# ARSENIC FRACTIONATION AND ITS REMEDIATION IN AGRICULTURAL SOILS OF BANGLADESH

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# ARSENIC FRACTIONATION AND ITS REMEDIATION IN AGRICULTURAL SOILS OF BANGLADESH

A Dissertation for the Partial Fulfilment of the Requirements of the Degree of Master of Philosophy in Soil, Water and Environment

Submitted by

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December 2015

**Dedicated to my beloved**

**Mother**

# Declaration

Declared that, except where specific references to other researches and publications are made, the thesis titled “Arsenic Fractionation and its Remediation in Agricultural Soils of Bangladesh” submitted by Shumana Zaman, Regd. No. 275/2009-10, Department of Soil, Water and Environment, University of Dhaka, represents an original research conducted under my supervision and has not been submitted elsewhere for any degree or diploma.

Prof. Dr. Sirajul Hoque
Thesis Supervisor

# Acknowledgement

The author of this dissertation expresses her deepest sense of gratitude, appreciation and thankfulness to her teacher and thesis supervisor Prof. Dr. Sirajul Hoque, Chairman, Department of Soil, Water and Environment, University of Dhaka for his excellent guidance, untiring support, enlightening suggestions, encouragements and inspiration, wholehearted co-operation to carry out the research without which it would have been impossible to materialize the work.

The author also expresses her sincere thanks and appreciation to Prof. Dr. Shah Mohammad Ullah for his inspiration, motivation and useful instruction for meaningful advancement of the work.

Special thanks and gratitude goes to Prof. Dr. Zakir Hossain Khan for his extremely valuable help in setting up the laboratory facilities without which the successful completion of this work would have been uncertain. Sincere thanks to Prof. Dr. ABM Badruzzaman, Department of Civil Engineering, BUET for his help in acquiring a few experimental data and materials.

The author shall remain ever grateful to Engr. Bazlul Hoque, Superintending Engineer, DPHE for his help and support in acquiring valuable resources and information related to the present research. The author expresses her sincere thankfulness to Mr. Md. Moniruzzaman, Senior Scientific Officer, BCSIR, Dhaka for his kind help and valuable advices throughout the work. Thanks go to Md. Nazmul Hasan, Principal Scientific Officer, SRDI and Ms. Abida Sultana, Senior Scientific Officer, SRDI for providing soil samples. Thanks to Dr. Sharmin Akhter, Scientific Officer, SRDI for providing valuable data for the work. Special thanks go to Mir Ferdous Ara of Advance Research Laboratory, Dept. of Soil, Water and Environment, The University of Dhaka for her help and support in carrying out the experimental works involving precision laboratory equipment.

Greatly acknowledged is the help of Md. Touhidul Islam for his support, help and valuable suggestion throughout the work as well as providing soil samples. The author also acknowledges the moral support received from Azizul Hakim, Rekha Rani, Nazmun Nahar, Pushpita Chowdhury, Maksuda Hossain, Afsana Parvin and Tamzid-Us-Sakib for their moral support and suggestions.

The author likes to thank all the laboratory staff especially Gazi Muhammad Babul, Md. Mostofa Kamal Sarker, Md. Alauddin, Md. Joynal Abedin, Md. Jahangir Alam Bhuiyan, Md. Alamgir and Md. Shafiq for their assistance during the work.

The author expresses her deepest sense of respect and honor to her mother who had always been a source of great aid, support and care for her family while carrying out the research. The author also expresses her thanks to her dearest kids Amanta and Aritha for their support.

Last but not the least, the author expresses her deepest sense of appreciation and thankfulness to her husband Prof. Dr. Khan Mahmud Amanat, Department of Civil Engineering, BUET for his untiring help in preparing the thesis and for his strong and affectionate encouragement, patience and moral support throughout the work.

# ABSTRACT

A laboratory batch experiment was conducted to find out the various fractions of arsenic in two contaminated calcareous high pH soils from Bagerhat and Kashiani and uncontaminated low pH soil from Madhupur of Bangladesh with an aim to understand arsenic dynamics in soils required to develop remedial measures against arsenic contamination. Study was conducted on soil samples by spiking with different combinations and sequence of anions – arsenic (As), phosphorous (P) and sulphur (S). Phosphate and sulphate were chosen as desorptive solutions because they are common soil nutrients. Seven different combinations of the anion application sequence at two different concentrations resulted in fourteen different treatments applied to soil samples which were subjected to fractionation study following the 5-step sequential extraction procedure (SEP) developed by Wenzel *et al*. (2001). Study on "Resident time effect" was also performed for by conducting the SEP at 0 day, 7 days and 30 days of incubation after spiking the samples. SEP was also carried out on the untreated samples.

The total concentration of Arsenic in Bagerhat, Kashiyani and Modhupur soils were found 22.0, 88.0 and 3.68 mg kg$^{-1}$, respectively. Very good correlation between total arsenic content and organic matter, phosphorus, calcium and carbonate content of the samples. Moderate correlation was obtained between arsenic content and CEC, pH and iron.

From the SEP study on untreated samples, highest fraction of arsenic was extracted as crystalline hydrous oxide bound form in SEP Step-4. Highest amount was found from Kashiani soil which was 54 mg kg$^{-1}$. The same fraction for Bagerhat and Madhupur soils were 7.0 and 2.5 mg kg$^{-1}$, respectively.

For all the spiked samples, most of the arsenic was extracted as specifically-bound form. When arsenic was added before or simultaneously with phosphate, the extracted amount of arsenic did not notably vary with incubation periods. When phosphate was added before arsenic, a gradual increase was observed in the extracted amount with residence times. Treatments involving arsenic and sulphate showed that the amount of desorbed arsenic did not appreciably vary with incubation period except for the uncontaminated Madhupur

soil. For all the treatments with sulphate and arsenic, the magnitude of extracted amount was similar. Comparison of the results showed that, in general, the extracted amount is notably higher in cases of treatments involving phosphate to that of sulphate. This might be due to the fact that sulphate is less strongly sorbed than phosphate and is thus a much less effective desorbent. The mixed treatment (As+S+P) resulted in much higher extraction from Bagerhat soil at higher concentration of treatments when compared to the extracted amount in treatments involving either phosphate or sulphate. It was thus appeared that in presence of sulphate, efficiency of phosphate may increase in desorbing arsenic from soils where phosphate alone is not strong enough to desorb arsenic.

Phosphate may not be able to mobilize the arsenic in amorphous or crystalline bound form which constituted the major fraction in the contaminated but unspiked samples. Use of phosphate fertilizer may not further aggravate the arsenic toxicity issue in such soils. In the present fractionation study of spiked samples, the species had been identified as the specifically bound form which can be mobilized due to addition of phosphate or sulphate anion. Therefore, fertilization of arsenic contaminated soils with phosphate will lead to increased arsenic mobility and leaching from soils and potential contamination of surface/groundwater only if arsenic is present as specifically-bound form found in the present study. Chemical remediation using $PO_4^{3-}$ or $SO_4^{2-}$ in such soils may not be effective for arsenic removal because, a significant proportion of arsenic can also be remobilized from soils through the process of anion exchange. Fertilization of such soils with sulphur may help in immobilization of arsenic.

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# Chapter 1

# INTRODUCTION

Earth environment and its pollution has become a widely discussed and debated topic all over the world in the recent days. With the advancement of civilization various types of human activities are causing a change in the environment. Besides such anthropological effects there are also natural geological causes which are changing the environment. Anthropological impacts are relatively easy to understand and their remedial measures are easy to formulate. On the contrary, geological causes are most difficult to understand due to the lack of proper understanding of geologic and geo-morphologic characteristics of earth. Arsenic pollution of ground water is such a phenomenon which has become an acute environmental problem in Bangladesh as well as in West Bengal of India in the recent past. The first reported case of arsenic-contaminated groundwater (greater than 50 $\mu g\ L^{-1}$) from the Bengal Basin was recorded in 1978 in West Bengal (Acharyya *et al.*, 2000) and the first cases of arsenic poisoning there were diagnosed in 1983. These early cases of arsenic induced skin lesions were identified by K.C. Saha of the Department of Dermatology, School of Tropical Medicine in Calcutta, India (Saha, 1997; Smith *et al.*, 2000). The first patients seen were from West Bengal but by 1987 several patients had already been identified who came from neighboring Bangladesh (Smith *et al.*, 2000). More than one hundred million people in this area are affected by arsenic pollution. This Arsenic pollution of ground water in Bangladesh has been termed as the worst environmental disaster in the history of mankind. Arsenic in water is tasteless, odorless and colorless, so it is not an easy task to determine the precise extent of the arsenic problems in Bangladesh.

In many areas of the Bengal basin, agriculture depends mainly on groundwater for irrigation, and in 40% of the net cultivable area in Bangladesh arsenic contaminated groundwater represents the main water source for irrigation

(Huq *et al*., 2003, 2006). A huge amount of arsenic is thus transferred every year from the contaminated aquifer to the surface water–soil–plant system (Ali *et al*., 2003). The arsenic reaching the soil by irrigation could accumulate in the soil solid phase, could be released to the deep or surface waterbodies, could be metabolized and possibly volatilized by microorganisms, and could be taken up by crops from the soil–water system. Among different crops, rice is particularly subjected to arsenic accumulation because of the required great amounts of irrigation water, potentially arsenic-polluted in this country, and the submerged cropping conditions that enhance the release of the arsenic accumulated in soils to the pore water, which can reach concentrations higher than those of the irrigation water itself (Garnier *et al*., 2010). In Bangladesh, rice cultivation represent one of the main arsenic inputs from groundwater to the soil–crop system (Brammer and Ravenscroft, 2009). Moreover, beside rice, different crops and vegetables grown in arsenic-affected areas, often in rotation with rice, can also accumulate high arsenic concentrations (e.g., arum), contributing to arsenic dietary intake (Huq *et al*., 2005; Smith *et al*., 2006). In the soil, the quantity and nature of adsorbing phases, mainly iron (Fe) and aluminum (Al) oxides, pH, redox potential, and presence of competing ligands play the most important role (Violante *et al*., 2011). Physicochemical characteristics of the soils of the Ganges floodplain are seldom directly related to the differences in the adsorbing phases and to the forms in which arsenic is retained (Martin *et al*., 2013). Thus, the differences in arsenic accumulation in soils are not yet completely explained and a prediction of arsenic fate in the contaminated sites is still difficult.

Although it is undoubtedly important to know the total concentrations of Arsenic in soils and sediments, these concentrations do not give any information about the solid-phase partitioning and potential mobility of arsenic within the soils. Arsenic is bound up in various fractions of soils. Some of it may be easily released and go into solution rendering it available to plants, while others are tightly bound or are fixed within the clay lattices. This is particularly important for arsenic, which in many areas is in too low abundance or is associated with such fine-grained solid phases that characterization by standard mineralogical techniques is extremely difficult or time-consuming. The pathways of arsenic from soil and sediment to water, plants and animals depend on the solid-phase partitioning of the arsenic. In order to be able to properly understand the global distribution of arsenic in soils and sediments and its pathways to water, plants and animals, it is vitally important to be able to collect accurate and precise total and solid-phase partitioning data for arsenic at high and low concentrations. Methods for determination of arsenic compounds are more diverse than those applied for other elements. Among them, there are methods applied for the analysis of phosphorus, an element similar to arsenic, and for the compounds of metals as well. Analysis of the arsenic content is more laborious. The use of flame atomic absorption spectrophotometry is almost impossible because of its low sensitivity. Electrothermal atomization of a sample makes its analysis more complicated. All these circumstances testify for the necessity of methodological and research works oriented to the study of the fractional composition of arsenic compounds in soils. A relatively simple and well-adopted method to assess trace element pools of differential relative lability in soils is the sequential extraction procedure (SEP) with reagents of increasing dissolution strength. It has also been shown that plant uptake or toxicity can be related to specific fractions of SEPs (Chlopecka and Adriano, 1996; Woolson *et al*., 1971). Thus, understanding the relation between arsenic toxicity and its solid-phase partitioning is important.

Arsenic (As) is toxic whereas phosphorus (P) is essential for plants. They are both Group VA elements and thus have similar electron configurations and chemical properties. In soil, therefore, arsenate and phosphate will compete with each other for soil sorption sites, resulting in a reduction in their sorption by soil and an increase in solution concentrations (Livesey and Huang, 1981; Manning and Goldberg, 1996; Smith *et al*., 2002). Similarly, it may be difficult for plants to distinguish between arsenate and phosphate. Thus uptake of arsenate and phosphate by plants is very likely to be competitive. Furthermore, after entering a plant, arsenate may replace phosphate in ATP synthesis, and/or in various phosphorolysis reactions, thus interfering with phosphate metabolisms and causing toxicity to a plant (Dixon, 1997). In contrast, phosphate may be able to alleviate arsenate toxicity by improving phosphate nutrition (Sneller *et al*., 1999). Tu and Ma (2003) reported that phosphate application may be an important strategy for efficient use to phytoremediate arsenic contaminated soils. However, further study is needed on the mechanisms of interactive effects of arsenate and other anions e.g. phosphate and sulphate. Thus, in the present investigation, phosphate and sulphate were chosen as desorptive solutions because they are common soil nutrients. Such an understanding is necessary to provide the much needed information on the mobility, persistence, and fate of arsenic in the environment through phytoremediation or to adopt appropriate chemical remediation or both.

Keeping the issues discussed above in the backdrop, the present study aims at understanding the different fractions of arsenic in some selected soils to find out the kinetics of arsenic desorption in the contaminated soil, interaction with different anions under different concentration levels at different ages in comparison with uncontaminated soils of Bangladesh. The specific objectives of the present study are,

a. To find out the solid-phase partitioning of arsenic in the soils, Sequential Extraction Procedure (SEP) on some selected arsenic contaminated agricultural soil samples and an uncontaminated soil sample will be performed.
b. To perform sequential extraction procedure on the same soil samples spiked with different concentrations of anions (phosphate and sulphate).
c. To study the effect of sequence of adding anions and the effect of aging on the arsenic fraction extracted in SEP.
d. To identify the mobilizable and non-mobilizable species of arsenic in soil samples to help adopting appropriate remediation measures.

# Chapter 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

Arsenic (As) exists widely in soil and groundwater environment, which is of increasing concern for its human toxicity. In recent decades, accidents involving arsenic contamination have occurred frequently worldwide and been recognized as a public health risk. In Bangladesh, the farmlands have been traditionally irrigated with arsenic-contaminated water and the concentration in rice grain harvested was 10-fold higher than the normal level (0.2 mg $kg^{-1}$) (Meharg and Rahman, 2003). Arsenic is mobilised in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. The mobility, the bioavailability, and the toxicity of arsenic in soil environments may be greatly affected by the nature of soil components, pH, presence of anions ($PO_4^{3-}$), and residence time. Most environmental arsenic problems are the result of mobilisation under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels and through the use of arsenic in pesticides, herbicides, crop desiccants and as an additive to animal feed. Although the use of arsenical products such as weed-killers and wood preservatives has decreased significantly in the last few years, their impact on the environment at least locally, is likely to remain for some years.

Resultant health problems were first identified in West Bengal in the late 1980s although the first confirmation in Bangladesh was not made until 1993. Around 6 million in West Bengal are believed to be at risk from drinking water with >50 μg $L^{-1}$ arsenic. Around 5000 patients have been identified with arsenic-related health problems in West Bengal (including skin pigmentation changes) and at least 6000–7000 in Bangladesh (Acharyya *et al*., 2000).

## 2.2 PHYSICAL PROPERTIES OF ARSENIC

Arsenic ranks twentieth in crystal abundance and is found in natural reservoirs. Although some forms of arsenic are metal-like, it is best classified as non-metal (Encyclopedia Britannica, 1994). Arsenic is a steel-gray, brittle, crystalline metalloid with three allotropic forms that are yellow, black and gray. It belongs to nitrogen family (group VA of the periodic table) and closely resembles to phosphorus chemically. Pure arsenic is usually found in the environment combined with other elements such as oxygen, sulphur and iron. Arsenic may be found in organic form when it is combined with carbon and hydrogen. Arsenic compounds compete with their phosphorus analogs for chemical binding sites. It is widely distributed in nature, and occasionally found un-combined, usually in association with such metals as antimony and silver. Arsenic bonds covalently with most nonmetals and metals and forms stable organic compounds in both its trivalent and pentavalent states. Arsenic and arsenical compounds are extremely toxic.

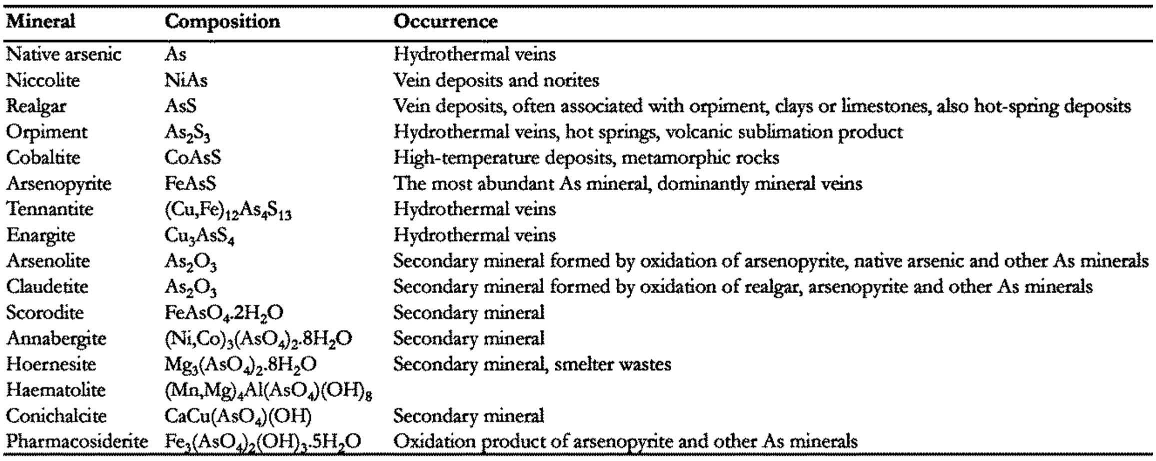
## 2.3 SOURCES OF ARSENIC

### 2.3.1 Arsenic Minerals

Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common arsenic minerals is given in Table 2.1. Most are ore minerals and their alteration products. The greatest concentrations of these minerals, therefore, occur in mineralised areas and are commonly found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most widespread arsenic ore mineral is arsenopyrite, FeAsS. It is generally assumed that arsenopyrite, together with the other dominant arsenic-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust, although there is currently some debate about whether arsenopyrite can form at low temperatures as an authigenic mineral.

Though not a major component, arsenic is also often present in varying concentrations in other common rock forming minerals. As the chemistry of arsenic follows closely that of Sulphur, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Arsenian pyrite is a relatively common mineral especially in ore bodies. Arsenic is also present in the crystal structure of many sulphide minerals as a substitute for sulphur.

Table 2.1. Major Arsenic Minerals Occurring in Nature (BGS and DPHE, 2001).



| Mineral | Composition | Occurrence |
|---|---|---|
| Native arsenic | As | Hydrothermal veins |
| Niccolite | NiAs | Vein deposits and norites |
| Realgar | AsS | Vein deposits, often associated with orpiment, clays or limestones, also hot-spring deposits |
| Orpiment | $As_2S_3$ | Hydrothermal veins, hot springs, volcanic sublimation product |
| Cobaltite | CoAsS | High-temperature deposits, metamorphic rocks |
| Arsenopyrite | FeAsS | The most abundant As mineral, dominantly mineral veins |
| Tennantite | $(Cu,Fe)_{12}As_4S_{13}$ | Hydrothermal veins |
| Enargite | $Cu_3AsS_4$ | Hydrothermal veins |
| Arsenolite | $As_2O_3$ | Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals |
| Claudetite | $As_2O_3$ | Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals |
| Scorodite | $FeAsO_4.2H_2O$ | Secondary mineral |
| Annabergite | $(Ni,Co)_3(AsO_4)_2.8H_2O$ | Secondary mineral |
| Hoernesite | $Mg_3(AsO_4)_2.8H_2O$ | Secondary mineral, smelter wastes |
| Haematolite | $(Mn,Mg)_4Al(AsO_4)(OH)_8$ | |
| Conichalcite | $CaCu(AsO_4)(OH)$ | Secondary mineral |
| Pharmacosiderite | $Fe_3(AsO_4)_2(OH)_3.5H_2O$ | Oxidation product of arsenopyrite and other As minerals |

Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions (authigenic pyrite). Authigenic pyrite plays a very important role in present day geochemical cycles. It is present in the sediments of many rivers, lakes and the oceans as well as in many aquifers. Pyrite commonly forms preferentially in zones of intense reduction such as around buried plant roots or other nuclei of decomposing organic matter. It is often present as framboidal grains.

Arsenic concentrations in phosphate minerals are variable but can also reach high values. However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic concentrations of most sediments. Arsenic can also substitute for $Si^{4+}$, $Al^{3+}$, $Fe^{3+}$ and $Ti^{4+}$ in many mineral structures and is therefore present in many other rock-forming minerals, albeit at much lower concentrations.

### 2.3.2 Arsenic in Rocks, Sediments and Soils

Arsenic is associated with igneous and sedimentary rocks, particularly with sulfidic ores. Natural phenomena such as weathering, biological activity and volcanic activity, together with anthropogenic inputs are responsible for the emission of arsenic into the atmosphere, from where it is redistributed on the earth's surface by rain and dry fallout. Even crustal levels, which are often quoted as 3 mg kg$^{-1}$, display values from 0.1 to several hundred ppm, depending on the types of rocks being considered (Cullen and Reimer, 1989). The natural content of arsenic in soils is usually 5 mg kg$^{-1}$ (Backer and Chesnin, 1975) to 6 mg kg$^{-1}$ (Bowen, 1979).

The presence of arsenic in igneous, metamorphic and sedimentary rocks generally results in its presence of in the water phase. In Table 2.2, arsenic concentrations in different rocks are presented. Arsenic concentrate in some minerals, for instance, arsenic readily substitutes Silicon, Iron(III) and Aluminum in crystal lattices of silicate minerals (Onishi and Sandell, 1955). Concentrations of arsenic tends to be high in volcanic glass, aluminisilicate minerals and igneous rocks containing iron oxide. Sedimentary rocks generally contain higher concentration of arsenic than igneous and metamorphic rocks.

Table 2.2 Typical Arsenic Concentrations in Rocks, Sediments, Soils and Other Surficial Deposits (BGS and DPHE, 2001).

| Rock/sediment type | As conc. average (range) (mg kg$^{-1}$) | Rock/sediment type | As conc. average (range) (mg kg$^{-1}$) |
|---|---|---|---|
| Igneous rocks: | | Unconsolidated sediments: | |
| Ultrabasic rocks (peridotite, dunite, kimberlite etc) | 1.5 (0.03–15.8) | Various | 3 (0.6–50) |
| Basic rocks (basalt) | 2.3 (0.18–113) | Alluvial sand (Bangladesh) | 2.9 (1.0–6.2) |
| Basic rocks (gabbro, dolerite) | 1.5 (0.06–28) | Alluvial mud/clay (Bangladesh) | 6.5 (2.7–14.7) |
| Intermediate (andesite, trachyte, latite) | 2.7 (0.5–5.8) | River bed sediments (Bangladesh) | 1.2–5.9 |
| Intermediate (diorite, granodiorite, syenite) | 1.0 (0.09–13.4) | Lake sediments, Lake Superior | 2.0 (0.5–8.0) |
| Acidic rocks (rhyolite) | 4.3 (3.2–5.4) | Lake sediments, British Colombia | 5.5 (0.9–44) |
| Acidic rocks (granite, aplite) | 1.3 (0.2–15) | Glacial till, British Colombia | 9.2 (1.9–170) |
| Acidic rocks (pitchstone) | 1.7 (0.5–3.3) | World average river sediments | 5 |
| Volcanic glasses | 5.9 (2.2–12.2) | Stream and lake silt (Canada) | 6 (<1–72) |
| Metamorphic rocks: | | Loess silts, Argentina | 3–18 |
| Quartzite | 5.5 (2.2–7.6) | Continental margin sediments (argillaceous, some anoxic) | 2.3–8.2 |
| Hornfels | 5.5 (0.7–11) | | |
| Phyllite/slate | 18 (0.5–143) | Soils: | |
| Schist/gneiss | 1.1 (<0.1–18.5) | Various | 7.2 (0.1–55) |
| Amphibolite and greenstone | 6.3 (0.4–45) | Peaty and bog soils | 13 (2–36) |
| Sedimentary rocks: | | Acid sulphate soils (Vietnam) | 6–41 |
| Marine shale/mudstone | 3–490 | Acid sulphate soils (Canada) | 1.5–45 |
| Shale (Mid-Atlantic Ridge) | 174 (48–361) | Soils near sulphide deposits | 126 (2–8000) |
| Non-marine shale/mudstone | 3.0–12 | Contaminated surficial deposits: | |
| Sandstone | 4.1 (0.6–120) | Mining-contaminated lake sediment, British Colombia | 342 (80–1104) |
| Limestone/dolomite | 2.6 (0.1–20.1) | Mining-contaminated reservoir sediment, Montana | 100–800 |
| Phosphorite | 21 (0.4–188) | Mine tailings, British Colombia | 903 (396–2000) |
| Iron formations and Fe-rich sediment | 1–2900 | Soils and tailings-contaminated soil, UK | 120–52,600 |
| Evaporites (gypsum/anhydrite) | 3.5 (0.1–10) | Tailings-contaminated soil, Montana | up to 1100 |
| Coals | 0.3–35,000 | Industrially polluted inter-tidal sediments, USA | 0.38–1260 |
| Bituminous shale (Kupferschiefer, Germany) | 100–900 | Soils below chemicals factory, USA | 1.3–4770 |
| | | Sewage sludge | 9.8 (2.4–39.6) |

Arsenic occurrence and distribution is mostly based on the result of dissolved arsenic concentration in ground water. Weathering of rocks converts arsenic sulphide to arsenic trioxide, which enters as dust or by dissolution in rain, rivers or groundwater (Clifford and Zhang, 1994). Volatile forms of arsenic e.g., arsine ($AsH_3$) and trimethyl arsine [$(CH_3)_3As$)] enter the atmosphere from land and water, are returned by rain and atmospheric fallout. The oxidized forms of arsenic are converted back to sulphides by anaerobic processes occurring on land and water sediments (Tamaki and Frankenberger, 1992).

Arsenic is found in natural reservoirs, such as ocean, soil and atmosphere. The concentration of arsenic in natural reservoirs showed that more than 99% of the total arsenic in the environment is present in rocks (Table 2.2). The high concentration of arsenic in rocks result from the ease with which arsenic substitutes for Si, Al, or Fe in lattices of silicate minerals (Onishi and Sandell, 1955). Arsenic concentration in rock type, with sedimentary rocks containing much higher concentrations of arsenic than igneous or metamorphic rocks. The average concentrations of arsenic in igneous, limestone, sandstone and shale are 1.5, 26, 4.1, and 14.5 mg kg$^{-1}$. respectively. However, concentrations in shales can ranges from 0.3 to 250 mg kg$^{-1}$ (Colbourn *et al.,* 1975).

Soils and oceans are the remaining major reservoirs that have much more inherent arsenic than do biota (pants, animals, man and microbes) and the atmosphere. The average concentration of arsenic in soils of world is 7.2 mg kg$^{-1}$. However, the total amounts of arsenic in reservoirs are much smaller in soils than in rocks, due to the difference in abundance of arsenic in soils and rocks.

According to Chilvers and Peterson (1987), volcanic activity and low temperature volatilization (biological methylation) are the two dominant natural sources. From their studies, it appeared that nearly 60% of the total natural flux comes from low temperature volatilization and the remainder from volcanoes. They found a low temperature volatilization to be 26200 tons As/yr, with volcanoes, on average contributing 17150 tons As/yr and arsenic emissions from natural sources of 45480 tons As/yr.

Although the dominant source of arsenic in soils is geological, additional inputs may be derived locally from industrial sources such as smelting and fossil-fuel combustion products and agricultural sources such as pesticides and phosphate fertilizers. Ure and Berrow (1982) quoted concentrations in the range 366–732 mg kg$^{-1}$ in orchard soils as a result of the historical application of arsenical pesticides to fruit crops. Continued irrigation of crops with arsenic-rich groundwater could also significantly enhance the arsenic concentration in the soil since much of the added arsenic can be expected to be retained in the soil layer.

### 2.3.3 Arsenic in Atmosphere

There is little evidence to suggest that atmospheric arsenic poses a real health threat for drinking-water sources. Atmospheric arsenic arising from coal burning has been postulated as a major cause of lung cancer in parts of China (Guizhou Province), but the threat is from direct inhalation of domestic coal-fire smoke together with the consumption of food, especially chillis dried over coal fires, rather than from drinking water affected by atmospheric inputs of arsenic. Arsine gas ($AsH_3$), like methane, would be expected to be released from strongly reducing soils. Mixing arsenic rich sludge material from small-scale arsenic removal plants with cow dung has been advocated as one way of dealing with the contaminated sludge. This procedure relies on the strongly reducing conditions created by the dung promoting the reduction of the arsenic and its loss to the atmosphere as arsine gas (BGS and DPHE, 2001).

### 2.3.4 Arsenic in Natural Water

As with most trace metals, the concentration of arsenic in natural waters is probably normally controlled by some form of solid-solution interaction. Knowing the types of interaction involved is important because this will govern the response of arsenic to changes in water chemistry. The importance of oxides in controlling the concentration of arsenic in natural waters has been appreciated for a long time (Korte, 1991; Korte and Fernando, 1991; Livesey and Huang, 1981; Matisoff *et al.,* 1982). Clays can also adsorb As(III) and As(V) (Manning and Goldberg, 1997). Frequently, one of the best correlations between the concentration of arsenic in sediments and other elements is with iron. This is also the basis for the use of iron , aluminium and manganese salts in water treatment, including for arsenic removal (Edwards, 1994). The arsenic content of residual sludges can be in the range 1,000–10,000 mg/kg (Driehaus *et al.,* 1998; Forstner and Haase, 1998). Arsenic adsorption onto iron oxides has been quite extensively studied and the data for hydrous ferric oxide in particular has been well documented (Dzombak and Morel, 1990). The extent of adsorption is strongly dependent on the arsenic speciation (and hence redox status), arsenic concentration, pH and the concentration of competing anions such as phosphate. The shapes of the As(III) and As(V) isotherms are very different reflecting the weak electrostatic contribution in the case of

As(III) and the strong electrostatic contribution in the case of As(V). The As(III) isotherm resembles a Langmuir isotherm with a near-linear isotherm at low arsenic concentrations and a maximum adsorption at high concentrations. The As(V) isotherm like phosphate is strongly nonlinear which means that As(V) loadings can be high even at very low solution arsenic concentrations. As(III) sorption is practically independent of pH over the range of pH of interest in groundwaters (pH 6–9) whereas As(V) sorption declines rapidly above pH 8.5 or so. Therefore while As(V) is much more strongly bound at low pH, at about pH 8–9 or above, As(III) binding can be greater than As(V) binding under similar conditions. This rapid decline in As(V) adsorption therefore occurs in a pH range that is found in groundwaters and is one factor that can lead to high arsenic groundwater. Groundwater invariably contain a range of other anions at concentrations exceeding that of arsenic and these can be expected to compete for binding sites. The most relevant are phosphate, silicate, bicarbonate and dissolved organic carbon. All of these can be high in arsenic-rich groundwaters and it can be difficult to differentiate 'cause' from 'effect'. The specific adsorption of positively charged $Ca^{2+}$ and $Mg^{2+}$ will tend to enhance the adsorption of As(V) thereby tending to counteract the some of the effects of anion competition. In reducing groundwater, $Fe^{2+}$ may also be important. These competitive interactions can have an important influence on the shape of the arsenic adsorption isotherms and hence on the partitioning and transport of arsenic in groundwater environments. For example, if the oxide surface is dominated by adsorbed phosphate (which is quite likely in many natural environments), then this phosphate will effectively control the electrostatic potential of the surface not the adsorbed As(V). This means that additional As(V) sorption will have little influence on the electrostatics and will lead to an adsorption isotherm that is more like a Langmuir isotherm than a Freundlich isotherm. In effect, the excess phosphate reduces the high loadings expected in low As(V), low phosphate systems. Interactions such as these could therefore play an important role in controlling the mobility of arsenic in natural waters. Korte (1991) speculated some time ago that desorption of arsenic from iron oxides could occur in reducing, alluvial sediments and that this could lead to high-arsenic groundwaters. He anticipated that this could be quite widespread but suggested that it would be most important in small, low yielding alluvial aquifers of local significance (Korte, 1991; Korte and Fernando, 1991) whereas it has in fact turned out to be most problematic in large, productive deltaic aquifers such as those of the Bengal Basin.

