ベンガルデルタの農村における泥炭質堆積物から地下水（井戸水）へのヒ素溶出のメカニズム

Md. Shamim, Uddin
Graduate School of Social and Cultural Studies, Kyushu University

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Mechanism of Arsenic Release from Peat Sediments into the Groundwater of Wells in the Rural Villages of the Bengal Delta

（ベンガルデルタの農村における泥炭質堆積物から
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Graduate School of Social and Cultural Studies
KYUSHU UNIVERSITY

MD. SHAMIM UDDIN

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Abstract

Groundwater arsenic (As) contamination in the Bengal Delta is one of the most severe environmental problems in Bangladesh. Millions of village people, who drink the As-contaminated groundwater of wells, are suffering from As poisoning. The main source of As is of geological origin, i.e., the As is contained in the sediments accumulated in the Bengal Delta. The problem has become apparent in the last 20-30 years, to which the release of As from the sediments into groundwater of wells is concerned. However, the mechanisms of the As release are still not well understood. The peat sediment, originated from decayed plant material, is often present in the sediments of the As-contaminated area. In addition, the chemical fertilizers are applied massively in recent decades in the rural villages of the delta. Therefore, this study was made to clarify the mechanism of As release from sediments into groundwater in the rural villages of the delta, considering the effects of peat sediment and massive chemical fertilizers application.

For the sediments bored from the As-contaminated village, the As concentration in the peat sediment was higher than in the other sediments, i.e., the order of the As concentration of sediments was peat>peaty clay> clay>silty clay>sand. A positive relationship between the As concentration, %C and %N was identified in these sediments. The N and C in the peat sediment were identified to be sourced from the chemical N fertilizer and aquatic plants, respectively, according to the $\delta^{15}N$ and $\delta^{13}C$ analyses. Thus, it is thought that As concentration in peat sediment is increased by the absorption of As by aquatic plants that had grown there long time ago, and the C concentration was increased by the accumulation of the decayed material of the plants. The positive correlation between %C and %N observed for the peat sediment may have been induced by the

mechanism that the C absorbed N sourced from the chemical N fertilizer with a comparatively weak chemical bond. The peat sediment had a thickness of 0.6-1.8 meters and was located in a shallow layer in between the groundwater table and the bottom of the well at the As-contaminated village. In contrast, peat sediment was not observed in the sediments bored from the non-As-contaminated village, where a thin peaty clay layer was observed at a deeper layer.

From the measurement of groundwater quality at the As-contaminated village, the As concentration of groundwater was maximally as high as 30 times the Bangladeshi drinking water standard. There was a positive relationship between the concentrations of As and ammonium-N. According to the $\delta^{15}N$ analysis on the groundwater, the inorganic-N, most of which was the ammonium-N, was identified to be sourced from the chemical N fertilizer, i.e., the same source as that of the peat sediment. The ORP of the groundwater was found to be low, showing a reducing condition of the groundwater. The release of As from peat sediment into groundwater was thought to be induced by the mechanism of "the reduction of iron hydroxides and release of involved As from the peat sediments," based on the fact that the groundwater As concentration was high when the groundwater was in the reducing condition. A large concentration of ammonium-N in the groundwater observed at a high As concentration may have been sourced from the N in the peat sediment. In the non-As-contaminated village, the concentrations of As and ammonium-N of the groundwater were very low, and the ORP showed that the groundwater was in non-reducing or oxidizing condition. The result of the $\delta^{15}N$ analysis showed that the source of the inorganic-N in the groundwater was not the chemical N fertilizer, but animal or human waste. Hence the above-mentioned release of As under the reducing condition did not occur in the village.

From the above comparisons, it was concluded that peat sediment is important and plays a critical role in groundwater As contamination. Concerning the substances of peat sediment to affect the As contamination, As is the most important substance, followed by N. The peat sediment is a place to preserve a lot of As and N. In addition, C and inorganic substances in the peat sediment are important to bond N and inorganic As, respectively. Concerning the groundwater quality parameters to affect the As contamination, ORP is the most important parameter, followed by ammonium-N. Both of them could prompt the release of As into groundwater. A substance of peat sediment can affect a groundwater quality parameter, i.e., N in peat sediment contributes to create the reducing ORP of groundwater through the microbial activity that consumes oxygen by using N as a nutrient. Chemical N fertilizer, i.e., the source of N in peat sediment, eventually contributes to provide the reducing condition. The release of As is prompted by the reducing condition.

Thus, it was concluded that the concentrations of As, C and N, and the source of C and N in the peat sediment, and groundwater parameters of ORP and ammonium-N affect groundwater As contamination. Based on the results, the mechanism of As release from peat sediment into groundwater of wells was clarified in the villages of the Bengal Delta. For further study, it is important to clarify the topographical conditions favorable for the formation of peat sediment, and the kinds of microorganisms living in peat sediment and their activity in terms of the release of As.

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CHAPTER 1

General Introduction

1.1 Background of the present study

Groundwater arsenic (As) pollution is one of the most severe environmental problems in Bangladesh, where millions of people are suffering from As poisoning. The main source of As in Bangladesh is of geological origin (British Geological Survey, 1999). Millions of shallow tube wells have been drilled in the delta to supply drinking water, but the water contains a lot of As.

Much research has been conducted on the groundwater As pollution in Bangladesh, but it has not produced an outcome that can satisfactorily mitigate the As poisoning. Year by year, the As poisoning problem becomes more severe. The mechanisms through which As is released from sediments into groundwater are still not well understood. It is thought that the complex geological and geochemical changes within the Ganges Delta (or Bengal Delta) may be responsible for the occurrence of As-rich groundwater. Rabbani *et al*. (1999) claimed that since the Bengal Delta is a most recently formed alluvium, the source of As in Bangladesh might be associated with the sedimentary deposits as a similar problem experienced in the adjoining Indian portion of the Gangetic alluvial aquifers in West Bengal of India. According to this source, mobilization of As is regulated by a chain of complex chemical reactions such as oxidation, reduction, precipitation, dissolution, absorption-desorption and methylation.

Arsenic comes into the sediments in the state involved in particles from the parent rock and is carried into the stream during erosion.

After the first identification of groundwater As contamination in 1993 in Bangladesh, peat and peaty sediments were considered to be the main sources of As in groundwater of the Bengal Basin due to their rich content of As.

The widespread occurrence of peat layer at a shallow depth in Bangladesh has been noted by Brammer (1996). Peat layer is common beneath the Old Meghna Estuarine Floodplain in Greater Comilla (*Ahmed et al.* 1998), Sylhet, and the Gopalganj-Khulna basins (*Reimann* 1993; *Brammer* 1996). Also, McArthur et al. (2004) suggested that the peat layer is the driver for the reduction of iron oxyhydroxides, which may be related to the mechanism of As release.

Peat layer occurs extensively beneath the As-affected areas of Samta Village in southwestern Bangladesh, which is the present study area (Ishiga et al. 2000; Yamazaki et al. 2000; AAN, 2000).

However, concentrations of not only As but also C and N of peat layer, all of which show larger values, and the relationship of depth between peat layer and groundwater table, and their contributions to the groundwater As contamination have not been studied well.

In Bangladesh, massive application of chemical N fertilizer to grow crops and vegetables might be considered a possible cause of As pollution in groundwater. On the other hand, the ammonium-N concentration in groundwater was found to be high in the same district of Bangladesh in the present study (Kurosawa *et al.*, 2008a). Thus, the concentration of N in groundwater and sediments were targeted in this study, and to know the source of N, the δ^{15}N values of groundwater and peat sediments were measured. The ORP of groundwater was measured to know the oxidation or reduction characteristic of groundwater. The %C of sediments was measured to know the total organic matter content of the sediments, and the $\delta^{13}C$ value of peat sediments was targeted to know the source of C in the sediments.

1.2 Natural arsenic in the environment

Arsenic is the twentieth most abundant element in the earth's crust, and naturally occurs as sulfide (S^{2-}) in a variety of mineral ores containing copper (Cu), lead (Pb), iron (Fe), nickel (Ni), cobalt (Co), and other metals. It is found in trace quantities in all living things, the atmosphere, water and geologic formations. High concentrations of As (>10 µg/L) in groundwater from natural geological sources have been reported in many countries, such as Bangladesh, India, Nepal, Pakistan, China, Myanmar, Cambodia, Vietnam, Taiwan, Iran, Mongolia, Hungary, Romania, Ghana, Nigeria, Nicaragua, Argentina, Chile, Bolivia, Peru, Mexico, Australia, Canada and many areas in the United States of America (Bhattacharya *et al.*, 1997, 2002, 2006; Welch *et al.*, 2000; BGS/DPHE, 2001; Mandal & Suzuki, 2002; Nickson *et al.*, 2005; Bundschuh *et al.*, 2006; Berg *et al.*, 2007; O'Shea *et al.*, 2007; Mukherjee *et al.*, 2008).

Arsenic is a toxic metalloid, typically low in concentration (1-5 mg/kg) in igneous and metamorphic rocks, but slightly high in concentration (5-10 mg/kg) in soils and sedimentary rocks (Bhattacharya *et al.*, 2002; Smedley & Kinniburgh, 2002). More than 200 As-bearing minerals are found in rocks in different forms, such as sulfides, oxides, arsenates, arsenites, etc., of which sulfides, especially arsenopyrite (FeAsS) and As-bearing pyrite (FeS_2), are the most common minerals. Arsenic is released into the environment (e.g. into air, water or soil) either from natural sources through volcanic activity and weathering of As-bearing minerals or by human activities such as mining, smelting, burning of coals, uses of pesticides, herbicides, fertilizers and wood preservatives, and as discharge from other chemical industries. Naturally occurring As is generally leached into the groundwater system by the interaction of water with rocks, minerals and soils in different geological, hydro-geological and geochemical environments. The As concentration in sea water is low, averaging about 2 µg/L (Ahmed, 2003a).

1.3 Geography and water resources in Bangladesh

Bangladesh, one of the largest deltaic countries of the world, occupies an area of 147,570 square kilometers. It lies in the north eastern part of South Asia, between 20°34́ and 26°38́ north latitude and 88°01́ and 92°41́ east longitude. The country is bounded by India on the west, north and north-east, Myanmar on the south-east, and the Bay of Bengal on the south. Most of the country is composed of the floodplains formed by the three major rivers of the Ganges, Brahmaputra and Meghna. These rivers and their distributaries discharge about 142 thousand cubic meters of water per second into the Bay of Bengal at the peak periods (Rahman *et al.,* 1990). About 80% of the country is floodplains, 12% is hills and 8% is uplifted fault blocks. Bangladesh is endowed with water resources from rainfall, river flow and groundwater. Besides these natural water bodies, there are over one million ponds of various sizes. The total area of the water bodies is over 12,000 square kilometers, which is equivalent to about 8% of the total land area of Bangladesh (BBS, 2009).

Groundwater is a major component of the water resource in Bangladesh. Use of groundwater becomes vital during the dry season and drought periods when surface water is insufficient. The groundwater, owing to its better quality, serves for agricultural and industrial uses in most parts of the country during the whole year and 90% of the population depends on the groundwater for drinking purposes. About 97% of the world's fresh water is groundwater, but its quality is seriously affected by pollution from human activities. The quality of groundwater is mostly good with some variation from place to place, but industrial, agricultural and domestic wastes seriously threaten groundwater quality.

In Bangladesh, groundwater exists in two aquifers, the upper and main aquifers, which probably interconnect hydraulically in most areas. About 90% of the annual rainfall occurs in the period between June and September. Thus, the groundwater level is highest during the monsoon season from August to October, and lowest in the dry season from April and May. Although Bangladesh is countries having one of the most accessible groundwater resources in the world, large-scale withdrawal of groundwater due to uses for irrigation and other household purposes has resulted in a lowering of the groundwater level in many parts of the country. In recent years, water shortages and scarcity have been an usual phenomena in the country during the dry season. The groundwater level in Dhaka City has been declining at a rate of 0.75 meter/year by the increased pumping for domestic water use. It has also been reported that dug wells are becoming dry in many areas of Bangladesh, suggesting that the lowering of the groundwater level is a serious problem for the water supply. It can also be considered that unplanned large-scale withdrawal of groundwater is likely to cause further lowering of groundwater level and widespread As contamination in many areas of Bangladesh.

1. 4 Arsenic in the groundwater, sediments and crops in Bangladesh

Groundwater As contamination occurs over a large area of Bangladesh, particularly in the southern half of the country where groundwater is primarily used for drinking purposes for millions of people and is pumped up from the upper aquifer (20-50 m depth). After gaining independence in 1971, the Government of Bangladesh undertook a massive program to provide safe drinking water for the people of the country. The Government of Bangladesh has installed around 8-10 million tube wells to pump up safe water for drinking and domestic purposes in rural areas. In 1993, a high concentration of dissolved As in the tube well groundwater was first reported by the Department of Public Health Engineering, Bangladesh. Since then, As concentrations exceeding 50 µg/L, i.e. the Bangladeshi drinking water standard, have been detected in groundwater in 61 out of 64 districts of Bangladesh by national surveys (BGS/DPHE, 2001; BAMWSP, 2002). According to the National Hydrochemical Survey of Bangladesh conducted in 1998-99, nearly 35 million people drink As contaminated tube well water (DPHE/BGS/DFID, 2000). The As contamination is mainly restricted to groundwater that is from shallower than a depth of 150 meters. The deeper aquifers are consistently low in As concentration. Arsenic contamination is restricted to young alluvial aquifers occurring in the floodplains. There are 8,540 villages in Bangladesh, where more than 80% of the wells, used as the single source of drinking water, are contaminated with As. A randomly sampled groundwater As contamination map of Bangladesh is shown in Fig.1.1 which was surveyed by DPHE/BGS/DFID (DPHE/BGS/DFID, 2000). The map shows that highly As-contaminated areas are found in the surrounding adjacent areas of the Ganges, Brahmaputra and Meghna rivers.

