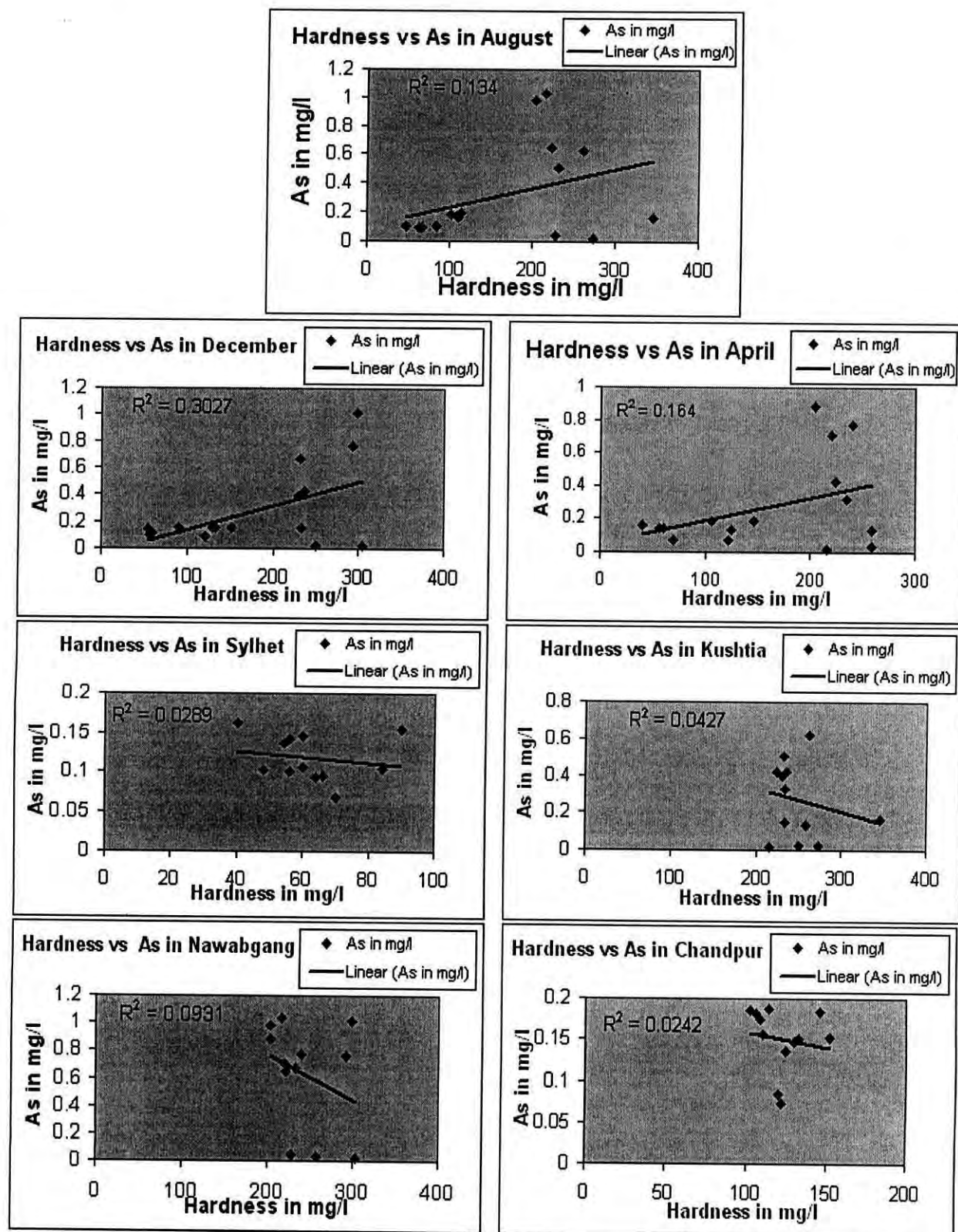


Fig A-6: Additional correlation between hardness and arsenic in study area

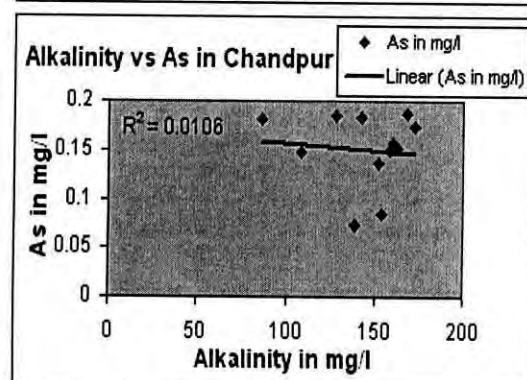
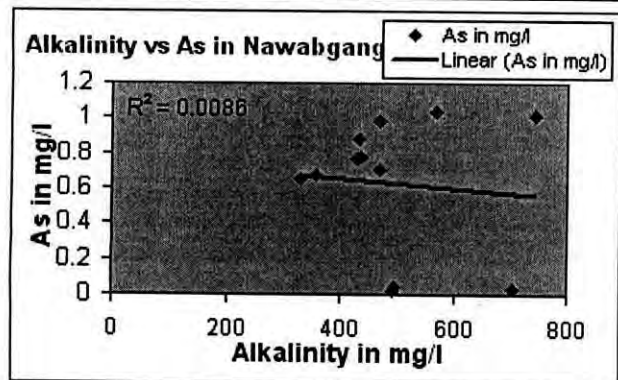
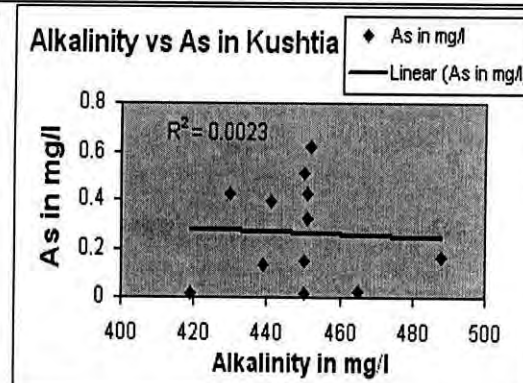
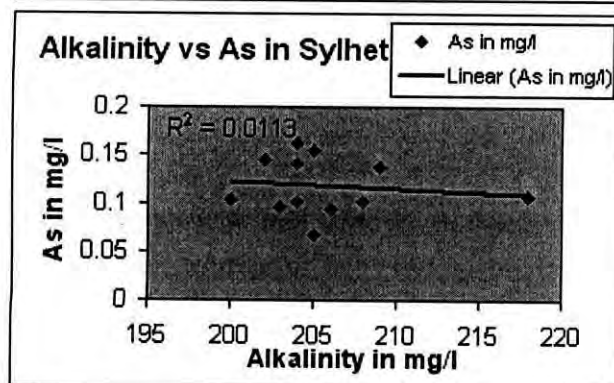
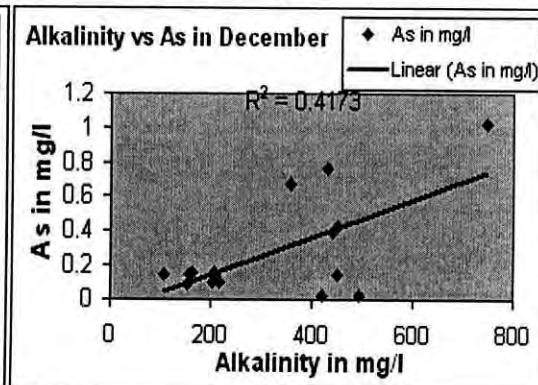
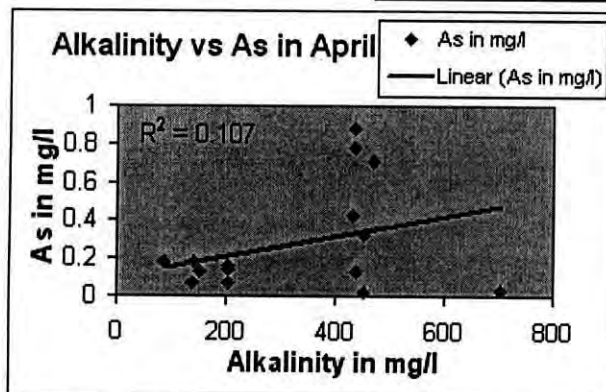
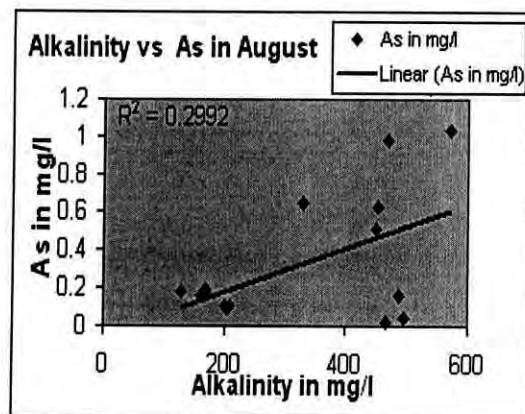