## 2.4 ARSENIC CONTAMINATION AROUND THE WORLD

A number of large aquifers in various parts of the world have been identified with problems from arsenic occurring at concentrations above 50 µg/l, often significantly so. The most noteworthy occurrences are in parts of West Bengal and Bangladesh, Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of the USA but particularly the south-west (Figure 2.1). Occurrences of mining related arsenic problems have also been recorded in many parts of the world, including Thailand, Ghana, Greece, Austria and parts of the USA (Figure 2.1). High arsenic groundwater do not usually appear to be directly related to areas of high arsenic concentrations in the source rocks. This is because of the high solid/solution ratio in aquifers and the low drinking water limits of arsenic – even a rock containing 1 mg kg$^{-1}$ arsenic would produce a groundwater with a concentration of some 3–10 mg L$^{-1}$ arsenic if all of the arsenic were to dissolve. Therefore only a small fraction of the arsenic needs to dissolve to produce a relatively high arsenic groundwater. Distinctive groundwater arsenic problems occur under both reducing and oxidizing groundwater conditions; also in both 'wet' and 'arid' environments. Below we discuss the characteristics of the arsenic problems worldwide through a series of type examples. These examples have been ordered according to the type of environment under which they are developed.

### 2.4.1 Contamination in Reducing Environments

#### 2.4.1.1 Bangladesh and West Bengal

In terms of the population exposed, Arsenic problems in groundwater from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. Concentrations in groundwater from the affected areas have a very large range from <0.5 µg L$^{-1}$ to ca. 3200 µg L$^{-1}$. As with Bangladesh, the affected aquifers in West Bengal are generally shallow (less than 100–150 m deep), of Holocene age and comprise a mixed sequence of micaceous sands, silts and clays deposited by the rivers Ganges and Hoogli and their

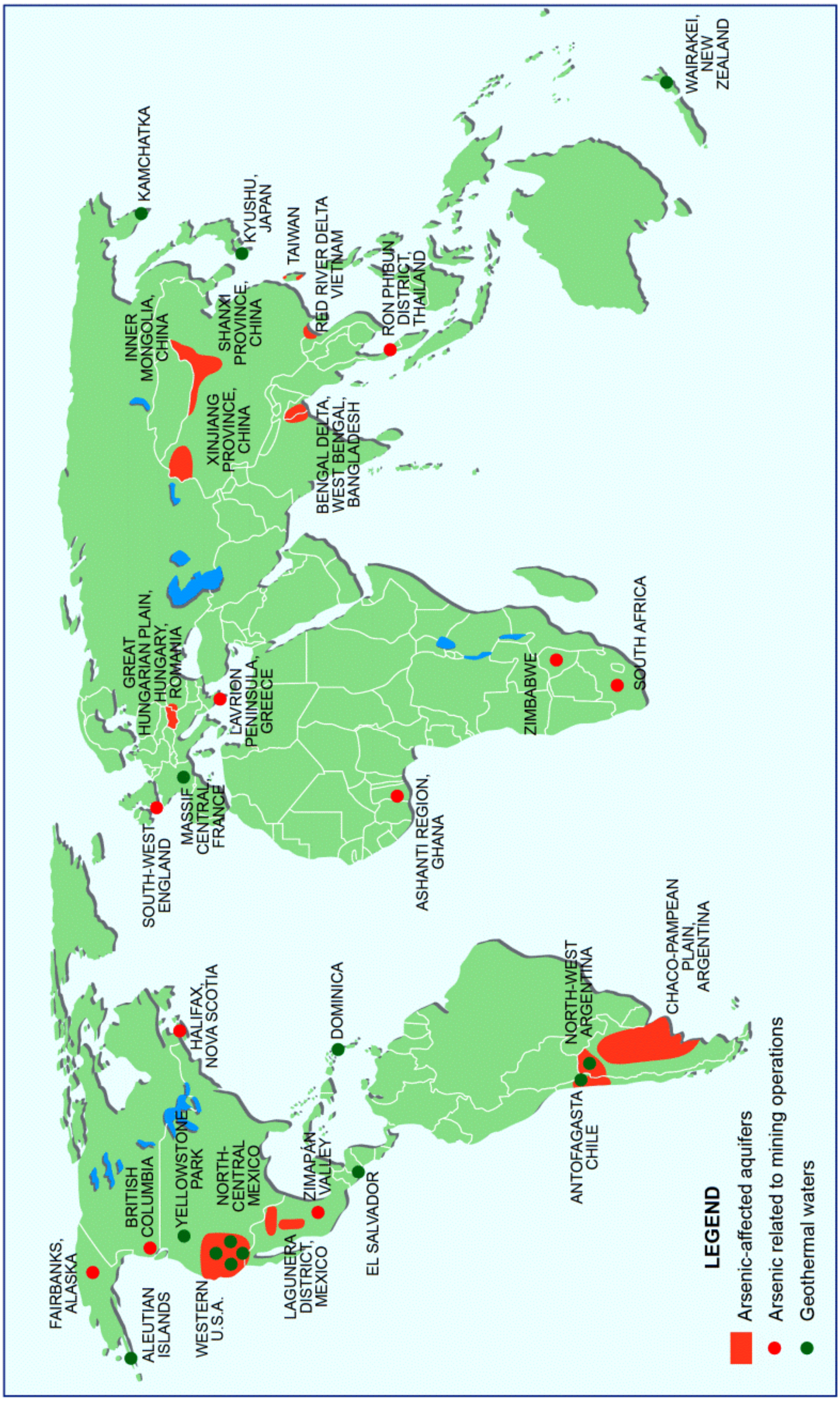


Fig. 2.1 Documented cases of arsenic problems in groundwater related to natural contamination. Cases include some of the major mining and geothermal occurrences reported in the literature (BGS and DPHE, 2001).

tributaries. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. In most affected areas, the sediment sequence is capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. This, together with an abundance of recent solid organic matter deposited with the sediments, has resulted in the development of highly reducing aquifer conditions and dominance of arsenic in solution as As(III). As with Bangladesh, deeper groundwaters from the sediment sequence in West Bengal (>100–150 m depth, probably of Pleistocene age) have generally low arsenic concentrations (<10 $\mu g\ L^{-1}$). As with Bangladesh, the regional distribution of the high-arsenic waters in West Bengal is known to be extremely patchy (AIP Steering Committee, 1991; CSME, 1997), presumably in part because of great variation in sedimentary characteristics and variations in abstraction depth. Estimates of the proportions of tubewells affected in West Bengal are not well-documented and difficult to assess. However, the indications are that the degree of contamination is not as severe in West Bengal as in the worst affected districts of Bangladesh (Dhar *et al.,* 1997). Certainly, the overall areal extent of contamination in West Bengal is less than in Bangladesh.

A map of ground water contamination by arsenic is shown in Fig. 2.2 (BGS and DPHE 2001). The worst-affected districts in Bangladesh are (percentage of sampled wells with greater than 50 $\mu g\ L^{-1}$ in parentheses): Chandpur (90%), Munshiganj (83%), Gopalganj (79%), Madaripur (69%), Noakhali (69%), Satkhira (67%), Comilla (65%), Faridpur (65%), Shariatpur (65%), Meherpur (60%), Bagerhat (60%) and Lakshmipur (56%). Percentages are the percentage of all wells sampled. The least-affected districts were: Thakurgaon, Barguna, Jaipurhat, Lalmonirhat, Natore, Nilphamari, Panchagarh, Patuakhali (all 0%), Rangpur (1 %), Dinajpur (2%), Naogaon (2%), Gazipur (2%), Cox's Bazar (2%), Bhola (4%), Nawabganj (4%), Jhalakati (6%), Rajshahi (6%), Gaibandha (7%), Tangail (9%) and Kurigram (9%). Again, percentages are the percentage of all wells sampled. Even in areas of generally low arsenic concentrations, there are occasionally 'hot spots' where a cluster of wells with unusually high concentrations of arsenic are found. Such hot spots are most noticeable in northern Bangladesh. The Chapai Nawabganj hot spot in north western Bangladesh was estimated to be about 5 km by 3 km in extent.

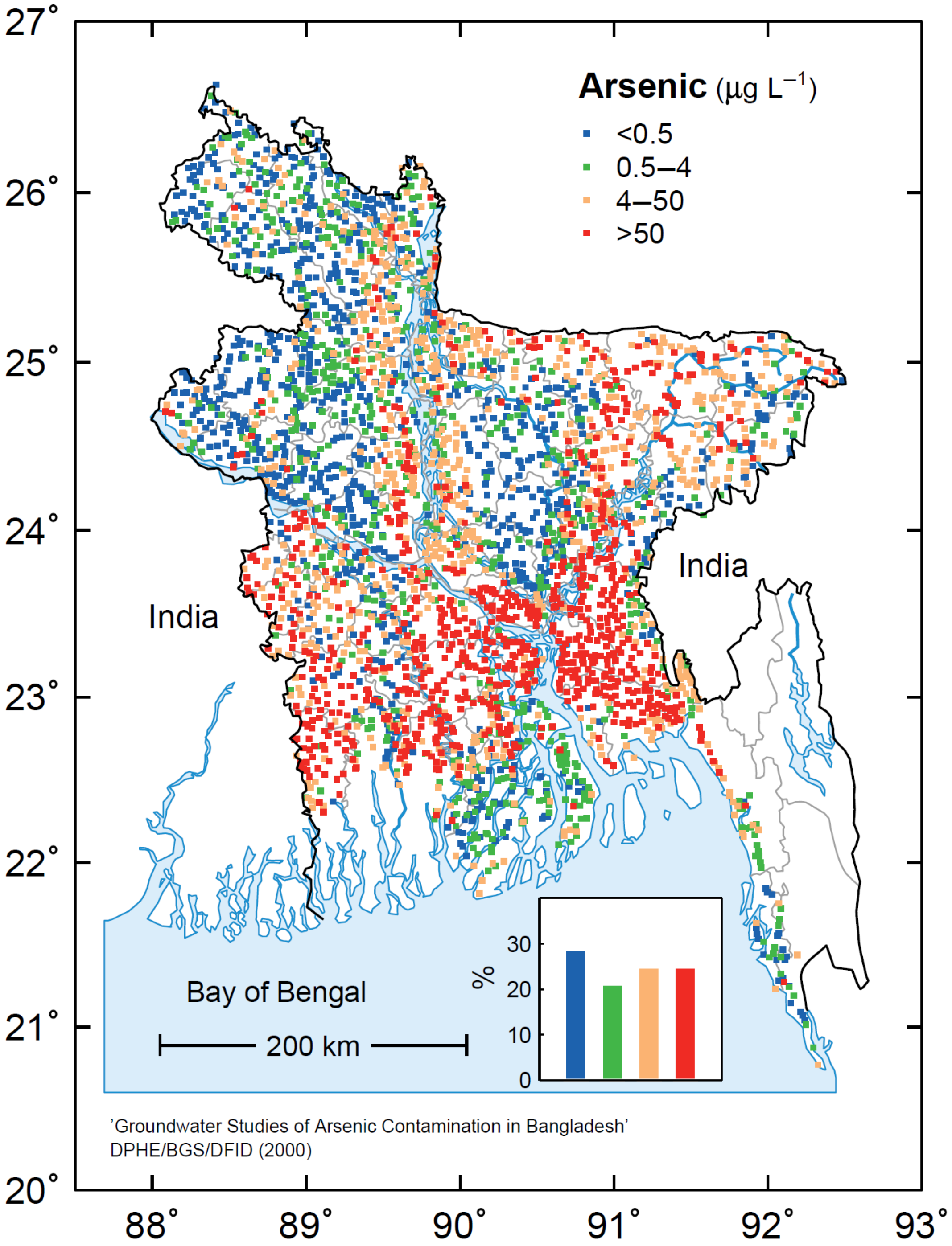


Fig. 2.2 Distribution of Arsenic in the Groundwater of Bangladesh (BGS-DPHE 2001).

#### 2.4.1.2 Other Places Around the World with Reducing Environment

Apart from Bangladesh and West Bengal, arsenic affected places in reducing environment are also found in Taiwan, Vietnam, Northern China, Hungary and Romania etc.

In Taiwan, high arsenic concentrations are found in deep artesian well waters abstracted from sediments which include fine sands, muds and black shale (Tseng *et al.,* 1968). The groundwater are therefore likely to be strongly reducing and hence may be analogous to groundwater in the affected areas of Bangladesh and West Bengal. This is supported by the observation that the arsenic is present largely as As(III) (Chen *et al.,* 1994). However, the hydro-geochemistry of the area is poorly understood in detail. Groundwater from shallow wells in the area has low arsenic concentrations (Guo *et al.,* 1994).

Little was known about the arsenic concentrations in groundwater in Vietnam until recently. UNICEF and EAWAG/CEC (Hanoi National University) are now carrying out extensive investigations to assess the scale of the problem. Preliminary results from Hanoi (Berg *et al.,* 2000; Wegelin *et al.,* 2000) indicate that there is a significant arsenic problem in shallow tubewells in the city, particularly in the south. There appears to be a seasonal pattern with significantly higher concentrations in the rainy season. This could be related to the local hydrology since there are significant interactions between the aquifer and the adjacent Red River. Little is known about the arsenic concentrations in groundwater from the middle and upper parts of the Mekong delta (and into adjacent Cambodia and Laos) and other smaller alluvial aquifers in Vietnam but investigations are presently taking place.

Arsenic occurrence has been found at high concentrations (in excess of the Chinese national standard of 50 $\mu g\ L^{-1}$) in groundwater from Inner Mongolia as well as Xinjiang and Shanxi Provinces (Figure 2.1) (Niu *et al.*, 1997; Wang, 1984; Wang and Huang, 1994). The first cases of arsenic poisoning were recognised in Xinjiang Province in the early 1980s. Wang (1984) found arsenic concentrations in groundwaters from the province at up to 1200 $\mu g\ L^{-1}$. Wang and Huang (1994) reported arsenic concentrations in between 40 $\mu g\ L^{-1}$ and 750 $\mu g\ L^{-1}$ in deep artesian groundwater from the Dzungaria Basin on the north side of the Tianshan Mountains (stretch of ca. 250 km). Arsenic concentrations in artesian groundwater from deep boreholes (up to 660 m) were found to increase with depth. Shallow (non-artesian) groundwaters had observed arsenic concentrations between <10 μg $L^{-1}$ and 68 μg $L^{-1}$. The concentration of arsenic in the saline Aibi Lake was reported as 175 μg $L^{-1}$, while local rivers had concentrations between 10 μg $L^{-1}$ and 30 μg $L^{-1}$. Artesian groundwater has been used for drinking in the region since the 1960s and chronic health problems have been identified as a result (Wang and Huang 1994).

Concentrations of arsenic above 50 μg $L^{-1}$ have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain and in parts of neighbouring Romania (Figure 2.1). Concentrations up to 150 μg $L^{-1}$ (average 32 μg $L^{-1}$, n=85) have been recorded by Varsányi *et al*. (1991). The Great Hungarian Plain, some 110,000 $km^2$ in area, consists of a thick sequence of subsiding Quaternary sediments. Groundwater vary from Ca-Mg-$HCO_3$-type in the recharge areas of the basin margins to Na-$HCO_3$-type in the low-lying discharge regions. groundwater in deep parts of the basin (80–560 m depth) with high arsenic concentrations are reducing with high concentrations of Fe and $NH_4$ and many have reported high concentrations of humic acid (up to 20 mg $L^{-1}$; Varsányi *et al*., 1991). The groundwater have highest arsenic concentrations in the lowest parts of the basin, where the sediment is fine grained.

### 2.4.2 Contamination in Arid Oxidizing Environment

Arsenic contamination in arid oxidizing environment is observed in many places including Mexico, Chile and Argentina. The Lagunera Region of north central Mexico has a well-documented groundwater arsenic problem with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwater from the region are predominantly oxidizing with neutral to high pH. Del Razo *et al*. (1990) quoted pH values for groundwater in the range 6.3 to 8.9. They found arsenic concentrations in the range 8 μg $L^{-1}$ to 624 μg $L^{-1}$ (average 100 μg $L^{-1}$, n=128), with half the samples having concentrations greater than 50 μg $L^{-1}$. They also noted that most (>90%) of the groundwater samples investigated had arsenic present predominantly as As(V). Del Razo *et al*. (1994) determined the average concentration of arsenic in drinking water from Santa Ana town in the region as 404 µg $L^{-1}$.

High arsenic concentrations have been recorded in surface waters and groundwaters from Administrative Region II (incorporating the cities of Antofagasta, Calama and Tocopilla) of northern Chile (Cáceres *et al*., 1992). The region is arid (Atacama Desert) and water resources are limited. High arsenic concentrations are accompanied by high salinity (due to evaporation) and high B concentrations. Arsenic values below 100 µg $L^{-1}$ in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 µg $L^{-1}$ have been found. Karcher *et al*. (1999) quoted ranges of 100 µg $L^{-1}$ to 1000 µg $L^{-1}$ in raw waters (average 440 µg $L^{-1}$). The arsenic is present in the waters mostly as arsenate.

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-arsenic groundwater known, covering around 1 million $km^2$. High concentrations of arsenic have been documented from Córdoba, La Pampa, Santa Fe and Buenos Aires Provinces in particular. The climate is temperate with increasing aridity towards the west. Groundwater are derived from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli *et al*., 1989; Smedley *et al*., 1998, 2002). The sediments display abundant evidence of post-depositional diagenetic changes under semi-arid conditions, with common occurrences of calcrete in the form of cements, nodules and discrete layers, sometimes many centimeters thick.

### 2.4.3 Arsenic Contamination in Mixed Oxidizing and Reducing Environments

Many areas have been identified in the USA with arsenic problems in groundwater (Welch *et al*., 2000). Most of the worst-affected and best-documented cases occur in the south-western states (Nevada, California, Arizona). However, within the last decade, parts of Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin have been found with concentrations of arsenic exceeding 10 µg $L^{-1}$ and smaller areas of high arsenic groundwater have been found in many other States. The arsenic is thought to derive from various sources, including natural dissolution/desorption reactions, geothermal water and mining activity. The natural occurrences of arsenic in groundwater are found under both reducing and oxidizing conditions in different areas.

### 2.4.4 Arsenic Contamination from Geo-thermal Sources

Arsenic associated with geothermal waters has been reported in several areas, including hot springs from parts of the USA, Japan, Chile, Kamchatka, New Zealand, France and Dominica (Criaud and Fouillac, 1989; Welch *et al.*, 1988). In the USA, occurrences of arsenic linked to geothermal sources have been summarized by Welch *et al.* (1988). Reported occurrences include Honey Lake Basin, California (As up to 2600 µg $L^{-1}$), Coso Hot Springs, California (up to 7500 µg L–1), Imperial Valley, California (up to 15,000 µg $L^{-1}$), Long Valley, California (up to 2500 µg $L^{-1}$) and Steamboat Springs, Nevada (up to 2700 µg $L^{-1}$). Geothermal waters in Yellowstone National Park also contain arsenic (<1–7800 µg $L^{-1}$ in geysers and hot springs) and have given rise to high concentrations (up to 370 µg $L^{-1}$) in waters of the Madison River (Nimick *et al.*, 1998). Geothermal inputs from Long Valley, California are believed to be responsible for high concentrations (20 µg $L^{-1}$) of arsenic in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie and Hering, 1998). Geothermal waters from Kyushu, Japan have been found to have arsenic concentrations in the range 500–4600 µg $L^{-1}$ (26 samples). The waters are typically of Na-Cl type and the arsenic is present almost entirely present as As(III) (Yokoyama *et al.*, 1993). Elevated arsenic concentrations have been documented in waters from the geothermal areas of New Zealand. Robinson *et al.* (1995) found an arsenic concentration in groundwater from the Wairakei geothermal field of 3800 µg $L^{-1}$ and found river and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei Korako and Atiamuri geothermal fields to have concentrations up to 121 µg $L^{-1}$.

### 2.4.5 Arsenic and Mining Related Problems

Probably the worst recorded case of arsenic poisoning related to mining activity is that of Ron Phibun District in Nakhon Si Thammarat Province of southern Thailand. Health problems were first recognised in the area in 1987. Around 1000 people have been diagnosed with arsenic-related skin disorders, particularly in and close to Ron Phibun town (Williams, 1997). The mobilisation of arsenic is believed to be caused by oxidation of arsenopyrite, exacerbated by the former tin-mining activities. Recent mobilisation in groundwater has occurred during post-mining groundwater rebound (Williams, 1997). In the gold mining areas of Ghana, arsenic mobilises in the local environment as a result of arsenopyrite oxidation, induced (or exacerbated) by the mining activity. Around the town of Obuasi, high arsenic concentrations have been noted in soils close to the mines and treatment works (Amasa 1975; Bowell 1992; 1993). Some high concentrations have also been reported in river waters close to the mining activity (Smedley *et al*., 1996). Arsenic contamination from mining activities has been identified in numerous areas of the USA, many of which have been summarized by Welch *et al*. (1988; 1999). Groundwater from some areas has been reported to have very high arsenic concentrations locally (up to 48,000 µg $L^{-1}$). Some mining areas of the USA have significant problems with acid mine drainage resulting from extensive oxidation of iron sulphides. In these, pH values can to extremely low and iron oxides dissolve and release bound arsenic. Iron Mountain has some extremely acidic mine-drainage waters with negative pHs and arsenic concentrations in the milligram per litre range (Nordstrom *et al*., 2000). Many other areas have increased concentrations of arsenic in soils, sediments and waters as a result of mining activity. Documented cases include the Lavrion region of Greece, associated with lead- and silver-mining activity (Komnitsas *et al*., 1995), the Zimapán Valley of Mexico, parts of southwest England (Thornton and Farago, 1997), South Africa, Zimbabwe and Bowen Island, British Columbia (Boyle *et al*., 1998). Although severe contamination of the environment has often been documented in these areas, the impact on groundwater used for potable supply is usually minor.

## 2.4.6 Anthropogenic Activities

Another source of arsenic in soil is human activities. At least 75% of the global atmospheric arsenic has been reported as anthropogenic and elevated arsenic concentrations in water result from anthropogenic activities (Nordstrom, 1998).

### 2.4.6.1 Coal Combustion

Arsenic can be present in coal mainly as arsenopyrite at concentration from <1 to > 90 mg/kg (Lim, 1979; Swaine, 1977). Bencko and Symon (1977) reported that arsenic concentration in brown coal from Czechosolovakia were as high as 1500 mg/kg.

Arsenic exists in the oxidation state of +3 and +5 and both are volatilized during coal combustion with an enrichment of the smaller particles. Total arsenic in coal combustion by products is extremely variable with little consistency within a single product. Arsenic is present in much larger amounts in fly ash than in bottom ash or flue gas desulfurization (FGD) sludge (Fulekar and Dave, 1985).

On the sources of arsenic contamination is coal fly ashes. During combustion arsenic and other chalcophiles (e.g. Cr, Se, Sr, Mo, and V) in the coal are volatilized and escaped in to the atmosphere which may eventually fallout in the surrounding areas, and can cause surface soil contamination (Boyle and Jonasson, 1973; Block and Dams, 1976; Coles *et .al.,* 1979; Hansen and Fisher, 1980; McElroy *et al.*, 1982). Arsenic is significantly enriched on the fly ash- particle surfaces by condensation during the cooling process following combustion of coal (Keefer and Murarka, 1994). Total chemical analysis of arsenic present in coal combustion by-products by X-ray spectroscopy showed alkaline, neutral and acidic fly ash to have 1871 and 82 mg/kg, respectively; and neutral FGD sludge to have 10 and 15 mg kg$^{-1}$ arsenic, respectively; and alkaline and neutral bottom ash to have 4.7 and <2.6 mg kg$^{-1}$ arsenic, respectively (Mason and Carlile, 1986).

### 2.4.6.2 Insecticides and Pesticides

Lead arsenate and calcium arsenate have been extensively used on cotton, tobacco and fruit crops as insecticides, e.g. sodium arsenite was used as a cotton desiccant (Levander, 1977; Steevans *et al.*, 1972; Tammes and Delint. 1969; Woo, 1965). Organic arsenical have been used as silvicides, herbicides and desiccants (Levander, 1977). Paris Green [$3Cu(AsO_2)_2 . Cu(C_2H_3O_2)$], calcium arsenate and lead arsenate being used as agricultural pesticides. Sodium arsenate is used for weed killer and increases arsenic concentration.

### 2.4.6.3 Feed Additives

Arsenic trioxide is used as a cattle dip which increases arsenic concentration. Arsanillic acid is used as a feed additive which increases arsenic concentration.

### 2.4.6.4 Wood Preservation

Arsenic trioxide is used for wood preservation. Anthropogenic inputs particularly due to the application and use of arsenical wood preservatives (Bhattacharya *et al*., 1998) as well as pesticides could also lead to significant emission of arsenic in ground water, especially under anoxic condition.

### 2.4.6.5 Industrial Burning

Wastes from industries of glass and ceramics cements, pigments, enamels, antifouling paints, iron and steel production, textile and fireworks. Introduction of organic compounds into aquifers from waste disposal and loss of petroleum products also can lead to $Fe(OH)_3$ dissolution and release of arsenic (Welch, 1998).

### 2.4.6.6 Sewage Sludge

Arsenic can be present in sewage sludge. Some researchers have reported concentrations from 3 to 46 mg As/kg in sludge from the United States (Furr *et al*., 1976) and the Netherlands (Haan, 1978). From 4 to 20 mg As/kg was reported in topsoil from a sewage treatment plant in Canada (Temple *et al.,* 1977). Sewage sludges usually contain relatively large amounts of phosphorus from 0.5±0.4% to 1.6±0.3% (Horvath and Koshut 1981) which could ameliorate the ill effects of the arsenic present (Temple *et al.,* 1977).

### 2.4.6.7 Irrigation Purpose

Need of water for domestic as well as irrigation purpose prompted development of groundwater resources. Such overdraft of groundwater could be envisaged as one of the key factors responsible for the spreading of arsenic epidemic in the part of the world. According to some scientists arsenic contamination may also arise from vigorous use of deep tube-well water for irrigation purpose during the draught. However, the extensive study by BGS and DPHE (2001) does not support such hypothesis.

## 2.5 PERMISSIBLE LIMIT VALUE OF ARSENIC

The Standard of arsenic concentration in drinking water varies in different countries of the world. A few typical permissible limits in different places are given below (WHO 2011).

| | | |
|---|---|---|
| European Union | - | 10 μg/l |
| Canada | - | 25 μg/l |
| Bangladesh | - | 50 μg/l |
| WHO | - | 10 μg/l |

## 2.6 CHEMISTRY OF ARSENIC

### 2.6.1 Forms of Arsenic

Arsenic is found in soil both in organic and inorganic forms. Arsenic joins with oxygen, chlorine and sulphur to make inorganic arsenic compounds. Inorganic arsenic species in contaminated industrial sites exist in the arsenate (oxidation form = V), arsenite (oxidation form = III), arsenic sulfide ($HAsS_2$), elemental arsenic (As) and arsine (oxidation form = III) gas ($AsH_3$) forms. Arsenate forms include $H_3AsO_4$, $H_2AsO_4^-$, $HAsO_4^{-2}$, and $AsO_4^{-3}$.

### 2.6.2 Speciation of Arsenic in Soil Environment

Four chemical forms of arsenic present in soil such as i) Arsenite-As(III), ii) Arsenate-As(V), monomethyl arsenic acid (MMAA) and iv) Dimethyl arsenic acid (Marin *et al.*, 1992). Inorganic arsenics have been found to be more toxic than the organics, while arsenite is four times more hazardous than arsenate. The last two are of organic form, which may be bound to metalic cations and form somewhat stable compounds, e.g. monosodium methane arsonate (MSMA) and disodium methane arsonate (DSMA).

**i) Arsenic (III)-Arsenite,** the reduced state of inorganic arsenic is a toxic pollutant in natural environments. It is much more toxic (Ferguson and Gavis, 1972) and more soluble and mobile (Deuel and Swoboda, 1972) than the oxidized state of inorganic arsenic, arsenate-As(V).

**ii) Arsenic (V)-Arsenate,** Arsenate can be sorbed onto calys, especially Kaolinite and Montmorillonite (Frost and Griffin, 1977). In Montmorillonite, calcereous clay, arsenate was highly adsorbed onto Kaolinite and Montmorillonite at low pH with a maximum near pH5.0, and became less adsorbed at high pH (Goldberg and Glaubig, 1988). Adsorption of arsenic (V) by calcite increased fromph 6 to 10, peaked at pH 10 to 12, and decreased above pH 12.

**iii) Organic arsenic,** A ubiquitous, volatile, arsenic compound, dimethyl-arsinic acid (cacodylic acid) seems to be present in all soils and may dominate in many (Braman, 1975).

### 2.6.3 Toxicity of Arsenic

Inorganic arsenic have been found to be more toxic than the organics, while arsenite is four more hazardous than arsenate (Khan, 1997). Toxicity of arsenic compounds varies to a large extent depending upon their chemical form (Table 2.3). Arsenic can enter into human body through ingestation and inhalition. The severity of the effect depends primarily on the level of exposure. Acute high-dose oral exposure to arsenic typically leads to gastrointestinal irritation accompanied by difficult in swallowing, thirst, abnormally low blood pressure and convulsions. Death may occur from cardiovascular collapse. Chronic exposure to low concentrations of arsenic are of primary interest when the health significant of arsenic in drinking water is evaluated (Pontius *et al.*, 1994). On the other side, there are still no well-established guidelines about to measure quantitatively the severity of arsenosis in a population.

Table 2.3 Arsenic Compounds and Species and their Environmental and Toxicological Importance in Water (Kartinen & Martin, 1995; WHO, 2011).

| **Compounds** | **Example** | **Aquatic Environment** | **Toxicity** |
|---|---|---|---|
| Arsenic | $As^{3-}$ | Major importance | Most toxic As species |
| Elemental Arsenic | As | Minor importance | Least toxic As species |
| Trivalent arsenic<br><br><br><br><br>MMAs(III)<br>DMAs(III)<br>TMAs(III)<br>Organo-As(III) | As(III)<br>$H_3AsO_3$<br>$H_2AsO_3^-$<br>$HAsO_3^{2-}$<br>$AsO_3^{3-}$<br>$CH_3As(III)O_2^{2-}$<br>$(CH_3)_2As(III)O^{1-}$<br>$(CH_3)_3As(III)$ | Anaerobic<br>pH=0-9<br>pH=10-12<br>pH=13<br>pH=14<br>Several fungi & bacterial can methylate As(V) Minor importance. | 10 x more than As(V)<br><br><br><br>Less than inorganic As(III) |
| Pentavalent arsenic<br>Arsenate<br><br><br><br>MMAs(V)<br>DMAs(V)<br>TMAs(V)<br>Organo-As(V) | As(V)<br>$H_3AsO_4$<br>$H_2AsO_4^-$<br>$HAsO_4^{2-}$<br>$AsO_4^{3-}$<br>$CH_3As(V)O_3^{2-}$<br>$(CH_3)_2As(V)O_2^{1-}$<br>$(CH_3)_3As(III)O$ | Aerobic<br>pH=0-2<br>pH=3<br>pH=7-11<br>pH=12-14<br>Methylation through reduction of As(V) to As(III) Minor importance. | 10x less than As(III)<br><br><br><br><br>Less than inorganic As(V) |

### 2.6.4 Release of Arsenic Compound

The arsenic is of natural origin and is believed to be released to groundwater as a result of a number of mechanisms which are poorly understood. This release appears to be associated with the burial of fresh sediment and the generation of anaerobic (oxygen-deficient) groundwater conditions. It probably occurred thousands of years ago. The arsenic is thought to be desorbed and dissolved from iron oxides which had earlier scavenged the arsenic from river water during their transport as part of the normal river sediment load. We call this the iron oxide reduction hypothesis. Natural variations in the amount of iron oxide at the time of sediment burial may be a key factor in controlling the distribution of high arsenic groundwater. Limited evidence suggests that the isolated arsenic hot spots found in northern Bangladesh occur in areas containing sediments particularly rich in iron oxides, and their accompanying adsorbed arsenic load. While there is evidence for sulphide minerals in some of the sediments, and in some cases indirect evidence for their oxidation, there is no support for the '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. There is no evidence to support the proposition that the groundwater arsenic problem is caused by the recent seasonal drawdown of the water table due to a recent increase in irrigation abstraction.

The most important commercial compounds are the oxides, the principle forms of which are arsenous oxide ($As_2O_3$) and arsenic pentoxide ($As_2O_5$). Arsenous oxide, commonly known as white oxide, is the material most used for synthesis of arsenic compounds. It is produced as by-product of the nonferrous metal industry, primarily from the smelting of copper ores. Naturally occurring metal arsenides, realgar and orpiment also convert to the trivalent oxide when roasted in air. The formation of the trioxide by the roasting of a sulfidic ore is illustrated in Eq. 2.1.