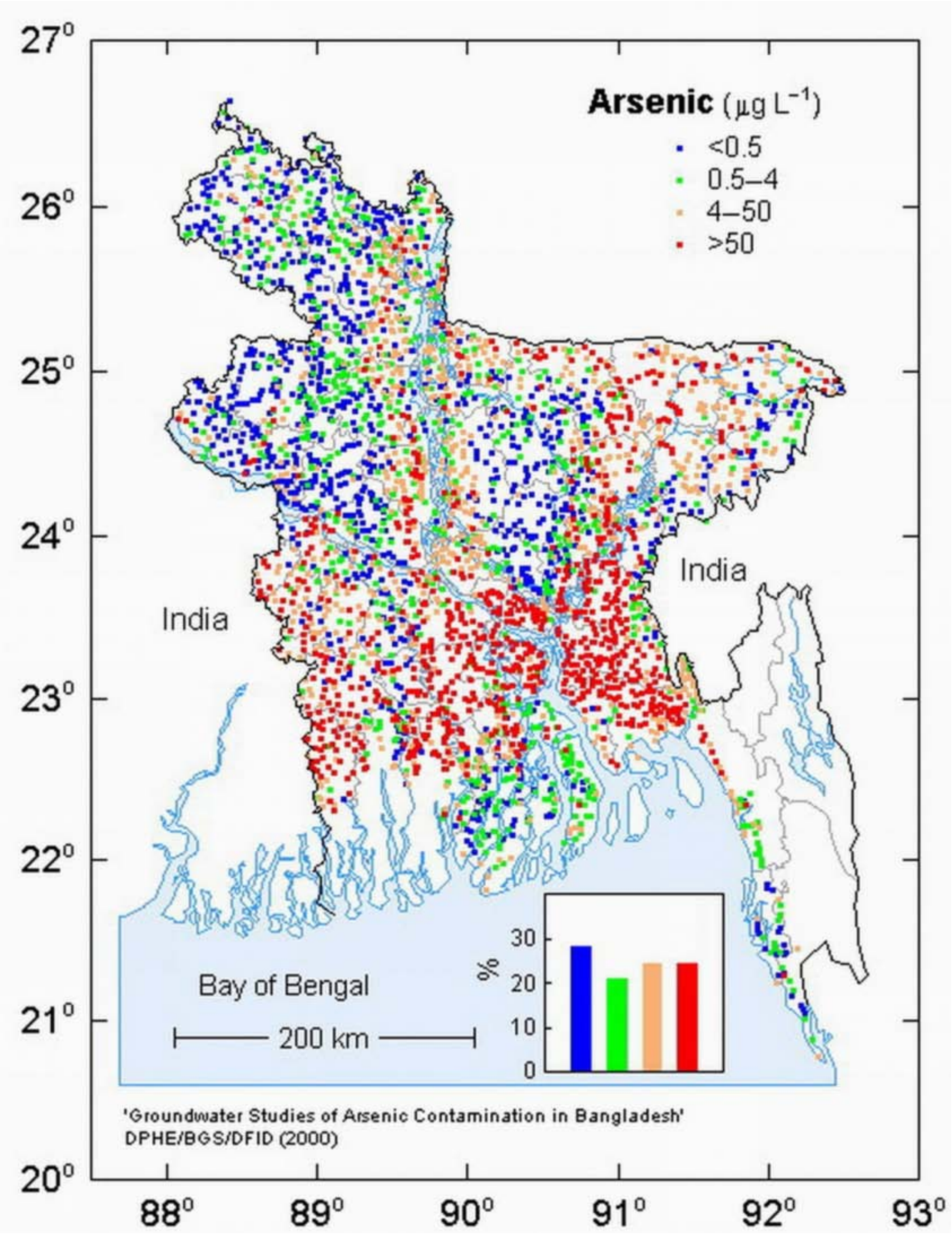

Figure 1.1 Groundwater arsenic contamination map of Bangladesh surveyed by DPHE/BGS/DFID in 2000

In addition to the use of groundwater for domestic purposes, a significant amount of groundwater is used for irrigation purposes during the dry season for rice planting. To meet the food demands for the increasing population in Bangladesh, the number of croppings has been expanded from one time to several times per year, and it is estimated that about 86% of the total groundwater pumped up is utilized for crop planting because of the limited rainfall during the rainy season. About 75% of the total irrigation water is provided by groundwater, and use of groundwater for irrigation may cause As contamination of paddy fields and rice grain. Apart from the health problem caused by drinking high As-containing groundwater, irrigation by As-contaminated groundwater threatens human health through intake of it by crops. There are some reports which have reported on the significant intake of As from rice and vegetables (Farid *et al.*, 2003; Meharg & Rahman, 2003; Correll *et al.*, 2006; Huq *et al.*, 2006). It has been estimated that more than 1,000 tons of As transferred annually from groundwater to arable land by groundwater irrigation, which poses a potential risk for future food production (Roberts *et al.*, 2007).

Numerous studies have been done on the As contamination of groundwater, soils and crops in Bangladesh, as introduced by Heikens (2006). Some other studies have focused on the relationships between groundwater-soils-crops (Kurosawa *et al.*, 2008b), groundwater-soils (Jahiruddin *et al.*, 2000; Ali *et al.*, 2003), and soils-rice (Chaturvedi, 2006) in the paddy fields. Heikens *et al.*(2007) stated that soil As concentration had increased with years due to the development of irrigation. The growth of rice plants was affected negatively by the amount of As in the soil, and As damaged the roots of the rice plants, resulting in suppression of the uptake of nutrients by the roots (Abedin *et al.*, 2002). Therefore, the contamination of soil and agricultural products by As is also of great concern.

1.5 Arsenic occurrence, sources and mobilization in the groundwater in Bangladesh

Arsenic can exist in groundwater with various oxidation numbers including +5 (arsenates), +3 (arsenites), +1 and -3 valences, and rarely in the elemental form. In these different oxidation numbers, As can form organic and inorganic compounds. The toxicity of As compounds depends largely on the oxidation number whether As is present in an organic form or not. The order of toxicity (from the highest to the lowest) is as follows: arsine (-3), arsenites (+3), arsenates (+5), and arsonium metals (+1). Under the reducing condition, As is a stable solid, and dissolved, As is present in oxygenated water. There are about 320 As-bearing minerals in nature, and the most commonly existing ones are: realgar (AsS), orpiment (As_2S_3), arsenopyrite (FeAsS), arsenolite (As_4O_6), and As pentoxide (As_2O_5). Among them, arsenopyrite is the most common (Ahmed, 2003a). Arsenic can occur in groundwater due to natural geochemical processes or anthropogenic activities. The groundwater As contamination in Bangladesh arises from the presence of As in the aquifer sediments and its release from the sediments into the groundwater.

Geological source of arsenic: The Ganges Delta (or the Bengal Delta) is the largest delta in the world, where these rivers contribute to the transport of one-third of the global sediments from the Himalayas to the world's oceans (Loving-bengal.net, 2007). It can be considered that these sediments are transported from the Himalayas created by the land in the present form and carry As. Thus, there is no doubt that the source of As in the sediments is of geological origin. Arsenic is usually contained in the range of 2-20 mg/kg in the alluvial sediments; which is greater than the range found in typical sediments (2-6 mg/kg) (British Geological Survey, 1999). However, it appears that a large proportion of As is present in a potentially soluble form. The greatest As concentrations are mainly found in the fine-grained sediments, especially of the grey clays (British Geological Survey, 1999). A large number of other elements, including iron, phosphorus and sulfur, are also enriched in the clays. The mobilization of As from sediments to water depends on the sediment-water interaction in different environments.

Mobilization of arsenic in the reducing condition: The reducing environment is believed to release As into groundwater because the reducing environment transforms ferric iron (III) to its ferrous (II) form, accompanied by the dissolution of both iron and As into groundwater (Ahmed, 2003b). A positive relationship was found between the degree of reduction and the As concentration in groundwater (British Geological Survey, 1999). It has been observed that high organic matter in sediments produces strong reducing condition in the sediments and groundwater (British Geological Survey, 1999). This process is aided by the high groundwater table and by the presence of fine-grained layers in the surface which impede entry of air to the aquifers. Microbial oxidation of organic carbon has depleted the dissolved oxygen in the groundwater. This is reflected by the high bicarbonate concentrations found in groundwater in recent sediments (British Geological Survey, 1999).

1.6 Proposed mechanisms of arsenic release from sediments into groundwater

The main source of As in the Bengal Delta is of geological origin, and As is contained in the sediments of the shallow Holocene aquifers of the delta (Ravenscroft *et al.*, 2005). Millions of shallow tube wells have been drilled in the Delta to supply drinking water to local people, but the water contains a lot of As. Much research has been conducted on the groundwater As pollution in Bangladesh, but the mechanism of As release from sediments into groundwater is still not well understood. Several hypotheses on the As release mechanism have been proposed, including (i) reduction of iron hydroxides and the release of involved As from the sediments (Nickson *et al.*, 2000; McArthur *et al.*, 2001; Dowling *et al.*, 2002), (ii) release of As following oxidation of As-rich pyrite in the sediments (Chowdhury *et al.*, 1999), and (iii) anion exchange of adsorbed As with P originating from fertilizers (Acharyya *et al.*, 2000). Among these mechanisms, (i) is the most widely accepted at present. Microbial activity is considered to be a factor to create the reducing condition in groundwater through decomposition of organic matter (Wang and Mulligan, 2006).

On the other hand, intensive cropping has been done in Bangladesh to produce food the 151.1 million people living in the small country area of only 147 thousand km^2. The Government of Bangladesh has subsidized chemical N fertilizer to farmers to grow crops and vegetables (Ministry of Industries, Bangladesh, 2008). However, massive application of chemical N fertilizer to the fields is a possible cause of the As contamination in the groundwater.

Three hypotheses regarding As release from sediments into groundwater leading to the As contamination of groundwater in the Bengal Delta, i.e., (i) reduction, (ii) oxidation, and (iii) anion exchange associated with phosphate fertilizer application, are described in detail below:

Reduction: Nickson *et al.* (1998) proposed the reduction hypothesis as the source of As in groundwater of the Bengal Delta. Therein, As is released by the reductive dissolution of As-rich iron hydroxides derived from the weathering of base-metal sulphides. It has been suggested that the As-rich groundwater is mostly restricted to the Holocene aquifers of the Bengal Delta. As the region where the concentration of iron and As is positively correlated is in the Bengal Delta, the source of As-rich iron hydroxides must lie in the Himalayas.

Oxidation: According to this hypothesis (Chowdhury *et al.*, 1999), As is derived from the oxidation of As-rich pyrite in the sediments of the Bengal Delta aquifer as atmospheric oxygen invades the aquifer in response to a lowering of the groundwater table carried by the excessive withdrawal of water.

Anion exchange associated with phosphate fertilizer application: Phosphate fertilizer itself contains As because it is made from phosphate rock that contains As. In addition, As in the sediments is combined with iron. When phosphate enters the sediments, the phosphate combines with the iron, resulting in the release of As into the groundwater (Acharyya *et al.*, 2000).

According to Kurosawa *et al.* (2008a), the ammonium-N concentration in groundwater was high in an As-contaminated area in Bangladesh, and the possible source of ammonium-N would be chemical N fertilizers.

1.7 Toxicity of arsenic

From ancient times, As compounds have been known as agents of committing suicide and murder, and as a common environmental agent. Arsenic has a metallic taste and slight garlicky odor. It is toxic and carcinogenic, and only a small quantity of it can cause serious health hazards. Dosages of 70-180 mg of As trioxide (As_2O_3) have been reported to be lethal to human beings in acute toxicity (Leonard, 1991). The toxicity and health effect of As depends on the chemical and physical states of gas, solution and powder particle size of the As compounds, the rate of absorption into cells, and of course, the preexisting state of the patient. Arsenic is present as organic and inorganic forms in the environment. Inorganic As is exist in groundwater and is more toxic than the organic As. High concentrations of inorganic As in groundwater induce a risk of As poisoning and poisons people slowly.

There is clear evidence that long-term use of As-contaminated water for drinking purposes increases the risk of getting cancer (Hopenhayn, 2006; Yuan *et al.*, 2007). It was confirmed from the epidemiological studies that long-term exposure to As-contaminated drinking water above the permissible limit causes melanosis, lewcomelanosis, keratosis, hyperkeratosis, skin pigments, Bowens, gangrene and causes cancer in the kidneys, bladder, skin, lungs and liver. These symptoms are the common types of chronic As poisoning. Arsenic is also deposited in bones, teeth and hair. For manifestation of the symptoms of As toxicity in a person’s body it may take several years after the start of drinking of As-contaminated water. 38,430 arsenicosis patients were identified in 270 out of the total 460 Upazilas (meaning sub-districts) up to 2004 in Bangladesh (NAMIC, 2005), where the drinking water quality did not meet the

Bangladeshi drinking water standard for As. The World Health Organization recommends a safety standard of 10 µg/L of As for drinking water, which is lower than the 50 µg/L of the standard set for the drinking water in Bangladesh.

In the present study, As concentrations of up to 1.5 mg/L were found in tube well water in Samta Village, which is 30 times higher than the Bangladeshi drinking water standard. In Samta village, 153 arsenicosis patients were identified in 2003 (JICA/AAN, 2004), and the photos of some patients are shown in Fig. 1.2. According to the national screening report of wells (NAMIC, 2005), groundwater As contamination has been identified in 61 out of 64 districts in Bangladesh where 38,430 arseniccosis patients were identified in 2005 (NAMIC, 2005). The groundwater As contamination map and the location map where patients were identified, both maps being divided by district, are shown in Fig. 1.3.

Figure 1.2 Photographs of the arsenicosis patients: (A) Melanosis, (B) Keratosis in palm, (C) keratosis in foot, (D) Severe melanosis, (E) Bowens, and (F) Cancer patients caused by chronic groundwater arsenic pollution in Bangladesh

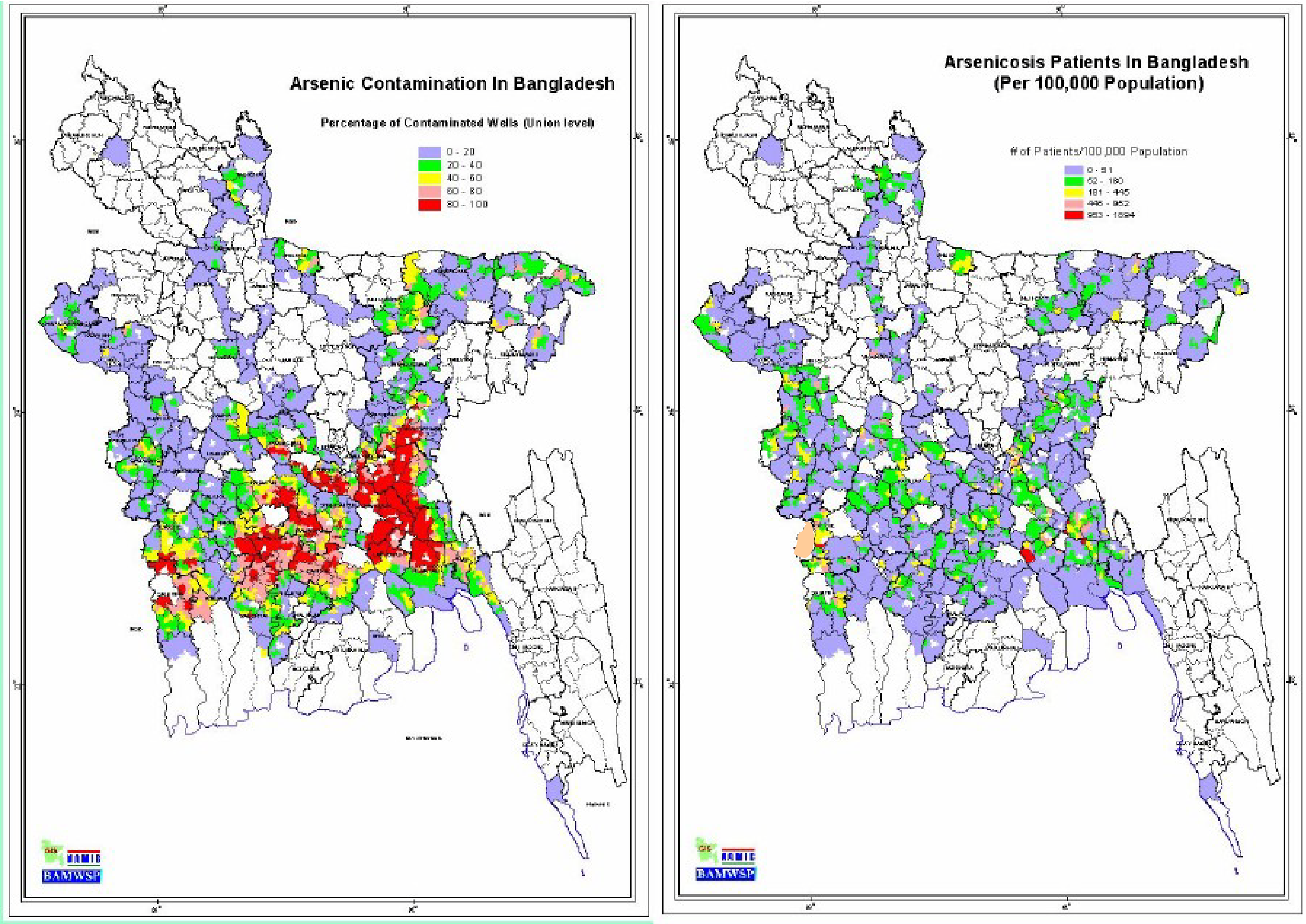

Figure 1.3 (A) Distribution of wells with As concentrations in the groundwater above the Bangladeshi standard, and (B) the location where arsenicosis patients were mainly identified

1.8 Acceptable limit of arsenic for human ingestion

Intake of As by the human body from foods, especially from sea food, is probably greater than that from drinking water. However, As species from sea food are mostly in organic form with a low toxicity. Arsenic present as an inorganic form in drinking water is more toxic. The World Health Organization established a guideline for drinking water quality in 1984 in the first edition (Ahmed, 2003a), where the water quality standard for As was set as 50µg/L, which was reduced to 10µg/L in 1993. The Government of Bangladesh adopted the value of 50µg/L in its Environmental Quality Standards (Ahmed, 2003a) in 1991.