Fig A-7: Additional correlation between Alkalinity and arsenic in study area

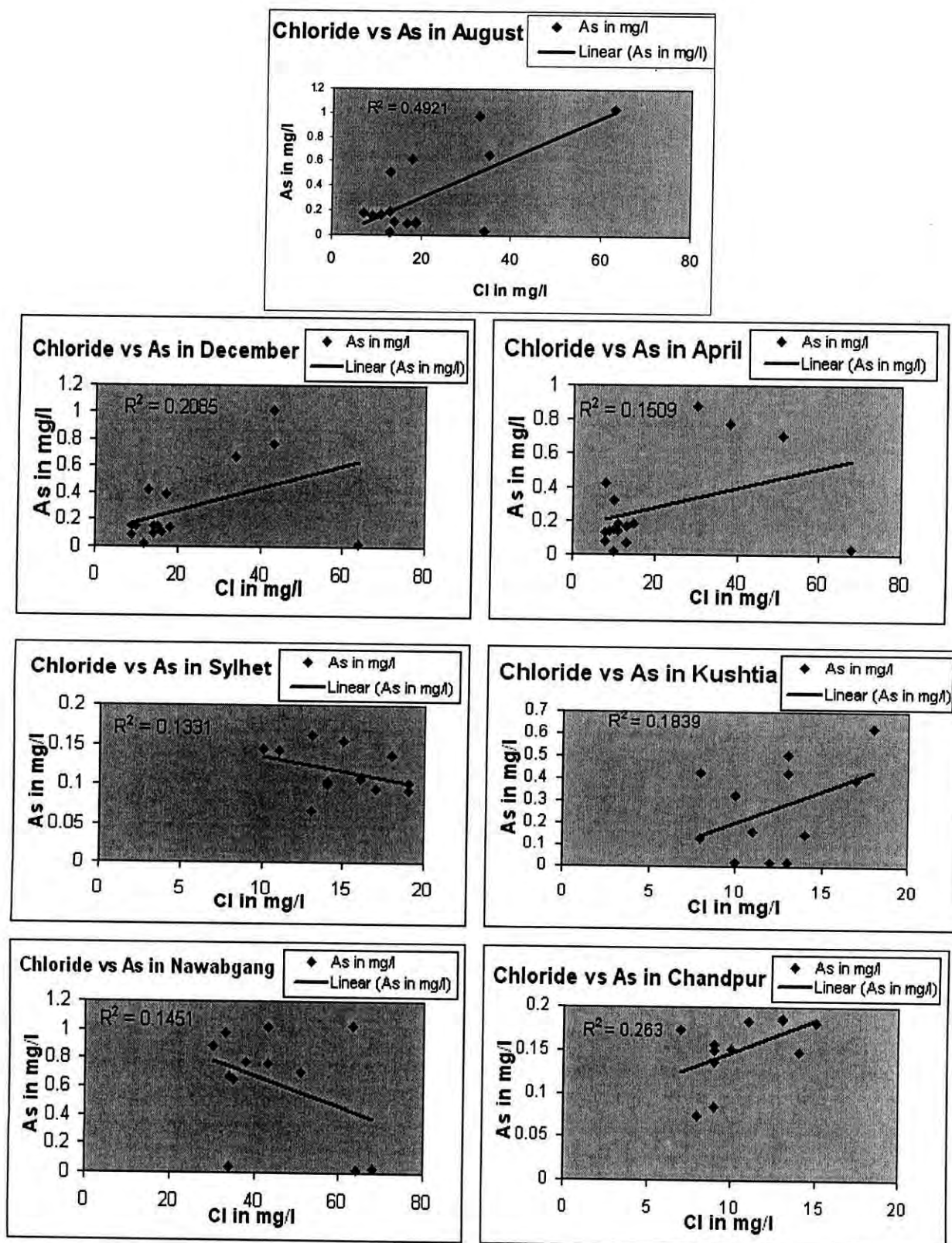


Fig A-8 : Additional correlation chloride and aarsenic concentration in the study areas.