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2 \qquad (2.1)$$

Elemental arsenic undergoes reaction with oxygen to yield the trioxide as follows:

$$4As + 3O_2 \rightarrow 2As_2O_3 \qquad (2.2)$$

The direct reaction between the elements yields the trioxide most exclusively. The reaction in air proceeds very slowly, but the rate increases rapidly with increasing temperature, decreasing particle size and the presence of moisture. The trioxide is moderately soluble in water, but dissolves easily in aqueous alkali to produce a solution of arsenic , $AsO_2^-$. Ti is slightly soluble in polar organic solvents such as alcohols and insoluble in benzene. The most useful reagent for the synthesis of pentoxide ($As_2O_5$) is concentrated nitric acid. The reaction between elemental and nitric acid gives $H_3AsO_4$. The controlled dehydration of this acid (Eq. 2.3) gives the pentaoxide. Hypochlorous, choric and perchloric acids also oxidize the metal or $As_2O_3$, to the pentavalent state. Arsenic pentoxide dissolves readily in water to produce arsenic acid, $H_3AsO_4$.

Arsenic ($AsH_3$) is the best known of the hydrides of arsenic. It is a colorless poisonous gas composed of arsenic and hydrogen. The gas also called arsenic hydride, is produced by the reduction by metals of arsenic compounds in acidic solutions. Other hydrides of arsenic are diarsine ($As_2H_4$), diarsinee dihydride ($As_2H_2$ ) and polymeric di-arsine monohydride $(As_2H)_x$.

## 2.6.5 Geochemical Processes Controlling Arsenic Mobility

Fe oxides are the main arsenic-bearing phases in soils (Martin *et al.*, 2013). Arsenite is in fact adsorbed in higher amounts than As(V) on all iron oxides, except at very low concentration. The arsenic retention capacity of soils is related to their content in clay and Fe and Al (hydr) oxides. Soil Fe and Al (hydr)oxides are mostly contained in the finest fractions (clay, fine silt), and they probably account for most of the retention of the clay fraction toward As(V), while Fe (hydr)oxides, in more or less crystalline forms or as coatings on clay minerals, appear to be mostly responsible for the soiladsorbing capacity toward As(III).

Two categories of processes largely control arsenic mobility in aquifers: (1) adsorption and desorption reactions and (2) solid-phase precipitation and dissolution reactions. Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface, is an example of desorption. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral calcite, from calcium and carbonate present in ground water, is an example of solid-phase precipitation. Dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution.

Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition.

Arsenic is a redox-sensitive element. This means that arsenic may gain or lose electrons in redox reactions. As a result, arsenic may be present in a variety of redox states. Arsenate and arsenite are the two forms of arsenic commonly found in ground water (Masscheleyn *et al.*, 1991). Arsenate generally predominates under oxidizing conditions. Arsenite predominates when conditions become sufficiently reducing. Under the pH conditions of most ground water, arsenate is present as the negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, whereas arsenite is present as the uncharged species $H_3AsO_3$. The strength of adsorption and desorption reactions between these different arsenic species and solid-phase surfaces in aquifers varies, in part, because of these differences in charge. Differences in species charge affect the character of electrostatic interactions between species and surfaces.

Arsenate and arsenite adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals. Adsorption and desorption reactions between arsenate and iron-oxide surfaces are particularly important controlling reactions because iron oxides are widespread in the hydrogeologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron-oxide surfaces in acidic and near-neutral-pH water (Dzombak and Morel, 1990; Waychunas *et al.*, 1993). However, desorption of arsenate from iron-oxide surfaces becomes favored as pH values become alkaline (Dzombak and Morel, 1990). The pH-dependence of arsenate adsorption to iron-oxide surfaces appears to be related to the change in iron-oxide net surface charge from positive to negative as pH increases above the zero-point-of-charge (pH at which the net surface charge is equal to zero) of about 7.7 for goethite (crystalline iron oxide) (Stumm and Morgan, 1996) or 8.0 for ferrihydrite (amorphous iron oxide) (Dzombak and Morel, 1990). Where pH values are above about 8, the negative net surface charge of iron oxide can repel negatively charged ions such as arsenate.

Iron-oxide surfaces also adsorb arsenite, and both arsenate and arsenite adsorb to aluminum oxides and clay-mineral surfaces. However, these adsorption reactions appear generally to be weaker than is the case for arsenate adsorption to iron-oxide surfaces under typical environmental pH conditions (Manning and Goldberg, 1997). Nevertheless, pH-dependent adsorption and desorption reactions other than those between arsenate and iron-oxide surfaces may be important controls over arsenic mobility in some settings. As is the case for adsorption of arsenate to iron-oxide surfaces, adsorption of arsenite to iron-oxide surfaces tends to decrease as pH increases, at least between the range from pH 6 to pH 9 (Dzombak and Morel, 1990). Unfortunately, arsenate and arsenite adsorption and desorption reactions with other common surfaces are less well characterized, and apparently more complex than is the case for adsorption and desorption reactions with iron-oxide surfaces (Manning and Goldberg, 1997).

Researchers have shown that arsenate is specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism (Fuller *et al.,* 1993; Fendorf *et al.,* 1997; Grossl *et al.,* 1997). Goethite ($\alpha$–FeOOH), the most common iron oxide in soils, has double bands of $FeO_3(OH)_3$ octahedra which share edges and corners to form 2 by 1 octahedra tunnels (only large enough to accommodate the passage of protons) partially bonded by H bonds (Cornell and Shwertmann, 1996; Schwertmann and Cornell, 1991; Sparks, 1995). On the basis of a pressure-jump relaxation study and confirmed by extended x-ray absorption fine structure (EXAFS) analysis, Grossl *et al*. (1997) and Fendorf *et al*. (1997) demonstrated that arsenate can form three types of surface complexes on goethite depending on the surface coverage level (Fig. 2.3). Grossl *et al*. (1997) proposed that, at extremely low surface coverages, a ligand exchange reaction of $H_2AsO_4^-$ with surface OH groups formed the monodentate complex. At high surface loadings, the sorption of arsenate was dominated by the formation of bidentate surface complexes after a second ligand exchange reaction occurred.

As a result of the pH dependence of arsenic adsorption, changes in ground-water pH can promote adsorption or desorption of arsenic. Because solid-phase diagenesis (water-rock interaction) typically consumes H+ (Stumm and Morgan, 1995), the pH of ground water tends to increase with residence time, which, in turn, increases along ground-water flow paths. Because iron-oxide surfaces can hold large amounts of adsorbed arsenate, geochemical evolution of ground water to high (alkaline) pH can induce desorption of arsenic sufficient to result in exceedances of the USEPA current MCL in some environments (Robertson, 1989).

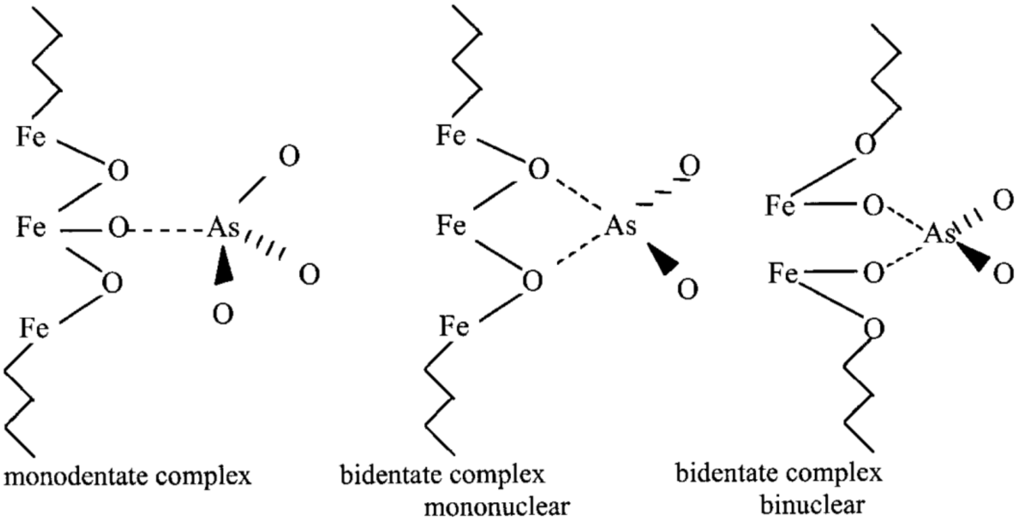


Fig. 2.3 Schematic illustration of the adsorption mechanisms of arsenate onto goethite (O'Reilly *et al.*, 2001).

Similarly, redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. For example, reduction of arsenate to arsenite can promote arsenic mobility because arsenite is generally less strongly adsorbed than is arsenate. Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility (Manning and Goldberg, 1997).

Structural changes in solid phases at the atomic level also affect arsenic adsorption and desorption. For example, conversion of ferrihydrite to goethite or to other crystalline iron-oxide phases may occur gradually over time (Dzombak and Morel, 1990). Fuller *et al.* (1993) demonstrated that as ferrihydrite crystallizes into goethite, the density of arsenic adsorption sites decreases. This decrease in density of adsorption sites can result in desorption of adsorbed arsenic. Structural changes in other solid phases may possibly affect arsenic mobility, too. The role of such solid-phase structural changes on ground-water arsenic concentrations has, however, received little attention to date.

### 2.6.6 Microbial Activity Affecting Arsenic Mobility

Numerous bacteria, fungi, yeasts and algae are able to transform arsenic compounds by oxidation, reduction, demethylation and methylation (Frankenberger and Arshad, 2002). Microbial reduction of As(V )to As(III) is known to occur by dissimilatory reduction and detoxification activities of microbes. In the process of dissimilatory reduction As(V) is utilised as a terminal electron acceptor during anareobic respiration (Dowdle *et al.*, 1996). Detoxification of arsenic by microbes involves an As(V) reductase and As(III) extrusion by an As(III)-efflux pump (Cervantes *et al.*, 1994). Inskeep *et al.* (2002) suggested that reduction of As(V) to As(III) via the detoxification pathway may be a widely-distributed trait of soil and aquatic microbes. However, the predominant arsenic-species found in soil solution of aerobic soil remains As(V) (Wenzel *et al.*, 2002). Bacterial oxidation has been described for many species and could be a feasible remediation strategy as As(V) is less toxic and less mobile than As(III) (Frankenberger and Losi, 1995). Microbial methylation is common for both bacteria and fungi and has been known for a long time (Cheng and Focht, 1979; Cullen *et al.*, 1984). Formation of volatile methylarsines offer the possibility to employ arsenic volatilization as remediation strategy. However, only marginal losses by formation of gaseous arsines have been reported for a Na cacodylate and methanarsonic-acid-amended soil (Goa and Burau, 1997), for a soil polluted by arsenic-containing wood preservatives (Turpeinen *et al.*, 1999) and a soil containing geogenic arsenic (Prohaska *et al.*, 1999).

## 2.7 INTERACTION OF ARSENIC WITH SULPHUR AND PHOSPHORUS

There were few significant correlations between arsenic and other elements. Darland and Inskeep (1997) conducted transport studies using free iron oxides in a sand column and found phosphate that effectively competes with arsenate; however, the phosphate was not able to desorb all of the applied arsenate, regardless of whether the arsenate was applied concurrently or prior to phosophate addition. Even when the applied phosphate surpassed the column adsorption capacity by twofold, some arsenate remained adsorbed to the free iron oxides in the sand. In contrast, Pierce and Moore (1982) found that once arsenate was sorbed to a natural surface in an aqueous system, the sorbed arsenate was not affected by the post addition of $PO_4^{3-}$ and and $SO_4^{2-}$. however, sorbed arsenate was affected, at low concentrations, by the prior addition of $PO_4^{3-}$ and and $SO_4^{2-}$ to the system. The ability of $PO_4^{3-}$ to compete with arsenate for goethite surface sites was somewhat expected since $PO_4^{3-}$, like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism (Parfitt, 1978; Persson *et al*., 1996). Also, Barrow (1992) concluded that $PO_4^{3-}$ become more competitive over time since it is capable of slow sorption. Phosphate is considered an analog of arsenate. They are both oxyanions in aqueous solution with three similar acid dissociation constants. The acid dissociation constants for $H_3PO_4$ are: $pK_1 = 2.13$, $pK_2 = 7.21$, $pK_3 = 12.44$, and for $H_3AsO_4$ are: $pK_1 = 3.60$, $pK_2 = 7.25$, and $pK_3 = 12.52$ (Whitten *et al*., 1992). Lumsdon *et al*. (1984) determined that arsenate may sorb more strongly because, unlike $PO_4^{3-}$, the arsenate ion is larger in size and interacts more strongly with some of the OH groups that remain on the surface.

Sulfate can be sorbed as either an outer- or inner- sphere complex (Gebhardt and Coleman, 1974; He *et al*., 1997). Myneni *et al*. (1997), working in alkaline environments with the solid ettringite, reported no arsenate desorption in the presence of $SO_4^{2-}$ in high ionic strength solutions. Xu *et al*. (1988) suggested that $SO_4^{2-}$ can compete with $H_2AsO_4^-$ and $HAsO_4^{2-}$ and occupy surface sites on the alumina. Since arsenate forms a strong, inner-sphere complex with goethite, to promote desorption an effective ion would have to compete for the same sorption sites (i.e., inner-sphere sorption). As discussed above, studies have shown that $PO_4^{3-}$ is able to form this type of bond with goethite while $SO_4^{2-}$ may or may not form this type of bond with the surface depending on the experimental conditions.

An interesting finding was the inverse relationship between sulphate (Fig. 2.4) and arsenic (Fig. 2.2), as found in the study of BGS-DPHE (2001). These two figures clearly show that sulphate content in groundwater is generally higher where arsenic concentration is lower or vice versa, probably reflecting the importance of strongly reducing conditions in promoting high arsenic in groundwater. Phosphorus distribution found from the study of BGS-DPHE (2001) as shown in Fig. 2.5 shows many similarities with that of arsenic (Fig. 2.2), although in contrast to arsenic, many of the deep groundwater of Barisal have relatively high

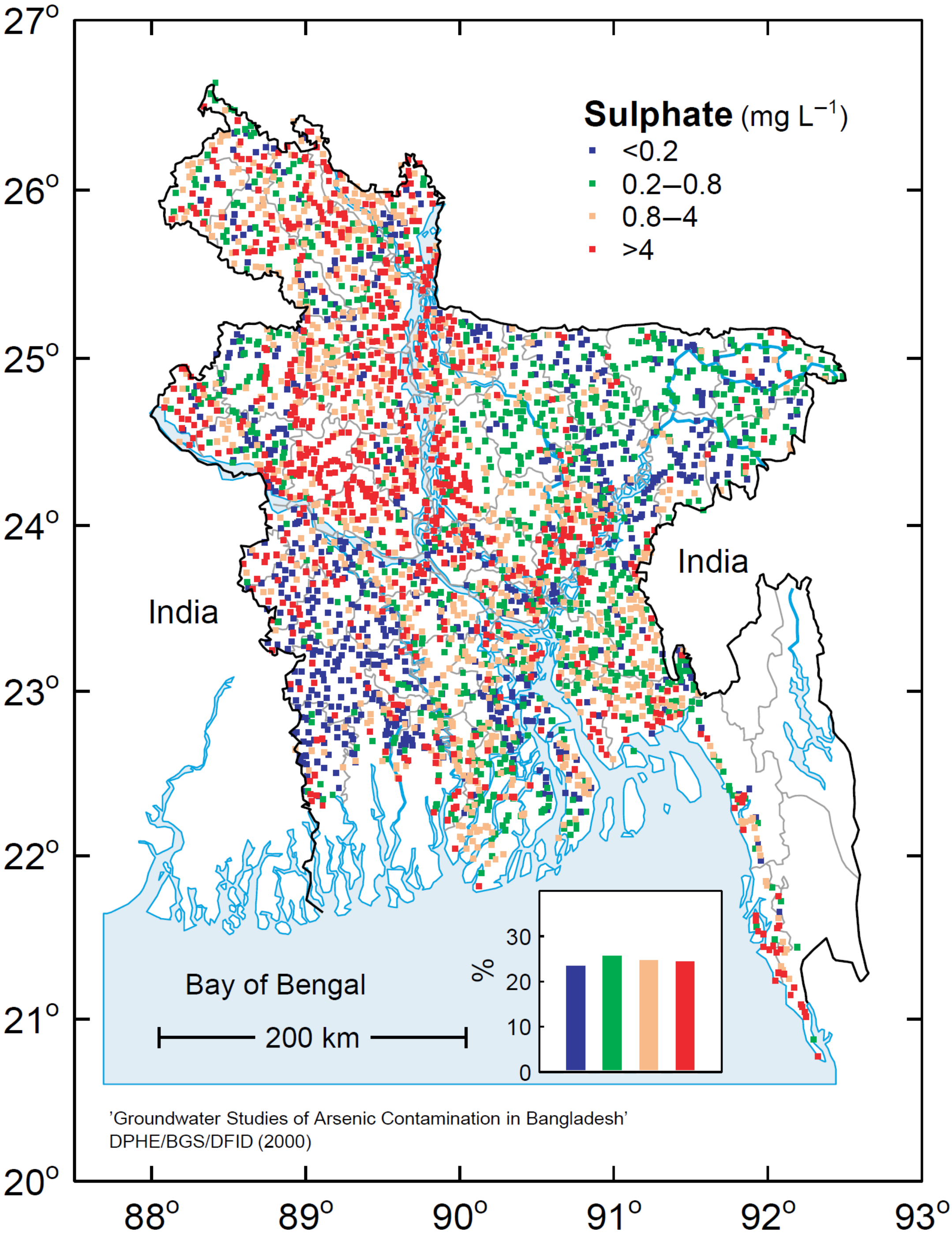


Fig. 2.4 Distribution of Sulphur in Groundwater of Bangladesh (BGS-DPHE 2001).

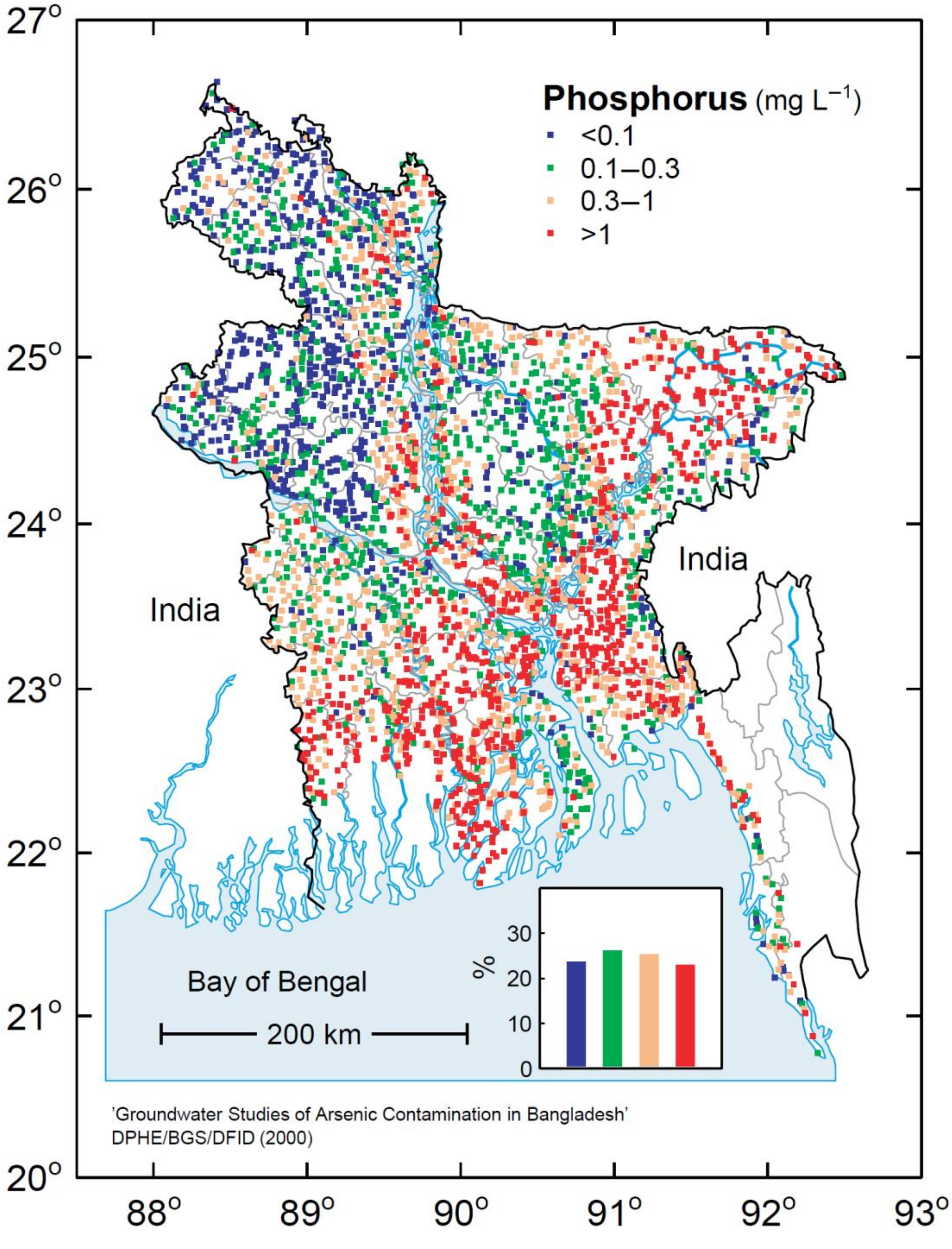


Fig. 2.5 Distribution of Phosphorus in Groundwater of Bangladesh (BGS-DPHE 2001).

concentrations (often >1 mg $L^{-1}$ P). The phosphorus is believed to derive by desorption from iron oxides and from organic matter. Dissolution of detrital apatite from sediments is also a likely contributor. The prevalence of high concentrations even in the deep groundwater (>150 m) precludes fertilizers as a major source. Dissolved phosphate is likely to compete with dissolved arsenic species (arsenite, arsenate) for adsorption sites on iron and other oxides and the high observed phosphorus concentrations may be an additional factor in the mechanism of arsenic mobilization in the Bangladesh groundwater. However, the presence of high phosphorus concentrations in many of the deep groundwater with low arsenic concentrations indicate that this may be only one of a number of factors involved in arsenic release.

## 2.8 REMEDIATION OF ARSENIC CONTAMINATION

A variety of remedial process are proposed (EPA, 2002; EPRI, 1997) for treatment of arsenic contamination in soil and water which are briefly discussed below.

### 2.8.1 Decontamination of Drinking Water

Precipitation/coprecipitation is frequently used to treat arsenic-contaminated water, and is capable of treating a wide range of influent concentrations to the revised maximum contaminant level (MCL) for arsenic (EPA, 2002). The effectiveness of this technology is less likely to be reduced by characteristics and contaminants other than arsenic, compared to other water treatment technologies. It is also capable of treating water characteristics or contaminants other than arsenic, such as hardness or heavy metals. Systems using this technology generally require skilled operators; therefore, precipitation/ coprecipitation is more cost effective at a large scale where labor costs can be spread over a larger amount of treated water produced. The effectiveness of adsorption and ion exchange for arsenic treatment is more likely than precipitation/coprecipitation to be affected by characteristics and contaminants other than arsenic. However, these technologies are capable of treating arsenic to the revised MCL of 0.01 mg $L^{-1}$. Small capacity systems using these technologies tend to have lower operating and maintenance costs, and require less operator expertise. Adsorption and ion exchange tend to be used more often when arsenic is the only contaminant to be treated, for relatively smaller systems, and as a polishing technology for the effluent from larger systems. Membrane filtration (reverse osmosis) is used less frequently because it tends to have higher costs and produce a larger volume of residuals than other arsenic treatment technologies.

Table 2.4 Technologies for Water Treatment (EPA 2002).

| | |
|---|---|
| Precipitation/ Coprecipitation | Uses chemicals to transform dissolved contaminants into an insoluble solid or form another insoluble solid onto which dissolved contaminants are adsorbed. The solid is then removed from the liquid phase by clarification or filtration. |
| Membrane Filtration | Separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some constituents to pass, while blocking others. |
| Adsorption | Concentrates solutes at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column. As contaminated water is passed through the column, contaminants are adsorbed. |
| Ion Exchange | Exchanges ions held electrostatically on the surface of a solid with ions of similar charge in a solution. The ion exchange media is usually packed into a column. As contaminated water is passed through the column, contaminants are removed. |
| Permeable Reactive Barriers | Walls containing reactive media that are installed across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through while the media remove the contaminants by precipitation, degradation, adsorption, or ion exchange. |

For all of these technologies (except membrane filtration) adsorption is the fundamental process governing arsenic removal (Hering *et al*., 1996). The current advanced treatment options to remove arsenic include activated alumina, iron-oxide-coated sand, reverse osmosis, ion-exchange and electro-dialysis. Some treatment options are shown in Table 2.4 (EPA 2002).

### 2.8.2 Remediation of Arsenic Contamination in Soil

Process of removing arsenic from water for drinking purpose is relatively easy when compared to remediation of arsenic toxicity from soil for plant uptake. Inorganic arsenic is classified as a well-known non-threshold carcinogen (National Research Council, 2001). The toxicity of arsenic (As) to humans has been well documented and reviewed (Duker *et al*., 2005). Numerous studies have reported that the increase in soil arsenic concentration can cause an enhancement of arsenic accumulation in rice grain and in turn threaten human health through food chain

(Williams *et al*., 2006; Zhu *et al*., 2008). The mobility and toxicity of arsenic in soil environment depend largely on its chemical species.

In general, soil and waste are treated by immobilizing the arsenic using solidification/stabilization (EPA, 2002). This technology is usually capable of reducing the leachability of arsenic to below 5.0 mg $L^{-1}$ as measured by the toxicity characteristic leaching procedure [TCLP], which is a common treatment goal for soil and waste. Solidification/stabilization is generally the least expensive technology for treatment of arsenic-contaminated soil and waste. Pyrometallurgical processes are applicable to some soil and waste from metals mining and smelting industries. Other soil and waste treatment technologies, including vitrification, soil washing/acid extraction, and soil flushing, have had only limited application to the treatment of arsenic. A summary of these treatments are given in Table 2.5. Although these technologies may be capable of effectively treating arsenic, data on performance are limited. In addition, these technologies tend to be more expensive than solidification/stabilization.

Innovative technologies, such as permeable reactive barriers, biological treatment, phytoremediation, and electrokinetic treatment, are also being used to treat arsenic-contaminated soil, waste, and water (EPA, 2002). Permeable reactive barriers are used to treat groundwater in situ. This technology tends to have lower operation and maintenance costs than ex situ (pump and treat) technologies, and typically requires a treatment time of many years. Biological treatment for arsenic is used primarily to treat water above-ground in processes that use microorganisms to enhance precipitation/ coprecipitation. Bioleaching of arsenic from soil has also been tested on a bench scale (EPA, 2002). This technology may require pretreatment or addition of nutrients and other treatment agents to encourage the growth of key microorganisms. Phytoremediation is an in situ technology intended to be applicable to soil, waste, and water. This technology tends to have low capital, operating, and maintenance costs relative to other arsenic treatment technologies because it relies on the activity and growth of plants. However, the effectiveness of this technology may be reduced by a variety of factors, such as the weather, soil and groundwater contaminants and characteristics, the presence of weeds or pests, and other factors. Electrokinetic treatment is an in situ technology intended to be applicable to soil, waste and

Table 2.5 Technologies for Soil and Waste Treatment (EPA 2002)

| | |
|---|---|
| Solidification/ Stabilization | Physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms. |
| Vitrification | High temperature treatment that reduces the mobility of metals by incorporating them into a chemically durable, leach resistant, vitreous mass. The process also may cause contaminants to volatilize, thereby reducing their concentration in the soil and waste. |
| Soil Washing/ Acid Extraction | An ex situ technology that takes advantage of the behavior of some contaminants to preferentially adsorb onto the fines fraction of soil. The soil is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentration in the remaining soil. |
| Pyrometallurgical Recovery | Uses heat to convert a contaminated waste feed into a product with a high concentration of the contaminant that can be reused or sold. |
| In Situ Soil Flushing | Extracts organic and inorganic contaminants from soil by using water, a solution of chemicals in water, or an organic extractant, without excavating the contaminated material itself. The solution is injected into or sprayed onto the area of contamination, causing the contaminants to become mobilized by dissolution or emulsification. After passing through the contamination zone, the contaminant-bearing flushing solution is collected and pumped to the surface for treatment, discharge, or reinjection. |

Table 2.6 Technologies for Soil, Waste, and Water Treatment (EPA 2002).

| | |
|---|---|
| Electrokinetic Treatment | Based on the theory that a low-density current applied to soil will mobilize contaminants in the form of charged species. A current passed between electrodes inserted into the subsurface is intended to cause water, ions, and particulates to move through the soil. Contaminants arriving at the electrodes can be removed by means of electroplating or electrodeposition, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or by pumping of water (or other fluid) near the electrode. |
| Phytoremediation | Involves the use of plants to degrade, extract, contain, or immobilize contaminants in soil, sediment, and groundwater. |
| Biological Treatment | Involves the use of microorganisms that act directly on contaminant species or create ambient conditions that cause the contaminant to leach from soil or precipitate/coprecipitate from water. |

water. This technology is most applicable to fine-grained soils, such as clays (EPA, 2002). These treatments are summarized in Table 2.6.

EPRI (1997) studied specific technologies such as including soil flushing, in-situ fixation, iron coprecipitation, and ceramic membrane filtration for arsenic remediation in soil and groundwater. Soil flushing, or in-situ soil washing, is the repeated passing of a solution through an aquifer in place to remove the contaminant(s) of interest from the aquifer media (soil) in an abbreviated time frame. The solution may contain a reagent specifically selected to remove the contaminant(s), or flushing may be done with water only. In-situ fixation is the introduction of a reagent into the aquifer to cause the contaminant to precipitate in place, in a relatively insoluble form. Iron coprecipitation is a wastewater treatment process pioneered by EPRI. In the iron coprecipitation process, an iron salt such as ferric chloride or ferric sulfate is added to the contaminated water, and the pH adjusted to induce precipitation of iron oxyhydroxides. Cross-flow ceramic membrane filtration can be used to remove any remaining contaminant (pin-point floc) in the feed stream. The filters replace a traditional clarifier in the system, occupy much less space than a clarifier, and produce a high-quality effluent stream.

### 2.8.3 Remediation of Arsenic Toxicity by Natural Attenuation

Natural attenuation (NA) is an environmentally compatible and cost-effective in situ remedial method that relies on the site intrinsic assimilative capacity. Regulatory definitions of NA generally include all types of processes that can reduce the concentration or minimize the toxicity of a contaminant (Wang and Mulligan, 2006; Yong and Mulligan, 2004). The naturally occurring physicochemical and biological processes give light to the use of NA processes to remediate arsenic-contaminated soils and groundwater. The NA of arsenic mainly involves processes such as immobilization by sorption to solid phases such as (hydro)oxides of iron (Fe), aluminum (Al) and manganese (Mn), organic matter, and clay minerals, the intra-conversion between As(III) and As(V) induced by the Fe and Mn (hydro)oxides and clay phases or natural organic matter, biotransformation, and hyperaccumulation of arsenic in plants.