As-contaminated groundwater is also used for irrigation. Therefore, a permissible limit for irrigation water should be established. The Food and Agriculture Organization showed that if As-contaminated water is used for agricultural purposes, As may enter in to the food chain (Meharg and Rahman, 2003; Dittmar *et al.*, 2007; Roberts *et al.*, 2007), and set the permissible limit of As, as 0.1 mg/L, 20 mg/kg and 1 mg/kg for irrigation water, soil and food, respectively.

1.9 Diagnosis and treatment of arsenicosis patients

No effective treatment is known for treating As poisoning, but drinking As-free water can help affected people get rid of or alleviate the symptoms of As poisoning. Hence, provision of As-free water is urgently needed to mitigate As poisoning and health damage caused by drinking As-contaminated water. The intake of high proteins and a vitamin-rich diet help affected people in the alleviation of arsenicosis diseases and protects them against the toxic effects of As. The antioxidant vitamins A, E and C also play an important role in the detoxification of As. The cancer and Bowens organs of the body caused by drinking As-contaminated water can be removed through surgical operation. Finally, the use of As-safe water for drinking and cooking purposes and an intake of high proteins and vitamin-rich diet most effectively help affected people to recover from arsenicosis diseases.

1.10 Screening of tube wells water for arsenic concentration and mitigation activities in Bangladesh

The As concentration of tube well water was screened in 270 out of the total 460 Upazilas (meaning sub-districts) by the Government of Bangladesh with the help of some donor agencies and NGOs. If the As concentration exceeded 50 µg/L, which is the Bangladeshi drinking water standard for As, the mouth of the tube well was painted red, while it was painted green when the As concentration was below the standard. At the same time as the screening of the tube well water, an awareness raising program was implemented to educate the village people about As poisoning from drinking water and it’s toxicity. However, many village people are still not aware of the groundwater As pollution and are still using the contaminated water.

The groundwater from non-As-contaminated wells, deep tube wells and dug wells, water from water treatment plants and rain water can be potential water supply sources to mitigate the As problem in Bangladesh. On the other hand, there are several As removal methods available for both household and community-based plants, which can also play a vital role in the supply of safe drinking water to many As-contaminated areas in

Bangladesh. These alternative safe water devices play an important role in mitigating the As problem in many victim areas in Bangladesh, a photo of some alternative devices is shown in Figure 1.4.

Figure 1.4 Photograph of alternative safe water devices: (A) Household As removal filter, (B) Dug well sand filter, (C) Rain water harvester, and (D) Pond sand filter

1.11 Annual consumption of chemical fertilizers in Bangladesh

Fertilizer provides the most important nutrient elements to soils and plays the most vital role in crop production in the 8.29 million hectares of lands used for agricultural purposes in Bangladesh. The annual consumption of chemical fertilizers for crop production has remarkably increased over the last 40 years, as shown in Fig. 1.5.

Rice is the staple food of the 151.1 million people in Bangladesh, and a large quantity of chemical N fertilizer (mainly urea) is used by farmers for rice cropping. The groundwater As contamination in Bangladesh is considered to have started at the time when the application of chemical fertilizers was initiated.

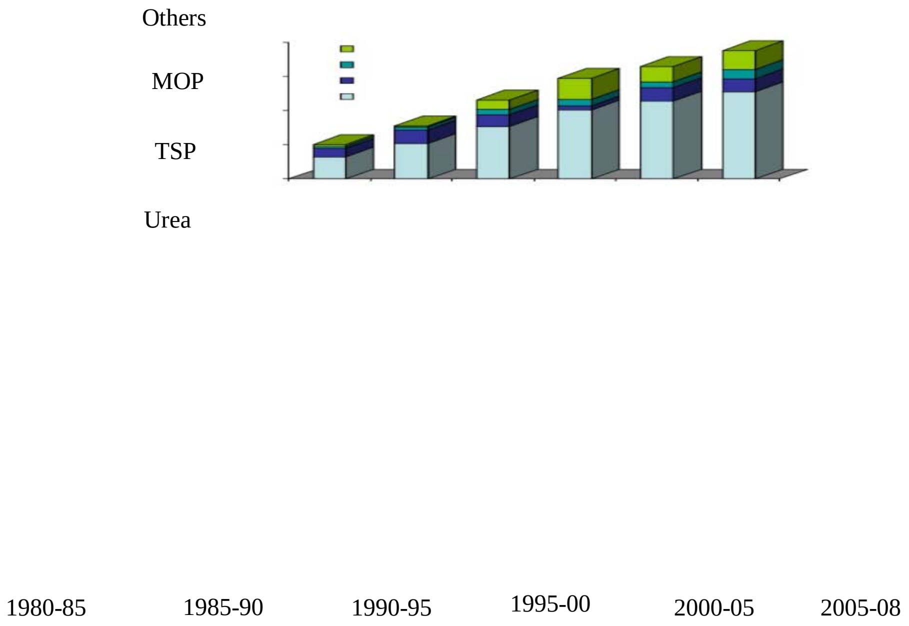

Fig. 1.5 Consumption of fertilizers with years in Bangladesh

1.12 Method of arsenic analysis

There are a number of instruments for the analysis of As in water. Commonly used instruments are spectrophotometers, atomic absorption spectrophotometers (AAS) and inductively coupled plasma mass spectrophotometers (ICP-MS). These instruments can measure As concentration down to a very low level. Field methods on site are also available, but give only a rough concentration of As. In Bangladesh, all the tube well water samples have been screened for As measurement by the field test kit, which is good to measure As concentration above 0.05 mg/L. However, the accuracy of the value measured by the field test kit is not good for scientific research, and the use of AAS or ICP-MS is preferable.

Pretreatment is necessary to determine As concentration for waste water, soils, sediments, crops, vegetables and biological samples. Several procedures are available for pretreatment, such as (1) decomposition with nitric acid and hydrochloric acid, (2) decomposition with nitric acid and perchloric acid, (3) decomposition with nitric acid and sulfuric acid (Japanese Standards Association, 2002), and (4) decomposition with nitric acid and hydrogen peroxide solution, USEPA 3050B method (USEPA, 1996).

1.13 Objective of the study

The As, observed in groundwater in the Bengal Delta, is of geological origin, but the level of As concentration differs from village to village in the delta, to which some factors of the mechanism of As release are thought to be concerned. In previous studies on mechanism of As release, the chemical properties of peat sediments, high ammonium-N in groundwater, application of huge amounts of chemical N fertilizer have not recently included.

Therefore, the specific objective of this research was to clarify the As releasing mechanism from sediments, in particular from peat sediments, into groundwater. Here, As concentration, oxidation-reduction-potential (ORP), inorganic-N (ammonium-N, nitrate-N, nitrite-N) and δ^{15}N of groundwater, As concentration, %C, %N, δ^{15}N and δ^{13}C of sediments, and δ^{15}N of the chemical N fertilizers were targeted. The following points were focused on:

(1) How the sediments structure is organized and how the %C is correlated with the concentration of As and %N in the sediments in the As-contaminated area.

(2) What the effects of C and N in sediments on the release of As from sediments, particularly peat sediment, into groundwater are, and what the source of C and N in the peat sediment is.

(3) What the effects of groundwater ORP, ammonium-N concentration and As, C, N contained in peat sediment on the groundwater As contamination are, and what the source of ammonium-N in the groundwater in the As-contaminated area is.

(4) Finally, the above parameters were compared with those of a non-As-contaminated village where peat sediment was not observed in the sediments.

CHAPTER 2

Materials and Methods

2.1 Study area

The present study was conducted in the rural villages of Samta and Dhannokola in Sharsha Upazila, Jessore District in southwestern Bangladesh. The location of these villages is shown in Fig. 2.1. Samta Village is an As-contaminated village, i.e., groundwater of 86% of tube wells was contaminated by As in concentrations of greater than 0.05 mg/L, and 153 arsenicosis patients were identified up to 2003 (JICA/AAN, 2004). Dhannokola Village is a non-As-contaminated village, where the As concentration of groundwater of all tube wells was less than the Bangladeshi drinking water standard and no arsenicosis patients were identified (JICA/AAN, 2004). The study area was located on the High Ganges River Floodplain in the agro-ecological regions of Bangladesh (UNDP/FAO, 1988). The soil distributed in the area is Calcareous Dark Grey or Brown Floodplain Soil with low fertility (Bangladesh Bureau of Statistics, 2004a). According to the meteorological data recorded at Jessore City from 1999 to 2007, the mean annual rainfall was 1,864 mm, mean annual maximum and minimum temperatures were 37°C and 10°C, respectively, and the mean annual relative humidity was 79% (Bangladesh Bureau of Statistics, 2003, 2004b, 2005, 2007, 2008, 2010). Groundwater is used for the purposes of domestic consumption and irrigation. In the area, large quantities of chemical N fertilizer have been used for crop and vegetable production. The main cropping patterns are rice-rice double cropping and sugarcane monoculture. Although the amount of fertilizers applied was not available for the study area, the national average rate of chemical N fertilizer application is 72 kg/ha for rice and 85 kg/ha for sugarcane for a single cropping (FAO, 2007).

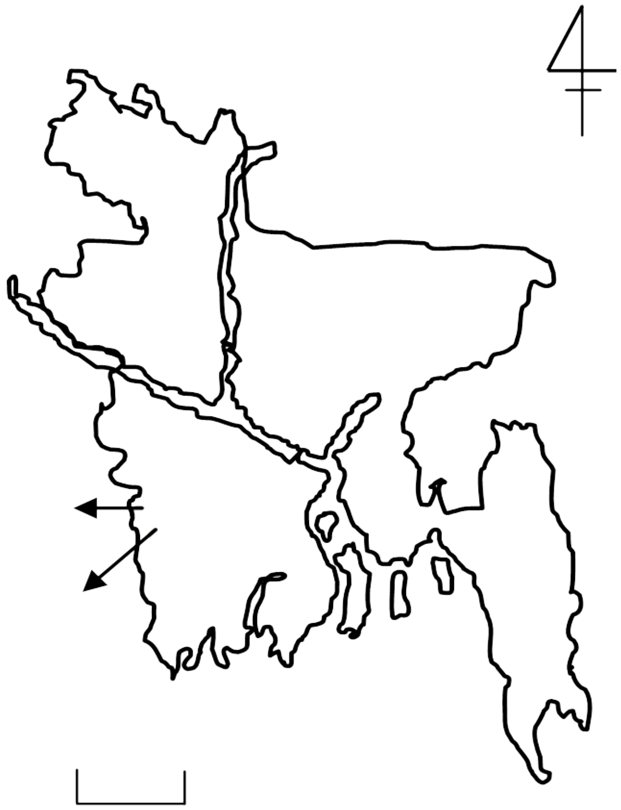

Fig. 1. Map of the study area.

Figure 2.1 Location of the study area

2.2 Samples of groundwater, sediments and chemical N fertilizer

Groundwater was sampled from shallow tube wells. In Samta Village, 30 water samples were collected, six at each of the five sites, and in Dhannokola Village, water was sampled from 12 tube wells, six at each of the two sites. A total 42 of sampling points are shown in Table 2.1. The ORP and concentrations of different forms of inorganic N of groundwater were measured immediately after sampling at each point. Each sample was preserved in a high density polyethylene bottle and acidified by addition of a nitric acid solution at the sampling point for the subsequent As analysis. Information on the depth of the tube wells from the ground surface was gathered through interviews with local people, and the depth of the groundwater table was measured with a surveying tape.

Next, two liters of groundwater samples were filtered using a 0.45-µm paper filter to remove suspended particles after back being brought to the AAN laboratory at Jessore City and preserved in a high density polyethylene bottle for measurement of the δ^{15}N value of the groundwater. The sampling was done at 5 selected points (well no. 2, 6, 16, 18 and 36 from Table 2.1), i.e. 4 from Samta and 1 from Dhannokola Villages, which showed high ammonium-N or nitrate-N concentrations of the groundwater.

Sediments were sampled using both hand and pressure boring methods (Fig. 2.2) from the ground surface to a depth of 60 m at intervals of 0.6 m. Here, each sample was taken from the sediments of 1-3 cm in thickness, and a total of 100 samples were collected from each site. Sediment samples were taken at five sites in Samta Village of S1-S5 sites and two sites in Dhannokola Village of S6 and S7 sites as shown in Table 2.1, and preserved in a zip-locked polyethylene bag. The chemical N fertilizer (Urea) used in the study area was sampled from fertilizer shops at a Jamtala Bazaar very close to Samta Village.

The groundwater sampling was done in February-March 2009, March 2010 and December 2010, and the sediments and fertilizer samplings were done in February-March 2009. The samples were brought to Japan for the analyses of As concentration and $\delta^{15}N$ for the groundwater, and chemical N fertilizers, and concentrations of As, N and C, and $\delta^{15}N$, and $\delta^{13}C$ for the sediments, respectively.