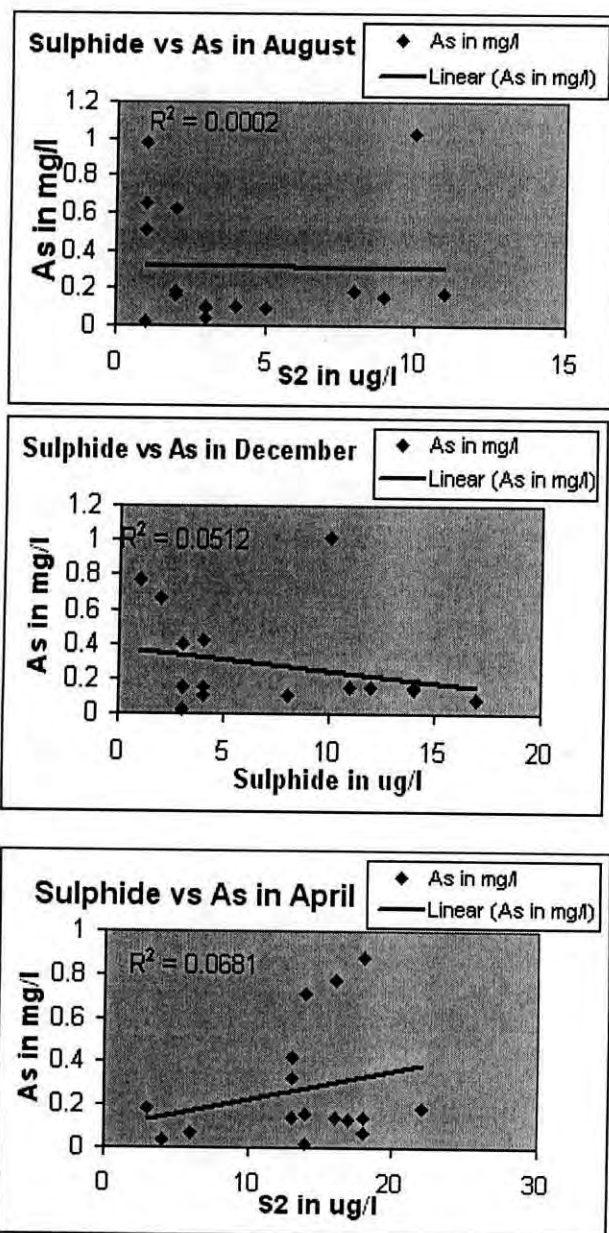


Fig A-9: Additional correlation between sulphide and arsenic in study areas

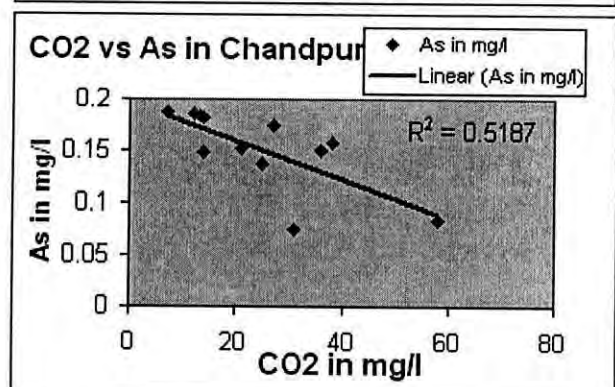
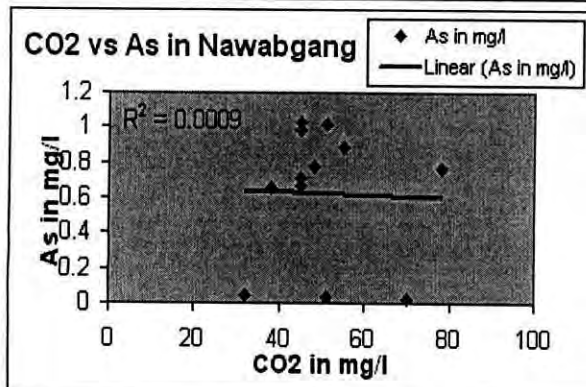
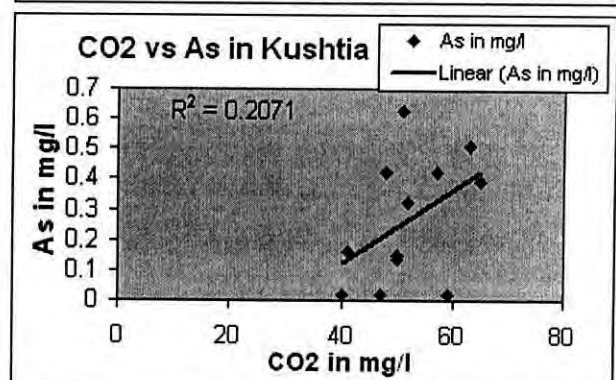
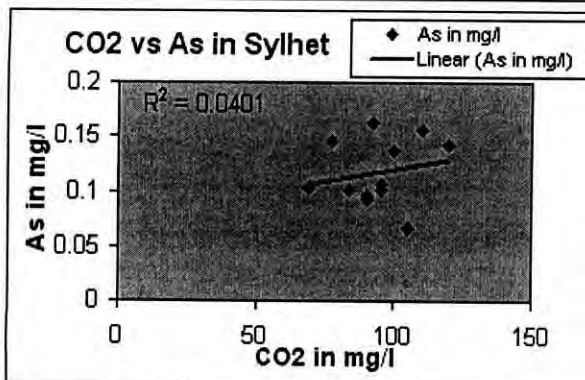
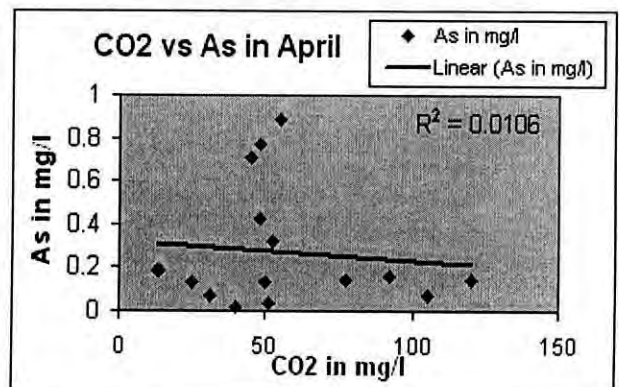
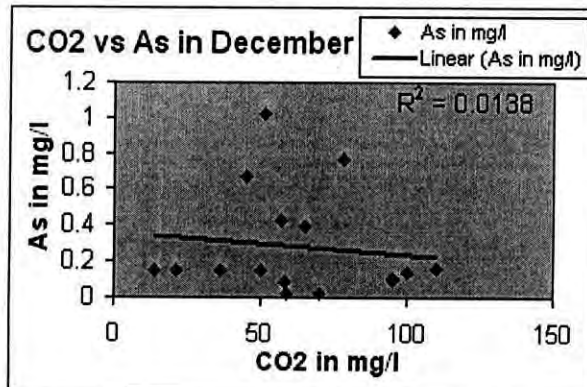
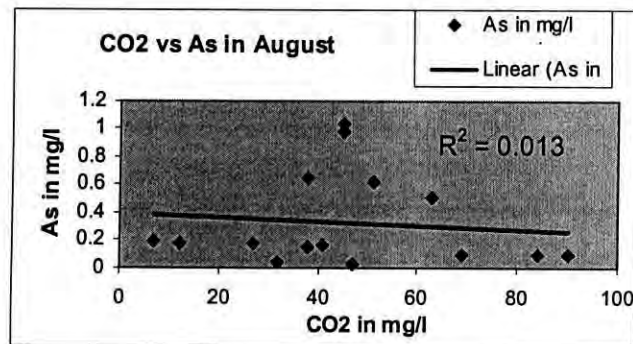