Natural attenuation of arsenic contamination in soils and groundwater is a complicated function of the co-occurring physicochemical and biological processes (Fig. 2.6) (Wang and Mulligan, 2006). Arsenic immobilization through sorption to solid phases currently is the best NA mechanism to retain arsenic in soils and remove it from groundwater, and this process can be enhanced by microbial activities. Hyperaccumulation is another applicable choice to remove arsenic from soils and shallow groundwater. However, NA is site specific and cannot be assumed to be operational at a given site. It will be effective only at sites with special environmental conditions conductive to the attenuation of As. Sufficient

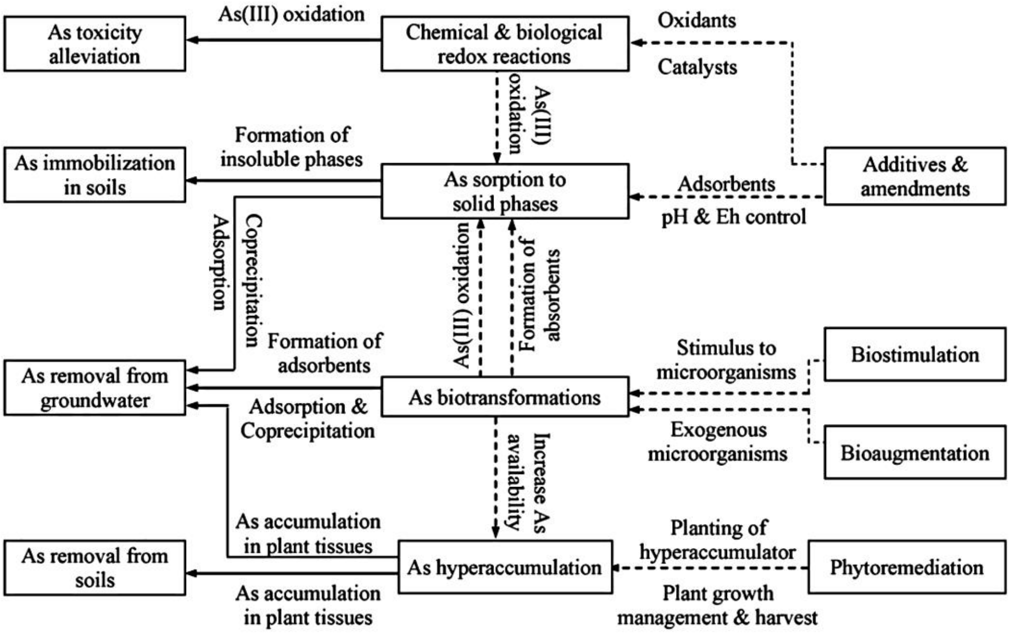


Fig. 2.6 Main arsenic natural attenuation processes and engineering enhancement strategies (Wang and Mulligan, 2006).

characterization of the site geology, hydrology, and microbiology is required to model the fate and transport of arsenic in the contaminated soils or groundwater. Conceptual and mathematical models developed then will be useful to predict whether the desired reactions can take place to obtain effective and optimal immobilization of the contaminant with solid phases and transformations that will enhance the immobilization or reduce the toxicity. Detailed investigation and long-term continued monitoring are absolutely necessary to ensure that the NA processes really occur at an acceptable rate, to ensure that conditions that do not favor NA occur, and to calibrate the models. Although various technical protocols have been established for NA, they are mainly adapted for organic contaminants in groundwater (Mulligan and Yong, 2004). Further efforts are needed to verify whether they are applicable to arsenic contaminated soils and groundwater, or to develop applicable alternatives.

## 2.9 ARSENIC FRACTIONATION

### 2.9.1 General

Fractionation is directed to the acquisition of data on the content of the main compounds of any element in soils. They include (1) firmly bound compounds of the soil solid phase, namely, mineral (in the structure of primary and clay minerals; not easily soluble salts; oxides; and hydroxides of Si, Fe, Al, and Mn), organic, and organomineral substances; (2) mobile compounds of the solid soil phase (exchangeable, specifically and nonspecifically sorbed, and chemically bound); (3) compounds of the soil solution; (4) compounds of the soil air; and (5) compounds of soil biota. These components interact permanently and characterize soil as a specific natural body. Being present in a minimal soil volume (pedon, horizon), they represent its elementary system of chemical compounds (Motuzova, 1999). According to the recommendation of the Bureau of Standards of the European Union (BCR) of 1987, fractionation implies a quantification of different kinds, forms, or phases of chemical compounds including the studied elements (Ure *et al*. 1993). According to the last recommendations of the International Union of Pure and Applied Chemistry (IUPAC), the term "fractionation" is determined as a taxonomic separation of substances by their physical (granulometric analysis) or chemical (bonds with other substances and reactivity) properties using corresponding physical and chemical methods.

Although it is undoubtedly important to know the total concentrations of arsenic in soils and sediments, these concentrations do not give any information about the solid-phase partitioning and potential mobility of arsenic within the soils. This is particularly important for arsenic, which in many areas is in too low abundance or is associated with such fine-grained solid phases that characterization by standard mineralogical techniques is extremely difficult or time-consuming.

### 2.9.2 Methods of Arsenic Fractionation

A relatively simple and well-adopted method to assess trace element pools of differential relative lability in soils is the sequential extraction with reagents of increasing dissolution strength. Ideally, each reagent should be targeting a specific solid phase associated with the trace element of interest (Wenzel *et al*., 2001). Many workers have devoted time and effort to devising sequential extraction chemical procedures for arsenic in soils and sediments to estimate the operationally defined phase associations, solubility and availability of arsenic, with a view to understanding the factors controlling arsenic mobility. At present, there is no universally agreed standard method for single or sequential extractions of arsenic in soils and sediments (Keon *et al*., 2001; Montperrus *et al*., 2002; Taggart *et al*., 2004).

Many sequential extraction schemes used for arsenic are based on conventional schemes used to extract metals and other elements that form cations (Quevauviller *et al*., 1994; Tessier *et al*., 1979; Ure *et al*., 1993; Voigt *et al*., 1996). However, other schemes recognize the anionic behavior of arsenic in soils and sediments, and are based on extraction procedures for phosphorus (Cappuyns *et al*., 2002; Johnson and Hiltbold, 1969). Schemes have also been developed for arsenic specifically (Herreweghe, 2003; Wenzel *et al*., 2001), and are based on the knowledge that arsenic is stable over a smaller range of Eh and pH than phosphorus, arsenic has a greater propensity to form bonds with sulphur and carbon than phosphorus, and organic arsenic is less common than organic phosphorus in soils (Herreweghe, 2003; Johnson, 1969; O'Neill, 1995).

A large number of different methodological approaches were developed over the last two decades defining the individual fractions of given elements in soil. The first sequential extraction procedure was described by McLaren and Crawford (1973) but an extended method was developed by Tessier *et al*. (1979), who performed fractionation of metals in samples of sediments into 5 parts. Filgueiras *et al*. (2002) reviewed a few hundred of these applications of various sequential extraction procedures applied to the fractionation of elements in environmental samples such as sediment, soil, sewage sludge, coal fly ash, solid waste incineration bottom ash, airborne dust, etc. A large diversity of sequential extraction schemes concerning the extraction reagents, operating conditions and number of stages involved is evident. Some researchers emphasized that small changes in the experimental conditions (e.g. pH, temperature, contact time, solid to extractant volume ratio, particle size, sample pretreatment) can lead to large variations in the fractionation, making it troublesome for comparisons between results. These findings were confirmed by many soil scientists (Bordas and Bourg, 1998; Chowdhury *et al*., 1992; Gray and McLaren, 2003) for both single and sequential extraction procedures.

A summary of a selection of sequential extraction schemes used presently for arsenic in soils and sediments is presented in Table 2.7 (Hudson-Edwards, 2004). The most obvious feature of the schemes is the different numbers of steps involved, and different extractions used. Shaking times for each step are also vastly different, but are not shown in the table; readers are referred to the specific articles for more information. Virtually all of the schemes extract an easily sorbed phase, an Al-, Fe- and/or Mn-oxyhydroxide phase and a residual phase. Other operationally defined phases extracted include water or easily soluble, acid volatile sulphide, organic matter, acid-soluble, Ca-associated, arsenic oxide and silicate, and arsenic or Fe sulphide (Table 2.7). In general, most soil or sediment arsenic is extracted by the Fe oxyhydroxide (reducible) phase, reflecting the well-known association of arsenic for Fe oxyhydroxides. The chemicals used for sequential extractions are introduced in increasing strengths and varying pHs, are chosen to minimize re-adsorption or precipitation between steps, and vary depending on the preference of the authors (Table 2.7) (e.g., ionically bound or exchangeable arsenic is extracted using $MgCl_2$ (Keon *et al*., 2001; Tessier *et al*., 1979), $(NH_4)_2SO_4$ (Wenzel *et al*., 2001), $NaNO_3$ (Cai *et al*., 2002) and anion exchange membrane strips (Cappuyns *et al*., type) is exchanged with one of the components of the chemical extractants or membrane strips. Cai *et al*. (2002), Keon *et al*. (2001) and Wenzel *et al*. (2001) have also extracted a specifically adsorbed arsenic fraction, using $NaH_2PO_4$, $NH_4H_2PO_4$ and $KH_2PO_4$, respectively (Table 2.7). The basis of this fraction is the competitive exchange between phosphate ($PO_4^{3-}$ ) and arsenate ($AsO_4^{3-}$) in soils, where, because of the smaller size and higher charge density of phosphate, arsenate is preferentially desorbed over phosphate (Manning and Goldberg, 1996). Obviously, 2002; Herreweghe *et al*., 2003). All of these extractants rely on the principle of ion exchange, whereby loosely bound arsenic (indiscriminate with respect to mineral the choice of single or sequential extraction scheme for arsenic will depend on the types of soils and sediments being analyzed. This was elegantly shown by Gleyzes *et al*. (2002) and by Montperrus *et al*. (2002), who found that orthophosphoric acid was the most efficient extractant for arsenic in river sediment and sludge, and ammonium oxalate the most efficient for arsenic in soil. A substantial amount of information about the soil or sediment should therefore be procured prior to undertaking the sequential extraction work. This should comprise analysis of the

Table 2.7 Examples of Sequential Extraction Schemes of Arsenic.

| **Reference** | **(Water) Soluble** | **Ionically-bound/ exchange-able** | **Strongly adsorbed** | **Acid volatile sulphides, carbonates, Mn oxides and amorphous Fe oxyhydr-oxides** | **Al-associated** | **Organic matter/ oxidisable** | **Amorphous and/or crystalline Fe oxyhydr-oxides/ reducible** | **Low (or acid) soluble** | **Arsenic oxides and silicates / residual** | **Pyrite and amor-phous $As_2S$** | **Orpiment and other recalcitrant minerals** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chang and Jackson (1957) | (1) 1 M $NH_4Cl$ | | | | (2) 0.5 M $NH_4F$ | | (3) 0.1 M NaOH | (4) 2 M $H_2SO_4$ (Ca-associated)<br>(5) CBD (reductant-soluble Fe-associated) | | | |
| Tessier et al. (1979) | (1) 1 M $MgCl_2$ | | | (2) 1 M NaOAc (carbonate) | | (4) 8.8 M $H_2O_2$ / $HNO_3$ + 0.8 M $NH_4OAc$ | (3) 0.04 M $NH_2OH{\cdot}HCl$ | | (5) HF/ $HClO_4$ | | |
| Amacher and Kotuby-Amacher (1994) | | | | | | | | | (1) 0.25 M $HN_2OH{\cdot}HCl$/0.2 M HCl/0.025 M $H_3PO_4$ (metal oxides) | (2) aqua regia + 8.8 M $H_2O_2$ (metal sulphides) | |
| Il'yin and Konarbayeva (1996) | (1) $NH_4Cl$ | | | (2) $(NH_4)_2CO_3$ (sulphides & As bound to Al compounds)<br>(3) Trilon B (enhanced dissolution of carbonates) | (2) $(NH_4)_2CO_3$ (sulphides & As bound to Al compounds) | | (4) NaOH (organic matter and Fe hydroxides) | (5) $H_2SO_4$ | (6) residual | | |

(Contd….)

Table 2.7 Examples of Sequential Extraction Schemes of Arsenic.

| Reference | (Water) Soluble | Ionically-bound/ exchange-able | Strongly adsorbed | Acid volatile sulphides, carbonates, Mn oxides and amorphous Fe oxyhydr-oxides | Al-associated | Organic matter/ oxidisable | Amorphous and/or crystalline Fe oxyhydr-oxides/ reducible | Low (or acid) soluble | Arsenic oxides and silicates / residual | Pyrite and amor-phous $As_2S$ | Orpiment and other recalcitrant minerals |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Montperrus et al. (2002) | (1) Ultra-pure water | | | | | | (2) 0.1 M hydroxylamine hydrochloride<br>(3) 0.2 M ammonium oxalate | | (4) 0.3 M $H_3PO_4$ | | |
| Gleyzes et al. (2002) | (1) 0.1 M $KH_2PO_4$/ $K_2HPO_4$ (easily extract-able) | | | | | | (2) 0.2 M oxalate/oxalic acid | | | | |
| Cai et al. (2002) | (1) 0.1 M $NaNO_3$ | (2) 0.1 M $KH_2PO_4$ | | | | | | | | | |
| Keon et al. (2001) | | (1) 1 M $MgCl_2$ | (2) 1 M $NaH_2PO_4$ | (3) 1 M HCl | | | (4) 0.2 M oxalate/oxalic acid<br>(5) 0.05 M Ti(III)-citrate-EDTA-bicarbonate | | (6) 10 M HF | (7) 16 M $HNO_3$ | (8) 16 M $HNO_3$ + 30% $H_2O_2$ |

(Contd…)

Table 2.7 Examples of Sequential Extraction Schemes of Arsenic.

| Reference | (Water) Soluble | Ionically-bound/ exchange-able | Strongly adsorbed | Acid volatile sulphides, carbonates, Mn oxides and amorphous Fe oxyhydr-oxides | Al-associated | Organic matter/ oxidisable | Amorphous and/or crystalline Fe oxyhydr-oxides/ reducible | Low (or acid) soluble | Arsenic oxides and silicates / residual | Pyrite and amor-phous $As_2S$ | Orpiment and other recalcitrant minerals |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wenzel et al. (2001) |  | (1) 0.05M $(NH_4)_2SO_4$ (non-specifically sorbed) | (2) 0.05 M $NH_4H_2PO_4$ (specifically sorbed) | (3) 0.2 M $NH_4^+$-oxalate buffer in the dark (amorphous and poorly-crystalline hydrous oxides of Fe and Al) |  |  | (4) 0.2 M $NH_4^+$ - oxalate buffer + ascorbic acid (well-crystallized hydrous oxides of Fe and Al) |  | (5) $HNO_3/H_2O_2$ (microwave digestion) (residual) |  |  |
| Cappuyns et al. (2002) and Van Herreweghe et al. (2003) | (1) 1 M $NH_4Cl$ (easily soluble) |  |  |  | (2) 0.5 M $NH_4F$ (pH 8.2) ($NH_4F$-extractable) |  | (3) 0.1 M NaOH (NaOH or Fe-bound)<br>(4) 0.5 M Na citrate & 1 M $NaHCO_3$ while adding 0.5 g $Na_2S_2O_4 \cdot 2H_2O$ | (5) 0.25 M $H_2SO_4$ | (6) HCl / $HNO_3$ / HF (residual) |  |  |
| Cappuyns et al. (2002) and Van Herreweghe et al. (2003) | (1) $H_2O$ | (2) 2 anion-exchange membrane (AEM) strips |  |  | (3) 0.5 M $NH_4F$ ($NH_4F$-extractable) | (6) 8.8 M $H_2O_2$ + $HNO_3$ (0.02 M) | (4) 0.1 M NaOH (NaOH or Fe-bound)<br>(5) 0.5 M Na citrate + 1 M $NaHCO_3$ 0.02 $MHNO_3$ |  | (7) HCl / $HNO_3$ / HF (residual) |  |  |

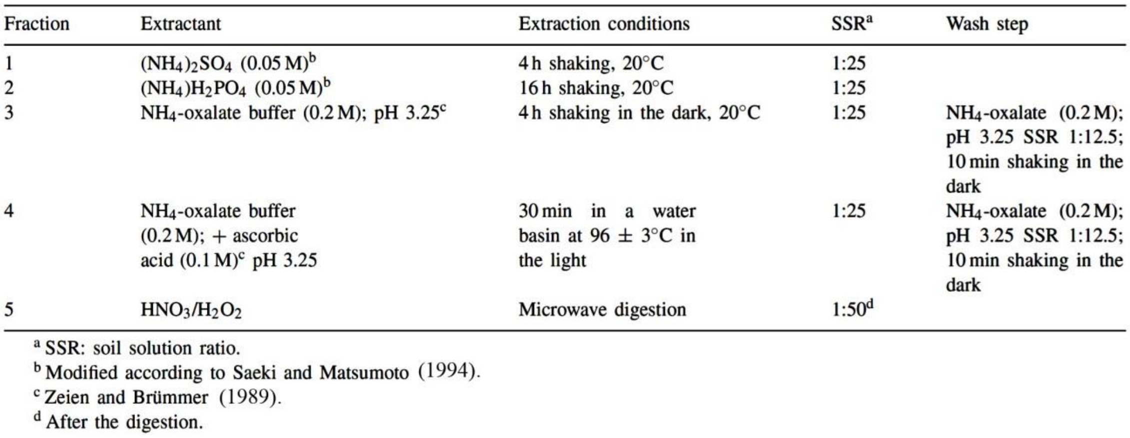
Where the descriptor of the operationally defined extraction for a given reference is different from that in the heading of the table, the difference name is given in parentheses after the chemical extractant used.

* Carried out in a single extraction rather than in sequential extractions.

organic matter and nutrient (N, P) content, mineralogy, cation-exchange capacity, and the major and trace element geochemistry of the whole sediment or soil.

The five-step procedure of Wenzel *et al*. (2001) is an updated or revised version of their originally proposed eight-step procedure (Wenzel *et al*., 1998). The Wenzel *et al*. (2001) protocol allows the prediction of changes in lability of arsenic in various solid phases as a result of soil remediation or alteration in environmental factors. In their method, based on the chemical similarity of phosphorus and arsenic, modified versions of the Chang and Jackson (1957) procedure for phosphorus have been adopted for arsenic. The final sequence obtained includes the following five extraction steps: (1) 0.05M $(NH_4)_2SO_4$, 20°C/4 h; (2) 0.05M $NH_4H_2PO_4$, 20°C/16 h; (3) 0.2M $NH_4^+$-oxalate buffer in the dark, pH 3.25, 20°C/4 h; (4) 0.2M $NH_4^+$-oxalate buffer + ascorbic acid, pH 3.25, 96°C/0.5 h; (5) $HNO_3/H_2O_2$ microwave digestion. Within the inherent limitations of chemical fractionation, these arsenic fractions appear to be primarily associated with (1) non-specifically bound; (2) specifically bound; (3) amorphous hydrous oxide bound (of Fe and Al); (4) crystalline hydrous oxide bound (of Fe and Al); and (5) residual phases. The final sequential extraction process is separately summarized in Table 2.8. In this study, five-step sequential extraction was performed following the procedure described by Wenzel *et al*. (2001). This method was chosen for this study because of its simplicity and high arsenic recovery rate, which has been confirmed by several recent studies (Mral *et al*., 2006; Nóvoa-Muñoz *et al*., 2007; Taggart *et al*., 2004).

Table 2.8 Five-Step Arsenic Fractionation by Wenzel *et al*. (2001)



| Fraction | Extractant | Extraction conditions | SSR[a] | Wash step |
|---|---|---|---|---|
| 1 | $(NH_4)_2SO_4$ (0.05 M)[b] | 4 h shaking, 20°C | 1:25 | |
| 2 | $(NH_4)H_2PO_4$ (0.05 M)[b] | 16 h shaking, 20°C | 1:25 | |
| 3 | $NH_4$-oxalate buffer (0.2 M); pH 3.25[c] | 4 h shaking in the dark, 20°C | 1:25 | $NH_4$-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark |
| 4 | $NH_4$-oxalate buffer (0.2 M); + ascorbic acid (0.1 M)[c] pH 3.25 | 30 min in a water basin at 96 ± 3°C in the light | 1:25 | $NH_4$-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark |
| 5 | $HNO_3/H_2O_2$ | Microwave digestion | 1:50[d] | |

[a] SSR: soil solution ratio.

[b] Modified according to Saeki and Matsumoto (1994).

[c] Zeien and Brümmer (1989).

[d] After the digestion.

## 2.10 RESEARCH SIGNIFICANCE

Compounds of arsenic in soil are of special interest for a number of reasons. The geochemistry and pedochemistry of arsenic have not been adequately investigated because of the limited data on its forms and content in components of the biosphere. Methods for determination of arsenic compounds are more diverse than those applied for other elements. Among them, there are methods applied for the analysis of phosphorus, an element similar to arsenic, and for the compounds of metals as well. Analysis of the arsenic content is more laborious. The use of flame atomic absorption spectrophotometry is almost impossible because of its low sensitivity. Electrothermal atomization of a sample makes its analysis more complicated. All these circumstances testify for the necessity of methodological and research works oriented to the study of the fractional composition of arsenic compounds in soils.

Remediation of metal(loid)-contaminated soils can be managed by manipulating the bioavailability of metal(loid)s. Phosphate compounds have often been used to increase the immobilization of metal(loid)s such as lead (Pb) and zinc (Zn), thereby reducing their mobility and bioavailability in soil (Bolan *et al*., 2013; Song *et al*., 2009). Alternatively soil remediation can be achieved by metal(loid)s' mobilization processes that include phytoremediation and chemical washing. Metal(loid)s' mobilization can be enhanced by the addition of soil amendments such as chelating (e.g., EDTA for Cu removal) and desorption (e.g., phosphorus for arsenic removal) agents (Cao *et al*., 2003; Lestan *et al*., 2008). Phosphorus influences arsenic uptake by plants by two processes. Firstly, it is well known that arsenate [As(V)] acts as a phosphorus analog and is taken up by plants via a phosphorus transporter system (Meharg and Macnair, 1992). While phosphorus deficiency can enhance arsenic uptake, high concentration of phosphorus in soil solution can inhibit the uptake of arsenic (Lei *et al*. 2012; Pigna *et al*. 2009). Secondly, phosphorus is more strongly adsorbed to soil than As(V) and hence competes for sorption sites, thereby facilitating the desorption of arsenic to soil solution and its subsequent uptake by plants (Ravenscroft *et al*., 2001). Thus the influence of phosphorus on arsenic mobilization depends on the charge characteristics of soils.

It is well established that (BGS-DPHE, 2001) southern part of Bangladesh groundwater is severely affected by Arsenic contamination which is also affecting the agricultural soil and crops grown therein. Phosphate fertilizers are very commonly used in agricultural soils in Bangladesh including these Arsenic affected areas. Arsenic is chemically similar to Phosphorus. Phosphorus (P) influences arsenic (As) mobility and bioavailability which depends on the charge components of soil. Dissolved phosphate is likely to compete with dissolved arsenic species (arsenite, arsenate) for adsorption sites on iron and other oxides in soil. Similarly, it may be difficult for plants to distinguish between arsenate and phosphate. Thus uptake of arsenate and phosphate by plants is very likely to be competitive. Furthermore, after entering a plant, arsenate may replace phosphate in ATP synthesis, and/or in various phosphorolysis reactions, thus interfering with phosphate metabolisms and causing toxicity to a plant (Dixon, 1997). In contrast, phosphate may be able to alleviate arsenate toxicity by improving phosphate nutrition (Sneller *et al*., 1999). Tu and Ma (2003) reported that phosphate application may be an important strategy for efficient use to phytoremediate arsenic contaminated soils. However, further study is needed on the mechanisms of interactive effects of arsenate and other anions e.g. phosphate and sulphate. Past studies on anion interaction (Begum and Huq, 2007; Cao *et al*., 2003; Davenport and Peryea, 1991; Fuller *et al*., 1993; Manning and Goldberg, 1996; O'Reilly *et al.,* 2001) found that $PO_4^{3-}$ causes arsenic mobilization but the exact species of arsenic was unknown. It is expected that the proposed fractionation study shall shed light on this issue and shall enable us to formulate appropriate remediation strategy based on the presence of different species of arsenic in the contaminated soils.

# Chapter 3

# MATERIALS AND METHODS

## 3.1 GENERAL

Laboratory experiments were conducted on soil samples collected from a few selected locations of Bangladesh. The laboratory facilities of the Department of Soil, Water and Environment, University of Dhaka were used. Experiments were conducted in both the regular chemical laboratory as well as the Advanced Laboratory which houses an Atomic Absorption Spectrophotometer (Model: Varian AA240). Some details of the experimental procedures are described in the following sections.

## 3.2 LOCATIONS OF SOIL SAMPLES

Soil samples are collected from different locations of agricultural fields of Bangladesh. These locations are as follows,

a. Tala, Satkhira
b. Sadar, Satkhira
c. Titas, Comilla
d. Subarnachar, Noakhali
e. Gournadi, Barisal
f. Fukura, Kashiani, Gopalgonj
g. Tungipara, Gopalgonj
h. Bagerhat
i. Khulna
j. Madhupur, Tangail

## 3.3 COLLECTING AND PROCESSING OF SOIL SAMPLES

The soil samples were collected from surface of paddy fields. Some of the samples were obtained through the curtesy of Soil Resource Development Institute

(SRDI), Govt. of Bangladesh. Soil samples were obtained on the basis of composite sampling method as suggested by the Soil Survey Staff of the USDA (1993). Each of the collected soil samples was dried in the air by spreading on separate sheet of paper after it was transported to the laboratory. For the purpose of hastening the drying process, these were exposed to sunlight. After air-drying, portions of larger and massive aggregates and gravels was broken by gentle crushing with a mallet. Then these samples were passed through a 2.0 mm sieve. The sieved soils were then preserved in plastic containers and labeled properly. These were used for analyses of both physical and chemical properties.

## 3.4 LABORATORY ANALYSES

## 3.4.1 Physical Properties

### 3.4.1.1 Particle Size Analysis

The particle size distribution of soil carried out by Hydrometer method as described (Bouyoucos, 1927). The textural classes were determined by Marshall's triangular co-ordinates as devised by the United States Department of Agriculture (USDA, 1993).

### 3.4.1.2 Moisture content

The moisture content of air-dried samples was determined by drying known amount of sample in an oven at $105^0$C for 24 hours until constant weight was obtained and the moisture percentage was calculated from the loss of the moisture from the samples.

## 3.4.2 Chemical Properties

### 3.4.2.1 Soil Reaction (pH)

The pH of the soil was measured by electrochemical method using a glass electrode pH meter (Model: Jenway 3305). The ratio of soil to water was 1:2.5 as suggested by Jackson (1962).

### 3.4.2.2 Electrical Conductivity

The Electrical conductivity (EC) of the soil was measured in the saturation extract of the soil with the help of an EC meter. The unit of EC is measured by micro-Simens per cm (μS/cm).

### 3.4.2.3 Organic Carbon

Soil organic carbon was determined volumetrically by Wet Oxidation method (Walkley and Black, 1934).

### 3.4.2.4 Organic Matter

Soil organic matter was calculated by multiplying the percent value of organic carbon by the van Bemmelen factor of 1.724.

### 3.4.2.5 Cation Exchange Capacity

The cation exchange capacity (CEC) of soil was determined by using ammonium acetate as described by Schollenberger and Simon (1945). The soil samples were treated with normal ammonium acetate followed by replacing ammonium on the exchange complex by 1N NaCl (pH 7). The displaced ammonium was distilled with 40% NaOH and $NH_3$ evolved was absorbed in 2% boric acid having mixed indicator. The excess of the acid was back titrated with standard $H_2SO_4$ acid.

### 3.4.2.6 Aqua-regia Digestible Nutrients

Soil samples were digested on hot plate with Aqua-regia ($HCl+HNO_3$ mixture, 3:1) (ISO 11466) for determination of total Sulphur (S), Phosphorus (P), Iron (Fe), Manganese (Mn), Magnesium (Mg), Calcium (Ca), Potassium (K), Sodium (Na) and total Arsenic (As).

**Total Sulphur:** The total sulphur content of soil was determined colorimetrically in the extract of digestion (Jackson, 1973) using a chemito visible spectrophotometer by turbidimetric method by recording the absorbance after 20 minute at 420 nm wavelength.

**Total Phosphorus**: The total phosphorus content of the soil was determined colorimetrically in the extract digestion using a chemito visible spectrophotometer after developing the yellow colour with vanadomolybdate as described by Jackson (1962). The intensity of the yellow colour was measured at 470 nm wavelength.

**Total Iron (Fe), Manganese (Mn), Calcium (Ca) and Magnesium (Mg):** Total Fe, Mn, Ca and Mg contents of soil were determined by analyzing the digested extract using atomic absorption spectrophotometer model Variant AA240.

**Total Potassium (K) and Sodium (Na):** Total Potassium (K) and Sodium (Na) was determined by using Jencons Flame Photometer (Model No. PFP 7) from aqua regia digestion.

**Total Arsenic:** The digested samples were filtered and amount of Arsenic was determined by an atomic absorption spectrophotometer (AAS: Varian AA240) fitted with a hydride generator system.

### 3.4.2.7 Free Carbonate

The amount of % free carbonate in the soil samples was determined using the Piper (1950) method.

## 3.5 SELECTION OF SITES FOR ARSENIC FRACTIONATION

The soils collected from the ten sites mentioned in Section 3.2 were tested for total arsenic concentration and pH values. The results are given in Table 3.1.

Table 3.1 Arsenic Concentration and pH of Soil Samples.

| Sl. | Location | As concentration, mg $kg^{-1}$ | Soil pH |
|---|---|---|---|
| a. | Tala, Satkhira | 6.73 | 6.06 |
| b. | Sadar, Satkhira | 3.45 | 6.11 |
| c. | Titas, Comilla | 3.98 | 6.26 |
| d. | Subarnachar, Noakhali | 2.07 | 6.33 |
| e. | Gournadi, Barisal | 2.08 | 6.50 |
| f. | Fukura, Kashiyani, Gopalgonj | 88.00 | 7.76 |
| g. | Tungipara, Gopalgonj | 3.35 | 7.3 |
| h. | Bagerhat | 21.95 | 7.1 |
| i. | Khulna | 22.55 | 6.9 |
| j. | Madhupur, Tangail | 3.68 | 5.31 |

Among these soil samples, three areas of Bangladesh (Fig 3.1) were chosen for incubation depending on soil pH and Arsenic concentration. These areas were,

a) Bagerhat.

b) Kashiyani, Gopalgonj and

c) Madhupur, Tangail

It can be observed from Table 3.1 that three locations – Khulna, Bagerhat and Kashiani had high Arsenic concentration. Among these, Bagerhat and Kashiani locations were chosen for fractionation. Khulna was omitted due to the limited scope of present investigation. Madhupur soil was selected as the control soil.

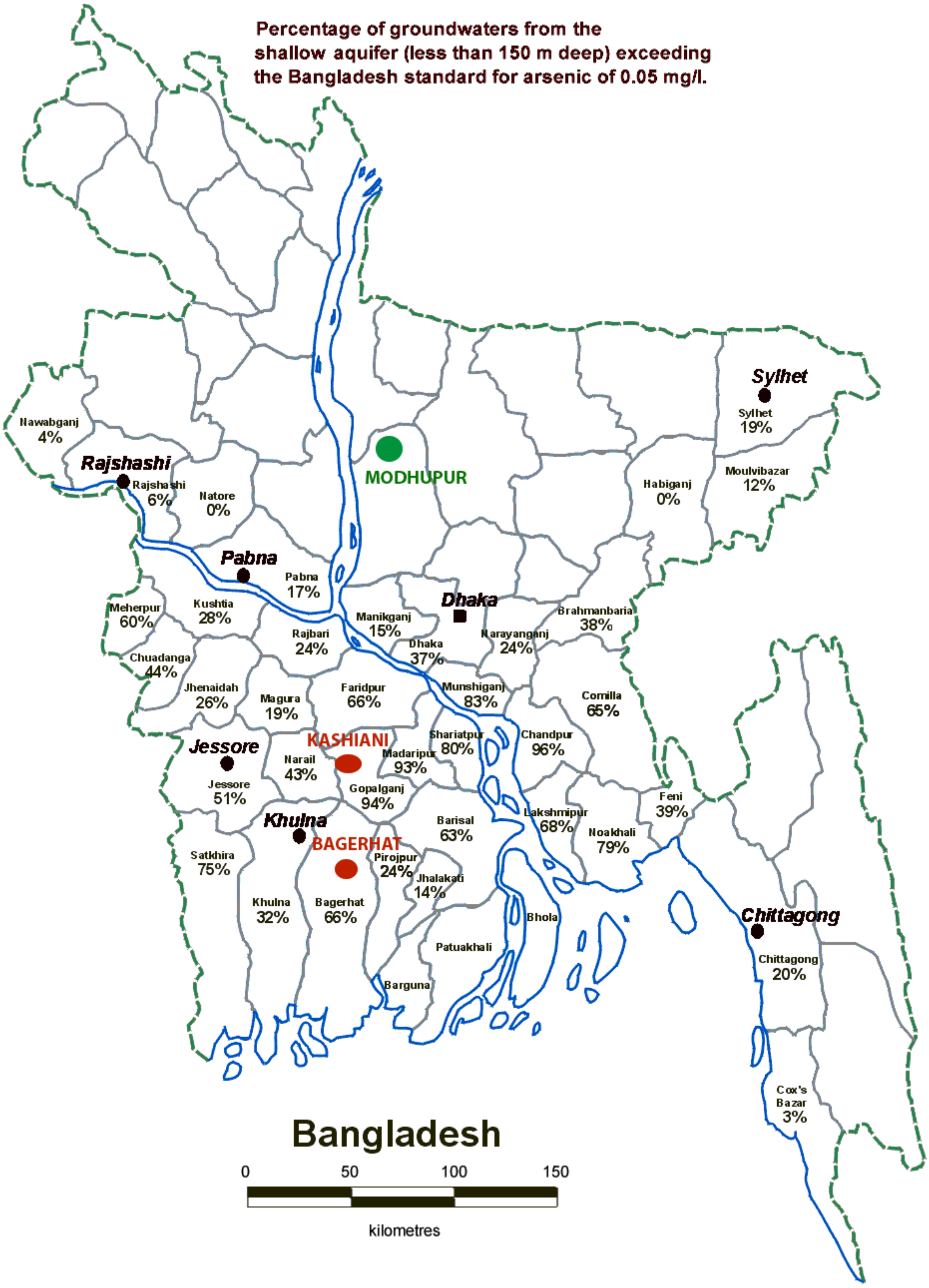


Fig. 3.1 Locations of soil samples selected for study.