Each sampling point in the Samta and Dhannokola Villages is shown in Table 2.1

Table 2.1 Latitude and longitude location of each point

Village	Site	Well No.	Caretaker Name	Depth of Wells (M)	Location of wells (°)	
					GPS (L)	GPS (N)
Samta	S1 (Bazer para)	1	Unus Ali	34	88.98756	22.99208
		2	Montaz	34	88.98725	22.99211
		3	Umor Ali	40	88.98764	22.99236
		4	Kuddus House	37	88.98758	22.99153
		5	Anwer House	23	88.98781	22.99214
		6	Observation well (S1)	17	88.94814	22.99194
	S2 (South para)	7	Abdul Mozid	37	88.98675	22.99656
		8	Abdus Samad	40	88.98744	22.99614
		9	Joynal Abedin	30	88.98644	22.99603
		10	Abdus Salam	32	88.98675	22.99575
		11	Farab	40	88.98681	22.99597
		12	Observation well (S2)	12	88.98694	22.99594
	S3 (West para)	13	Kudrul	27	88.98058	22.99417
		14	DW-Obs.well	46	88.98061	22.99408
		15	Jalal Molla	21	88.98017	22.99386
		16	Awal Hossain	27	88.98058	22.99339
		17	Ser Ali	18	88.98092	22.99464
		18	Observation well (S3)	15	88.98069	22.99403
	S4 (Patient Para)	19	Robiul	34	88.98417	22.99350
		20	Idris Ali	34	88.98425	22.99378
		21	Laltu Gazi	40	88.98392	22.99344
		22	Domser Ali	34	88.98444	22.99308
		23	Kamrul	23	88.98364	22.99389
		24	Observation well (S4)	13	88.98406	22.99361
	S5 (Pal para)	25	Mosque	35	88.98972	22.98956
		26	Abul Kasem	35	88.99006	22.98950
		27	Ismail Gazi	40	88.98953	22.98889
		28	Mundir	27	88.99031	22.99031
		29	Anser Ali	37	88.98903	22.99081
		30	Observation well (S5)	14	88.98953	22.98997
Dhannokola	S6 (South para)	31	Owler Rahman	23	88.89322	23.08839
		32	A. Khalek	27	88.89328	23.08814
		33	A. Hamid	41	88.89306	23.08814
		34	M. Motiar Rahman	23	88.89347	23.08825
		35	A. Kader	38	88.89347	23.08872
		36	Observation well (S6)	12	88.89322	23.08839
	S7 (Council para)	37	Jahangir	30	88.89358	23.09258
		38	Sohidul-A	37	88.89369	23.09258
		39	Sohidul-B	76	88.89367	23.09244
		40	Kobirul	27	88.89389	23.09331
		41	Romjan	18	88.89347	23.09322
		42	Observation well (S7)	12	88.89364	23.09261

Figure 2.2 Photograph of the sampling: (A) Sediment collection using pressure boring, (B) Sediments in a collection tube, (C) Sediment collection using local boring method, (D) Collected sediments in a rack, and (E) Groundwater sampling from wells

2.3 Measurements of ORP, and concentrations of inorganic-N and As for the groundwater samples

The ORP of groundwater was measured immediately after sampling using a portable ORP meter (Horiba D53, Horiba Co. Ltd). The measured ORP value was then converted to a value corresponding to the standard hydrogen electrode. Concentrations of ammonium-N (NH_4-N), nitrate-N (NO_3-N) and nitrite-N (NO_2-N) of the groundwater were measured immediately after sampling using a field kit (Aqua tester, KRK). The As concentration of groundwater was determined by the inductively coupled plasma mass spectroscope (ICP-MS) (Agilent 7500, Agilent Technologies) at Kyushu University after being brought to Japan. A photo of the field water quality testing and laboratory As test by ICP-MS is shown in Fig. 2.3.

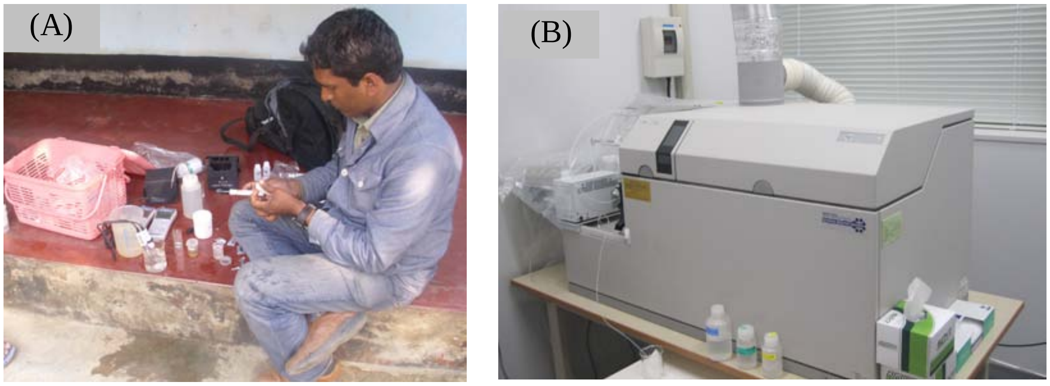

Figure 2.3 Photograph of the water quality testing (A) Field water quality test and (B) As test by ICP-MS in the laboratory

2.4 Classification of the sediments

After collecting sediment samples from the sites in Samta (S1-S5) and Dhanokola (S6-S7) Villages, the samples were classified as peat, peaty clay, clay, silty clay and sand in a wet condition, according to the soil textural classification system given by Roy *et al*. (2005). Sediments were air-dried at room temperature for 3 to 4 days at Kyushu University and then ground to a powder by using a porcelain mortar pestle. The pretreatment for As analysis for the sediments was done from the powdered sediments. A photo of the air-dried sediments samples is shown in Fig. 2.4.

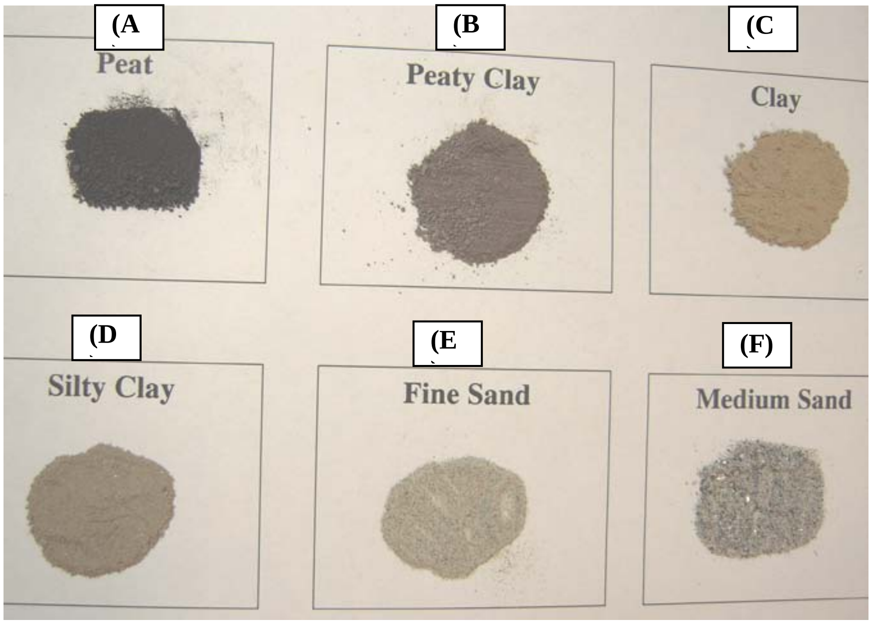

Figure 2.4 Photograph of the classified sediments: (A) Peat, (B) Peaty clay, (C) Clay, (D) Silty clay, (E) Fine sand, and (F) Medium sand

The soil textural classification chart of the sediments is shown in Table 2.2, and the clay sediments are divided into the 3 groups of peat, peaty clay and clay, depending on the color, touch and smell. The peat sediment was a tropical peat and which belongs to the low moor peat according to Andriesse (1988).

Table 2.2 Soil textural classification chart of the sediments

Soil Textural Classification	Grain Size (diameter in mm)
Clay	<0.004
Silty clay	<0.004 - 0.063
Silt	0.004 - 0.063
Very fine sand	0.063 - 0.125
Fine sand	0.125 - 0.250
Medium sand	0.25 - 0.50
Coarse sand	0.5 - 1.0
Very coarse sand	1.0 - 2.0

2.5 Pretreatment of the sediments for As analysis

The air-dried sediment samples were mixed homogeneously, and 0.5 - 1.0 g of the sample (dry-weight basis) was taken into a digestion vessel. After that, 10 mL of a 1:1 nitric acid (HNO_3) solution was added and the vessel was covered with a watch glass. The mixture was heated at 95°C on a hot plate and refluxed for 30 minutes without boiling. Then, 5 mL of concentrated HNO_3 was put into the mixture and the mixture was refluxed for 30 minutes. This reflux process was repeated until no brown fumes appeared from the mixture. After that, the mixture was cooled, and 2 mL of water and 3 mL of 30% hydrogen peroxide (H_2O_2) were added. The mixture was heated at 95°C on a hot plate for peroxide reaction until effervescence subsided and then was cooled. The peroxide reaction was continued by adding 1 mL of 30% H_2O_2 until the mixture appeared to be unchanged. Finally, the mixture was covered with a watch glass and heating was continued until the volume was reduced to approximately 5 mL. After cooling, the mixture was diluted to 100 mL by adding pure water and was filtered through Whatman no. 41 filter paper. This method of digestion is the USEPA 3050B method (USEPA, 1996), and the filtered mixture was provided for the determination of As by ICP-MS.

2.6 Measurement of %N, %C, δ^{15}N and δ^{13}C values of the sediments and δ^{15}N values of groundwater and chemical N fertilizer

Sediment samples were pre-frozen in a deep freezer for a minimum of 10 minutes and then freeze-dried overnight by using an Eyela freeze dryer (Tokyo-Rika, FDU 506). The samples were powdered with a porcelain mortar and pestle. Exactly 0.80 mg (duplicate measurements for each sample) was weighed in a tin capsule, and %N, %C, and $\delta^{15}N$ and $\delta^{13}C$ values of the sediments were measured using continuous-flow stable isotope ratio mass-spectrometry by an ANCA mass-spectrophotometer (SL/20-20, SerCon) at Kyushu University. Glycine and citric acid were used as running standards. Measurement errors were within 0.3% for $\delta^{15}N$ and within 0.1% for $\delta^{13}C$. If the difference of the duplicate values was larger than the measurement error, the measurement was repeated. With reference to the $\delta^{15}N$ and $\delta^{13}C$ values, the sources of N and C in the peat sediments were identified. The $\delta^{15}N$ value of the chemical N fertilizer was measured the same way as for the sediments. The $\delta^{15}N$ analysis of groundwater to identify the source of inorganic-N (ammonium-N plus nitrate-N plus nitrite-N) in the water was done at Shoko Co. Ltd., Japan. A photo of the ANCA mass-spectrophotometer is shown in Fig. 2.5.

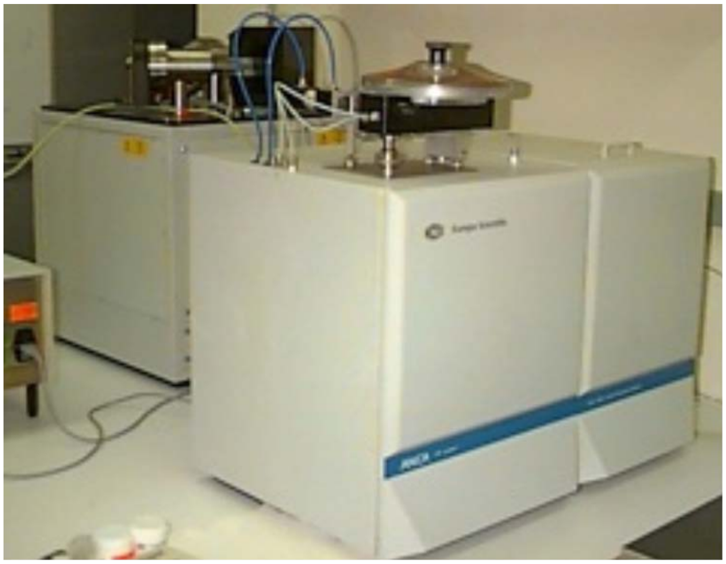

Figure 2.5 Photograph of the ANCA mass-spectrometer (SL/20-20, SerCon) in the laboratory

2.7 Chemicals and reagents

All the chemicals and reagents used in this study were of analytical grade. MilliQ water was used in all steps. Stock solution of As with a concentration of 100 mg/L (Wako Pure Chemical Industries Ltd., Japan) was used in the preparation of the standard solution for ICP-MS analysis. The chemicals used for the digestion of sediment samples were concentrated nitric acid (HNO_3 69%) and high purity hydrogen peroxide (H_2O_2 30%) manufactured by Wako Pure Chemical Industries Ltd., Japan.

CHAPTER 3

Comparison of Arsenic Status between Arsenic Contaminated and Non-Contaminated Villages

3.1 Introduction

The occurrence of groundwater As contamination has been identified in many areas of Bangladesh, and most of the rural people face serious environmental health hazards of As poisoning. According to UNICEF (2010), 12.6% of drinking water samples collected from nearly 13,000 households around the country did not meet the Bangladesh drinking water standard of As (≤0.05 mg/L). This is equivalent to approximately 20 million people being exposed to excessive quantities of As. The As poisoning problem is becoming more severe with time, but details of the As releasing mechanism have not yet been clarified. A possible mechanism of As contamination in water for streams in mountain areas is the weathering of As-rich minerals (McArthur *et al.*, 2001). Harvey *et al*. (2002) and Islam *et al.* (2004) suggested that the penetration of labile dissolved organic carbon compounds into the shallow aquifers by pumping for irrigation enhances the significant reduction of As-rich iron oxyhydroxides, thereby resulting in increased As concentration in groundwater.

Geochemical studies have suggested that the reducing condition of the subsurface aquifers and the reductive dissolution of As-rich iron oxyhydroxides through microbial oxidation of organic matter could be the dominant factor controlling As mobilization in groundwater (Anawar *et al.*, 2003; Nickson *et al.*, 2000). The microbial oxidation of organic matter coupled with the reduction of iron (III) to iron (II) appears to be an important process in the mobilization of As in a variety of subsurface environments. Iron-reducing bacteria may play a significant role in mobilizing As from As-rich iron oxyhydroxides and iron-arsenate minerals by direct reduction of iron (III) in sediments. It has been also observed that a great deal of chemical fertilizer is used for cultivating crops and vegetables in Bangladesh. Chemical N fertilizer application is considered a possible cause of As pollution in groundwater. According to Uddin and Kurosawa (2011), the groundwater, collected from the same area as the present study, showed to be in the reducing condition accompanied with high concentrations of As and ammonium-N, where the source of ammonium-N could be chemical N fertilizer.

Sharsha Upazila of southwestern Bangladesh, which is included in the present study area, is one of the most seriously As contaminated areas in Bangladesh (Rahman *et al.*, 2006). There were 312 arsenicosis patients identified in 2003 in Sharsha Upazila, and the number of patients increased to 478 in 2008 (JICA/AAN, 2004; LGD/JICA, 2008), indicating a severe environmental health hazard problem in the area.

The sediment samples collected from the As-contaminated and non-contaminated areas were measured for As concentration, %C (organic matter) and %N. These values are supposed to play an important role in the release of As from peat sediments into groundwater. The stable isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) were measured to identify the origin of the C and N in the peat sediment. The specific objectives of this chapter are to clarify: (1) difference of As status of sediments between As-contaminated and non-contaminated villages, (2) the relationship of As-C-N in sediments, (3) the source of C and N and the chemical bond of As-C-N in peat sediment that has the highest As concentration among the sediments, and (4) the role of C and N in the release of As from peat sediment, respectively.

3.2 Results

3.2.1 Geological features of sediments

Figure 3.1 shows the geological profiles of the sediments from the ground surface to a 60 m depth at sites S1 through S5 in As-contaminated Samta Village. From Fig. 3.1, silty clay, clay, peaty clay and peat layers were mainly located within a 12 m depth from the ground surface at each site, and a sandy layer was located below this depth. A peat layer, with a thickness of 0.6-1.8 m, was located in the 6-9 m depth from the ground surface at sites S1, S3, S4 and S5, however at site S2 the peat layer was not observed until a depth of 60 m. At depths of deeper than 13 m, the sandy layer was more than 15 m thick at most sites, whereas the peat and peaty clay layers were less than 2 m thick. The peat or peaty clay layers were also located at a 36 m to 48 m depth at sites S1, S2, S3 and S5, but were not observed at site S4 at these depths.