Fig A-10: Additional correlation between carbon dioxide and arsenic in study areas

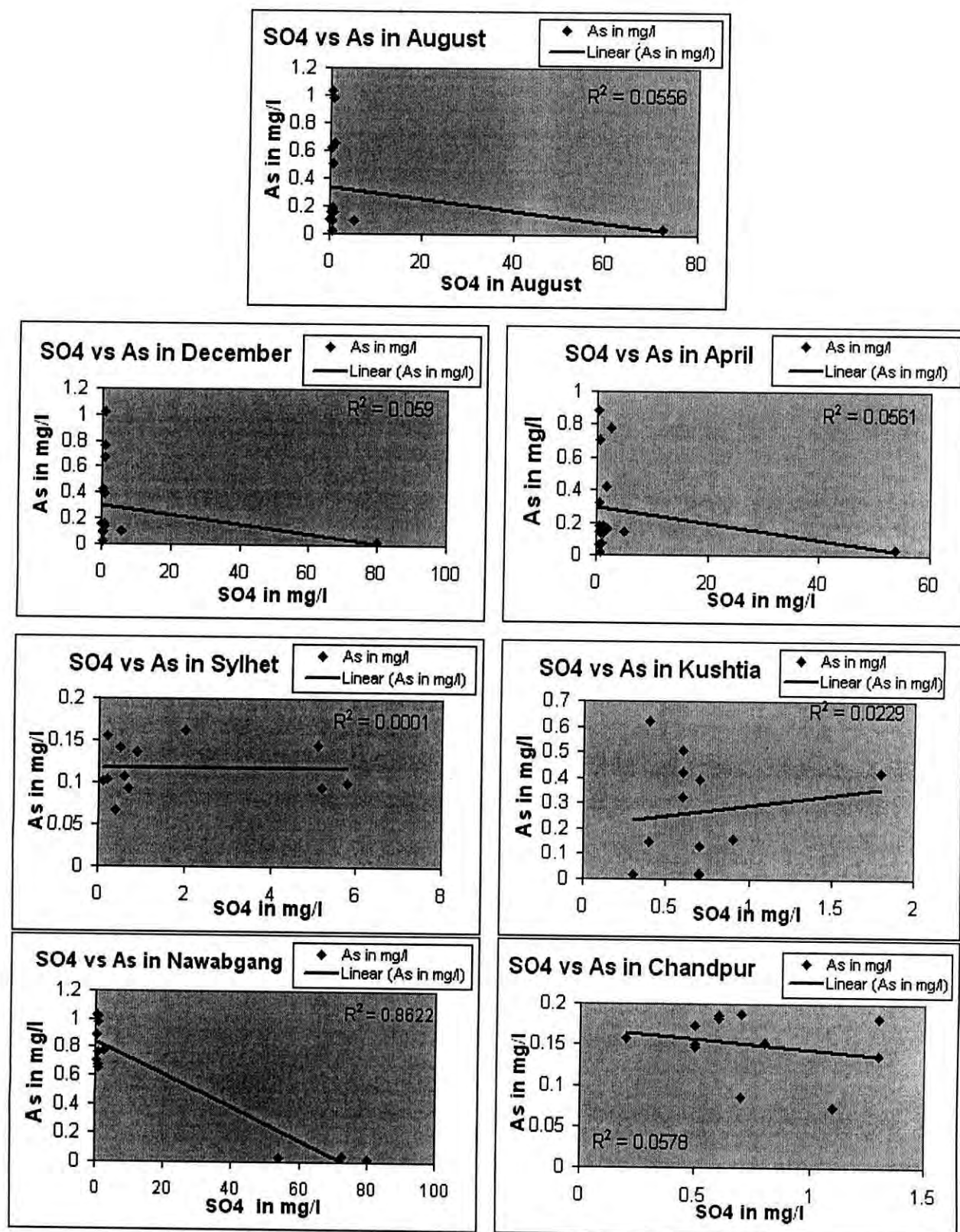


Fig A-11: Additional correlation between sulfate and arsenic study areas

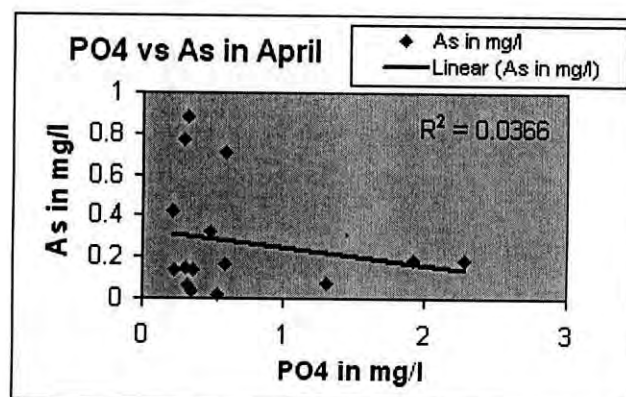
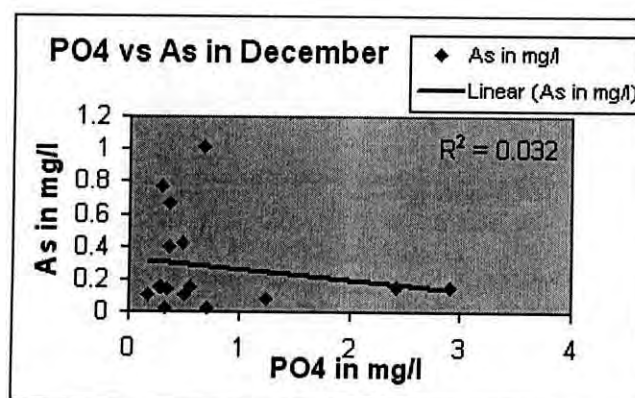
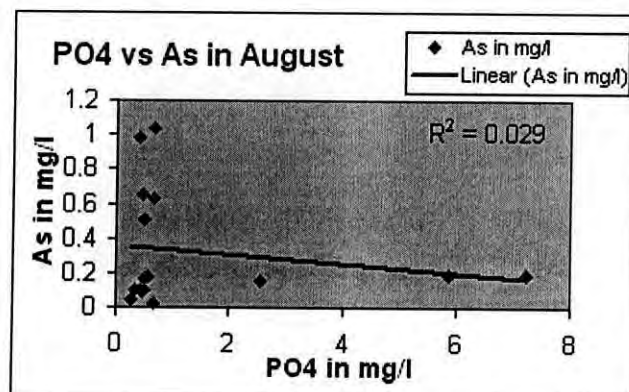