## 3.6 CHOICE OF ANION INTERACTION WITH ARSENIC

Arsenic release may occur due to competition from other strongly bound anions such as phosphate, bicarbonate and silicate and sulphate (BGS and DPHE, 2001). There is also often a good correlation between the iron content of the sediment and its arsenic content. While iron is found in both iron oxides and iron sulphides, the low sulphur content of most the sediments of Bangladesh indicate that the dominant source of iron in these sediments is the oxides not sulphides (BGS and DPHE 2001). Woolson *et al*. (1973) showed that arsenate could be leached from soil by $PO_4^{3-}$ and Melamed *et al.* (1995) and Davenport and Peryea (1991) showed that arsenate mobility was vastly enhanced by treatments with increasing amounts of $PO_4^{3-}$. Phosphate-released arsenic was not significantly resorbed in the presence of added $PO_4^{3-}$ (Amacher and Amacher, 1994; Peryea, 1991). Pierce and Moore (1982) found that once arsenate was sorbed to a natural surface in an aqueous system, the sorbed arsenate was not affected by the post addition of $PO_4^{3-}$ and $SO_4^{2-}$. However, sorbed arsenate was affected, at low concentrations, by the prior addition of $PO_4^{3-}$ and $SO_4^{2-}$ to the system.

These studies give us some important ideas about the interaction of Arsenic with $PO_4^{3-}$ and $SO_4^{2-}$ anions. However, the exact solid phase fraction of arsenic which is interacting with these anions is not fully clear. Therefore, a fractionation study is justified to get a closer insight into the interaction of arsenic with phosphate and sulphate anions.

## 3.7 INCUBATION WITH ARSENIC, PHOSPHORUS AND SULPHUR SOLUTION

Soil samples were spiked with fourteen different treatments with three elements – Arsenic (As), Phosphorous (P) and Sulphur (S). For each treatment 5-step sequential extraction process was carried out following the procedure of Wenzel *et al.* (2001). The whole procedure was performed for three incubation periods – 0 day, 7 days and 30 days. The fourteen incubated treatments are shown in Table 3.2.

In order to carry out the treatment effects shown in Table 3.2, 1000 mg $L^{-1}$ solution of arsenic, phosphorus and sulphur were prepared from Sodium Arsenite

Table 3.2 The Fourteen Treatments for Arsenic Fractionation.

| Treatment No. | Description | Designation |
|---|---|---|
| $T_1$ | 10 mg kg$^{-1}$ As solution + 10 mg kg$^{-1}$ P solution after 24 hours | As-P(10) |
| $T_2$ | 10 mg kg$^{-1}$ As and P solutions simultaneously | As+P(10) |
| $T_3$ | 10 mg kg$^{-1}$ P solution + 10 mg kg$^{-1}$ As solution after 24 hours | P-As(10) |
| $T_4$ | 30 mg kg$^{-1}$ As solution + 30 mg kg$^{-1}$ P solution after 24 hours | As-P(30) |
| $T_5$ | 30 mg kg$^{-1}$ As and P solutions simultaneously | As+P(30) |
| $T_6$ | 30 mg kg$^{-1}$ P solution + 30 mg kg$^{-1}$ As solution after 24 hours | P-As(30) |
| $T_7$ | 10 mg kg$^{-1}$ As solution + 10 mg kg$^{-1}$ S solution after 24 hours | As-S(10) |
| $T_8$ | 10 mg kg$^{-1}$ As and S solutions simultaneously | As+S(10) |
| $T_9$ | 10 mg kg$^{-1}$ S solution + 10 mg kg$^{-1}$ As solution after 24 hours | S-As(10) |
| $T_{10}$ | 30 mg kg$^{-1}$ As solution + 30 mg kg$^{-1}$ S solution after 24 hours | As-S(30) |
| $T_{11}$ | 30 mg kg$^{-1}$ As and S solutions simultaneously | As+S(30) |
| $T_{12}$ | 30 mg kg$^{-1}$ S solution + 30 mg kg$^{-1}$ As solution after 24 hours | P-As(30) |
| $T_{13}$ | 10 mg kg$^{-1}$ As, S and P solutions simultaneously | As+S+P(10) |
| $T_{14}$ | 30 mg kg$^{-1}$ As, S and P solutions simultaneously | As+S+P(30) |

($NaASO_2$), Potassium-di-hydrogen Phosphate ($KH_2PO_4$) and Sodium Sulphate ($Na_2SO_4$) respectively. Then 10 mg L$^{-1}$ and 30 mg L$^{-1}$ solutions of arsenic, phosphorus and sulphur were obtained by diluting these 1000 mg L$^{-1}$ solutions (Fig. 3.2.a). For incubation study, 10gm soil sample was placed in a test tube and then the fourteen treatments were applied to each soil. Thus for each of the three sample locations, there were a total of 42 (3x14) tubes for incubation (Fig. 3.2.b). The treatments were performed at field moisture capacity. To maintain the moisture level, the test tubes were covered with parafilm wrap. The tubes were kept at room temperature in the laboratory. Approximate 1.3 gm moist samples were taken from the test tubes and were put into centrifuge tube after incubation period of 0 day, 7 days and 30 days interval for 5-step arsenic fractionation. Each treatment was replicated twice. For each 1.3 gm moist sample, the percent moisture content were determined so that results corresponding to 1 gm dry soil can be obtained.

Fig. 3.2.a Laboratory procedure: Extracted samples awaiting AAS operation.

Fig. 3.2.b Laboratory procedure: Spiked samples.

## 3.8 SELECTION OF ARSENIC FRACTIONATION METHODOLOGY

Wenzel *et al*. (1998) proposed an eight-step sequential procedure for extraction of Arsenic from soils of Austria. Keon *et al*. (2001) also adopted an eight-step sequential extraction procedure to validate the mobility of Arsenic in sediments. Both of these methods required extended laboratory procedures. In 2001, Wenzel *et al*. proposed a revised sequential extraction procedure (SEP) involving five steps. According to Wenzel *et al*. (2001), this later procedure is recommended over the previous 8-step SEP. In the current research, the 5-step SEP as recommended by Wenzel *et al*. (2001) was adopted for its accuracy and reproducibility of results.

## 3.9 FIVE-STEP SEQUENTIAL ARSENIC FRACTIONATION (Wenzel *et al.*, 2001)

A relatively simple and well-adopted method to assess trace element pools of differential relative lability in soils is the sequential extraction with reagents of increasing dissolution strength. Wenzel *et al*. (2001), developed a 5-step sequential extraction procedure (SEP) of arsenic from Austrian soil. In this procedure, each reagent targets a specific solid phase associated with the trace element of interest. Sequence of extractants of decreasing pH are aimed at minimizing adverse interactions (re-adsorption, precipitation) between subsequent extractants. The SEP is easily adaptable in routine soil analysis, is dependable as indicated by repeatability and recovery test. The SEP can be useful in predicting the changes in the lability of arsenic in various solid phases as a result of soil remediation or alteration in environmental factors. Details of the 5-Step SEP are shown in Table 3.3. Ammonium sulfate $(NH_4)_2SO_4$) extraction in Step -1 was shown to correlate well with the arsenic in the field collected soil solutions and hence it can be used for predicting the solute arsenic (Wenzel *et al.*, 2002). Step - 2 of the scheme employs the phosphate solution to extract specifically sorbed arsenic based on anion exchange between phosphate and arsenate. Ortophosphoric acid was previously shown to be very efficient in arsenic extraction from soils (Gallardo *et al.*, 2001). Potassium phosphate ($KH_2PO_4$) was suggested as an extractant for the mobilisable arsenic fraction in a simplified arsenic fractionation method proposed by Cai *et al*. (2002). Steps - 3 and 4 of the Wenzel *et al*. (2001) protocol involve extraction with

Table 3.3 The Five-Step SEP of Wenzel *et al*. (2001).

| Fractionation steps | Extractant | Extraction Cond. | SSR | Wash step |
|---|---|---|---|---|
| 1. Non-specifically-bound | $(NH_4)_2SO_4$ (0.05M)[b] | 4h shaking, 20°C | 1:25 | |
| 2. Specifically-bound | $(NH_4)H_2PO_4$ (0.05M)[b] | 16h shaking, 20°C | 1:25 | |
| 3. Amorphous hydrous oxide-bound | NH4-oxalate buffer (0.2M); pH 3.25[c] adjusted with diluted $NH_3$ solution. | 4h shaking in dark, 20°C | 1:25 | $NH_4$-oxalate (0.2M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark |
| 4. Crystalline hydrous oxide-bound | NH4-oxalate buffer (0.2M); + ascorbic acid (0.1M)[c] pH 3.25 | 30 min in a water basin at 96±3°C in the light | 1:25 | $NH_4$-oxalate (0.2M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark |
| 5. Residual | $HNO_3$ - $H_2O_2$ | Microwave digestion | 1:50[d] | |

[a] SSR: soil solution ratio
[b] Modified according to Saeki and Matsumoto (1994)
[c] Zeien and Brümmer (1989)
[d] After the digestion

the oxalate buffer in the dark to solubilise the amorphous Fe-oxides and the oxalate buffer in ascorbic acid in the light for solubilisation of the crystalline forms. The oxalate method is widely used in the soil research and it has been shown effective in a separation of the amorphous Fe-oxides (mainly in the form of ferrihydrite) from better crystalline oxides such as hematite and goethite (Cornell and Schwertmann, 1996). The oxalate ions form very stable complexes with polyvalent cations such as Fe(III). In the absence of the catalysing effect of light, oxalate does not dissolve crystalline Fe-oxides and thus allows for separation of both forms (Shuman, 1982). Ascorbic acid is a more reducing agent and allows for solubilisation of crystalline forms of Fe-oxides in the soils (Cornell and Schwertman, 1996). It should be noted however that in the Steps 3 and 4 of the Wenzel method Al and Mn oxides are also solubilised and thus these fractions should be assigned as amorphous oxide bound and crystalline oxide bound. The Wenzel method does not allow for differentiation between arsenic bound to Fe, Al and Mn- oxides.

In the present study, after 5-step fractionation, the number of samples tested for arsenic for each soil is 630. Thus a total of 1890 samples were tested for arsenic for three samples of soil. The supernatant were preserved in plastic container after centrifuging at 2000 rpm for 20 minutes. But in 5th step, the residual soil was digested with the $HNO_3$-$H_2O_2$. After digestion, the sample was filtered and the extract was made to 50ml by adding de-ionized water. After preparation of the above mentioned 1890 nos. of samples, the three replicates were mixed to obtain 630 samples which were used in AAS for arsenic determination.

# Chapter 4

# RESULTS AND DISCUSSION

## 4.1 GENERAL

The soil samples under investigation were collected from different locations. Their physical appearance and characteristics were also different. The Bagerhat soil had an olive-grey appearance while the Kashiani soil was brownish grey. On the other hand, the Madhupur soil appeared typical red. Kashiani soil showed high effervescence on addition of hydrochloric acid (HCl) solution, while the Bagerhat soil showed low and the Madhupur soil showed no effervescence supporting the fact that Kashiani sample was highly calcareous while the calcareousness of Bagerhat sample was relatively low.

## 4.2 PROPERTIES OF SOILS

### 4.2.1 Physical Properties of Soil Samples

Bagerhat soil consisted mainly of silt and clay fractions of about equal proportions with a small sand fraction (8.17%) giving it a silty clay texture. On the other hand, the Kashiani soil was dominated by all the fractions of sand, silt and clay resulting in a sandy clay loam texture. The Madhupur soil was characterized by almost equal proportions of sand and silt, both being about 39% and the rest being the clay fraction. These physical properties are summarized in Table 4.1.

Table 4.1 Physical Properties of Soil Samples.

| Location | Moisture % | Particle size distribution (%) | | | Texture |
|---|---|---|---|---|---|
| | | Sand | Silt | Clay | |
| Bagerhat | 4.71 | 8.17 | 47.23 | 44.60 | Silty clay |
| Kashiani | 6.45 | 46.55 | 21.38 | 32.07 | Sandy Clay Loam |
| Madhupur | 2.31 | 38.58 | 38.39 | 23.03 | Loam |

### 4.2.2 Chemical Properties of Soil Samples

Arsenic concentration was found to be quite high in the Kashiani soil (88 mg kg$^{-1}$). Bagerhat soil also contained 22 mg kg$^{-1}$ of arsenic (Table 4.2). Sulphur content was found to be low for all the samples which was also supported by the findings of BGS and DPHE (2001), the values were less than 0.4 mg L$^{-1}$ in the groundwater of arsenic affected areas. These observations support the finding of BGS and DPHE (2001) that an inverse relationship exists between arsenic and sulphur.

Table 4.2 Chemical Properties of Soil Samples

| Properties | Locations | | |
|---|---|---|---|
| | Kashiani | Bagerhat | Madhupur |
| pH | 7.76 | 7.10 | 5.31 |
| EC, μS/cm | 365 | 2330 | 266 |
| Org. Carbon (%) | 1.72 | 0.87 | 0.57 |
| Org. matter (%) | 2.96 | 1.5 | 0.98 |
| CEC, cmol/kg | 13.74 | 12.76 | 9.0 |
| Total As, mg kg$^{-1}$ | 88 | 22 | 3.68 |
| Total Ca, mg kg$^{-1}$ | 2080 | 441 | BDL |
| Total Mg, mg kg$^{-1}$ | 45.4 | 99.5 | 34.6 |
| Total Mn, mg kg$^{-1}$ | 3.4 | 5.95 | 1.6 |
| Total Fe, mg kg$^{-1}$ | 300 | 159 | 241 |
| Total N, % | 17.29 | 10.41 | 17.7 |
| Total P, % | 0.421 | 0.092 | 0.029 |
| Total K, % | 0.37 | 0.33 | 0.16 |
| Total S, % | 0.063 | 0.076 | 0.044 |
| Total Na, % | 0.037 | 0.085 | 0.021 |
| Free $CO_3^{2-}$, % | 9 | 2 | Nil |

Content of both calcium (2080 mg kg$^{-1}$) and free carbonate (9%) was considerably higher in the Kashiani sample giving it a more calcareous characteristic than the Bagerhat soil while the acidic Madhupur soil did not contain any calcium or carbonate (Table 4.2). According to Huq and Naidu (2003), in Bangladesh, the soils developed on Gangetic alluvium have been found to contain relatively higher amount of arsenic. Moreover, the soils of Gangetic alluvium are in general have pH values above 7.0 with many soils being calcareous in nature

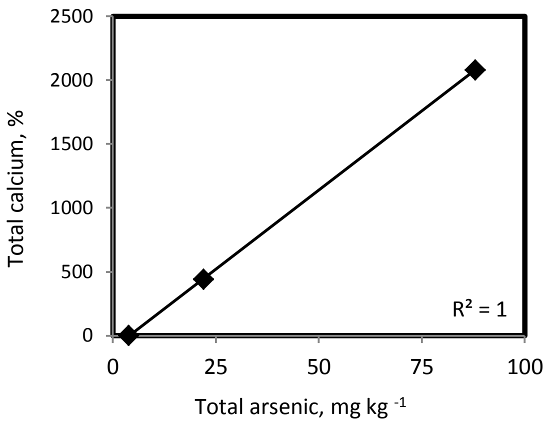


Fig. 4.1.a Correlation between arsenic and total calcium.

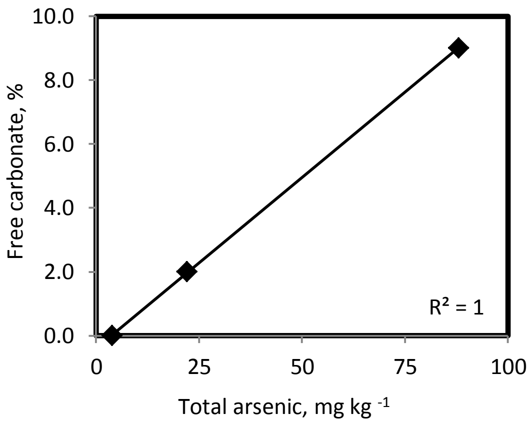


Fig. 4.1.b Correlation between arsenic and free carbonate.

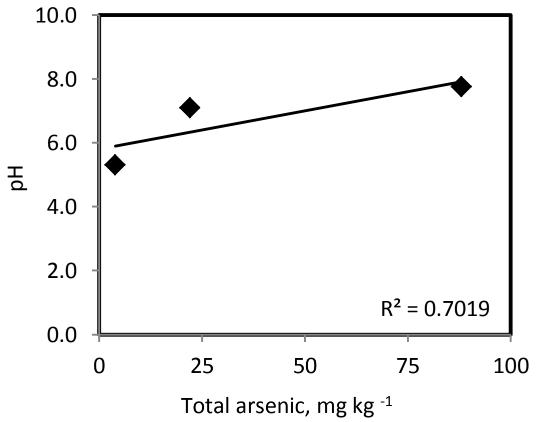


Fig. 4.1.c Correlation between arsenic and pH.

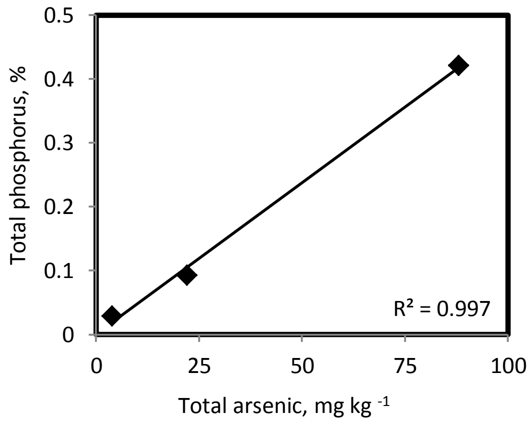


Fig. 4.1.d Correlation between arsenic and total phosphorus.

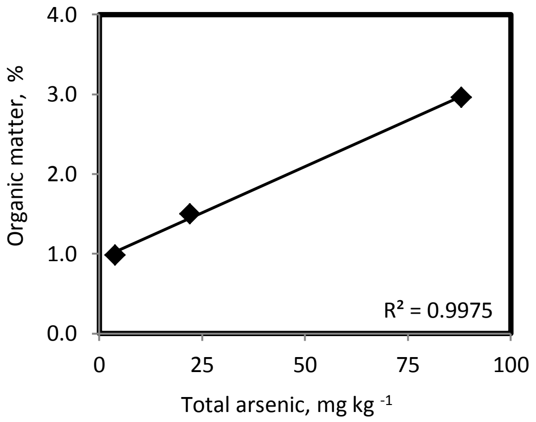


Fig. 4.1.e Correlation between arsenic and organic matter.

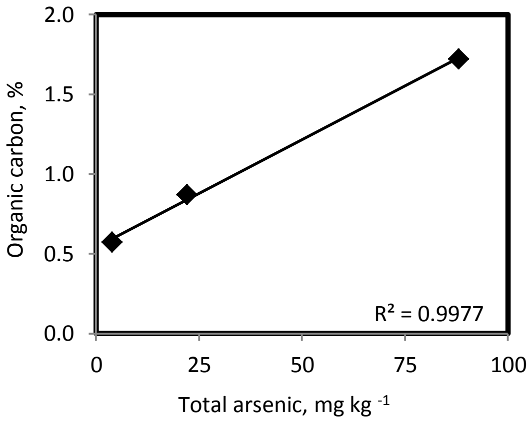


Fig. 4.1.f Correlation between arsenic and organic carbon.

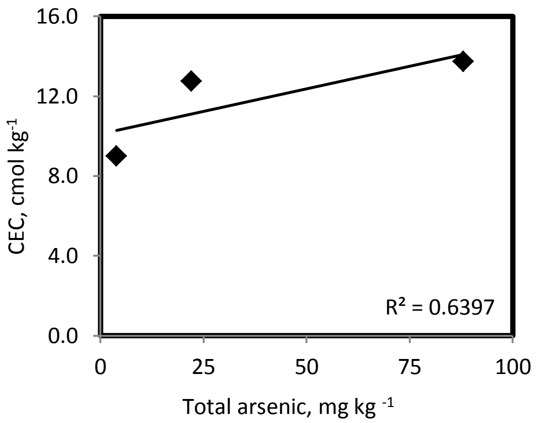


Fig. 4.1.g Correlation between arsenic and CEC.

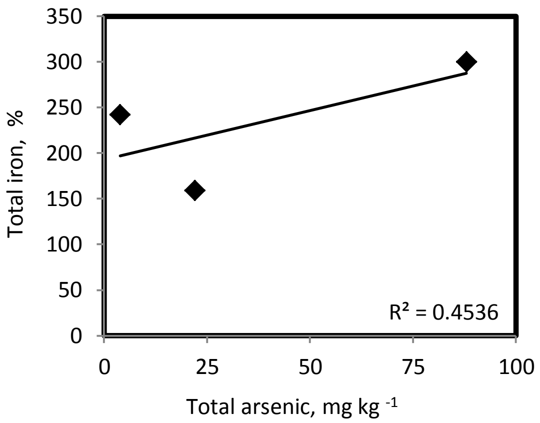


Fig. 4.1.h Correlation between arsenic and total iron.

(having free $CaCO_3$). Correlation between total arsenic content and calcium (Fig. 4.1.a) shows strong correlation ($R^2 \approx 1.0$). Similar strong correlation also exists between arsenic and free carbonate (Fig. 4.1.b) too ($R^2 \approx 1.0$). A possible reason could be that minerals in the clay fraction of soils, such as carbonates can contribute to arsenic adsorption due to their abundance (Goldberg and Glaubig, 1988; Goldberg, 2002; Ladeira and Ciminelli, 2004).

The Bagerhat sample had neutral pH. The Kashiani sample was slightly alkaline (pH 7.76) while the Madhupur sample had slightly acidic reactivity. Moderate correlation ($R^2$ = 0.702) exists between total arsenic and corresponding soil pH as shown in Fig. 4.1.c

The electrical conductivity of the Bagerhat soil was found to be quite high (2330 μS/cm) compared to the other two samples. This is probably due to the higher salinity of Bagerhat soil which has also been substantiated by the relatively higher sodium content (850 mg kg$^{-1}$).

Phosphorus content was found to be highest in the Kashiani soil (4207 mg kg$^{-1}$) which also showed highest arsenic contamination. Total phosphorus content of Bagerhat soil was found to be 924 mg kg$^{-1}$ while the uncontaminated Madhupur soil had only 289 mg kg$^{-1}$. A close similarity in the arsenic and phosphorus distribution in the groundwater of Bangladesh can be observed form Fig. 2.2 and Fig. 2.5 (BGS & DPHE, 2001). The pattern of phosphorus concentration in the samples was also very similar to that of arsenic concentration of the soil samples.

Strong correlation ($R^2$ = 0.997) was found between total arsenic and total phosphorus (Fig. 4.1.d).

The amount of organic matter in the Bagerhat, Kashiani and Madhupur samples were found to be 1.5, 2.96 and 0.98 percent, respectively. According to Faust *et al*. (1987) as reported by Wenzel *et al*. (2001), there is growing evidence that in contrast to phosphate, arsenic is virtually not associated with soil organic matter (SOM) when in competition with other soil constituents such as hydrous iron oxides as sorption sites. However, according to the study of BGS and DPHE (2001), decomposition of organic matter will undoubtedly release some phosphate (and arsenic as well). The competition of organic molecules for surface adsorbing sites can enhance arsenic release and, under submerged conditions, by favoring the microbial activity, may accelerate the reduction of arsenic-bearing solids and of arsenic itself (Williams *et al*., 2011). Huq *et al*. (2008) found a positive relationship of arsenic content with organic carbon along several Bangladesh soil profiles. A possible explanation is the formation of cation bridging and/or of arsenic-bearing iron-organic colloids with large reactive surface and a disordered structure stabilized by the organic molecules (Bauer *et al*., 2008). According to Harvey *et al*. (2002) respiration of organic carbon plays a role in arsenic mobilization. Mobilization may be driven by reduction with organic carbon despite the paucity of ferric oxy-hydroxides. Findings of the present study also favor these findings. The correlation between arsenic and organic content in present study appeared to be very strong (Fig. 4.1.e) among the soil samples studied ($R^2$=0.9975). Similar correlation was also found between total arsenic and organic carbon (Fig. 4.1.f, $R^2$=0.9977). The cation exchange capacity also showed correlation (Fig. 4.1.g) with arsenic content ($R^2$=0.6397).

The total iron content of Kashiani, Bagerhat and Madhupur samples were 300, 159 and 241 mg $kg^{-1}$, respectively. Correlation of these iron content with respective arsenic content, however, did not show any strong correlation (Fig. 4.1.h, $R^2$=0.4536). It is a generally accepted fact that there is a good correlation between As, Fe and Mn in their occurrence, transport and exposure to the environment (Baviskar *et al*., 2011; Manning and Goldberg 1997; O'Reilly *et al*., 2001; Sarifuzzaman *et al*., 2007). In the present study, the respective concentrations of arsenic and iron in both Kashiani and Bagerhat soils support the fact. The high associativity of Fe with arsenic in Kashiani and Bagerhat soil is probably due to presence of iron oxy-hydroxides (Islam *et al*., 2009). The Madhupur soil, despite having high Fe concentration, contains very low amount of arsenic. This is due to the fact that Madhupur soil contains large amount of Fe(III) oxides which are quite stable and therefore incapable of bonding arsenic.

## 4.3 ARSENIC FRACTIONS OF ORIGINAL SOIL SAMPLES

A few studies revealed that the average background concentration of arsenic in Bangladesh is much below 10 mg $kg^{-1}$ soil (Ali *et al*., 2003; Huq *et al*., 2001). However, in some areas, the concentration has been found to be as high as 80 mg $kg^{-1}$ soil. The soil arsenic varies both spatially and vertically. The soil formation and the aquifer characters control the spatial variation, while the vertical distribution is controlled by the clay contents (Huq and Naidu, 2005). In the present study, the total concentration of arsenic in Bagerhat, Kashiani and Madhupur samples were found to be 22.0, 88.0 and 3.68 mg $kg^{-1}$, respectively. Arsenic is bound up in various fractions of soils. Some of it may be easily released and go into solution rendering it available to plants, while others are tightly bound or are fixed within the clay lattices. Therefore, a five-step sequential fractionation (Wenzel *et al*., 2001) of the untreated samples was conducted to determine the various fractions of arsenic in the samples and the results are graphically represented in Fig. 4.2 (see Appendix - I). The findings of the fractionation of the untreated samples would help in understanding and comparing the anion-anion interaction (arsenic with phosphate and sulphate) study of the spiked samples. The fractionation results showed that for all soil samples, the highest amount of arsenic fraction was bound with crystalline hydrous oxide in SEP step-4 using $NH_4$-oxalate/ascorbic acid extractant. The highest concentration was found from Kashiani soil (53.45 mg $kg^{-1}$). For Bagerhat soil, the maximum amount was found as crystalline hydrous oxide-bound (7.14 mg $kg^{-1}$) followed by amorphous hydrous oxide bound (4.21 mg $kg^{-1}$). It can be noted that the uncontaminated Madhupur soil showed very low arsenic fraction in all steps of SEP indicating that this soil did not have arsenic bonding active mechanism. The study of Wenzel *et al*. (1998) also reported highest amount of arsenic extraction with oxalate extractant indicating that arsenic is primarily associated with amorphous or crystalline hydrous oxide bound. The amount of readily mobile arsenic extracted by $(NH_4)_2SO_4$ in Step-1 was generally small but represented the most important fraction for risk assessment. The amount of arsenic extracted by $(NH_4)H_2PO_4$ in Step-2 provide a relative measure of specifically-bound arsenic in soil. The residual fraction was typically small.

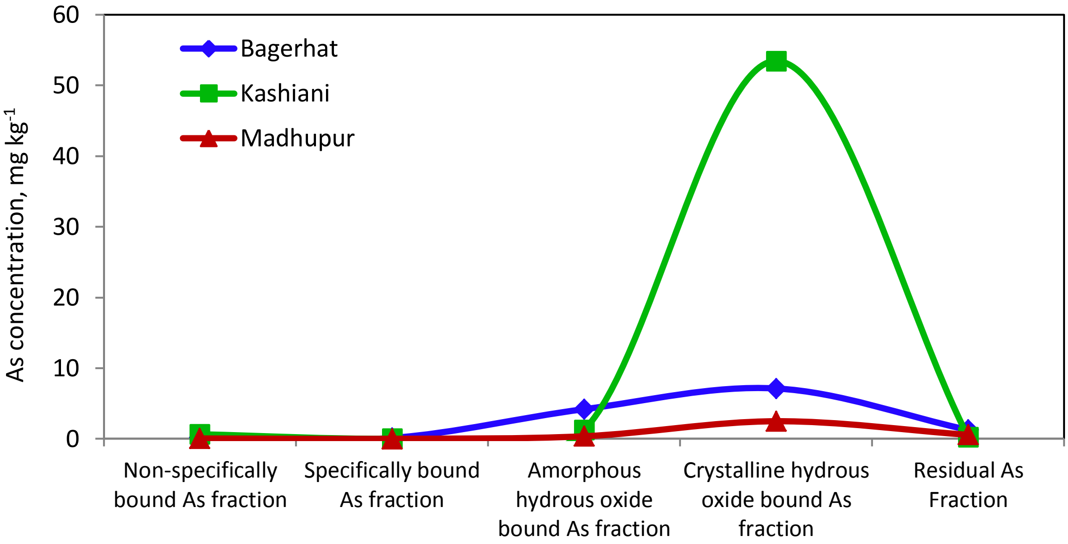


Fig. 4.2 Five-step arsenic fractionation of untreated samples from three locations.

## 4.4 INTERACTION OF ARSENIC WITH PHOSPHORUS

It has been described earlier that a total fourteen treatments (spiking) were applied to all the three soil samples (Table 3.2) for three incubation periods. Of these treatments, the first six ($T_1$ to $T_6$) were aimed at examining the interaction with phosphate anion. Soil samples subjected to each of the six treatments of a particular incubation period underwent 5-Step sequential extractions procedure (SEP) developed by Wenzel *et al*. (2001). Results of these fractionations are described and discussed in the following sections.

### 4.4.1 SEP Step-1: Non-Specifically-Bound Arsenic Fraction

An examination of data presented in Fig. 4.3.a to Fig. 4.3.f showed that whenever incubed soil was extracted with $(NH_4)_2SO_4$ in SEP Step-1, the amount of non -specifically- bound arsenic fraction was always higher for 0-day and 7-day

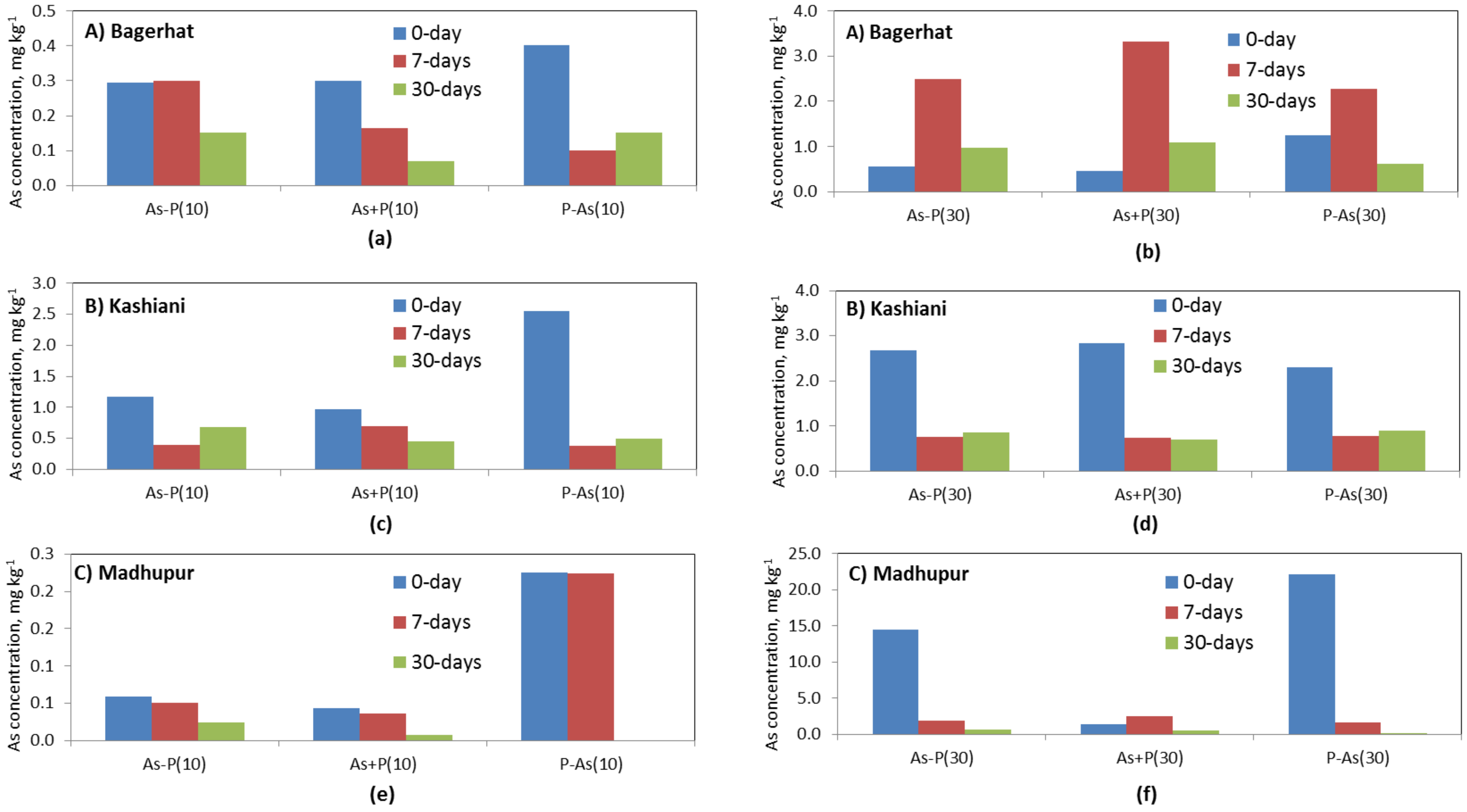


Fig. 4.3 Non-specifically bound As fraction as affected by phosphorus treatments.

periods. The amount considerably decreased for 30-day of incubation regardless of all sequences of arsenic and phosphorous application, i.e., arsenic was given before phosphorous [As-P(10) and As-P(30)], arsenic and phosphorus given simultaneously [As+P(10) and As+P(30)] or phosphorous was given before arsenic [P-As(10) and P-As(30)].