The geological profile of non-As-contaminated Dhannokola Village is shown in Fig.3.2. Here, the sites are S6 and S7. In both S6 and S7, peat layer was not observed at any depth. Peaty clay layer was not observed either, but clay and silty clay layers were observed within a 6 m depth from the ground surface at sites S6 and S7. Thick sandy layer was observed below a 6 m depth, and a thin peaty clay layer was observed at the relatively deeper zone of 51 m and 28 m from the ground surface at sites S6 and S7, respectively.

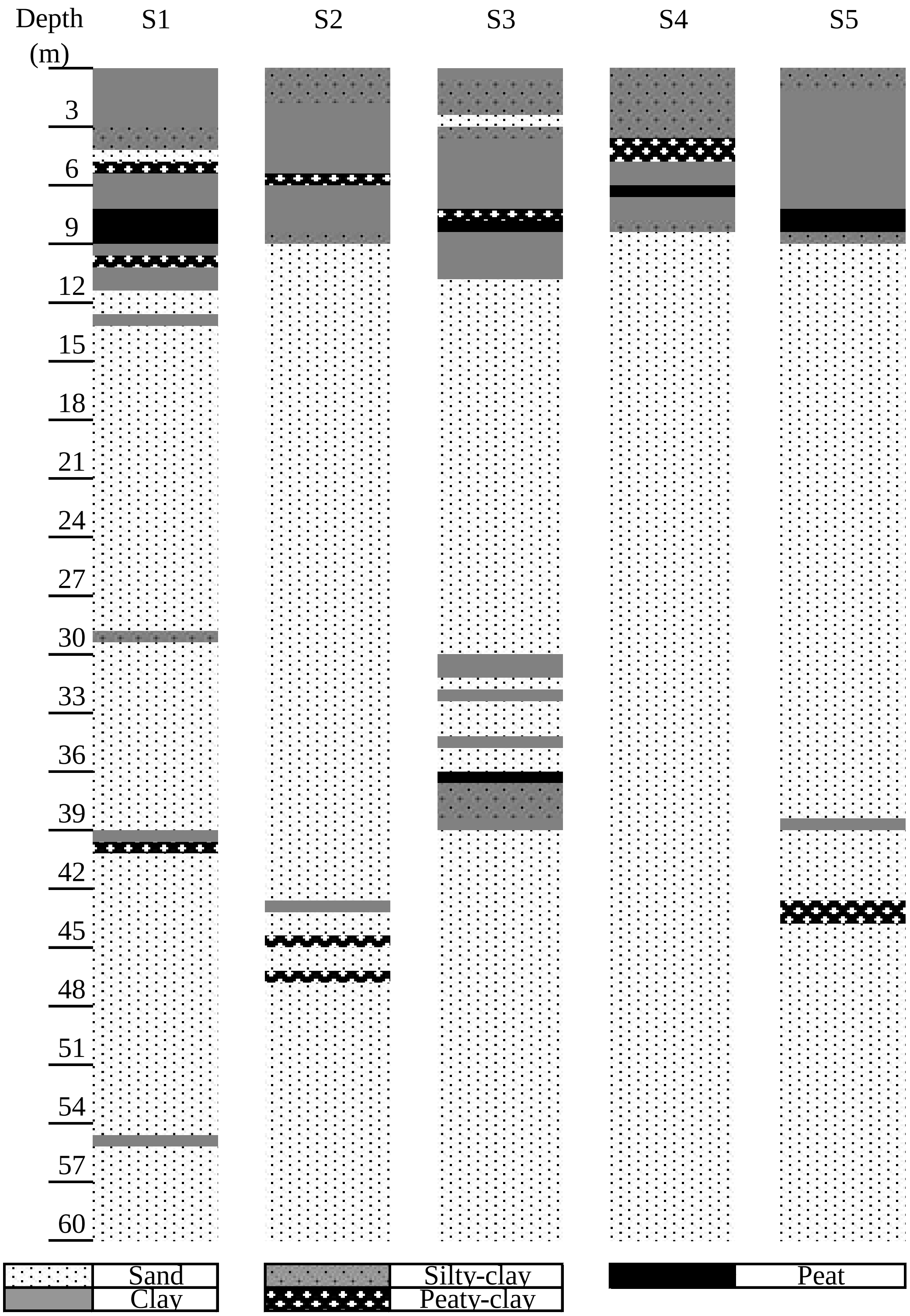

Figure 3.1 Geological profiles of the sediments in the As-contaminated village

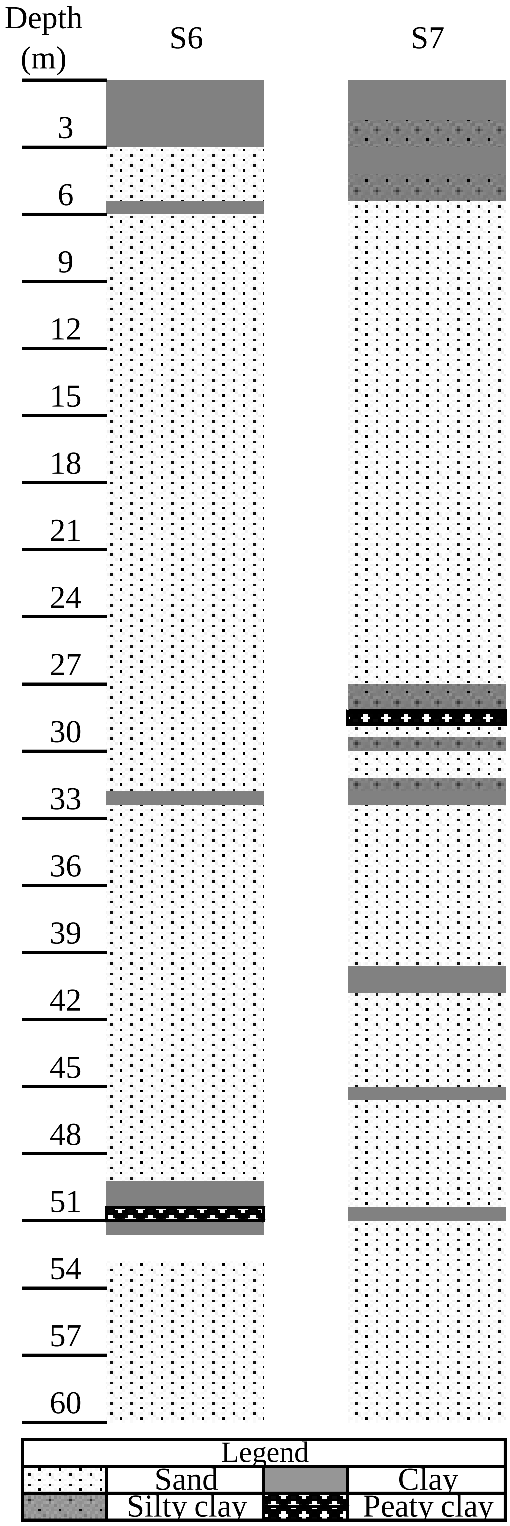

Figure 3.2 Geological profiles of the sediments in the non-As-contaminated village

3.2.2 Arsenic status of sediments and relevant parameters

Figure 3.3 shows the As concentration of sediments at site S1 by depth. The As concentration varied with sediment and ranged from 34.9 mg/kg to 75.3 mg/kg for peat, 16.5 mg/kg to 19.8 mg/kg for peaty clay, 5.9 mg/kg to 15.6 mg/kg for clay, 1.7 mg/kg to 3.2 mg/kg for silty clay and 0.7 mg/kg to 2.8 mg/kg for sand. The As concentration of the peat sediment was higher by more than 3 times compared to that of the peaty clay sediment, which had the second highest As concentration among the sediments.

Although the sediments were collected from the five sites of S1-S5 in Samta Village, the As concentration in the sediments was measured only for the S1 site because the measurement took a long time and the S1 site can represent Samta Village because it is located at the middle of the village.

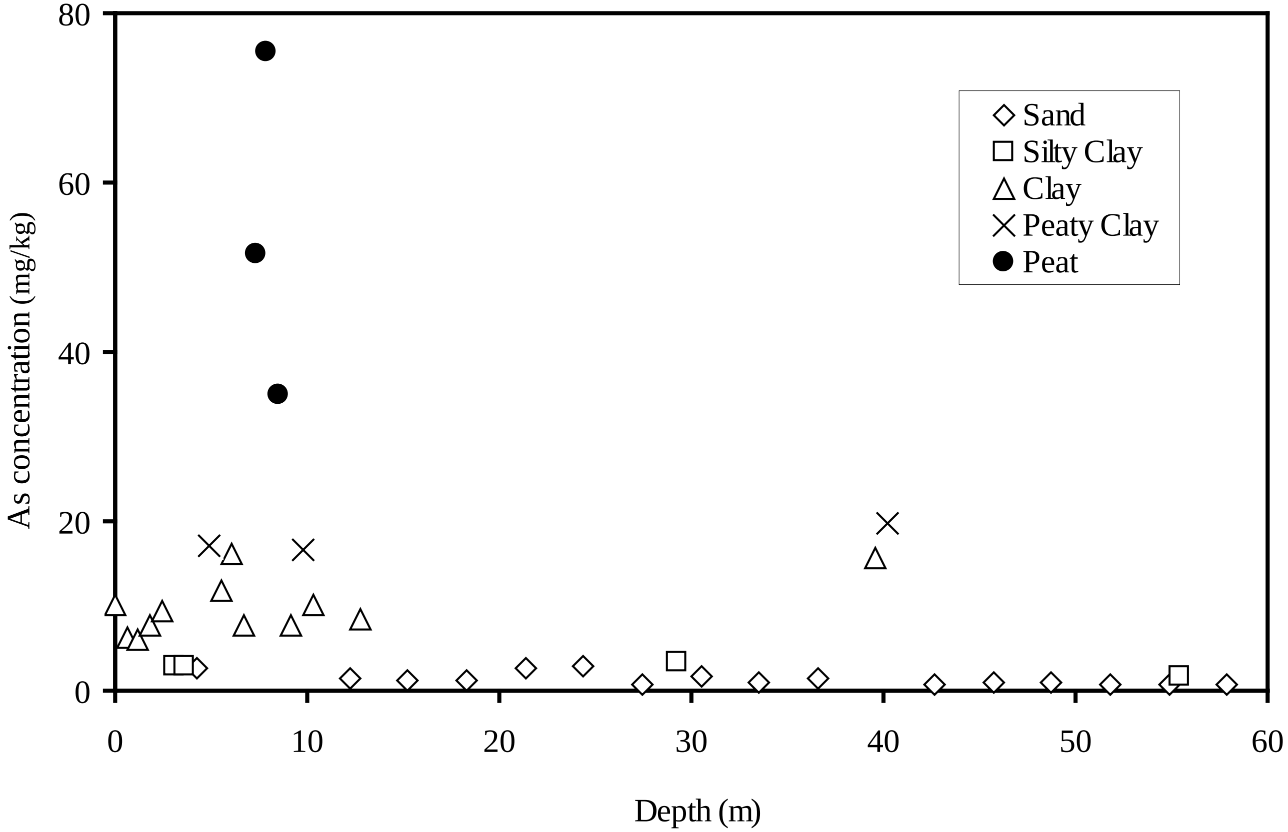

Figure 3.3 The As concentration of each sediment by depth at site S1

In Dhannokola Village, the maximum, minimum and average As concentrations of the sediment at site 6 are shown in Table 3.1. The As concentration of the peaty clay sediment was 6.9 mg/kg, that of clay ranged from 2.8 to 4.8 mg/kg, and that of sand ranged from 0.4 to 2.2 mg/kg; peat and silty clay layers were not observed. The average As concentrations of the sediments were in the order of peaty clay > silty clay > sand, and were nearly half of those corresponding sediments of site S1 in Samta Village (Table 3.3).

Table 3.1 The concentration of As of each sediment at the S6 site of Dhannokola Village

Concen-tration	Param-eters	Peat	Peaty Clay	Clay	Silty Clay	Sand
As (mg/kg)	Min	N.A.	6.9	2.8	N.A.	0.4
	Max	N.A.	6.9	4.8	N.A.	2.2
	Ave	N.A.	6.9	4.1	N.A.	0.6
	n	N.A.	1	7	N.A.	18

When the As concentrations of peaty clay and clay sediments are compared between the As-contaminated and non-contaminated villages, the As concentration of peaty clay and clay sediments were observed to be 2-3 times higher in the contaminated village than the non-contaminated village from Table 3.1 and Table 3.3.

The values of $\delta^{15}N$ and $\delta^{13}C$ of peat sediment and $\delta^{15}N$ of chemical N fertilizer are shown in Table 3.2. According to Table 3.2, $\delta^{15}N$ was 2.81, 0.26 and -1.68‰, and $\delta^{13}C$ was -24.0, -35.3 and -27.1‰ for the peat sediment (sample number P1, P2 and P3) at sites S1, S3 and S4, respectively. The $\delta^{15}N$ value of urea was 1.81‰. Here, the $\delta^{15}N$ value of the peat sediment was in a range from 4 to -4‰, and also close to that of urea.

Table 3.2 The %N, $\delta^{15}N$, %C and $\delta^{13}C$ values of the peat sediment, and %N and $\delta^{15}N$ value of the chemical N fertilizer (Urea)

Sample No.	Site	N (%)	$\delta^{15}N$ (‰)	C (%)	$\delta^{13}C$ (‰)
P1	S1	0.39	2.81	4.81	-24.0
P2	S3	1.30	0.26	17.63	-35.3
P3	S4	0.75	-1.68	14.45	-27.1
Urea		45.20	1.81		

3.2.3 Relationship of arsenic-carbon-nitrogen in sediments

Figure 3.4 shows the relationship between As concentration and %C in the sediments at S1 site representatively. Here, the concentration of As was positively correlated with %C. According to Table 3.3, the peat sediment had the highest As concentration (35-75 mg/kg) and %C (5-15 %), the peaty clay sediment had the second highest concentration of As (17-20 mg/kg) and %C (1.7-2.5 %), and the other sediments had lower concentrations of As (0.7-15.6 mg/kg) and %C (0.5-2.7 %). Figure 3.5 shows the relationship between %N and %C in the sediments, where %N showed an increasing trend with the increased %C, peat sediment had the highest %N (0.30-0.86 %), peaty clay sediment had the second highest %N (0.09-0.17 %), and the other sediments had a lower value of %N (0.01-0.16 %).