Fig A-12: Additional correlation between phosphate and arsenic in study areas

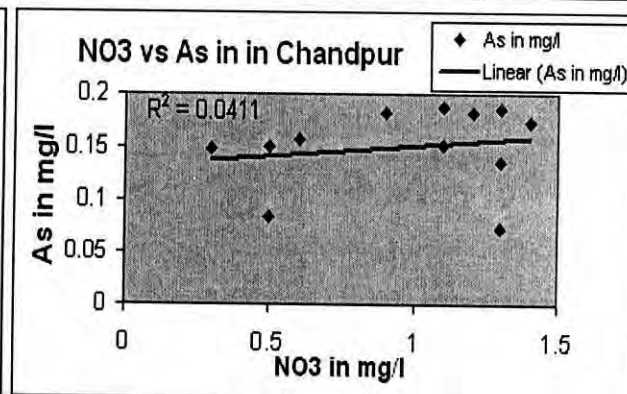
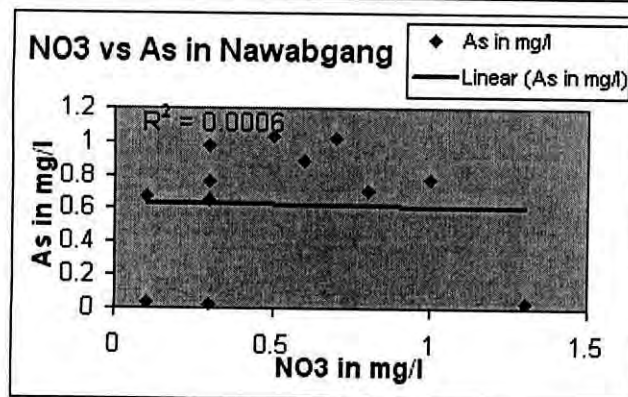
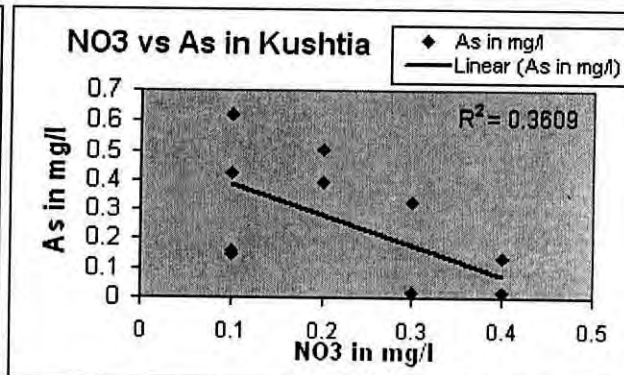
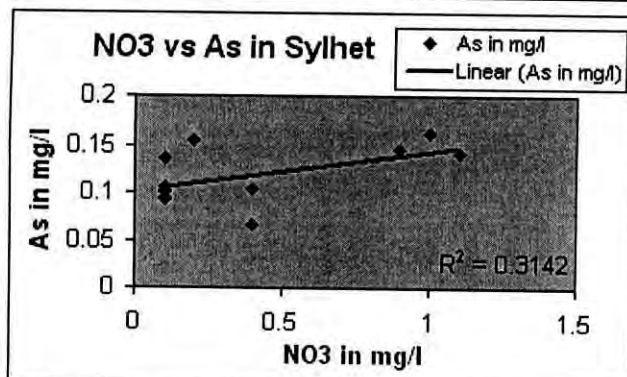
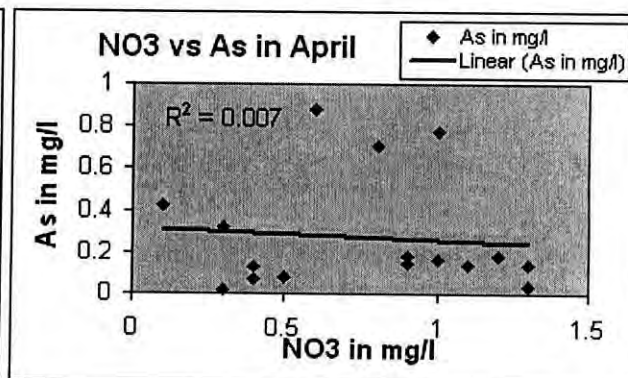
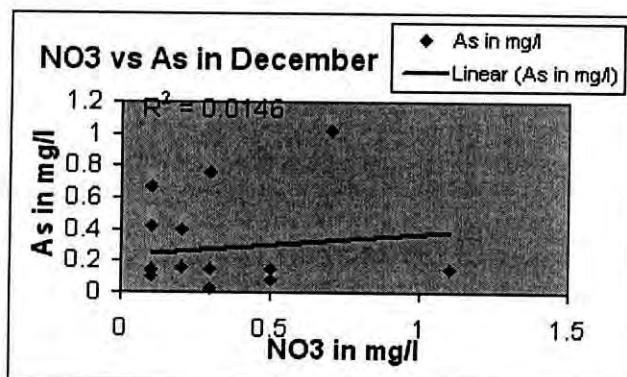
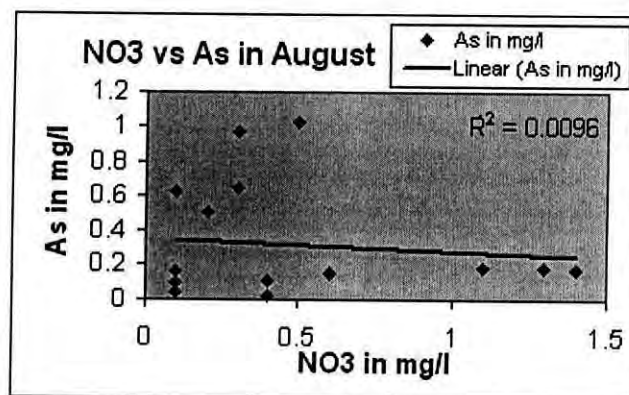