For Bagerhat soil spiked with 10 mg $kg^{-1}$ dose (Fig. 4.3.a) SEP Step-1 extracts for non-specifically-bound arsenic fraction considerably more in 0-day or 7-day of incubation compared to 30-day of incubation regardless of the treatments e.g., As-P(10), As+P(10) or P-As(10). For 30 mg $kg^{-1}$ dose (Fig. 4.3.b), extraction of this fraction maximizes at 7-day of incubation. For this case, the extraction was lower at both 0-day and 30-day of incubation period which did not show any trend.

For Kashiani soil spiked with 10 mg $kg^{-1}$ dose (Fig. 4.3.c), SEP Step-1 extracts for non-specifically-bound arsenic fraction considerably more in 0-day incubation compared to 7-day or 30-day of incubation regardless of the arsenic treatment sequence e.g., As-P(10), As+P(10) and P-As(10). When the concentration of treatment was increased, i.e. 30 mg $kg^{-1}$ dose (Fig. 4.3.d), extraction of for non-specifically-bound arsenic fraction decreased with increased incubation period.

For Madhupur soil (control soil) spiked with 10 mg $kg^{-1}$ dose (Fig. 4.3.e, SEP Step-1 extracted non-specifically-bound arsenic fraction more in 0-day incubation which gradually decreased with increase in incubation period for treatments As-P(10) and As+P(10). For P-As(10) treatment the amount of non-specifically-bound arsenic fraction was considerably higher compared to other two treatments for 0-day and 7-day of incubation periods. However, at 30-day of incubation period, this amount was almost non-detectable. For 30 mg $kg^{-1}$ dose (Fig. 4.3.f), extraction maximized at 0-day incubation for treatments As-P(30) and P-As(30) which almost vanishes with increased period of incubation. When arsenic and phosphorus doses were given together, that was As+P(30), the non-specifically-bound amount of arsenic was almost nil.

Generally, non-specifically-bound arsenic fraction decreases for all soil samples at 30 days compared to 0 or 7-day of incubation. From the results presented (Fig. 4.3.a to Fig. 4.3.f), it could be inferred that the non-specifically-bound arsenic fraction needs more than 7-day to come to a stable state. This might happen due to increased desorption of arsenic with aging which is similar to that of phosphorus desorption mechanism. This characteristic is independent of all treatment types. This means the amount of phosphate ions do not have any influence on the amount of non-specifically-bound arsenic fraction.

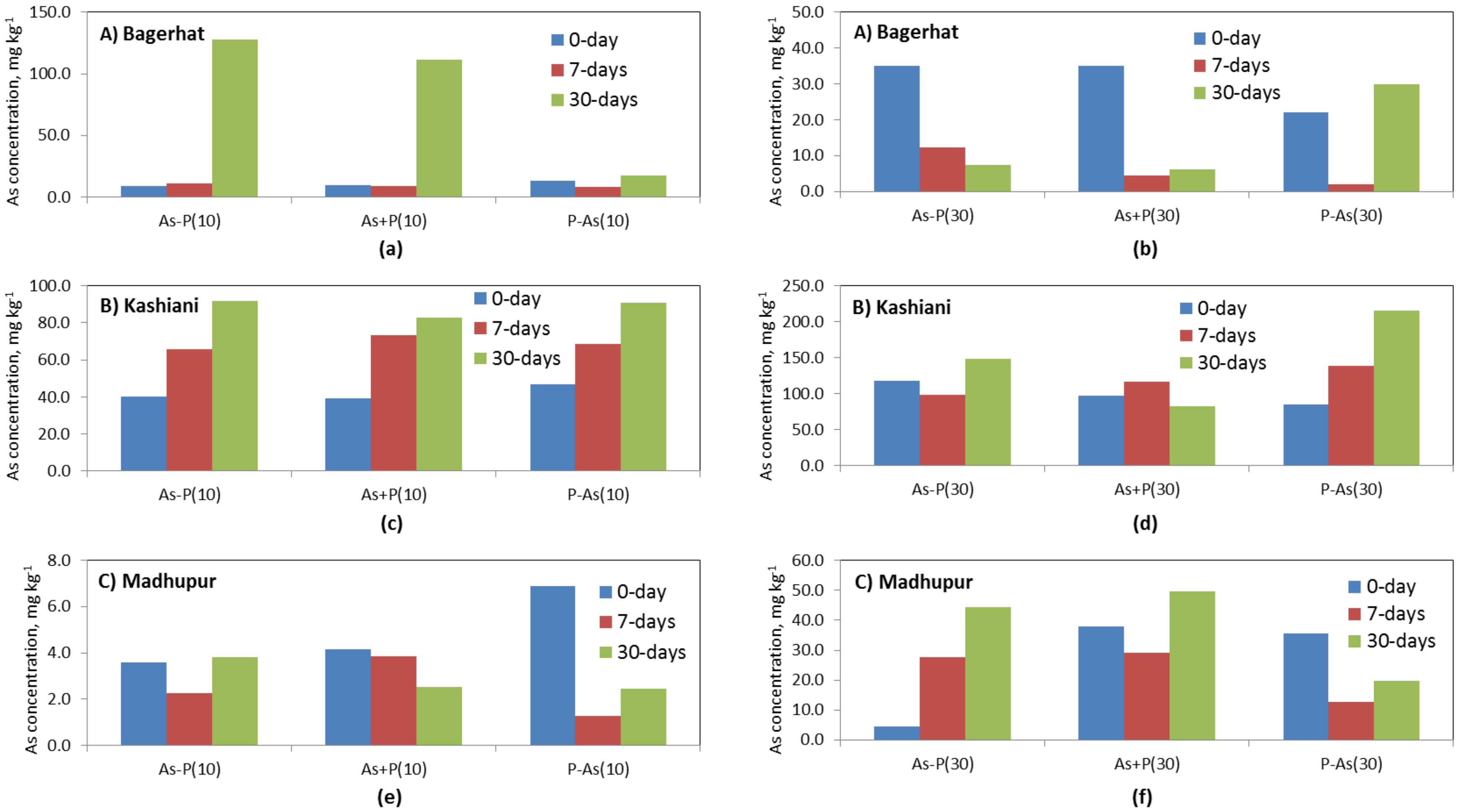
### 4.4.2 SEP Step-2: Specifically-Bound Arsenic Fraction

For treatment As-P(10), the Bagerhat soil showed initially (0-day and 7-day) low specifically-bound arsenic fraction which suddenly increased after 30-day period of incubation (Fig. 4.4.a). On the other hand, Kashiani soil showed gradual increase with time as shown in Fig. 4.4.c. But Madhupur soil did not show any particular trend (Fig. 4.4.e). When the dose increased to 30 mg kg$^{-1}$ as in treatment As-P(30), specifically-bound arsenic concentration gradually decreased from 0-day to 30-day for Bagerhat soil (Fig. 4.4.b) while Madhupur soil showed opposite trend (Fig. 4.4.f). Kashiani soil did not show any trend (Fig. 4.4.d).

For treatment As+P(10), the Bagerhat soil showed behavior similar to treatment As-P(10) as shown in Fig. 4.4.a. On the other hand, Kashiani soil showed gradual increase with time as shown in Fig. 4.4.c. For Madhupur soil, the specifically-bound arsenic concentration gradually decreased with increased time of incubation (Fig. 4.4.e). When the dose increased to 30 mg kg$^{-1}$ in treatment As-P(30), specifically-bound arsenic concentration decreased from 0-day to 30-day (Fig. 4.4.b) for Bagerhat soil while Kashiani and Madhupur soils did not show any trend (Figs.4.4.d and 4.4.f).

Specifically-bound arsenic concentration for Bagerhat soil was low for treatment P-As(10) for all incubation periods as observed from Fig. 4.4.a But for P-As(30) treatment, the arsenic extraction at 0-day and 30-day showed higher amount than that of 7-day amount (Fig. 4.4.b). For treatment P-As(30), Kashiani and Madhupur soils showed similar behavior to that of P-As(10) treatment (Fig. 4.4.d and 4.4.f).

Background analysis of the soil samples showed that contaminated Kashiani soil had a high concentration of Fe (208 mg kg$^{-1}$) compared to Bagerhat soil (62.5 mg kg$^{-1}$). Uncontaminated Madhupur soil also contained high Fe concentration (238 mg kg$^{-1}$). However, it was a red soil where Fe was present in oxide form and is incapable of specifically bonding arsenic. In accordance with



(a) (b)

(c) (d)

(e) (f)

Fig. 4.4 Specifically bound As fraction due to phosphorus treatments.

Wenzel *et al.* (1998), $(NH_4)H_2PO_4$ was used to extract the specifically-bound arsenic from hydrous iron oxides. Thus the magnitude of arsenic extraction in this step depends on the amount of hydrous iron oxides present in the contaminated soil. Extraction of specifically-bound arsenic by $(NH_4)H_2PO_4$ can be expected to be higher with soils having higher hydrous iron oxide concentration. This is clearly supported by the results of the present investigation. The amount of specifically-bound arsenic extracted from Kashiani soil was of the order of 100 ~ 200 mg $kg^{-1}$ while for Bagerhat soil it was about 10 ~ 100 mg $kg^{-1}$.

### 4.4.3 SEP Step-3: Amorphous Hydrous Oxide-Bound Arsenic Fraction

For Bagerhat soil amount of amorphous hydrous oxide-bound arsenic fraction was initially low which gradually increased with the time of incubation (Figs. 4.5.a and 4.5.b). This was same for all the treatments – As-P, As+P and P-As for both 10 mg $kg^{-1}$ and 30 mg $kg^{-1}$ doses.

For Kashiani soil amount of amorphous hydrous oxide-bound arsenic fraction was initially high for 0-day incubation which decreased with time of incubation for all treatments of 10 mg $kg^{-1}$ doses as shown in Fig. 4.5.c. For treatment As-P(30), arsenic extraction was high at 0-day and 7-day but low at 30-day. Treatment As+P(30) showed similar behavior to As+P(10) as shown in Fig. 4.5.d. For P-As(30) treatment, amount of extraction was initially low which gradually increased with period of incubation. For Madhupur soil amount of amorphous hydrous oxide-bound arsenic fraction was initially low which gradually increased with the time of incubation (Figs. 4.5.e and 4.5.f). This was same for all the treatments – As-P, As+P and P-As for both 10 mg $kg^{-1}$ and 30 mg $kg^{-1}$ doses.

Amorphous hydrous oxide-bound arsenic fraction was initially (0 or 7-day of incubation) low and increased with time of incubation for Bagerhat and Madhupur soils for all doses of phosphorus. But Kashiani soil did not show any definite trend in this change of arsenic with time. Of the three samples, Kashiani soil was contaminated about four times than Bagerhat soil while the Madhupur soil was almost uncontaminated. When additional arsenic and phosphorus was added (spiked), the amorphous hydrous oxide-bound arsenic continued to increase with time for all sequence of treatments. On the other hand, since Kashiani soil was

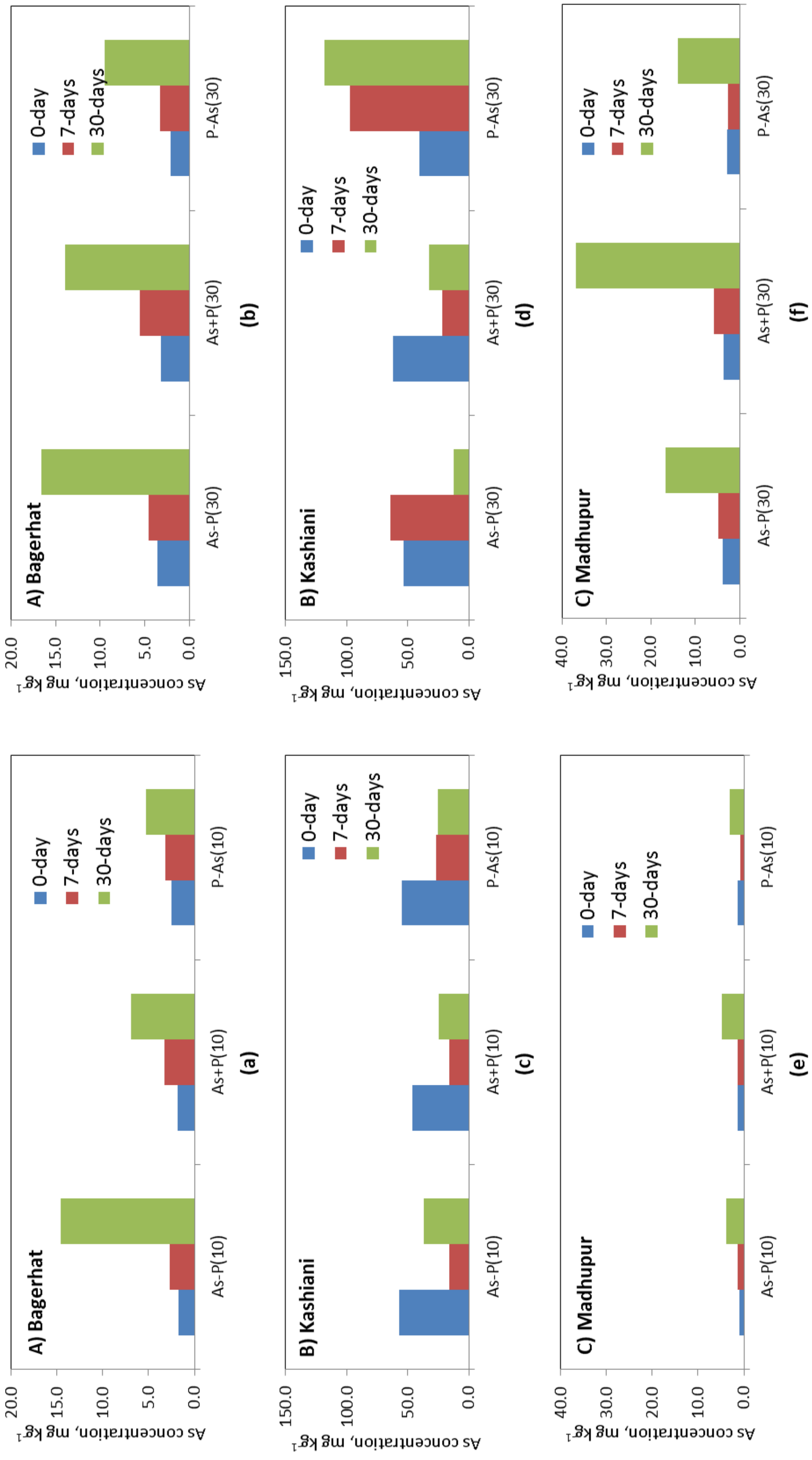


Fig. 4.5 Amorphous hydrous oxide bound As fraction as affected by phosphorus treatments.

already heavily contaminated, its capacity of increasing amorphous hydrous oxide-bound arsenic was probably less. This caused arsenic to be bound with amorphous iron at slower and irregular rate and did not show any specific trend with incubation time. In addition, it is to be noted that, though the trend was irregular, the magnitude of extracted amount of arsenic for Kashiani soil was generally much higher (of the order of 50 ~ 100 mg kg$^{-1}$) than the Bagerhat (about 15 mg kg$^{-1}$) or Madhupur soil (about 10 mg kg$^{-1}$). This was consistent with the finding that Kashiani soil contains more amount of arsenic than the other two samples. Only As+P(30) treatment for Madhupur soil showed considerably higher values than that of all other SEP steps for.

### 4.4.4 SEP Step-4: Crystalline Hydrous Oxide-Bound Arsenic Fraction

Amount of crystalline hydrous oxide-bound arsenic fraction in Bagerhat soil was almost same at 0, 7 and 30 days of incubation for all sequence of treatments of phosphorus with 10 mg kg$^{-1}$ dose (Fig. 4.6.a). For 30 mg kg$^{-1}$ dose, the amount extracted generally increased at 30-day of incubation (Fig. 4.6.b).

For Kashiani soil the amount of crystalline hydrous oxide-bound arsenic fraction was higher at 0 and 30-day of incubation but lower at 7-day of incubation for all sequences of treatment with both 10 and 30 mg kg$^{-1}$ doses (Figs. 4.6.c and 4.6.d). Behavior of Madhupur soil was similar to that of Kashiani soil for all doses and treatments (Figs. 4.6.e and 4.6.f). When fractionation was conducted for the untreated samples, most of the arsenic was extracted as crystalline hydrous oxide-bound as shown in Fig. 4.1. Of the three samples, highest amount was extracted from Kashiani sample which was 53.5 mg kg$^{-1}$. After spiking the samples with phosphorus and arsenic, the overall magnitude of extraction was comparatively lower than the amount extracted in the previous step (SEP Step-3, Figs. 4.5.a through 4.5.f). This is due to the fact that crystalline hydrous oxide-bound form is the most stable form of arsenic in soil that bounds with iron oxy-hydroxides. Spiking of soil samples for even 30-day residence time is probably not enough for arsenic to bound in crystalline hydrous oxide from. Therefore, amount of extraction of arsenic was higher in earlier SEP steps.

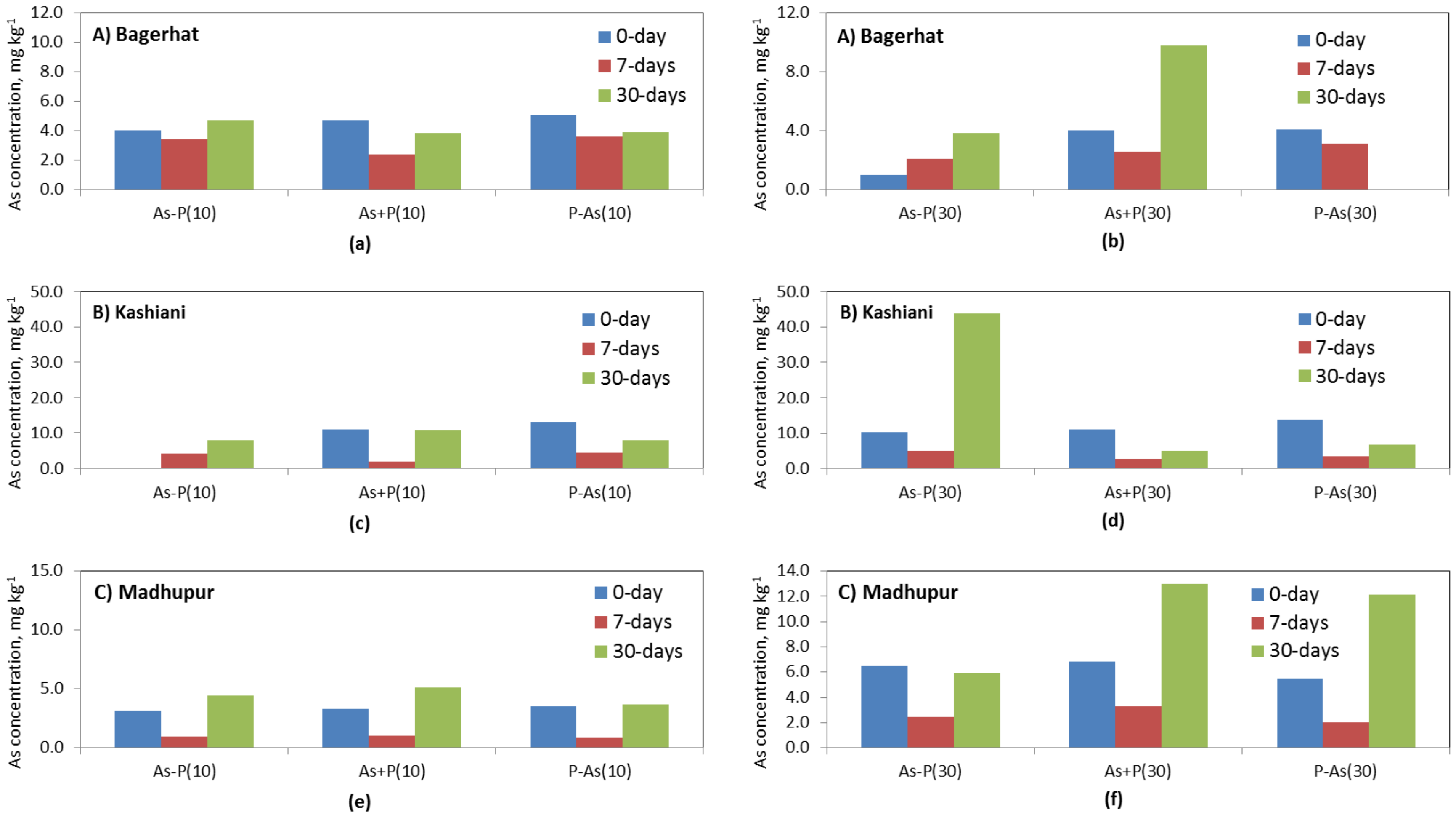
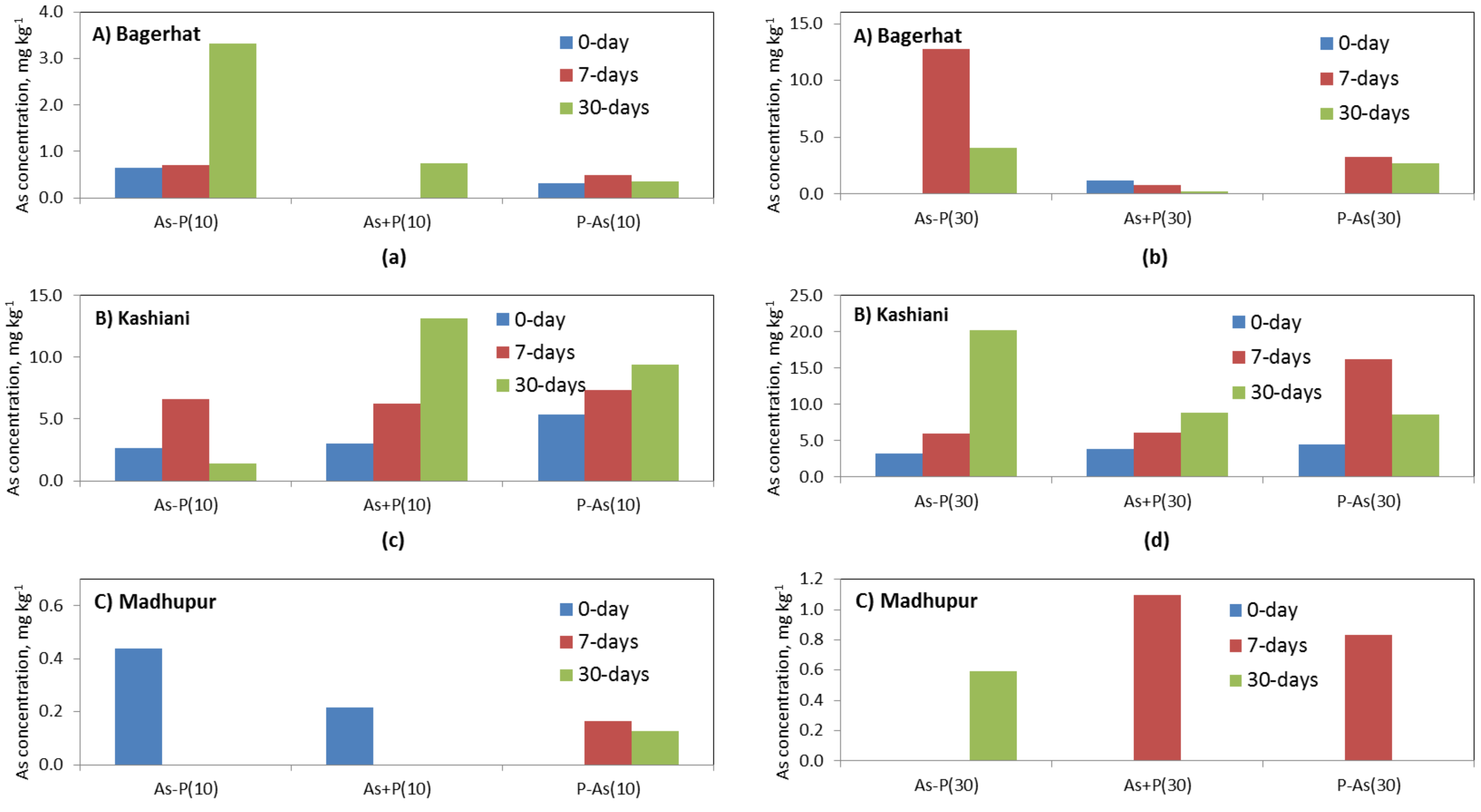


Fig. 4.6 Crystalline hydrous oxide bound As fraction due to phosphorus treatments.



(a) (b)

(c) (d)

(e) (f)

Fig. 4.7 Residual As fraction due to phosphorus treatments.

### 4.4.5 SEP Step-5: Residual Arsenic Fraction

The results of arsenic fraction extracted in Step-5 are shown in Figs. 4.7.a through 4.7.f. Most of the extractable portions of arsenic was detected in the earlier steps. For this reason arsenic fraction extracted in the acid digestion was below the detection level of the AAS apparatus for many instances except for the Kashiani sample which showed higher extracted amount compared to the other soil samples. Of the three soil samples studied, Kashiani soil was the highest contaminated with arsenic and also had the capability of retaining greater amount of residual arsenic. As a result, these figures do not show any particular trend.

## 4.5 INTERACTION OF ARSENIC WITH SULPHUR

Of the fourteen treatments (spiking) described in Table 3.2, six ($T_7$ to $T_{12}$) were aimed at examining the interaction of arsenic with sulphate anion. Each of the six treatments of a particular incubation period was subjected to 5-Step sequential extractions procedure (SEP) developed by Wenzel *et al*. (2001). Results of these fractionations are described and discussed in the following sections.

### 4.5.1 SEP Step-1: Non-Specifically-Bound Arsenic Fraction

For Bagerhat soil spiked with 10 mg $kg^{-1}$ dose (Fig. 4.8.a) SEP Step-1 extracted non-specifically-bound arsenic fraction using $(NH_4)_2SO_4$ considerably more in 0-day or 7-day of incubation compared to 30-day of incubation for treatments As+S(10) or S-As(10). For treatment As-S(10), there was no non-specifically-bound arsenic fraction at 30-day of incubation. For 30 mg $kg^{-1}$ dose (Fig. 4.8.b), extraction of non-specifically-bound arsenic fraction was maximum at 7-day of incubation. For this case, the extraction was lower at both 0-day and 30-day of incubation periods.

For Kashiani soil spiked with 10 mg $kg^{-1}$ dose (Fig. 4.8.c), SEP Step-1 extracted non-specifically-bound arsenic fraction considerably more in 0-day incubation compared to 7-day or 30-day of incubation regardless of the sequence of treatments, e.g., As-S(10), As+S(10) or S-As(10). When the concentration of dose was increased to 30 mg $kg^{-1}$ (Fig. 4.8.d), extraction of non-specifically-bound arsenic fraction decreased with increasing incubation period. This interaction of

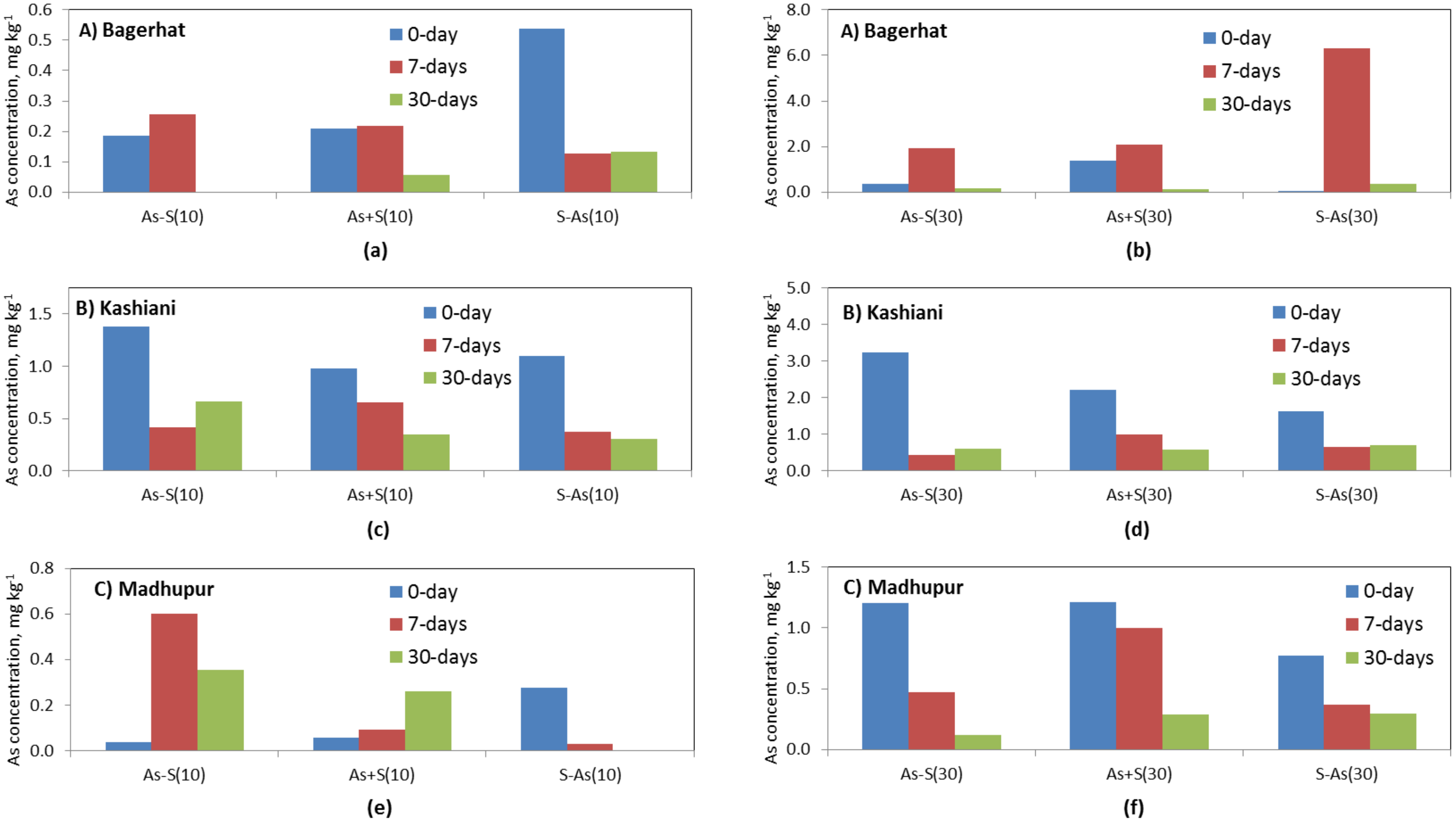


Fig. 4.8 Non-specifically bound As fraction as affected by sulphur treatments.

sulphur with arsenic was very similar to the interaction with phosphorus discussed before.