Table 3.3 The concentration of As, %N and %C of each sediment at the S1 site of Samta Village

Concen-tration	Param-eters	Peat	Peaty Clay	Clay	Silty Clay	Sand
As (mg/kg)	Min	34.9	16.5	5.9	1.7	0.7
	Max	75.3	19.8	15.6	3.2	2.8
	Ave	53.9	17.8	9.7	2.7	1.3
	n	3	3	12	4	17
N (%)	Min	0.3	0.09	0.02	0.01	0.01
	Max	0.86	0.17	0.16	0.02	0.01
	Ave	0.62	0.12	0.05	0.02	0.01
	n	3	3	12	4	2
C (%)	Min	5.1	1.7	0.5	0.4	0.5
	Max	15.1	2.5	2.7	1.5	0.6
	Ave	10.1	2.1	1.3	0.8	0.6
	n	3	3	12	4	2

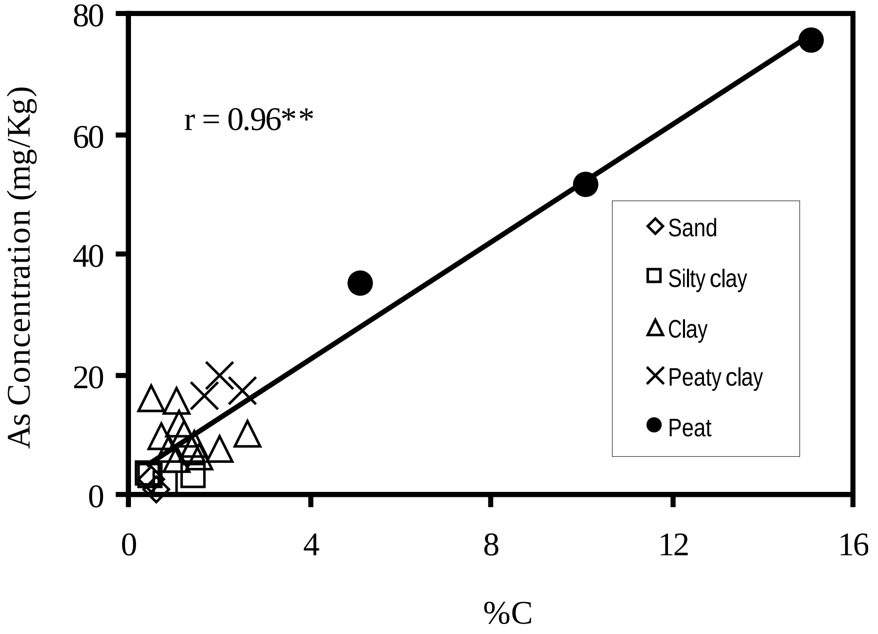

Figure 3.4 Relationship between concentration of As and %C in sediments (**: significant at 1% level)

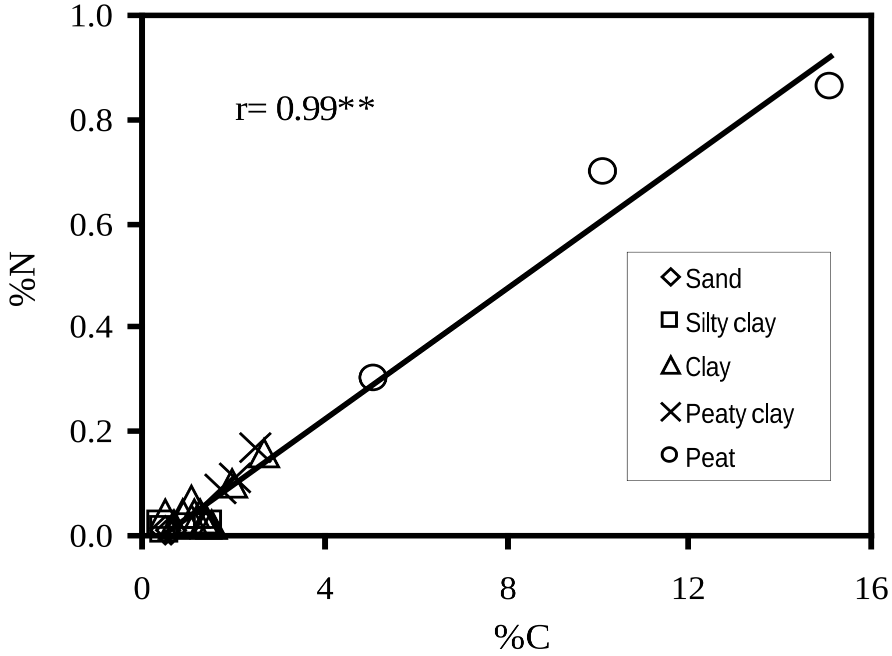

Figure 3.5 Relationship between %N and %C in sediments (**: significant at 1% level)

3.3 Discussion

3.3.1 Source of N and C of the peat sediment and their bonding

According to the grouping of $\delta^{13}C$ on the organic sources of sedimentary material (Anderson *et al.*, 2008), the source of C in peat sediment, whose $\delta^{13}C$ is -19.3 to -24.0 ‰, is aquatic plants. Aquatic plants have a wider range of $\delta^{13}C$, from -10 to -50 ‰, in the grouping.

According to Ulrich (2009), the chemical composition of aquatic plants is woody cellulose ($C_{12}H_{32}O_{14}$) and charcoal (C_7H_4O). Of course, peat sediments possibly include some N with the decay of the plants. Seiler (1996) showed that the $\delta^{15}N$ of the chemical N fertilizer is -4 to +4 ‰, soil organic N is +4 to +9 ‰, and animal and human wastes are more than +10 ‰. According to this criterion, the source of N of peat sediment collected from S1, S3 and S4 sites (Table 3.2) is regarded to be from chemical N fertilizer.

The $\delta^{15}N$ value of the sediments other than the peat sediment was also measured at S1 site representatively, though the detailed data is not shown here. Those $\delta^{15}N$ values were different from those of the peat sediment, indicating that the source of N in the other sediments is different from the chemical N fertilizer.

Peat sediments containing high As is thought to have been created a long time ago in the study area. The maximum concentrations of C, N and As in the peat sediments were 15.1%, 0.86% and 75.3 mg/kg, respectively (Table 3.3). The ratio of C: N: As is 2005:114:1, showing that the N is 114 times larger than As in amount in peat sediments. Thus, when the N, sourced from chemical N fertilizer, reaches the surface of the peat sediment, most the N is adsorbed to C in the peat sediments. Here, N is probably absorbed by the decomposed wooden materials, which originated from woody cellulose and charcoal in aquatic plants, and a comparatively weak chemical bond between N and C is thought to be formed, which will be mentioned later. It is also considered that As is connected with C by a weak chemical bond. These bonds can be disconnected easily, for instance, by microbial activity. When the N entered into the peat sediments, the microbial activity was heightened, and the bond could be disconnected. The bond of C -N-As and the process of As release from peat sediments is shown in Fig. 3.6.

Iron oxyhydroxide has been identified in the sediments by a number of studies as occurring mainly as grain coatings (Nickson, 1997; Imam *et al*, 1997; Madhavan and Subramanian, 2006), and it may be that iron oxyhydroxides can exist together in peat sediments. In this case, the idea of the As release from peat sediments presented in this study could not conflict with the theory previously mentioned on the As release of “the reductive dissolution of iron oxyhydroxides.”

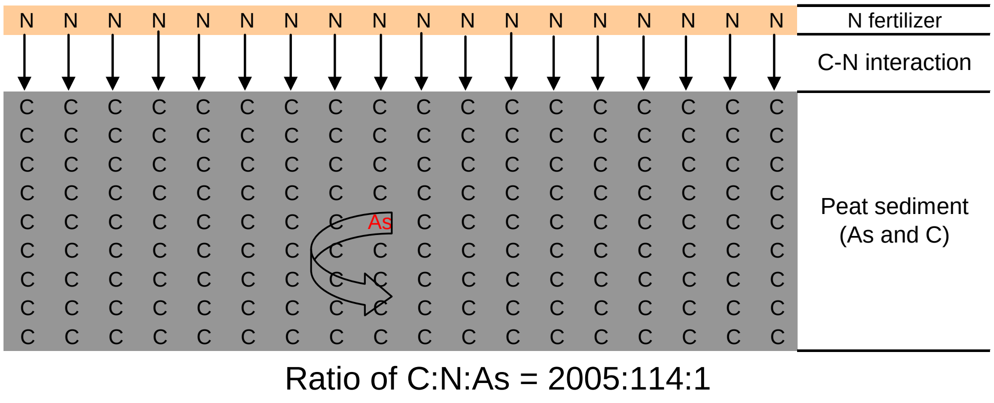

Figure 3.6 Bond between N, C and As molecules in peat sediments, and As release

3.3.2 The existence of C and N in peat sediments and the role of it on the release of As from the sediments

Aquatic plants, which are the source of C in peat sediments, are thought to have grown from a long time ago, but the subsequent plants have decayed and have been buried, resulting in the high concentration of C in the peat sediments. Since the δ^{13}C and δ^{15}N values were measured only for peat sediments, the following discussion is restricted to peat sediment among all the sediments.

The positive relationship observed between As concentration and %C in the peat sediment is perhaps due to the absorption of As by aquatic plants from when the plants had grown there.

N concentration was higher for the peat sediment than for the other sediments (Table 3.3). A great deal of N, sourced from the chemical N fertilizer, is considered to have become present with the development of intensive agriculture in recent decades. The heightened N in peat sediment is thought to have an important role in the occurrence of As in groundwater.

The granular form of activated C binds materials by the van der Waals force (Weli, 2010), because the force physically acts between molecules. By visual observation and handling the peat sediments, the granular particles, which are thought to be decomposed wooden material, were identified. Various substances can be bound by the force, including N compounds. Thus, the %N is positively related to %C. However, the coordination bond between C and N, which is also a weak bond, is also conceivable for the coexistence of C and N.

3.4 Conclusion

In the present chapter, it was clarified that As concentration in the peat sediment was higher than in the other sediments, and a positive relationship between the As concentration, %C and %N was identified in the sediment. Peat sediment with a thickness of 0.6-1.8 meters was located in the 6-9 meters depth from the ground surface in the As-contaminated area. The results of the $\delta^{15}N$ analysis performed on the N in the peat sediment showed that the N was perhaps sourced from the chemical N fertilizer.

The results of the $\delta^{13}C$ analysis for peat sediments showed that C is sourced mostly from aquatic plants. Thus, it is thought that As concentration in peat sediments is heightened by the absorption of As by the plants, and the concentration of C is heightened by the decay and burying of the aquatic plants.

Since the peat sediment had the largest %C and %N among the sediments, influence of the existence of peat sediment on groundwater As contamination would be significant. The positive correlation between %C and %N in peat sediment was perhaps produced by the adsorption of N from the chemical N fertilizer by C through the comparatively weak chemical bond.

However, a peat or peaty layer was not observed in the upper part of the sediments of the non-As-contaminated village, and only a thin peaty layer was observed in the relatively deeper part of the sediments. The As concentration of the sediments in the non-As-contaminated area was low compared to the sediments of the As-contaminated village. Therefore, peat sediment might play a critical role on groundwater As contamination.

CHAPTER 4

Mechanism of Arsenic Release from Peat Sediments into Groundwater

4.1 Introduction

Though groundwater is the primary source of drinking water in Bangladesh, the groundwater is contaminated by As, threatening the health of millions of people. The use of groundwater which contains a high level of the inorganic form of As is the cause of one of the worst environmental disasters in Bangladesh. Arsenic in various forms is also known to be very toxic to many microorganisms (Yamauchi *et al.*, 1994). The type of As depends on the underground geochemical conditions. The stable pentavalent As (V) in the sediments is converted to water-soluble trivalent As (III) in groundwater, primarily through mobilization due to the dissolution in the sediments by virtual quantitative reduction (Azcue and Nrigu, 1994; Korte and Fernando, 1991; Ferguson and Gavis, 1972; Uthe and Reinke, 1975). The dominant redox states of As in the environment are As (III) and As (V). Under slightly oxidized conditions, As (V) is the stable redox species, while under more reducing conditions As (III) is the dominant species (William, 1997). Much research has been conducted to elucidate the mechanism of As release into groundwater, but these researches have not yet established the actual As releasing mechanism into groundwater. It is believed that one-third of the people in Bangladesh have been exposed to As-contaminated water in their daily life, and thus the diseases related to As-contaminated drinking water has been reported in Bangladesh (NAMIC, 2005).

In Bangladesh, groundwater is used not only for domestic purposes, but also for irrigation purposes because only limited rainfall occurs during the dry season. For irrigation purposes, several thousands of shallow irrigation wells have been installed in the agricultural land. In addition, several million metric tons of chemical fertilizers are applied to the agricultural land to cultivate the crops and vegetables.

The use of chemical fertilizers in agriculture started in the year 1975. At that time, N fertilizer was much larger than the other fertilizers in application amount. Since then, fertilizer application has increased with years and the amount of application reached 4.0 million metric tons in 2008-09 (Fig. 1.5), among which 2.8 million metric tons were chemical N fertilizer. However, when chemical N fertilizer is percolates downward, it could act on the peat sediments those contain high As to release As, as was described Chapter 3. Thus, it is very important to know the concentration of inorganic-N in the groundwater and its sources.

In this chapter, the groundwater samples collected from Samta and Dhanokola Villages, i.e., As-contaminated and non-contaminated villages, respectively, are used to clarify the followings: (1) the difference in groundwater quality between the As-contaminated and non-contaminated villages, (2) the relationships between concentrations of As, ammonium-N and ORP in the groundwater, (3) the source of inorganic-N in the groundwater, and (4) the location of the peat layer, groundwater table and depth of the wells. For (2), (3), and (4), only the As-contaminated village was targeted.

From these points, the mechanism of As release from peat sediments into groundwater is discussed and determined.

4.2 Results

4.2.1 Groundwater quality

Table 4.1 shows the sampling depth, ORP and the concentrations of As, ammonium-N, nitrate-N and nitrite-N for the groundwater of wells at each point of Samta Village. Six wells were targeted at each site. According to Kazakovskaya (2006) and USEPA (1998), if the ORP is below 100 mV, 100-200 mV, and above 200 mV, the groundwater is in the reducing, non-reducing and oxidizing conditions, respectively. Under this criterion, the groundwater of the wells was in the reducing condition, except for wells no. 6, 18, 24 and 30 among the 30 total samples. The As concentration of groundwater ranged from 0.073 mg/L to 1.480 mg/L for all the wells, which exceeds the Bangladeshi drinking water standard of 0.05 mg/L. The ammonium-N concentration was high, more than 1.0 mg/L, but concentrations of nitrate-N and nitrite-N were low, less than 0.05 mg/L for all the wells.

Table 4.1 The depth of the sampled groundwater, and ORP and concentrations of As, ammonium-N, nitrate-N and nitrite-N for each groundwater sample at the S1-S5 sites of Samta Village

Site	Well No.	Depth of the sampled water (m)	ORP (mV)	As (mg/L)	Ammonium-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)
S1	1	34	77	0.432	4.0	0.01	0.01
	2	34	76	0.507	3.0	0.01	0.01
	3	40	81	0.240	3.0	0.01	0.01
	4	37	95	0.195	3.0	0.01	0.00
	5	23	75	0.200	3.0	0.01	0.01
	6	17	116	0.223	4.0	0.01	0.02
S2	7	37	94	0.124	1.5	0.01	0.01
	8	40	97	0.130	1.5	0.01	0.01
	9	30	87	0.105	1.5	0.01	0.01
	10	32	70	0.189	2.0	0.01	0.01
	11	40	73	0.073	1.5	0.01	0.02
	12	12	95	0.569	3.0	0.01	0.02
S3	13	27	79	0.129	2.0	0.01	0.02
	14	46	70	0.296	3.0	0.01	0.02
	15	21	88	0.410	3.0	0.01	0.02
	16	27	78	0.906	4.0	0.01	0.01
	17	18	92	0.166	3.0	0.01	0.02
	18	15	153	0.187	2.0	0.01	0.02
S4	19	34	83	0.827	4.0	0.01	0.01
	20	34	86	0.853	4.0	0.01	0.01
	21	40	88	0.827	4.0	0.01	0.01
	22	34	85	0.561	4.0	0.01	0.01
	23	23	83	1.480	4.0	0.05	0.01
	24	13	192	0.077	1.2	0.02	0.00
S5	25	35	38	0.136	2.0	0.01	0.01
	26	35	84	0.352	2.0	0.01	0.01
	27	40	88	0.157	2.0	0.01	0.01
	28	27	94	0.133	2.0	0.01	0.02
	29	37	93	0.164	2.0	0.01	0.01
	30	14	155	0.104	5.0	0.02	0.01

Table 4.2 shows the sampling depth, ORP and concentrations of As, ammonium-N, nitrate-N and nitrite-N for the groundwater of the wells in Dhannokola Village. The minimum, maximum and average sampling depths of water were 12, 76 and 30 m, respectively. The ORP ranged from 94 to 300 mV. Here, the groundwater in the village was mostly in the non-reducing condition, and only two points (well no. 31 and 32) were in the oxidizing condition.