Fig A-13: Additional correlation between nitrate and arsenic in the study areas

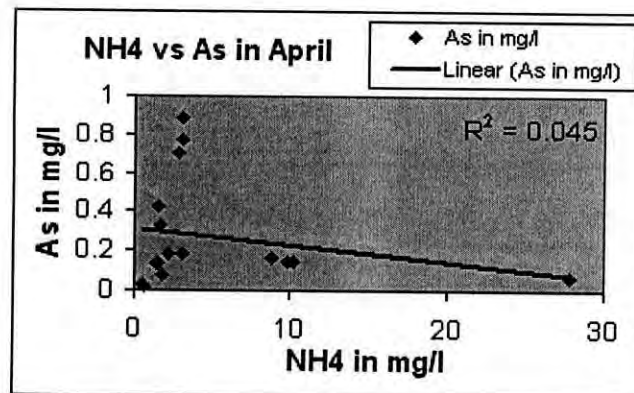
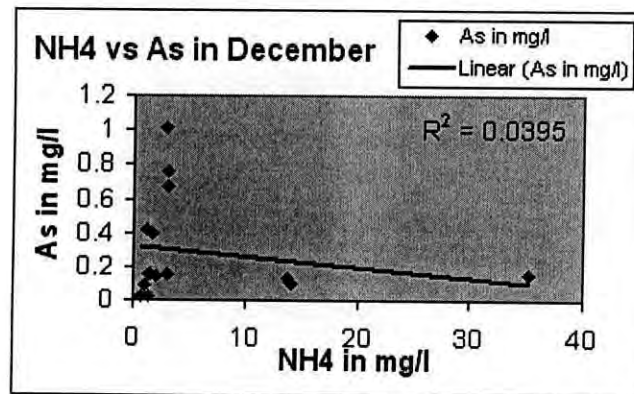
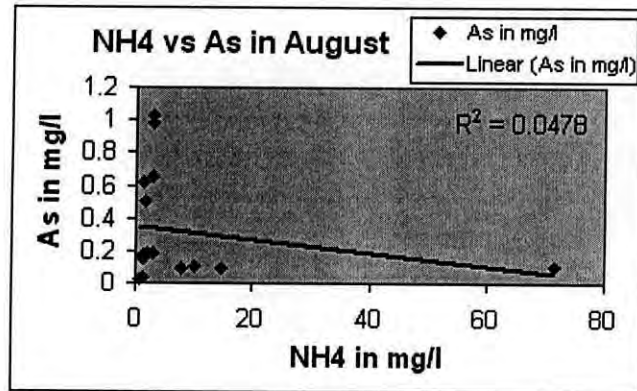


Fig A-14: Additional correlation between ammonium and arsenic in study areas

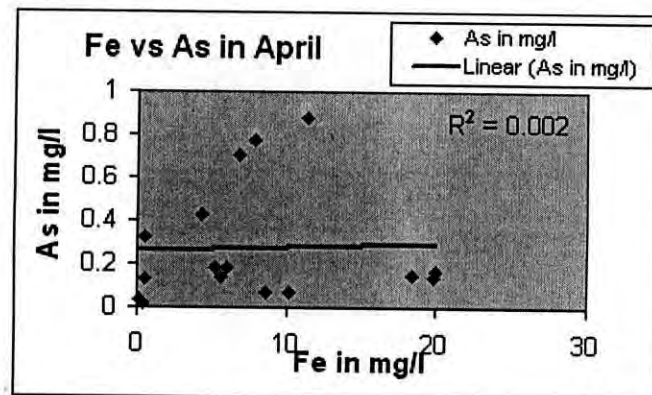
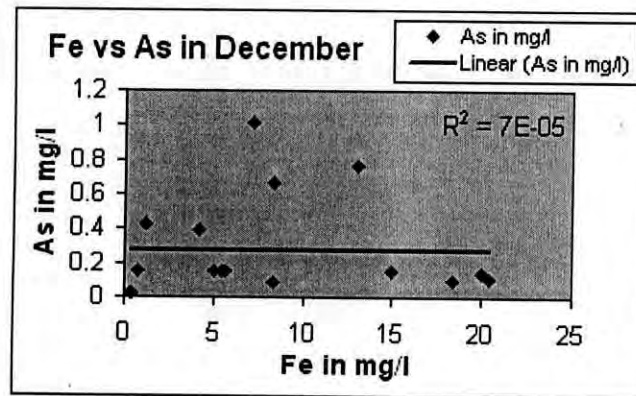
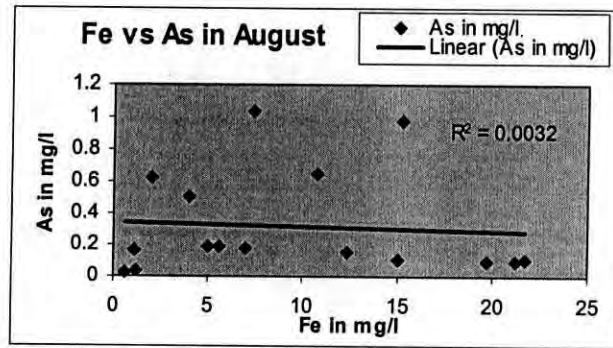