For Madhupur soil (control soil), spiked with 10 mg kg$^{-1}$ dose (Fig. 4.8.e), SEP Step-1 extracted non-specifically-bound arsenic fraction less in 0-day incubation. The extracted arsenic fraction increased at 7-day but again decreased at 30-day for treatment As-S(10). For As+S(10) treatment, initially non-specifically-bound arsenic fractionation is low but gradually increased a bit with time. For S-As(10) treatment, the amount of non-specifically-bound arsenic fraction was more at 0-day which decreased with increased period of incubation. For this treatment the non-specifically-bound amount of arsenic was almost nil at 30-day of incubation. For 30 mg kg$^{-1}$ dose (Fig. 4.8.f), non-specifically-bound arsenic fraction was high at 0-day which gradually decreased with higher periods of incubation for all sequences of treatment.

Overall desorption of arsenic in SEP step-1 for treatments with sulphur was found to be low in magnitude ranging from 0.5 to 6 mg kg$^{-1}$. Similar behavior was observed for treatments with phosphorus in this step. It is thus indicated that both the phosphate and sulphate anions did not have any notable effect on non-specifically-bound arsenic fraction.

### 4.5.2 SEP Step-2: Specifically-Bound Arsenic Fraction

The amount of specifically-bound arsenic fraction by $(NH_4)H_2PO_4$ was almost similar for all treatments with 10 mg kg$^{-1}$ dose except the 7-day fraction of As-S(10) treatment which was considerably lower (Fig. 4.9.a). For 30 mg kg$^{-1}$ dose, the extracted amount was initially high at 0-day incubation for all sequence of treatments (Fig. 4.9.b). At 7-day of incubation, the extracted amount got much smaller for As-S(30) and As+S(30) treatments. For S-As(30) treatment, extracted amount of arsenic after 7-day of incubation was similar to that of 0-day incubation.

Amount of specifically-bound arsenic was high in Kashiani soil and similar for all sequence of treatments with both the 10 and 30 mg kg$^{-1}$ doses for all incubation periods (Figs. 4.9.c and 4.9.d).

The Madhupur soil generally showed higher amount of specifically-bound arsenic extraction at 30-day of incubation periods compared to 0 and 7-day of

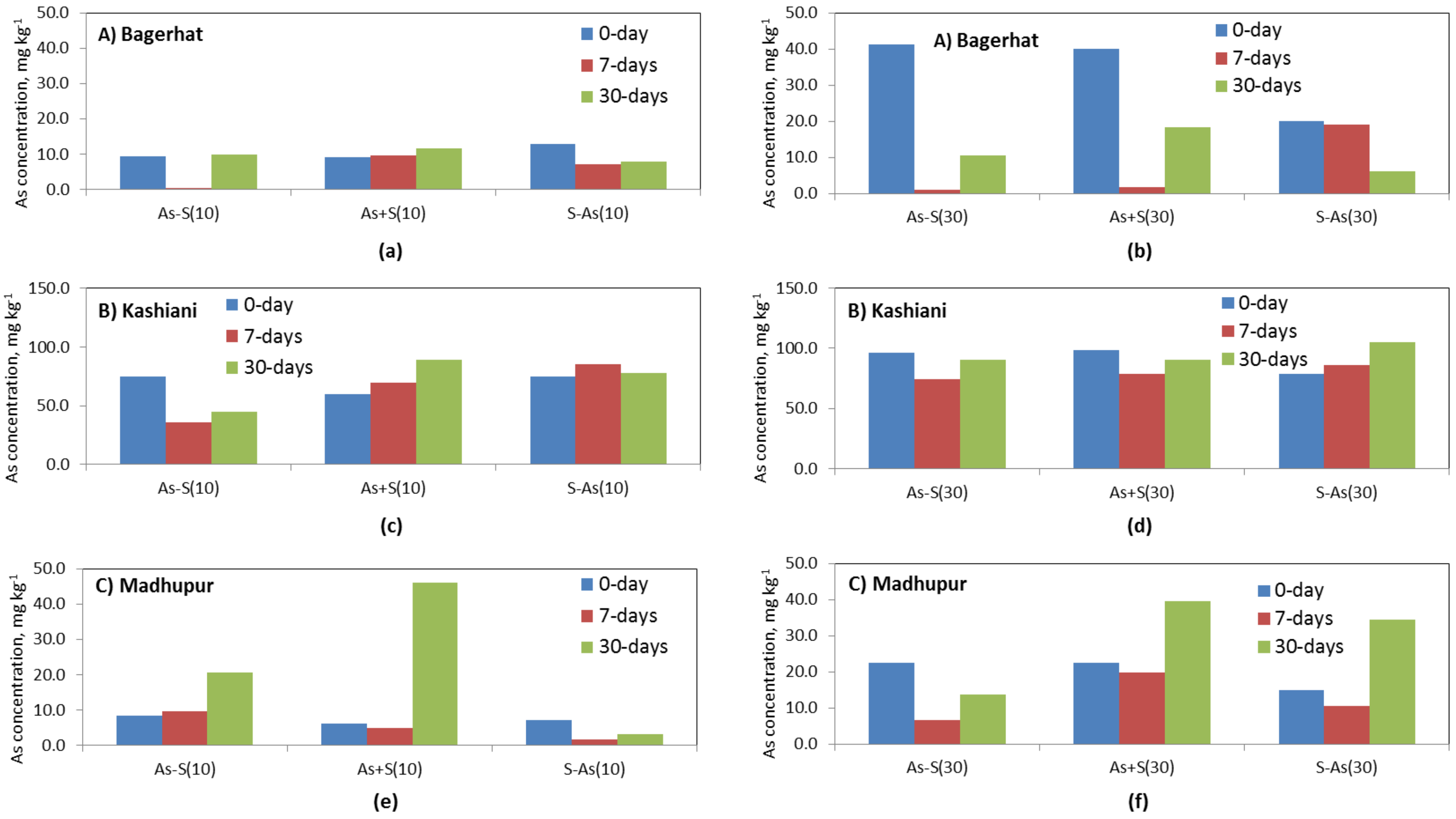


Fig. 4.9 Specifically bound As fraction as affected by sulphur treatments.

incubation period except treatments S-As(10) and As-S(30) as shown in Figs. 4.9.e and 4.9.f.

The overall amount of specifically-bound arsenic fraction extracted in this step was quite high (~ 100 mg kg$^{-1}$) compared to other steps. Among the three samples, Kashiani soil showed the highest magnitude of extraction. For similar treatment with phosphorus, the extraction amount was about 216 mg kg$^{-1}$. When the dose of treatments increased from 10 to 30 mg kg$^{-1}$, Bagerhat and Madhupur soil, in general, showed significant increase in the magnitude of arsenic extraction. However, the Kashiani sample did not show any variation due to change of concentration of treatments. For all the soil samples, the no trend was observed for specifically-bound arsenic fraction as affected by the residence time.

### 4.5.3 SEP Step-3: Amorphous Hydrous Oxide-Bound Arsenic Fraction

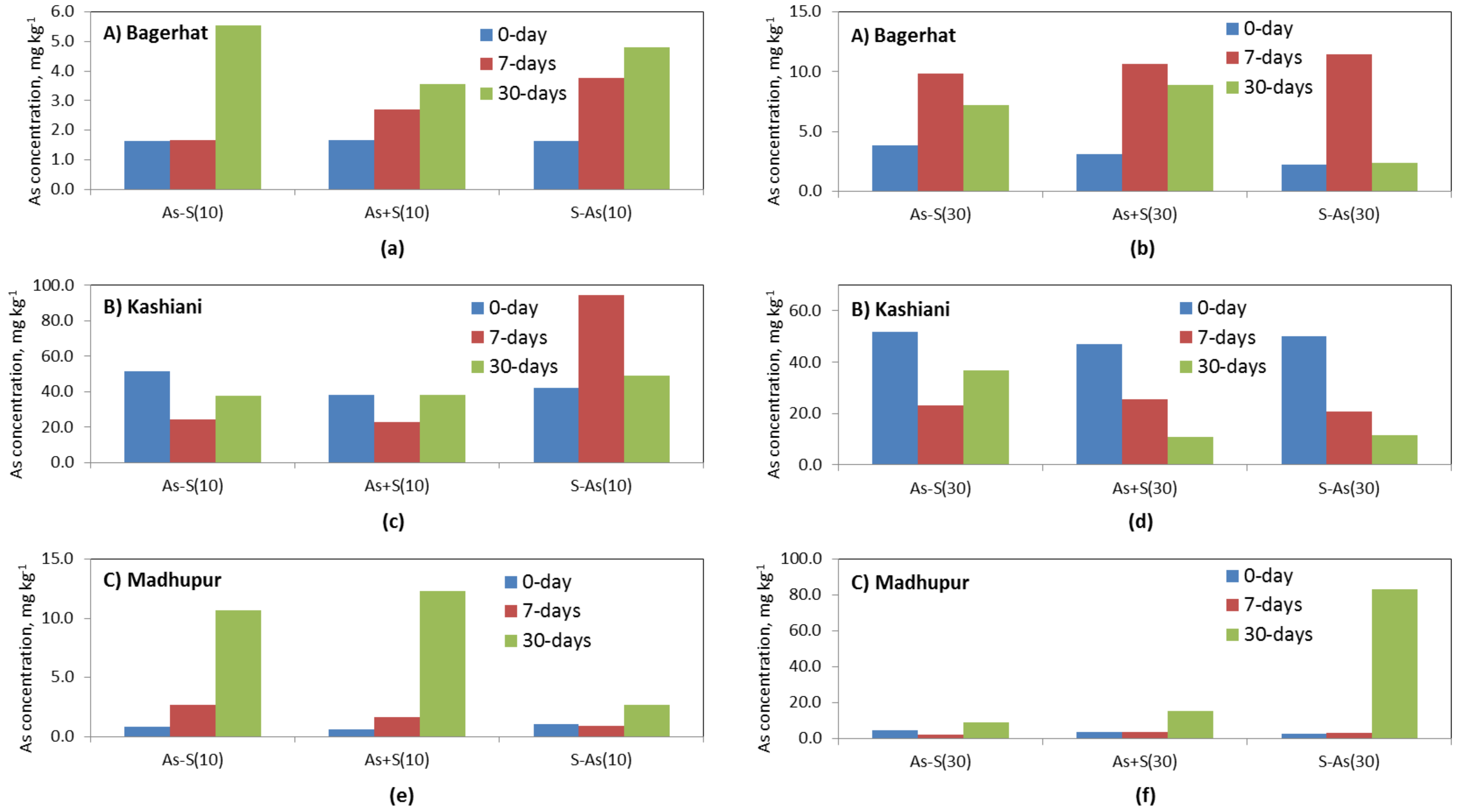
Extracted amount of amorphous hydrous oxide-bound arsenic fraction in Bagerhat soil was same at 0-day incubation for all treatments. Amount of extraction was higher with increased period of incubation (Figs. 4.10.a and 4.10.b) except for treatment S-As(30).

For Kashiani soil, the amount of amorphous hydrous oxide-bound arsenic fraction was generally same for all treatments with 10 mg kg$^{-1}$ dose except for treatment S-As(10) where the extracted amount was higher at 7-day of incubation period (Fig. 4.10.c). For all treatments of 30 mg kg$^{-1}$ dose, the extracted amount was initially higher which became lower with increased period of incubation (Fig. 4.10.d).

There was no notable amount of amorphous hydrous oxide-bound arsenic fraction in Madhupur soil for all doses with all sequences of treatment at 0 and 7-day of incubation. The amount of arsenic extraction was higher at 30-day of incubation for treatments As-S(10), As+S(10) and S-As(30) as shown in Figs. 4.10.e and 4.10.f.

### 4.5.4 SEP Step-4: Crystalline Hydrous Oxide-Bound Arsenic Fraction

Values obtained with treatments As-S(10), As+S(10) and S-As(10) showed that (Fig. 4.11.a) crystalline hydrous oxide-bound arsenic fraction of Bagerhat soil



(a) (b) (c) (d) (e) (f)

Fig. 4.10 Amorphous hydrous oxide bound As fraction as affected by sulphur treatments.

was higher at 0-day and 30-day of incubation but somewhat lower at 7-day of incubation. As-S(30) treatment in Fig. 4.11.b showed that crystalline hydrous oxide-bound arsenic fraction was initially higher and gradually decreased with increased period of incubation. For treatments As+S(30) and S-As(30), the extracted amount of arsenic was similar for all incubation periods.

All treatments with both 10 and 30 mg kg$^{-1}$ doses showed that (Figs. 4.11.c and 4.11.d) crystalline hydrous oxide-bound arsenic fraction of Kashiani soil was higher at 0-day and 30-day of incubation but somewhat lower at 7-day of incubation.

Madhupur soil showed behavior similar to that of Kashiani soil as can be observed from Figs. 4.11.e and 4.11.f.

### 4.5.5 SEP Step-5: Residual Arsenic Fraction

Amount of arsenic fraction remained as residual determined in SEP Step-5 for both the Bagerhat and Kashiani soils were not comparable to SEP Steps 2, 3 and 4 (Figs. 4.12.a, 4.12.b, 4.12.c and 4.12.d). Amount of residual arsenic fraction in Madhupur soil was below detection level (Figs. 4.12.e and 4.12.f). Most of the extractable portions of arsenic had been detected in the earlier SEP steps. For this reason the arsenic fractions extracted in the acid digestion phase were below the detection level of the AAS for many instances. As a result, these figures do not show any particular trend.

## 4.6 INTERACTION OF ARSENIC WITH MIXED SULPHUR AND PHOSPHORUS

Of the fourteen treatments (spiking) described in Table 3.2, last two ($T_{13}$ and $T_{14}$) were aimed at examining the combined interaction of arsenic with both phosphate and sulphate anions. Each of these treatments of a particular incubation period was subjected to 5-Step sequential extraction procedure (SEP) developed by Wenzel *et al*. (2001). Results of these fractionations are described and discussed in the following sections.

### 4.6.1 SEP Step-1: Non-Specifically-Bound Arsenic Fraction

For contaminated Bagerhat and Kashiani soils and control Madhupur soil as shown in Figs. 4.13.a, 4.13.b and 4.13.c – there was not any notable amount of

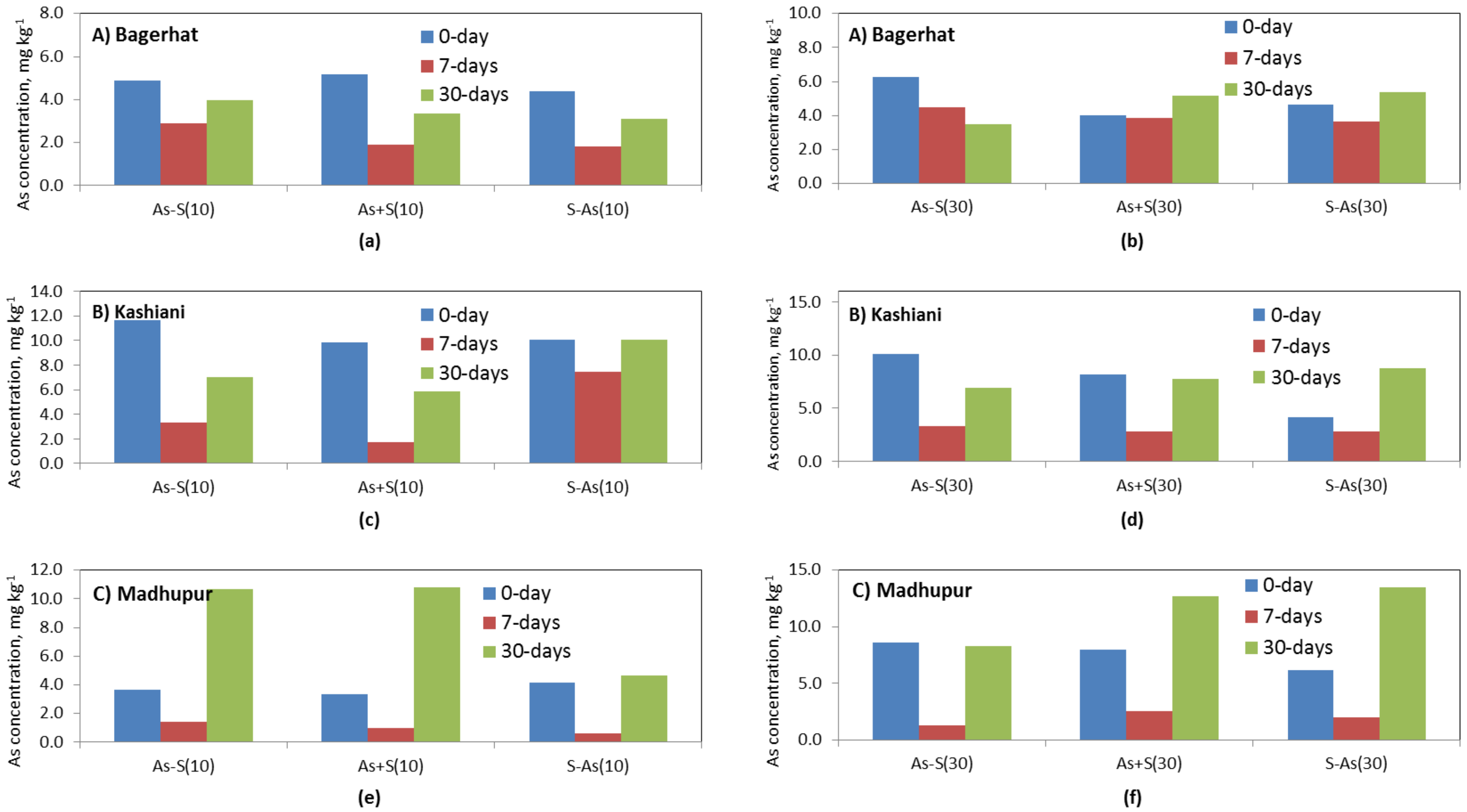


Fig. 4.11 Crystalline hydrous oxide bound As fraction due to sulphur treatments.

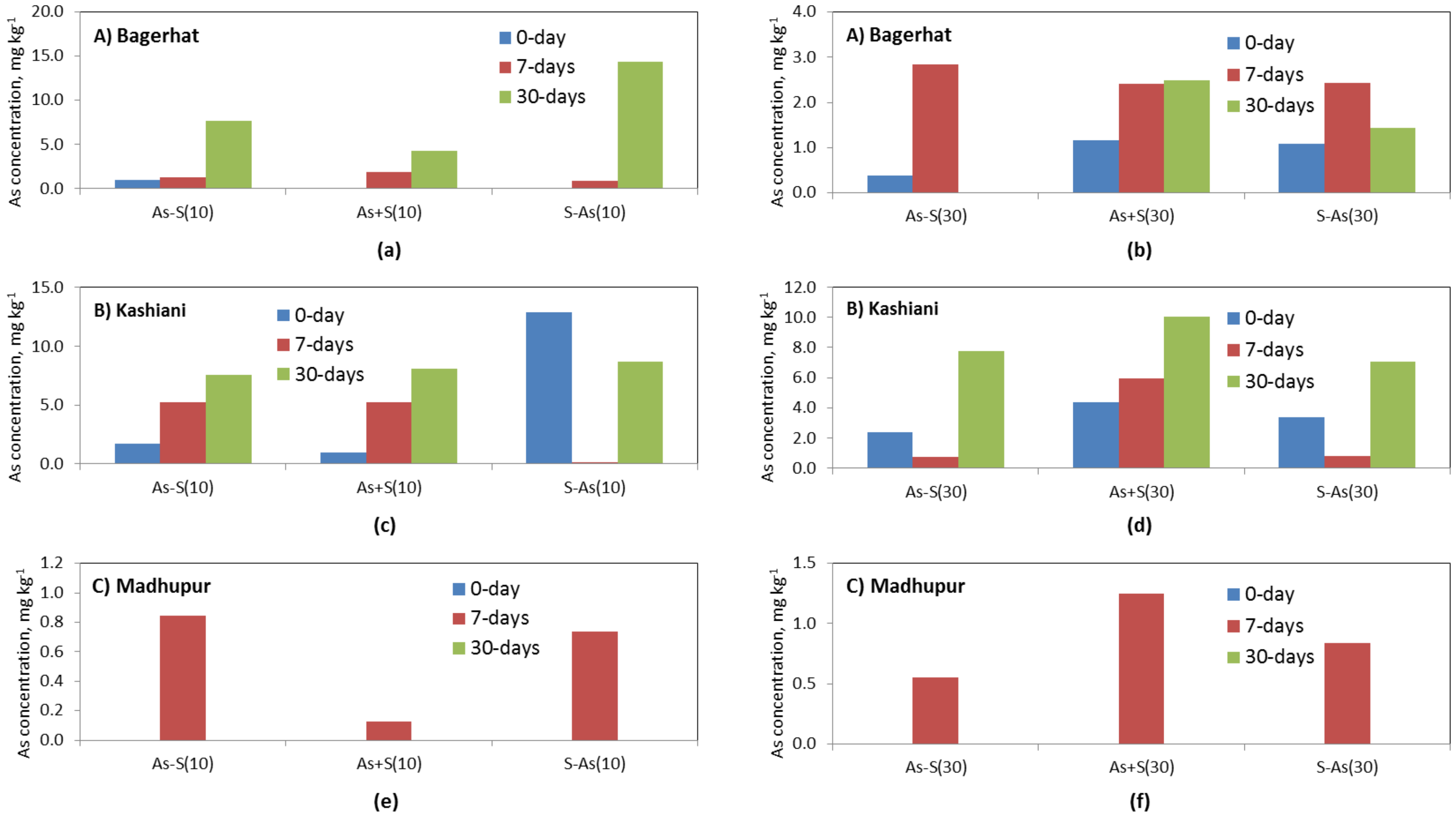


Fig. 4.12 Residual As fraction due to sulphur treatments.

non-specifically-bound arsenic obtained with 10 mg kg$^{-1}$ dose. For 30 mg kg$^{-1}$ dose, amount of non-specifically-bound arsenic of Bagerhat soil gradually increased with period of incubation (7 mg kg$^{-1}$ max.). Amount of non-specifically-bound arsenic for Kashiani and Madhupur soils was higher at 7-day of incubation and decreases with increased period of incubation.

### 4.6.2 SEP Step-2: Specifically-Bound Arsenic Fraction

The amount of specifically-bound arsenic fraction was very small for Bagerhat soil with treatment As+P+S(10), but for treatment As+P+S(30) the extracted amount gradually increased with the increase in period of incubation (Fig. 4.14.a).

For Kashiani soil, the amount of specifically-bound arsenic fraction was almost similar for As+P+S(10) treatment for all incubation periods. For treatment As+P+S(30), the extracted amount generally increased with period of incubation (Fig. 4.14.b).

For Madhupur soil, the amount of extracted arsenic was quite low for treatment As+P+S(10) for all incubation periods. For treatment As+P+S(30), some amount of specifically-bound arsenic fraction was available in 0-day and 7-day of incubation which suddenly dropped at 30-day of incubation period (Fig. 4.14.c). It was found that generally the SEP Step-2 extracted the highest proportion of arsenic as specifically-bound fraction when compared to the other SEP steps. Similar behavior was observed in other fractionations for treatments with either phosphate or sulphate as described in the preceding sections 4.4.2 and 4.14. However, unlike the preceding fractionation studies, the extracted amount of specifically-bound arsenic fraction increased notably with increased concentration (30 mg kg$^{-1}$) of doses. For Bagerhat soil sample, the extraction was about 5 mg kg$^{-1}$ for 10 mg kg$^{-1}$ dose at 30-day of incubation which increased to about 125 mg kg$^{-1}$ for 30 mg kg$^{-1}$ dose treatment at 30-day of incubation. For similar conditions, the extraction amount for Kashiani sample were about 50 and 175 mg kg$^{-1}$.

### 4.6.3 SEP Step-3: Amorphous Hydrous Oxide-Bound Arsenic Fraction

The amount of amorphous hydrous oxide-bound arsenic fraction was very small for Bagerhat soil with treatment As+P+S(10), but for treatment As+P+S(30)

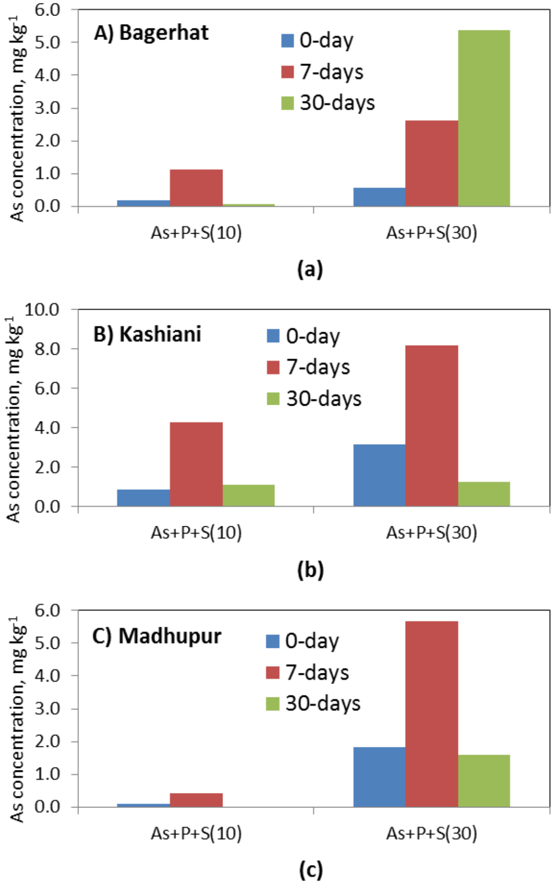


Fig. 4.13 Non-specifically bound As fraction as affected by mixed treatments.

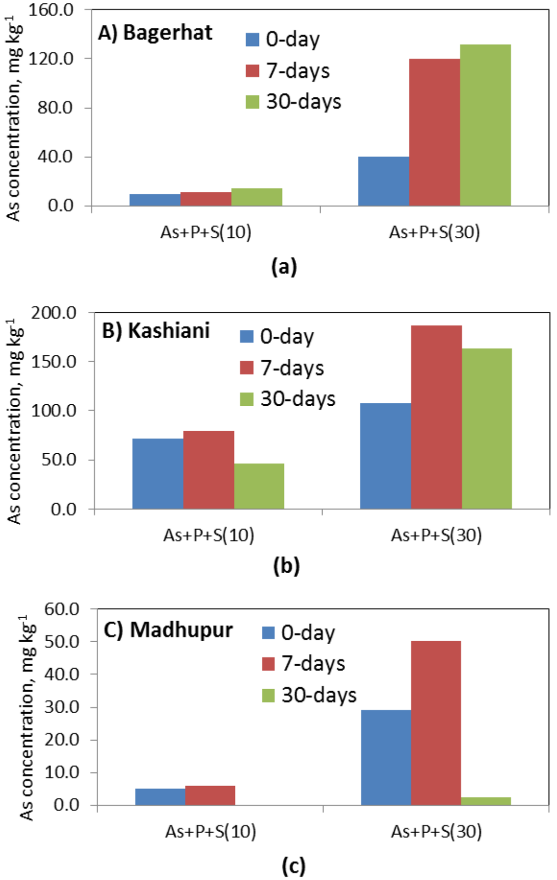


Fig. 4.14 Specifically bound As fraction as affected by mixed treatments.

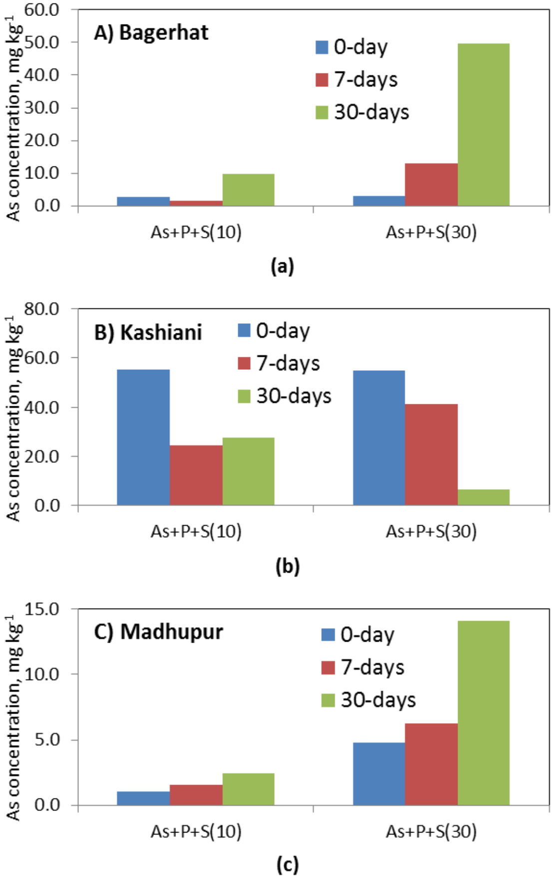


Fig. 4.15 Amorphous hydrous oxide bound As fraction as affected by mixed treatments.

the extracted amount gradually increased with the period of incubation (Fig. 4.15.a).

For Kashiani soil, the amount of amorphous hydrous oxide-bound arsenic fraction was initially high which decreased with period of incubation for both As+P+S(10) and As+P+S(30) treatments (Fig. 4.15.b).

The Madhupur soil showed behavior similar to that of Bagerhat soil (Fig. 4.15.c).

### 4.6.4 SEP Step-4: Crystalline Hydrous Oxide-Bound Arsenic Fraction

For Bagerhat soil, the amount of crystalline hydrous oxide-bound arsenic was similar for As+P+S(10) treatment at all incubation periods (Fig. 4.16.a). For treatment As+P+S(30), the initial extraction was low at 0-day which increases with period of incubation.

For Kashiani soil, the extracted amounts of crystalline hydrous oxide-bound arsenic were similar to As+P+S(10) treatment and for all incubation periods. For treatment As+P+S(30), the values obtained at 0-day and 30 days of incubation were almost similar but lower after 7 day incubation (Fig. 4.16.b).

The Madhupur soil showed trends similar to that of Kashiani soil except that the amount of extracted arsenic was lower for As+P+S(10) treatment (Fig. 4.16.c).

### 4.6.5 SEP Step-5: Residual Arsenic Fraction

Amount of arsenic fraction remained as residual determined in SEP Step-5 for the Bagerhat and Madhupur soils were trace or below detection level compared to SEP Steps 2, 3 and 4 (Figs. 4.17.a and 4.17.c) for many instances. Amount of residual arsenic fraction in Kashiani soil was found to increase with the longer period of incubation (Fig. 4.17.b). Generally, most of the extractable portions of arsenic was detected in previous steps. For this reason the arsenic fraction extracted in the acid digestion phase were below the detection level of the AAS apparatus for many instances. As a result, these figures did not show any particular trend.

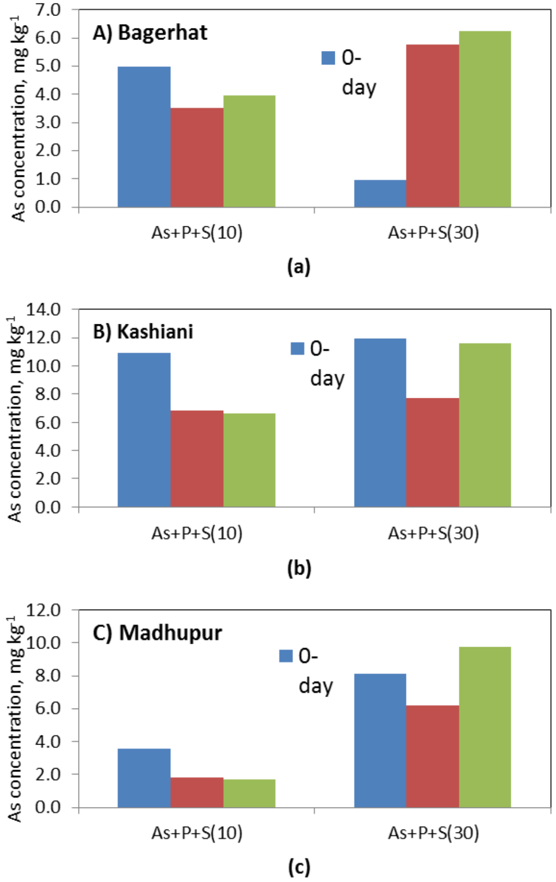


Fig. 4.16 Crystalline hydrous oxide bound As fraction as affected by mixed treatments.