The As concentration ranged from 0.007 mg/L to 0.013 mg/L, which is collectively less than the drinking water standard of Bangladesh. The ammonium-N concentration was overall low, less than 1 mg/L, while the concentrations of nitrate-N and nitrite-N varied widely from 0.0 to 8.80 mg/L and from 0.0 to 0.46 mg/L, respectively. Here, the nitrate-N and nitrite-N concentrations were high at 3 points (well no. 31, 32 and 36) compared to those of the other wells, i.e., 8.8, 2.2, 5.0 mg/L for nitrate-N concentration and 0.34, 0.46, 0.18 mg/L for nitrite-N concentration, respectively. At these 3 points, the ORP was very high, 197-300 (mV), showing that the groundwater was mostly in the oxidizing condition. In this condition, N is thought to exist as a form of nitrate-N and/or nitrite-N in the groundwater.

Table 4.2 The depth of the sampled water, ORP and concentrations of As, ammonium-N, nitrate-N and nitrite-N of each groundwater samples at the S6-S7 sites of Dhannokola Village

Site	Well No.	Depth of the sampled water (m)	ORP (mV)	As (mg/L)	Ammonium-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)
S6	31	23	300	0.007	0.2	8.8	0.34
	32	27	261	0.007	0.2	2.2	0.46
	33	41	108	0.017	0.2	0.0	0.01
	34	23	128	0.007	0.2	0.0	0.01
	35	38	119	0.012	0.2	0.0	0.01
	36	12	197	0.007	0.6	5.0	0.18
S7	37	30	117	0.012	0.2	0.01	0.02
	38	37	110	0.011	0.2	0.01	0.01
	39	76	95	0.012	0.2	0.01	0.01
	40	27	94	0.011	0.2	0.01	0.02
	41	18	94	0.012	0.2	0.01	0.02
	42	12	137	0.013	0.8	0.01	0.00
Average		30	147	0.011	0.3	1.3	0.09

4.2.2 Relationships between concentrations of As and ammonium-N, and ORP for the groundwater

Figures 4.1 and 4.2 show the As concentration in relation to the ammonium-N concentration and ORP, respectively, for the groundwater at sites S1 to S5 of Samta Village. From Fig. 4.1, it appears that the As concentration increases as the ammonium-N concentration increases, but a wide variation in As concentration can be observed when the ammonium-N concentration is at a high of from 3 mg/L to 4 mg/L. The ammonium-N concentration was as high as 5 mg/L at well no. 30, but the As concentration was at a low level of 0.104 mg/L (Table 4.1). Well no. 30 was located quite near an abandoned dug-well which had the depth of 10 m. Groundwater of well no. 30 was sampled at a shallow depth of 14 m. Therefore, it is thought that the high ammonium-N concentration of well no. 30 was affected by the waste dumping due to the adjacency of the dug well.

In Fig. 4.2, high As concentration was observed ranging up to 1.48 mg/L, when the ORP of the groundwater was low of a reducing condition in Samta Village. Therefore, it can be said that the As was released from peat sediments largely in the reducing condition of the groundwater except for the 4 samples of wells no. 6, 18, 24 and 30 (Table 4.1) that showed ORPs above 100 mV. Since these 4 tube wells passed only several days after installation, there may have been some negative effect on the reducing condition of groundwater. In addition, the depth of these wells was shallow, 13-17 m from the ground surface, providing a favorable condition for the groundwater to become a non-reducing or oxidizing condition.

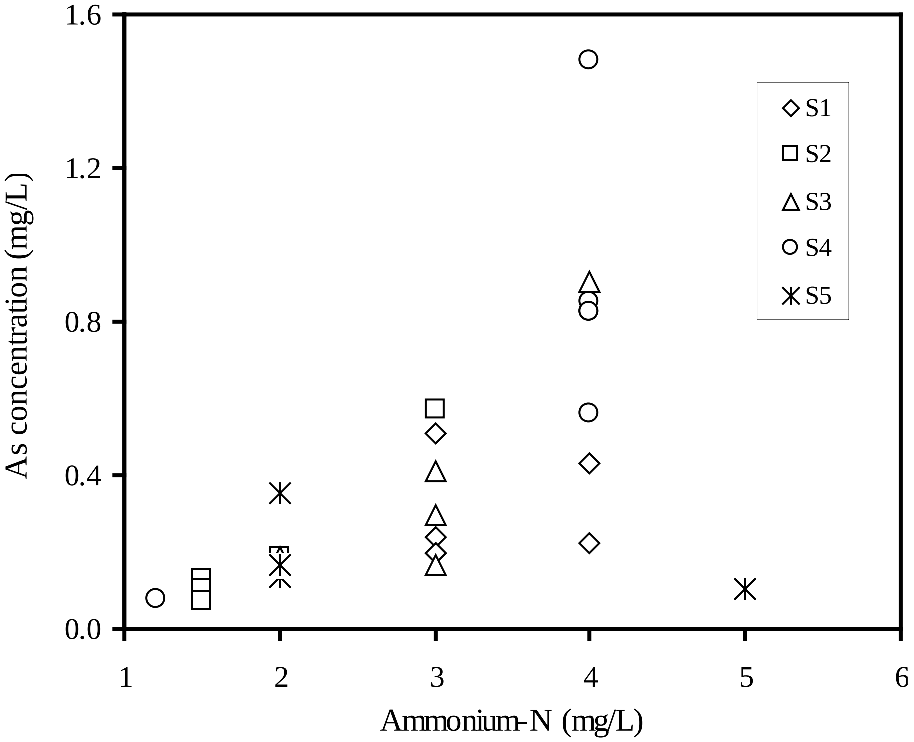

Figure 4.1 Relationship between concentrations of As and ammonium-N in groundwater samples in the As-contaminated village

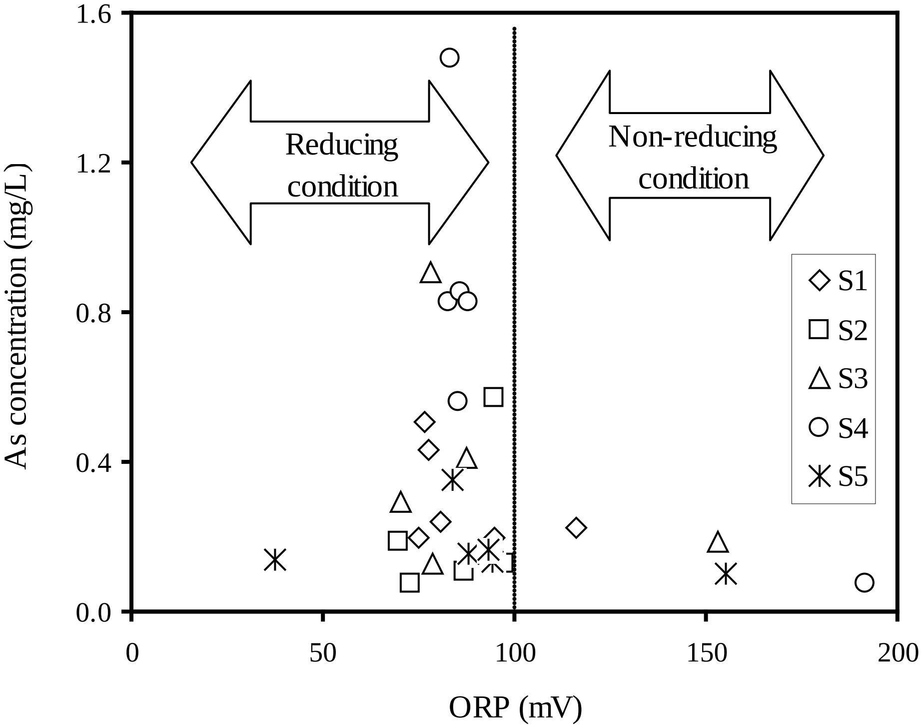

Figure 4.2 Relationship between As concentration and ORP of groundwater samples in the As-contaminated village

The relationship between ORP and As concentration for groundwater samples taken in Dhannokola Village is shown in Fig. 4.3. Here, the groundwater shows mostly non-reducing or oxidizing conditions. The As concentration was a little higher when the groundwater was 90-120 mV (reducing or near to the reducing condition) than that when the groundwater was in the oxidizing or near to the oxidizing condition. For all ORP ranges, the As concentration was low, less than 0.02 mg/L.

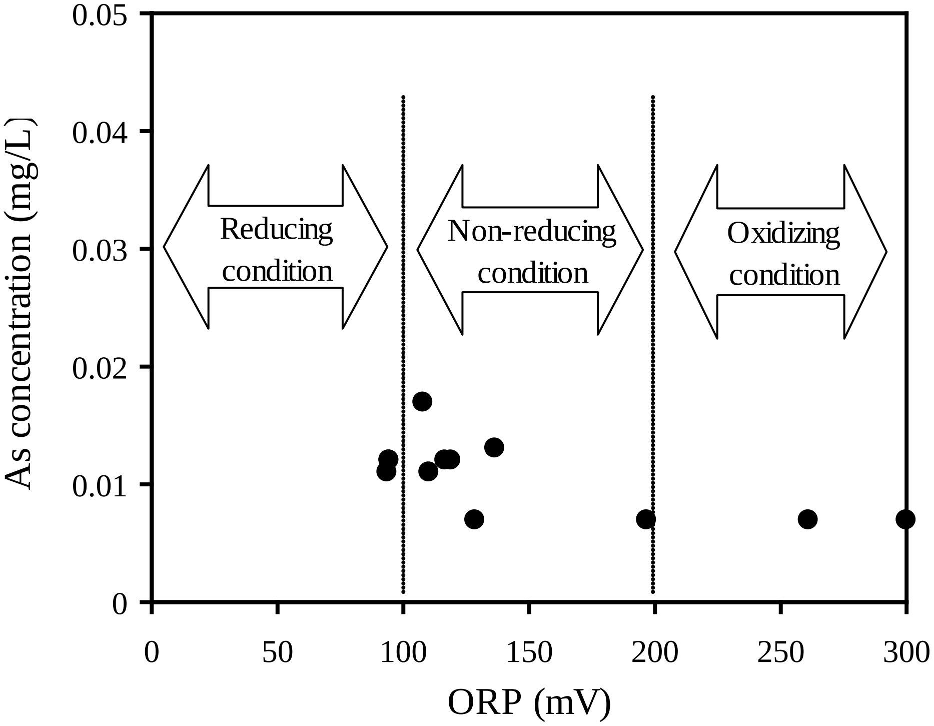

Figure 4.3 Relationship between As concentration and ORP of groundwater samples in the non-As-contaminated village

4.2.3 Depth of the groundwater table and bottom of the tube wells

The depths from the ground surface to the groundwater table and to the bottom of the well were 7.0 m and 16.8 m, respectively, at the S1 site (Table 4.3). These depths were 5.1 m and 15.2 m at the S3 site, 5.5 m and 12.8 m at the S4 site, and 6.8 m and 14.0 m at the S5 site, respectively. The depths of the peat layer were read from Fig. 3.1 and were 7.2-9.0 m, 7.8-8.4 m, 6.0-6.6 m and 7.2-8.4 m at sites S1, S3, S4 and S5, respectively.

From the comparison of the depths of the peat layer with those of the groundwater table and bottom of the wells (Table 4.3), the peat layer was found to be present in between the groundwater table and the bottom of the well, i.e., the peat layer was contacted with the groundwater at all sites except site S2, where a peat layer was not present, as known from Fig. 3.1. Thus the release of As from the peat layer to the groundwater is possible.

When the groundwater As concentration was compared between those of the sites of Samta Village, the As concentration at the sites where peat layer was observed was higher than that at the site where peat layer was not observed according to the following calculation.

By using Table 4.1, the vertical average of As concentration at each site was calculated to be 0.300, 0.198, 0.349, 0.771 and 0.174 mg/L at S1, S2, S3, S4 and S5, respectively. Although the peat layer was not observed at S2, the average As concentration of S2 was higher than that of S5, where the peat layer was observed. At the S2 site, the As concentration of a point (well no. 12) was very high (0.569 mg/L) compared to those of the other points, although its cause was unknown, raising the average As concentration at the S2 site. If the As concentration at the well no. 12 is excluded, the average As concentration of the S2 site becomes 0.124 mg/L, which is lower than those not only of S5, but also of S1, S3 and S4.

It is expected that groundwater As concentration is positively related to the thickness of peat layer, but there seems to be no relationship between the groundwater As concentration and the thickness of the peat layer at the S1, S3, S4 and S5 sites. To this, the thickness of peaty clay layer, depth of well, etc. might be related, but to determine the relationship is difficult here.

Table 4.3 The depth of the peat layer, groundwater table and bottom of wells from the ground surface at the S1 to S5 sites in Samta Village

Site	Depth from ground surface to (m)		
	peat layer	groundwater table	bottom of the well
S1	7.2 – 9.0	7.0	16.8
S2	NA		
S3	7.8 – 8.4	5.1	15.2
S4	6.0 – 6.6	5.5	12.8
S5	7.2 – 8.4	6.8	14.0

4.2.4 $\delta^{15}N$ values of the groundwater samples

The $\delta^{15}N$ values of the groundwater sampled from five representative wells at S1 and S3 of Samta Village and S6 of Dhannokola Village are shown in Table 4.4. These wells were targeted because they showed high inorganic-N concentration.

From Table 4.4, the $\delta^{15}N$ value ranged from 1.83‰ to 2.54‰, showing low values with minor variation in Samta Village. Since the concentration of ammonium-N was far larger than those of nitrate-N and nitrite-N, the $\delta^{15}N$ value is considered to represent the value for ammonium-N.

Table 4.4 The depth of the sampled water, $\delta^{15}N$ and the concentrations of ammonium-N, nitrate-N and nitrite-N of the groundwater samples for the 5 selected wells at sites S1, S3 and S6

Village	Site	Depth of Well (m)	$\delta^{15}N$ (‰)	Ammonium-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)
Samta	S1	16.8	2.39	4.0	0.01	0.01
		33.5	2.54	3.0	0.01	0.02
	S3	15.2	2.28	2.0	0.01	0.01
		27.4	1.83	4.0	0.01	0.02
Dhannokola	S6	12.2	28.20	0.6	5.00	0.18

However, in Dhannokola Village, the $\delta^{15}N$ value for the groundwater sample at site 6, given in Table 4.4, also include the concentrations of ammonium-N, nitrate-N and nitrite-N. The $\delta^{15}N$ value was very high, 28.20‰, and the concentration of nitrate-N was far higher than those of ammonium-N and nitrite-N, thus the $\delta^{15}N$ value is considered to represent the value for nitrate-N.