Fig A - 15: Additional correlation between iron and arsenic in study areas

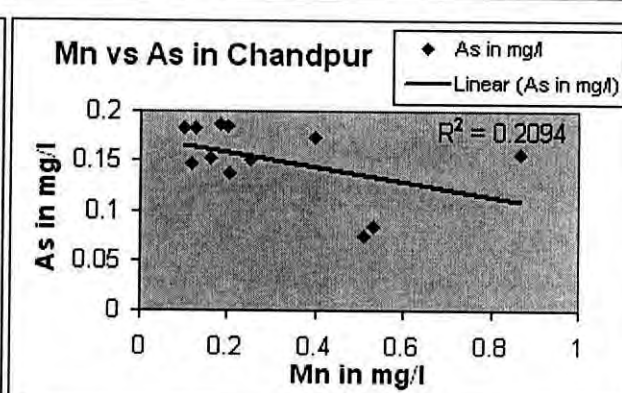
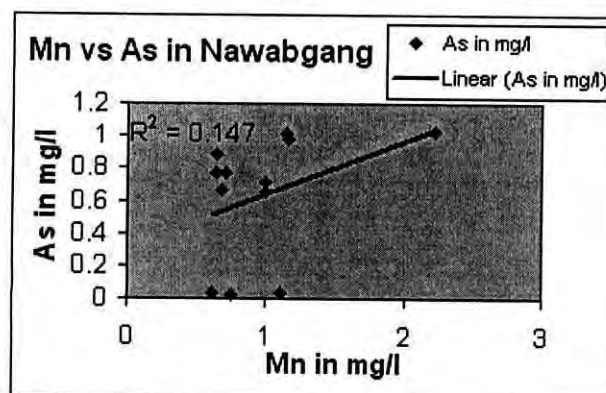
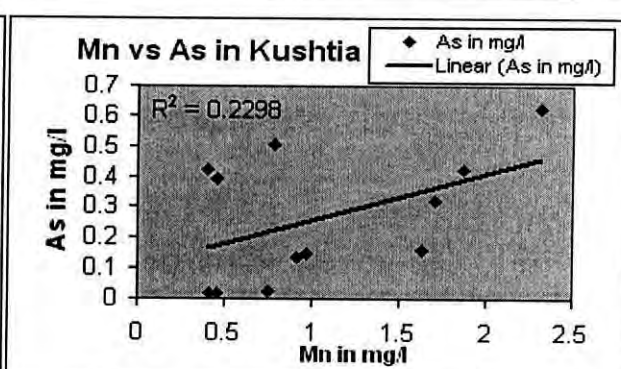
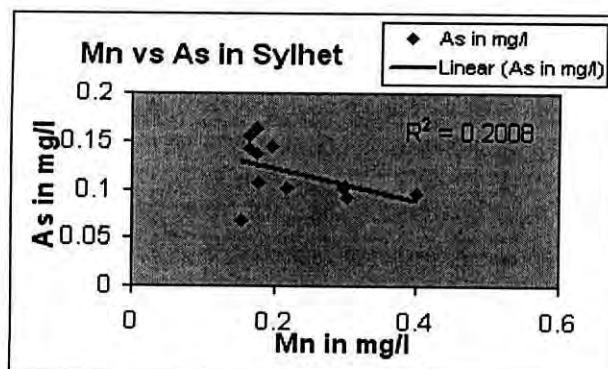
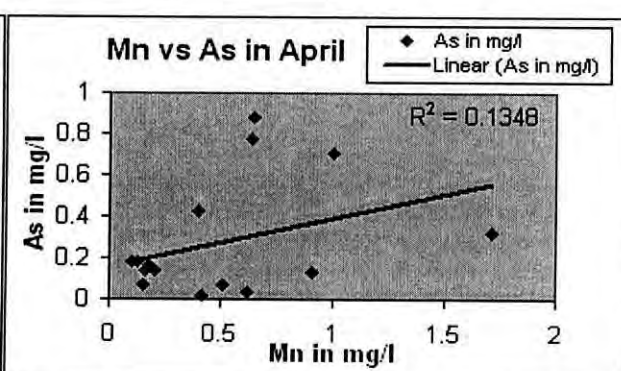
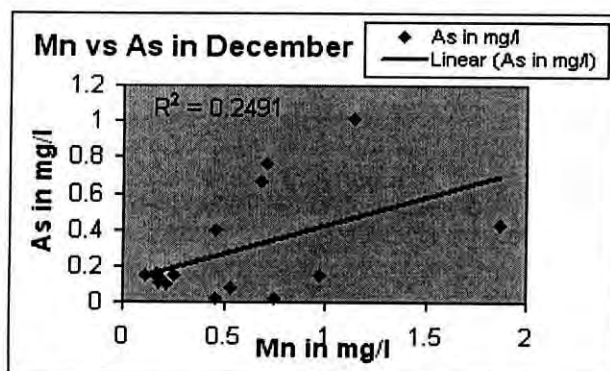
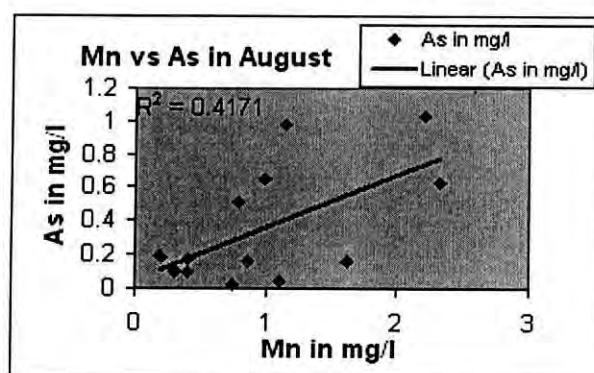