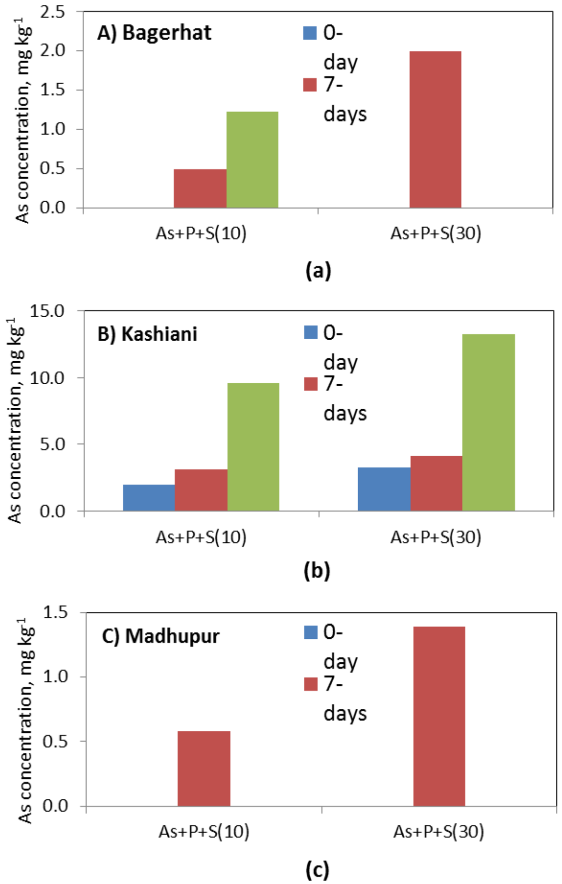


Fig. 4.17 Residual As fraction as affected by mixed treatments.

## 4.7 ASSESSMENT OF INTERACTION OF ARSENIC WITH PHOSPHATE ANION

In order to get a better understanding of the effect of the different sequences of arsenic treatment, results are grouped and compared. Sequences of treatment with phosphate anion, i.e. arsenic was added before phosphorous application [As-P(10) and As-P(30)], simultaneous application of arsenic and phosphorus [As+P(10) and As+P(30)] and arsenic added after application of phosphorus [P-As(10) and P-As(30)] are grouped in Figs. 4.18.a. 4.18.b and 4.18.c, respectively and are discussed in the following sections.

### 4.7.1 As-P Treatment

From Fig. 4.18.a it was observed that generally, after spiking of contaminated soils of Bagerhat and Kashiani with As-P treatment at 10 mg kg$^{-1}$ dose, highest amount of arsenic was extracted from specifically-bound state in SEP Step-2 compared to the arsenic extracted in other steps. This was true for all periods of incubation. The corresponding amount of arsenic extracted from Madhupur soil was much lower than the contaminated samples. Thus it was clear that the Madhupur soil did not have the characteristic to adsorb arsenic from this treatment.

Desorption behavior of Kashiani soil for As-P(30) treatment was high even at early stage of incubation. Begum and Huq (2007) had similar finding in their study where highly imposed treatment of arsenic caused high desorption. After incubation of 30-day, the desorption of arsenic by Bagerhat soil became comparable to that of Kashiani soil for As-P(10) treatment. However, for higher concentration of treatment e.g. As-P(30), Bagerhat soil showed lower amount of extracted arsenic at higher residence time (30-day). At lower dose of treatment As-P(10), arsenic was found to be more amorphous hydrous oxide bound rather than specifically-bound (SEP Step-3) at initial stage of incubation (0-day) for the Kashiani soil. It was also observed that for both the contaminated soils of Bagerhat and Kashiani, arsenic desorption increased with time of incubation. At 30 days of incubation Bagerhat soil showed an exception where the extracted arsenic for As-P(30) treatment was less than that of As-P(10) treatment which might be due to the high salinity (EC=2330 μS/cm). Since most of the arsenic was extracted from sorbed states (except Bagerhat soil at 0-day incubation with 10 mg kg$^{-1}$ dose), it indicated that 30-day of incubation period is generally not enough to cause arsenic to chemically bond with iron in amorphous or crystalline form.

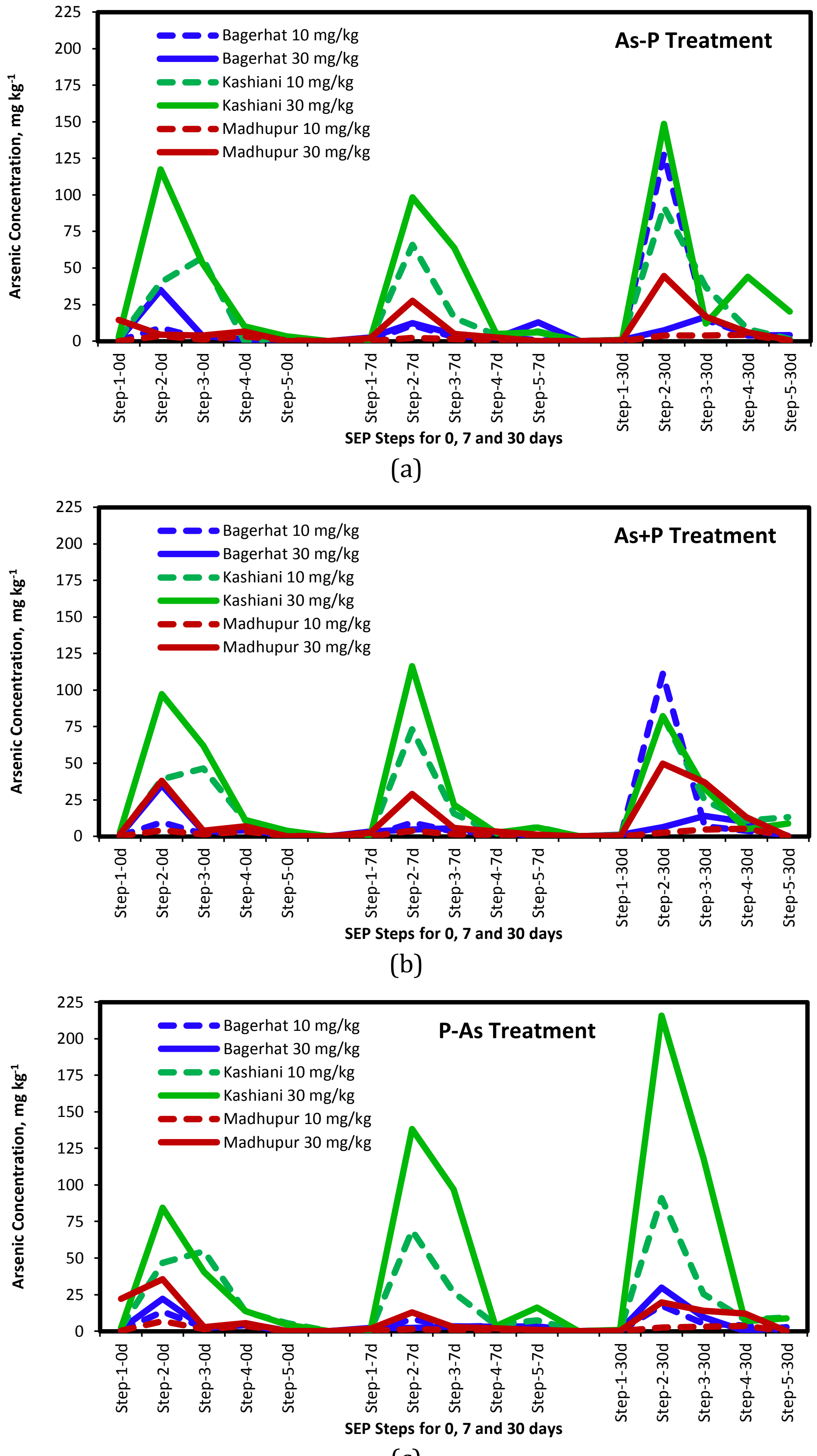
### 4.7.2 As+P Treatment

The amount of arsenic extracted when the arsenite and phosphate anions were added to the samples at the same time is shown in Fig. 4.18.b. When arsenic and phosphorus (As+P) were spiked together into the soil samples, the fractionation behavior was similar to that of As-P treatment, i.e. most of the arsenic was extracted as specifically bound fraction in SEP Step-2 extracted by $(NH_4)H_2PO_4$. However, the magnitude of arsenic desorption was relatively lower than the As-P treatment at 30-day of incubation. One exception showed by the Bagerhat soil sample was that the arsenic extracted with 10 mg kg$^{-1}$ dose was higher than the corresponding 30 mg kg$^{-1}$ dose at 30-day of incubation. Similar exception was also exhibited by the Bagerhat soil for As-P treatment discussed earlier (Sec. 4.7.1).

### 4.7.3 P-As Treatment

As shown in Fig. 4.18.c, a general trend was observed that, like other treatments, larger amount of arsenic extraction occurred as specifically bound arsenic. Also, the amount of extracted arsenic increased with the time of incubation. It was apparent that arsenic adsorption was affected by the presence of competing ions. In particular, phosphate and arsenate have similar geochemical behavior, and as such, both compete for sorption sites (Hingston *et al.*, 1971; Livesey and Huang, 1981; Manning and Goldberg, 1996). Oxyanions in addition to phosphate also may compete for sorption sites. In the present study, as phosphate dose was applied before arsenic, it was likely that phosphate anions occupied the sorption sites of soil colloids. When arsenic was applied after the day of phosphate treatment, the arsenate might have sorbed more strongly because, unlike $PO_4^{3-}$, the arsenate ion is larger in size and interacts more strongly with some of the OH groups that remain on the surface as found by Lumsdon *et al.* (1984).

An important observation was that the magnitude of extracted amount was highest in this P-As treatment especially for the Kashiani soil (216 mg kg$^{-1}$). The



(a)

(b)

(c)

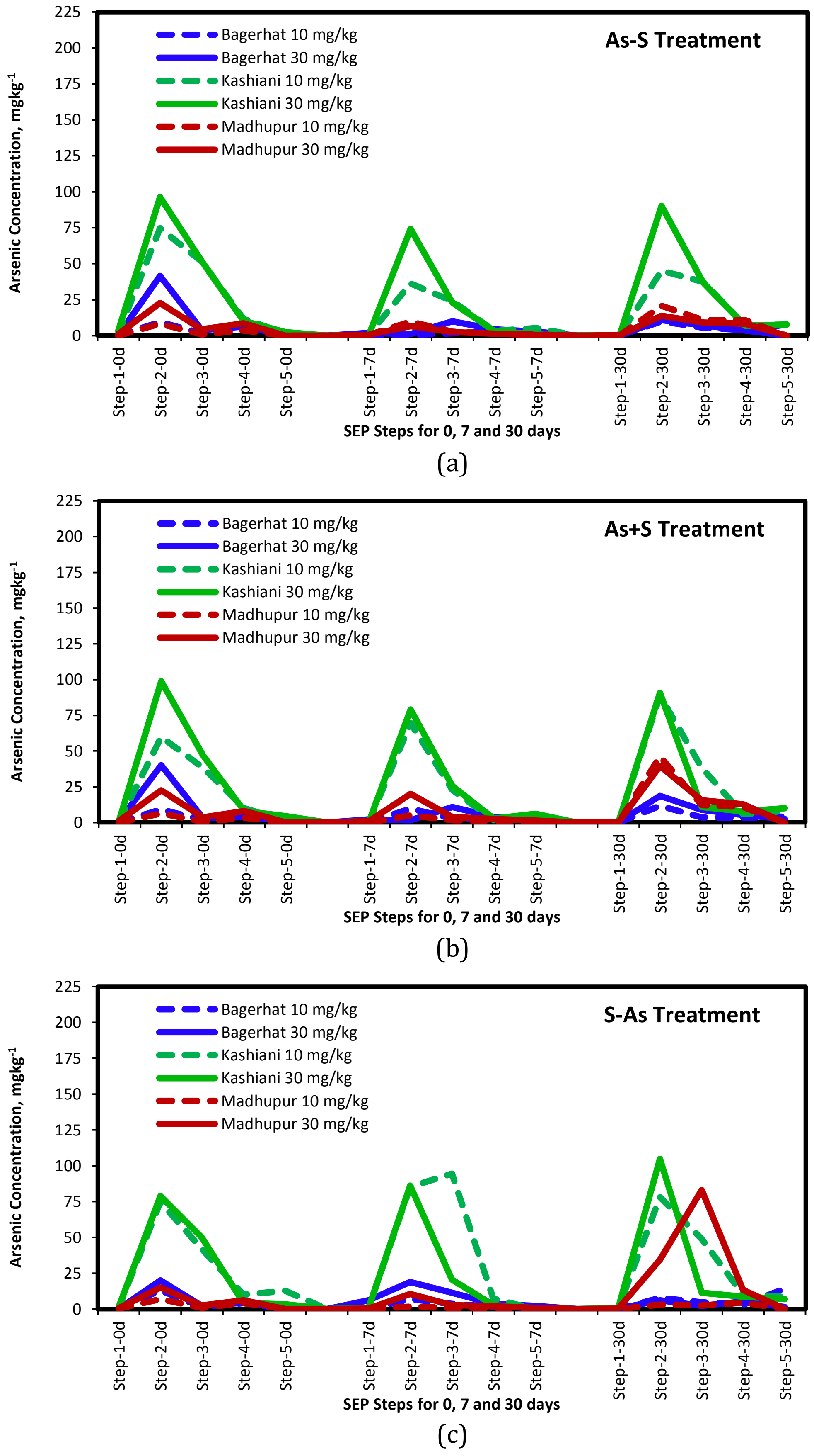
Fig. 4.18 Comparison of extracted arsenic fractions for treatments with phosphate and arsenite anions for different incubation periods.

amount of extracted arsenic gradually increased with period of incubation. This might be attributed to the soil having a high phosphate fixation capacity and available phosphate probably does not increase much after phosphate addition (Tu and Ma 2003). Thus the increase in the extracted amount with time as found in the present study is probably justified.

Comparing the results of treatments involving arsenic and phosphorus as shown in Figs. 4.18.a, 4.18.b and 4.18.c, it becomes apparent that when arsenic was added prior to (Fig. 4.18.a) or simultaneously with phosphate (Fig. 4.18.b), the extracted amount of arsenic does not notably vary with incubation periods (0, 7 or 30 days). This observation is similar to that obtained by Darland and Inskeep (1997) who found that phosphate effectively competes with arsenic, however, phosphate was not able to desorb all the applied arsenic regardless of whether the arsenic was applied concurrently or prior to phosphate addition. When phosphate was added before arsenic (P-As), a gradual increase in the extracted amount was observed with residence times (0, 7 and 30 days) as shown in Fig. 4.18.c. This is in agreement with the findings of Pierce and Moore (1982) who found that once arsenate was sorbed to a natural surface, the sorbed arsenate was not affected by the post addition of phosphate and sulphate, however, sorbed arsenate was affected, at low concentrations, by the prior addition of phosphate (P-As) and sulphate to the system.

## 4.8 ASSESSMENT OF INTERACTION OF ARSENIC WITH SULPHATE ANION

In a sequence similar to treatments with phosphate, results of different sulphate treatments are grouped. The results are shown in Fig. 4.19.a. 4.19.b and 4.19.c for As-S, As+S and S-As treatments, respectively. A general observation of these results showed that $(NH_4)H_2PO_4$ extractable specifically bound arsenic were higher in amount in SEP Step-2 compared to other steps. An exception was found that S-As treatment at 10 mg kg$^{-1}$ dose for Kashiani soil at 7-day where the extracted amount of amorphous hydrous oxide bound arsenic was more than the specifically bound fraction. Madhupur soil showed similar behavior at 30-day for 30 mg kg$^{-1}$ dose for the same treatment.



(a)

(b)

(c)

Fig. 4.19 Comparison of extracted arsenic fractions for treatments with sulphate and arsenite anions for different incubation periods.

For all the treatments with sulphate and arsenic, the magnitude of extracted amount was similar (75 ~100 mg $kg^{-1}$) and did not vary with time. This indicates poor or no correlation of arsenic with sulphate anion during retention by soils. This is because arsenic has a greater propensity to form bonds with sulphur and carbon than phosphorus (Herreweghe, 2003; Johnson and Hiltbold, 1969; O'Neill, 1995). Sulphate anion probably did not have the same sorption site. Phosphate anion may have similar sorption mechanism to that of arsenic. Reseracher postulated that sulphate anion may have different sorption mechanism (Gebhardt and Coleman, 1974; He *et al.*, 1997). Therefore, treatments with sulphate did not show any appreciable variation with time in relation to arsenic retention.

Comparison of the results showed that, in general, the extracted amount was notably higher in cases of treatments involving phosphate to that of sulphate. This was quite in agreement with the past studies (Geelhoed *et al.*, 1997; O'Reilly, 2001) which stipulated that sulphate is less strongly sorbed than phosphate and is thus a much less effective desorbent. The mechanisms for adsorption of arsenate and sulphate were probably not identical because arsenate adsorption should have decreased with increased sulphate concentration if the mechanisms were the same. In fact, Geelhoed *et al*. (1997) found that phosphate was a stronger competitor for adsorption on goethite than sulphate in competitive adsorption systems with phosphate and sulphate.

## 4.9 ASSESSMENT OF INTERACTION OF ARSENIC WITH MIXED PHOSPHATE AND SULPHATE ANIONS

The results of the mixed As+P+S treatments are shown in Fig. 4.20. Like the previous treatments, the $(NH_4)H_2PO_4$ extractable specifically bound arsenic could generally be attributed as the highest extracted amount in SEP Step-2 for all soils and for all doses. The magnitude of extraction showed a generally increasing trend with time for the 30 mg $kg^{-1}$ dose. Unlike other treatments, the amount of extraction for Bagerhat soil was found to be higher at 7 and 30-day of incubation for the 30 mg $kg^{-1}$ dose.In the present study, the application of all three anions at the same time have caused higher extracted amount of arsenic for the higher 30 mg $kg^{-1}$ dose for both the Kashiani and Bagerhat soil. It may be mentioned that

Kashiani soil also showed higher extraction in other treatments especially the treatments involving arsenic and phosphorus only. On the other hand, Bagerhat soil showed high extraction only in the As+S+P treatment at high concentration. Like other treatments, maximum amount of arsenic was extracted as specifically–bound fraction. The effect of mixed treatment is comparable to treatment with arsenic-

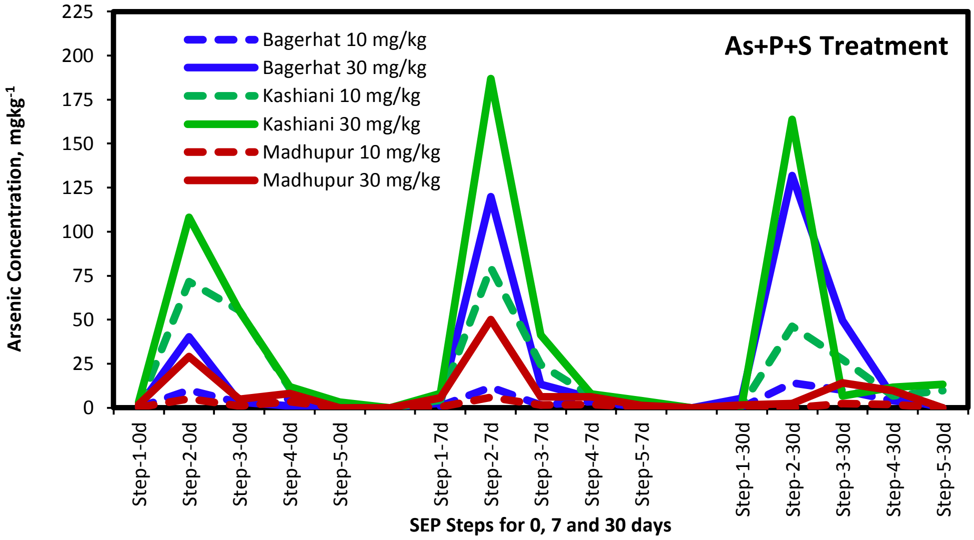


Fig. 4.20 Comparison of extracted arsenic fractions for treatments with phosphate, sulphate and arsenite anions for different incubation periods..

phosphate for Kashiani soil. On the other hand, the mixed treatment (As+S+P) resulted in much higher extraction for Bagerhat soil specifically at higher concentration when compared to the extracted amount in previous treatments. It is thus appeared that in presence of sulphate, efficiency of phosphate might increase in desorbing arsenic for soils where phosphate alone is not strong enough to desorb arsenic. These findings were in agreement with Ali and Ahmed (2003). In the subsurface environment, adsorption-desorption of arsenic onto iron oxy-hydroxides is an important mechanism controlling its mobility. Presence of ligands, which may compete with arsenic for adsorption sites on iron oxy-hydroxides, e.g., phosphate, silicate and sulfate can also influence the desorption or mobility of arsenic in the subsurface, if present in large enough concentrations (Ali and Ahmed, 2003).

## 4.10 DISCUSSION

By using a novel method for arsenic sequential extraction in this study (Wenzel *et al*., 2001), arsenic fractionation of two contaminated (Kashiani and Bagerhat) samples and an uncontaminated (Madhupur) sample were carried under various conditions of treatment and incubation period. The sequential extraction of arsenic from the studied soils allowed for studying the speciation pattern of when the soils samples were treated with different sequences and doses of mixed oxyanions (arsenic with phosphorus and/or sulphur).

In the present study, the un-spiked contaminated soils of Kashiani and Bagerhat showed crystalline bound form as the major fraction of arsenic. On the other hand, for the spiked samples, most of the arsenic was extracted as specifically bound. Treatments on uncontaminated Madhupur soil showed small arsenic extraction even with treatments with higher arsenic concentration. The difference between the crystalline and specifically bound is important from the risk assessment point of view. The present study is similar to that of Dybowska *et al*. (2005). They observed that a much higher fraction of arsenic is solubilised with ammonium phosphate (specifically bound). The basis of this fraction is the competitive exchange between phosphate ($PO_4^{3-}$) and arsenate ($AsO_4^{3-}$) in soils, where, because of the smaller size and higher charge density of phosphate, arsenate is preferentially desorbed over phosphate (Manning and Goldberg, 1996). This fraction provides a useful indication of arsenic which may be potentially mobilized due to anion exchange and the risks of this remobilization in the soils studied have to be taken into consideration. A significant proportion of arsenic which are in non-specifically or specifically bound can be remobilized from the contaminated soils by anion exchange with phosphates. Fertilization of such soils with phosphate will lead to increased arsenic mobility and leaching from soils and risk for potential contamination of surface/groundwater.

Previous studies on anion interaction (Begum and Huq, 2007; Cao *et al*., 2003; Davenport and Peryea, 1991; Fuller *et al*., 1993; Manning and Goldberg, 1996; O'Reilly *et al.,* 2001) showed that $PO_4^{3-}$ causes arsenic mobilization but the exact species of arsenic was unknown. In the present fractionation study, the species had been identified as the non-specifically and specifically bound which can be mobilized due to addition of phosphate fertilizer. However, $PO_4^{3-}$ may not be able to mobilize the arsenic from amorphous or crystalline bound form (Dybowska *et al*., 2005). O'Reilly *et al*. (2001) also pointed out that arsenic is not easily desorbable or removable. Their study on the effect of highly concentrated phosphate anion in affecting arsenic leaching from a arsenic contaminated soil column showed that a major fraction of arsenic is non-extractable. In the spiked contaminated soil samples of present study, most of the arsenic was $(NH_4)H_2PO_4$ extractable specifically bound form. Arsenic added (spiked) to the samples during application of treatment sequences (As and P) was the source of this fraction of arsenic. On the other hand, fractionation of the untreated contaminated samples showed that most of the arsenic is in crystalline bound form. The "aged" oxides with more crystalline character (crystalline Fe oxides) are more resistant to changes in the oxidation-reduction conditions and the pH in the soil (Cornell and Schwertmann, 1996). Therefore, use of phosphate fertilizer may not further aggravate the arsenic toxicity issue in such soils.

# Chapter 5

# SUMMARY AND CONCLUSIONS

## 5.1 FINDINGS OF THE STUDY

A laboratory batch experiment was conducted using three soil samples of different pH to evaluate anion-anion interaction (arsenic, phosphorous and sulphur) using a five-step sequential extraction procedure of arsenic fractionation with an aim to understand arsenic dynamics in soils which might be helpful in developing remedial measures against arsenic contamination. Research work was directed to acquaint with various fractions of arsenic in two contaminated calcareous high pH soils from Bagerhat and Kashiani and uncontaminated low pH soil from Madhupur of Bangladesh. These three sites were selected on the basis of studying the total arsenic content, pH and calcareousness of soil samples collected from eleven different sites. Background analysis of these soils was conducted to determine their physical and chemical properties. Correlation study of different soil nutrients with arsenic content was also carried out. The results of the present study are summarized as follows,

a. The total concentration of Arsenic in Bagerhat, Kashiyani and Modhupur soils were found to be 22.0, 88.0 and 3.68 mg kg$^{-1}$, respectively. Study of the physical and chemical properties of the samples showed very good correlation between total arsenic content and % organic matter ($R^2$=0.9975), phosphorus ($R^2$=0.997), calcium ($R^2$≈1.0) and carbonate ($R^2$≈1.0) content of the samples. Moderate correlation was obtained between % arsenic content and CEC ($R^2$=0.64), pH ($R^2$=0.702) and iron ($R^2$=0.454).

b. The carbonate content of Kashiani soil was nine percent while the same for Bagerhat soil was only two percent. The corresponding arsenic content was 88 and 22 mg kg$^{-1}$, respectively. It appears that there had been a good correlation between carbonate and arsenic concentration. A possible reason could be that minerals in the clay fraction of soils, such as carbonates can contribute to arsenic adsorption due to their abundance.

c. The total iron content of Kashiani, Bagerhat and Madhupur samples were 300, 159 and 241 mg kg$^{-1}$, respectively. Arsenic adsorption is significantly positively correlated with Al and Fe (hydrous)oxide and clay content of soils. Inorganic constituents of soils that adsorb significant amounts of arsenic are Al and Fe oxides, clay minerals, and carbonates. In the present study, the respective concentrations of arsenic and iron in both Kashiani and Bagerhat soils support the fact. The high associativity of Fe with arsenic in Kashiani and Bagerhat soil was probably due to presence of iron oxy-hydroxides. Low arsenic content in Madhupur soil is possibly due to the fact that Madhupur soil contains large amount of Fe(III) oxides which are quite stable and therefore incapable of bonding arsenic.

d. Fractionation of the un-spiked soil samples showed that most of the arsenic was bound with crystalline hydrous oxides as was revealed in SEP Step-4. Highest amount of crystalline hydrous oxide bound arsenic fraction was found from Kashiani soil which was 54 mg kg$^{-1}$. The same for Bagerhat and Madhupur soils were 7.0 and 2.5 mg kg$^{-1}$, respectively. For Bagerhat soil, the maximum amount was found as crystalline hydrous oxide-bound followed by amorphous hydrous oxide bound. It can be noted that the uncontaminated Madhupur soil showed very low arsenic fraction in all steps of SEP indicating that this soil has poor arsenic bonding capacity.

e. Comparing the results of treatments involving arsenic and phosphorus it became apparent the when arsenic was added before or simultaneously with phosphate, the extracted amount of arsenic does not notably vary with incubation periods. The amount of specifically sorbed arsenic was highest in P-As treatment than As-P or As+P treatment. When phosphate was added before arsenic (P-As), a gradual increase in the extracted amount with residence times (0, 7 and 30 days) was found. The basis of this fraction is the competitive exchange between phosphate ($PO_4^{3-}$) and arsenate ($AsO_4^{3-}$) in soils, where, because of the smaller size and higher charge density of phosphate, arsenate is preferentially desorbed over phosphate.

f. Treatments involving arsenic and sulphate showed that the amount of desorbed arsenic did not appreciably vary with incubation except for the uncontaminated Madhupur soil in S-As treatment. For all the treatments with sulphate and arsenic, the magnitude of extracted amount was similar. This indicates that sulphate anion probably did not have the same sorption site. Phosphate anion may have similar sorption mechanism to that of arsenic. Therefore, treatments with sulphate did not show any appreciable variation with time with respect to arsenic retention.

g. Comparison of the results showed that, in general, the extracted amount was notably higher in cases of treatments involving phosphate to that of sulphate. This might be due to the fact that the mechanisms for adsorption of arsenate and sulphate were probably not identical because arsenate adsorption should have decreased with increased sulphate concentration if the mechanisms were the same. Sulphate is less strongly sorbed than phosphate and is thus a much less effective desorbent. In competitive adsorption systems with phosphate and sulphate, phosphate was a stronger competitor for adsorption than sulphate anion.

h. In the present study, the application of all three anions at the same time had caused higher extracted amount of arsenic for the higher 30 mg kg$^{-1}$ dose for both the Kashiani and Bagerhat soil. Unlike previous treatments, Bagerhat soil showed high extraction only in the As+S+P treatment at high concentration. Like previous treatments, maximum amount of arsenic was extracted as specifically–bound fraction. The effect of mixed treatment is comparable to treatment with arsenic-phosphate for Kashiani soil. On the other hand, the mixed treatment (As+S+P) resulted in much higher extraction for Bagerhat soil specifically at higher concentration when compared to the extracted amount in previous treatments. It is thus appeared that in presence of sulphate, efficiency of phosphate might increase in desorbing arsenic for soils where phosphate alone is not strong enough to desorb arsenic.

## 5.2 REMEDIATION

Past studies on anion interaction found that $PO_4^{3-}$ causes arsenic mobilization but the exact species of arsenic was unknown in most of the cases. In the present fractionation study, the species had been identified as the specifically bound form which can be mobilized due to addition of phosphate fertilizer. However, $PO_4^{3-}$ may not be able to mobilize the arsenic in amorphous or crystalline bound form. In the spiked contaminated soil samples of present study, most of the arsenic was $(NH_4)H_2PO_4$ extractable specifically bound form. Arsenic added (spiked) to the samples during application of treatment sequences (As and P) was the source of this fraction of arsenic. On the other hand, fractionation of the untreated contaminated samples showed that most of the arsenic is in crystalline bound form. The "aged" oxides with more crystalline character (crystalline Fe oxides) are more resistant to changes in the oxidation-reduction conditions and the pH in the soil. Therefore, use of phosphate fertilizer may not further aggravate the arsenic toxicity issue in such soils.

Fertilization of arsenic contaminated soils with phosphate will lead to increased arsenic mobility and leaching from soils and potential contamination of surface/groundwater only if arsenic is present as specifically-bound form found in the present study. Chemical remediation using $PO_4^{3-}$ or $SO_4^{2-}$ in such soils may not be effective for arsenic removal because, a significant proportion of arsenic can also be remobilized from soils through the process of anion exchange. Fertilization of such soils with sulphur may help in the immobilization of arsenic.

## 5.3 RECOMMENDATION

Arsenic can be retained in soils or removed from groundwater by sorption to metal (hydro)oxides, clay mineral phases and natural organic matter, forming insoluble solids. Chemically and microbially mediated oxidation and reduction reactions may produce less mobile arsenic species and mixed solid phases capable of sorbing arsenic, thus enhancing the immobilization processes. However, the immobilization processes by sorption is reversible and the remobilization of sorbed arsenic may occur when biogeochemical conditions of site change with time. Arsenic immobilization through sorption to solid phases is probably the best mechanism to retain arsenic in soils and remove it from groundwater, and this process can be enhanced by microbial activities. Hyperaccumulation is another applicable choice to remove arsenic from soils and shallow groundwater. However, adoption of any such remedial measures requires prior characterization of soils of different areas.

Although it is undoubtedly important to know the total concentrations of Arsenic in soils and sediments, these concentrations do not give any information about the solid-phase partitioning and potential mobility of arsenic within the soils. Fractionation study of all the spiked soil samples in the present study reveals that the majority of the arsenic had been extracted as specifically-bound form which is extractable by phosphate anion. On the other hand, contaminated original (unspiked) soil samples contained arsenic mostly in crystalline bound form which may not be easily mobilized by addition of phosphate. Therefore, proper site characterization is critical to the success in application of any arsenic remediation measures. Based on the findings of the present study, it may be recommended that fractionation study should be conducted for different soils of Bangladesh to identify the species of arsenic. This shall enable to select the appropriate remediation measures specific to a site.

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# APPENDIX - I

Table A-1 Five-step arsenic fractionation of untreated samples from three locations, mg kg$^{-1}$.

| | Step-1: $(NH_4)_2SO_4$ for non-specifically-bound As fraction | Step-2: $(NH_4)H_2PO_4$ for specifically - bound As | Step-3: $NH_4$-Oxalate for amorphous hydrous oxide- bound As fraction | Step-4: $NH_4$-Oxalate/ Ascorbic acid for crystalline hydrous oxide-bound As fraction | Step:-5: Acid digestion for residual As fraction |
|---|---|---|---|---|---|
| Bagerhat | 0.226 | 0.137 | 4.205 | 7.138 | 1.270 |
| Kashiani | 0.657 | 0.040 | 1.291 | 53.450 | 0.270 |
| Modhupur | 0.062 | 0.020 | 0.374 | 2.500 | 0.580 |