Fig A-16: Additional correlation between iron and arsenic in study areas

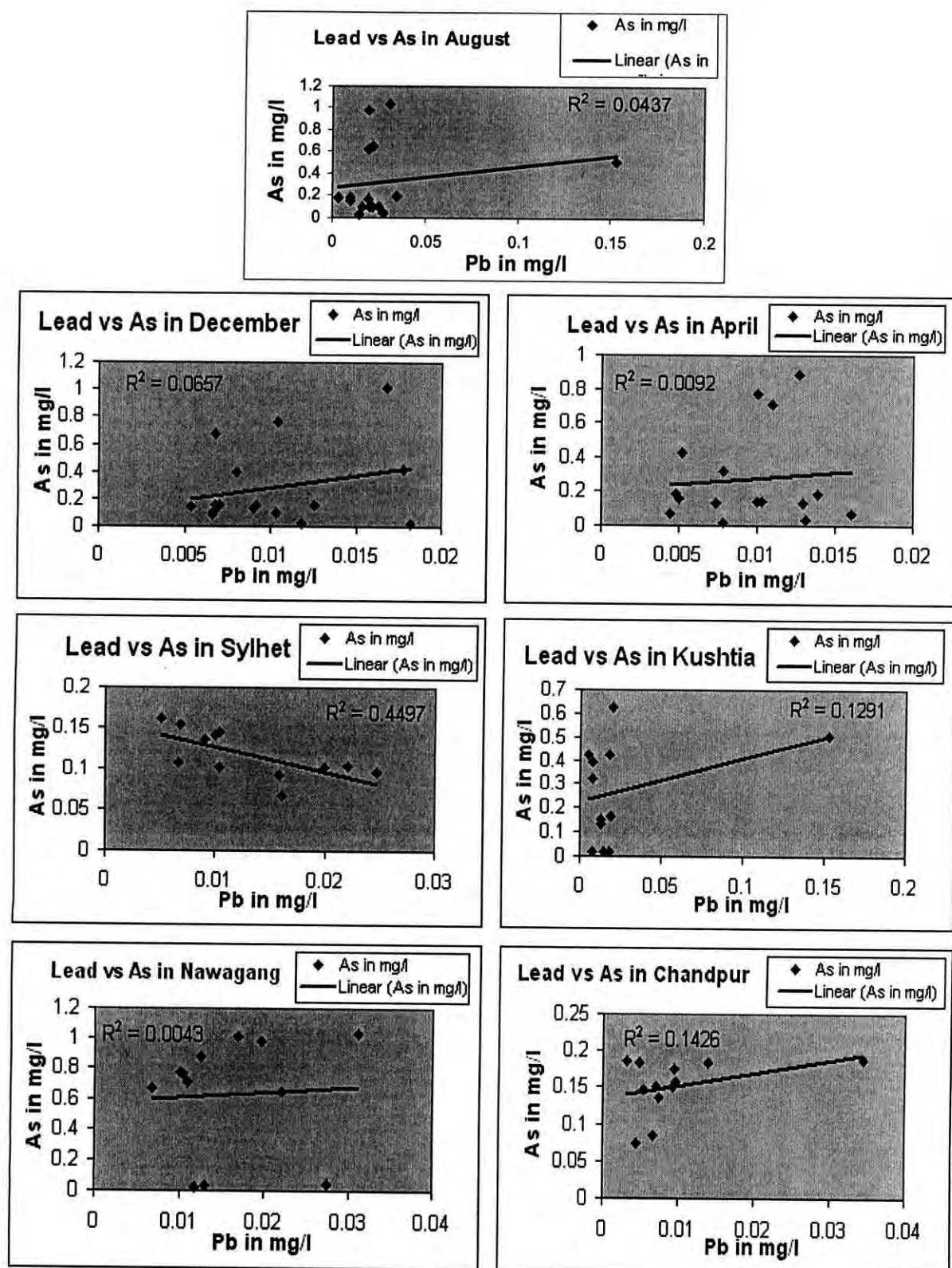


Fig A-17: Additional correlation between lead and arsenic in study areas

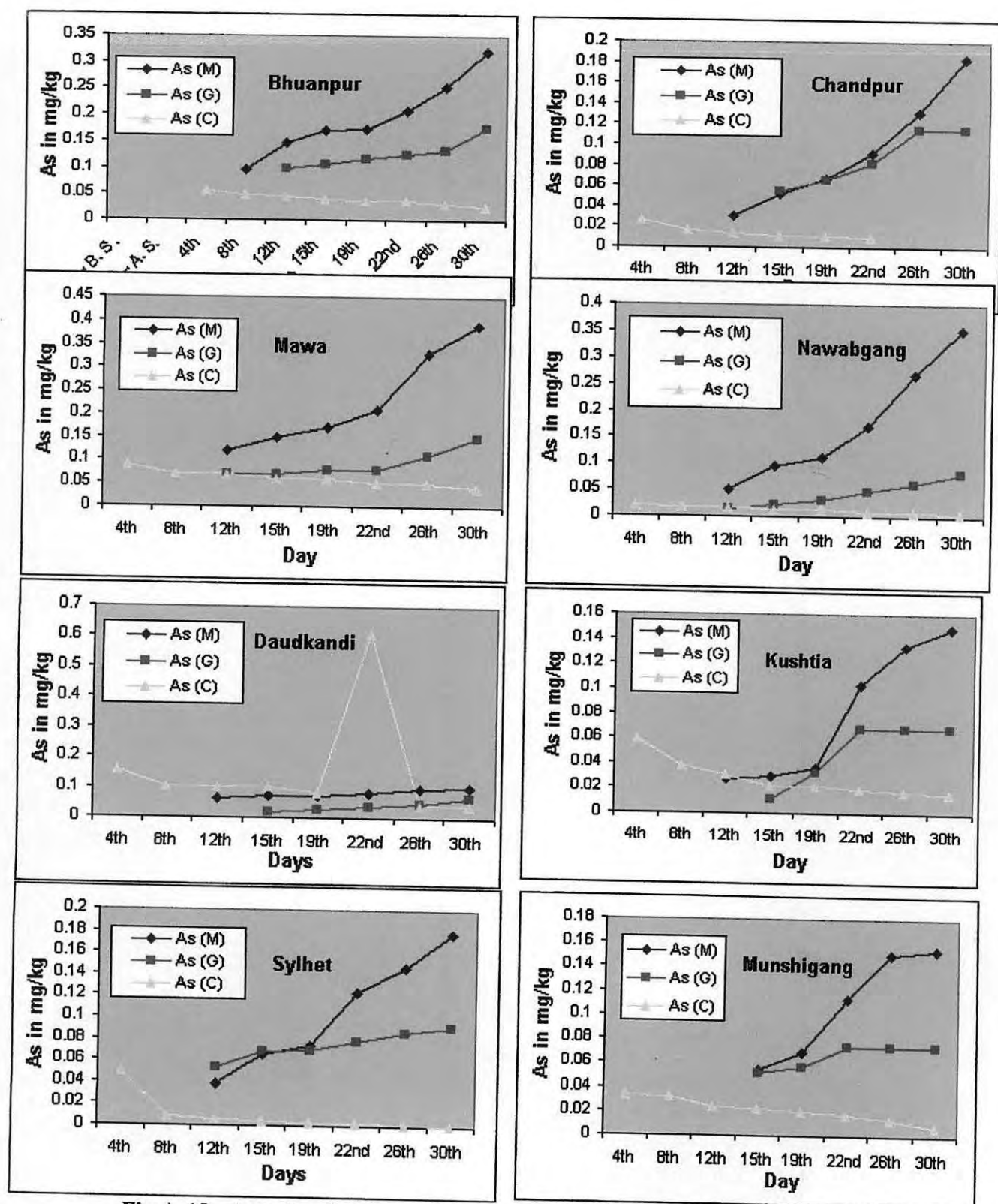


Fig A-18: Arsenic release w.r.t. time in the sediments of different locations.



Fig A-19 : Measurement of water level in the field

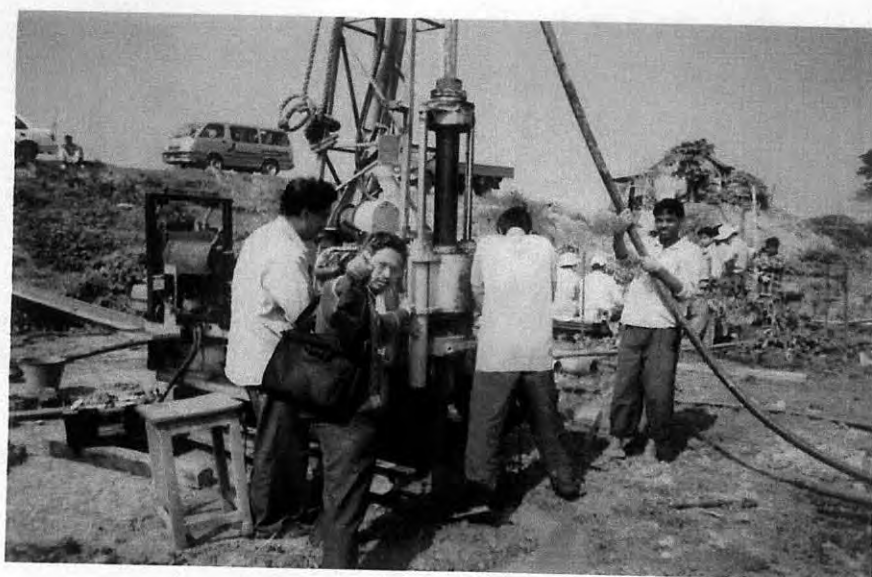


Fig. A- 20 : Boring works for collection of borehole sediment from Nunshiganj