4.3 Discussion

4.3.1 Source of N in the groundwater samples

In Samta Village, the source of N in the groundwater samples was identified to be chemical N fertilizer according to the values of δ^{15}N ranging from 1.83 to 2.54‰ (Table 4.4), and which were very close to the measured value of δ^{15}N of urea (1.81‰) (Table 3.2). The groundwater was contacting to the peat layer (Table 4.3), and the source of N in the groundwater was perhaps sourced from the peat layer with the release of As. The source of N in other sediments was different from that of peat sediment based on the δ^{15}N as mentioned before.

The source of inorganic-N in the groundwater in Dhannokola Village, whose δ^{15}N was 28.2‰, was animal or human wastes according to the criterion shown by Seiler (1996). Here, nitrate-N of inorganic-N was produced, perhaps due to an oxidizing condition of the groundwater (Fig. 4.3) with sufficient oxygen. At the sampling site of Dhannokola Village, the toilet was located close to the well, probably affecting the δ^{15}N value of the groundwater.

4.3.2 Mechanism of As release from peat sediments into groundwater

Arsenic is considered to be released in a reducing groundwater environment from Fig. 4.2. Among the three hypotheses of As release from the sediments described in Chapter 1, the present release mechanism corresponds to the “reduction of iron hydroxides and release of involved As from the sediments” hypothesis. When the reducing condition of groundwater becomes stronger, the As release from the peat layer, which has an abundant amount of As, as shown in Fig. 3.3, occurs more intensively. The release of As from the peaty clay layer may also contribute to the increase, but the contribution was not so large as that of the peat layer, because the As concentration was considerably lower in the peaty clay sediment than that in the peat sediment. However, the contribution of the peaty clay sediment becomes larger when the thickness of the peaty clay layer is larger. A very high As concentration in the groundwater was observed at site S4 (Table 4.1), where not only a peat layer, but also a very thick peaty clay layer compared to the other sites, was observed (Fig. 3.1). This may be one cause of the high As concentration at site S4. In addition, there has been high anthropogenic activity around site S4, which might additionally be concerned to the occurrence of the high As concentration.

Peat sediments contain Fe and As, where the Fe concentration was far higher than that of As. Release of Fe and As into the groundwater is thought to be done from an iron compound of arsenopyrite (FeAsS) contained in peat sediments in a reducing condition. However, peat sediments usually contain other iron compounds of Fe_2O_3, Fe_3O_4, $FeCl_3$, $Fe_2(SO_4)_3$, etc., and these compounds can also release Fe into groundwater affected by various redox conditions of groundwater. Some of these compounds may not release Fe in a reducing condition.

Thus, the concentration of Fe could not correlate with that of As in groundwater. By using the concentration of Fe measured for groundwater, which was shown in Table 7 of the Appendix, its relation to the concentration of As was examined, but any correlation was not observed, though their results were not shown here. Although the Fe in peat sediments may have some relation with the As release, the concentration of Fe in groundwater or even in peat sediments does not show its exact relation to the As release in the mechanism, thus Fe was not targeted here.

For the release of As, the hypotheses other than the reduction hypothesis, i.e. (1) oxidation hypothesis and (2) hypothesis of anion exchange associated with phosphate fertilizer application, which are mentioned in Chapter 1, will be denied. According to the (1) oxidation hypothesis, As in groundwater is produced from the oxidation of As-rich pyrite in sediments by intrusion of atmospheric oxygen due to the lowering of the groundwater table. However, in the As-contaminated Samta Village, the peat sediment (As rich pyrite is present in peat sediment, according to Ishiga, 2000) was lower than the groundwater table, and thus the atmospheric oxygen could not intrude into the sediment, and As release could not occur through the mechanism. However, concerning hypothesis (2), only a small quantity of phosphate fertilizer is applied compared to nitrogen and potassium fertilizers in cropping in Bangladesh (Jahiruddin et al., 2010). Therefore, the phosphate originating from fertilizer combines only a small quantity of iron that is contained in the compound of As and iron, resulting in a minor release of As from the sediment into the groundwater.

Furthermore, it is not clear why the reducing condition is created, however, a possible cause of the reducing condition is discussed in Chapter 5, based on the chemical properties of peat sediments and the characteristic on groundwater that, when the As concentration was high, the concentration of ammonium-N was high.

4.4 Conclusion

The following conclusions are drawn in this chapter.

From the measurement of groundwater quality at sites of the As-contaminated village where the peat layer is located at a shallow depth, the As concentration of groundwater was as high as 30 times the maximum of the Bangladeshi drinking water standard, and there was a positive relationship between the concentrations of As and ammonium-N. By the stable isotope analysis on inorganic-N, the N in groundwater was identified to be sourced from chemical N fertilizer, i.e., the same source as that of the peat sediments.

The ORP of the groundwater was found to be low, showing a reducing condition of the groundwater. The release of As from the peat layer was identified to occur through the mechanism of “reduction of iron hydroxides and release of involved As from the peat sediments” based on the relationship that when the groundwater was in the reducing condition, the As concentration of the groundwater was high. The above mechanism is the prevailing hypothesis on the release of As. A large quantity of ammonium-N in groundwater observed at high As concentration was thought to be produced from the N in the peat sediment. The peat layer containing a high amount of As is thought to contribute greatly to the release of As under the proposed mechanism.

In the non-As-contaminated village, the peat or peaty clay layer sediment was not located at a shallow depth, the concentrations of As and ammonium-N of the groundwater were very low, and the ORP showed that the groundwater was in the non-reducing or oxidizing condition. The result of the δ^{15}N analysis showed that the source of N in the groundwater was not the chemical N fertilizer but animal or human waste.

At the site where peat layer did not exist, the ammonium-N concentration was low, and the ORP showed the non-reducing or oxidizing condition of the groundwater. Hence the reductive release of As is not to occur at this site.

CHAPTER 5

Factors Affecting Arsenic Concentration of the Groundwater in the Arsenic Contaminated Village

5.1 Introduction

The substances contained in the peat sediment and the groundwater quality parameters are thought to be the important factors which affect the groundwater As concentration in the contaminated village.

This is because the As-contaminated village had peat in its sediments, whereas the non-contaminated village did not have it (Figs.3.1 and 3.2). The peat sediment had higher concentrations of As, %C and %N than those of other sediments in the As contaminated village (Fig. 3.3 and Table 3.3). Furthermore, concerning the groundwater quality in the As-contaminated village, the As concentration was positively related to the ammonium-N concentration to some extent (Fig. 4.1), while the As concentration was related neither positively nor negatively to the ORP, but was high when the ORP was in between 50 mV and 100 mV (Fig.4.2), showing the reducing condition of the groundwater.

Based on these features, the following points are clarified in this chapter: (1) effect of substances of peat sediment, (2) effect of the groundwater quality parameter on groundwater As concentration, and (3) relationship between the effects of the substances of peat sediment and the groundwater quality parameters, respectively. These points finally affect the groundwater As concentration in the As contaminated village.

5.2 Factors affecting groundwater As concentration

5.2.1 Effects of the substances of the peat sediment

According to Madhavan and Subramanian (2006), groundwater As contamination occurs in the areas where Holocene sediments are observed in the Bengal Delta. The Holocene sediments in the delta often contain peat sediment, which has a high concentration of As, as shown in Fig. 3.3. However, the As species observed in the groundwater of the As-contaminated area in Bangladesh are arsenate [As(V)] and arsenite [As(III)] (Ahmed, 2003a). Peat sediment contains a certain amount of C, 15.1 % in concentration at maximum (Table 3.3). However, organic substances, consisted of C together with H, O, N, S, P, etc., are thought to occupy far more than 15.1% in the peat sediment, and the other remaining part in the sediment is inorganic substances. By these inorganic substances, inorganic As species of arsenate and arsenite will be absorbed in peat sediment. Farooqui and Usha (2003) suggested that peat sediment could be a place for residing arsenopyrite, which is an inorganic compound composed of As (arsenate and/or arsenite), iron and sulfur.

Furthermore, the concentration of N in peat sediment is usually high (Moor, 1998). In the present study, the concentration of N in the peat sediment was much higher than those in the other sediments (Table 3.3). Here, the source of N in the peat sediment was chemical N fertilizers, as learned from $\delta^{15}N$ analysis (Table 3.2). N is the most important nutrient element for crops and vegetables, and thus the chemical N fertilizer has been intensively used in agriculture in Bangladesh recently (Fig.1.5). The N is probably combined with C in the peat sediment through a weak chemical bond.

From the above, peat sediment is important as a place for preserving As and N. In addition, C and inorganic substances in peat sediment are important substances to bond N and inorganic As, respectively.

According to AAN (2000) and Ishiga *et al*. (2000), peat layer was identified in the sediments of the Bengal Delta, including the study area, but the topographical conditions favorable for the formation of peat layer have not yet been clarified.

Samta Village of the As-contaminated village is a low-lying area and located adjacent to the Betna River. In the village, flooding occurs frequently. In addition, the village has a gently undulating topography, thus, flooded water is easy to stay longer in the concave area of the village. Concave areas are located at some places around the villages. Considering the topography, aquatic plants, which are the source material of peat sediment, are thought to grow easily in the area. Though the village topography from a long time ago may have been greatly changed, and the aquatic plants might not be the same as those in the current topography.

In contrast, Dhannokola Village, where peat layer was not observed in the sediments, is a low-lying area, but no river is located in or near the village. The area has a comparatively flat topography and has less number of concave areas. Therefore, even when flooding occurs, the water will not stay there long. This topography is not favorable for the growth of aquatic plants.

Since only two villages were targeted in this study, further study is necessary to examine the topographical conditions favorable for the aquatic plant's growth.

5.2.2 Effects of groundwater quality parameters

In Samta Village of the As-contaminated village, the groundwater As concentration was high, ranging up to 1.48 mg/L when the ORP showed the reducing condition of the groundwater. Meng *et al.* (2001) and Nickson *et al*. (1998) also mentioned that the mobility of As in groundwater is influenced by the redox potential of groundwater.

A certain concentration of As was observed in the non-reducing condition of the groundwater, but the concentration was rather low (0.013 mg/L at maximum). In the oxidizing condition, the As concentration of the groundwater was very low (0.007 mg/L at maximum). Therefore, the reducing condition of groundwater is a very important parameter of groundwater quality affecting the As concentration.

While showing a positive relationship between the concentrations of As and ammonium-N observed in groundwater (Fig. 4.1), the As concentration varied widely (0.166 - 1.48 mg/L), when the ammonium-N concentration was high, 3 mg/L to 4 mg/L. This relationship shows that the ammonium-N concentration can be a factor affecting the As concentration, but its effect is not strong compared to that of ORP due to the variation.

Except for ORP and ammonium-N concentration, there were no other groundwater quality parameters that affected the As concentration.

5.2.3 Relationship between the effects of the substances of peat sediment and groundwater quality parameters

Among the substances of peat sediment, As is the most important one to affect the As concentration, because As in groundwater is thought to be provided mainly from peat sediment. If peat sediment did not exist in the sediments, the As concentration of the groundwater was very low, as shown in Dhannokola Village (0.013 mg/L at maximum from Table 4.2).

For the groundwater quality parameters, ORP is the most important one. A high As concentration was observed only when the groundwater was in the reducing range shown by the ORP. The second most important factor is ammonium-N from its relationship with As concentration.

N in peat sediment is an important factor next to the As. The release of As is done by the mechanism of reductive release. Through this mechanism, N in peat sediment may serve as a nutrient for microorganisms. By the activity of microorganisms, oxygen is consumed, and then reducing condition is created, as suggested by Kurosawa *et al.* (2008a). According to Matsumoto *et al.* (2011), N using bacteria were isolated from the peat sediment of the As-contaminated Samta Village.

In the reducing condition, As release from peat sediment can be prompted. At the same time, ammonium-N in groundwater is thought to be provided from N in peat sediment.

From the above, the N in peat sediment eventually contributes to create the reducing condition of peat sediment/groundwater, which increases the As concentration of groundwater. This indicates a relationship between the effects of substances of peat sediment and groundwater quality parameters.

Since the N in peat sediment is thought to be sourced from chemical N fertilizer, the fertilizer probably creates the reducing condition in peat sediment.

5.3 Conclusion

Concerning the effect of the substances of peat sediment, As is the most important, followed by N. The peat sediment is suitable as a place for preserving As and N. In addition, C and inorganic substances in peat sediment are important to bond N and inorganic As, respectively. Identification of the topographical conditions favorable for peat formation, i.e. for the growth of aquatic plants, is important.

Concerning the effect of groundwater quality parameters, ORP is the most important, followed by ammonium-N. Both of these could prompt As release.

The N in peat sediment eventually creates the reducing condition of groundwater, which indicates the relationship between the effects of the substances of peat sediment and groundwater quality parameters. Chemical N fertilizer, i.e. the source of N in peat sediment, probably produces the reducing condition.

CHAPTER 6

General Conclusions

From the present study, it was clarified first that As concentration in the peat sediment was higher than in the other sediments in the As-contaminated village, i.e., the order of the As concentration of sediments was peat>peaty clay> clay>silty clay>sand. A positive relationship between the As concentration, %C and %N was identified in these sediments.

The N and C in the peat sediment were identified to be sourced from the chemical N fertilizer and aquatic plants, respectively, according to the $\delta^{15}N$ and $\delta^{13}C$ analyses. Thus, it is thought that As concentration in peat sediment is increased by the absorption of As by aquatic plants that had grown there long time ago, and the C concentration was increased by the accumulation of the decayed material of the plants.

The positive correlation between %C and %N observed for the peat sediment may have been induced by the mechanism that the C absorbed N sourced from the chemical N fertilizer with a comparatively weak chemical bond.

The peat layer had a thickness of 0.6-1.8 meters and was located in a shallow layer in between the groundwater table and the bottom of the well at the As-contaminated village. In contrast, peat layer was not observed in the sediments of the non-As-contaminated village, where a thin peaty clay layer was observed at a deeper layer.

From the groundwater quality at the As-contaminated village, the As concentration of groundwater was maximally as high as 30 times the Bangladeshi drinking water standard. There was a positive relationship between the concentrations of As and ammonium-N. According to the δ^{15}N analysis on the groundwater, the inorganic-N, most of which was the ammonium-N, was identified to be sourced from the chemical N fertilizer, i.e., the same source as that of the peat sediment.

The ORP of the groundwater was found to be low, showing a reducing condition of the groundwater. The release of As from peat sediment into groundwater was thought to be induced by the mechanism of “the reduction of iron hydroxides and release of involved As from the peat sediments,” based on the fact that the groundwater As concentration was high when the groundwater was in the reducing condition. A large concentration of ammonium-N in the groundwater observed at a high As concentration may have been sourced from the N in the peat sediment.

In the non-As-contaminated village, the concentrations of As and ammonium-N of the groundwater were very low, and the ORP showed that the groundwater was in non-reducing or oxidizing condition. The result of the δ^{15}N analysis showed that the source of the inorganic-N in the groundwater was not the chemical N fertilizer, but animal or human waste. Hence the above-mentioned release of As under the reducing condition did not occur in the village.

From the above comparisons, it was concluded that peat sediment is important and plays a critical role in groundwater As contamination.

Concerning the effect of the substances of peat sediment, As is the most important substance, followed by N. The peat sediment is a place to preserve a lot of As and N. In addition, C and inorganic substances in the peat sediment are important to bond N and inorganic As, respectively. Concerning the effect of groundwater quality parameters, ORP is the most important parameter, followed by ammonium-N. Both of them could prompt the release of As into groundwater.

A substance of peat sediment can affect a groundwater quality parameter, i.e., N in peat sediment contributes to create the reducing ORP of groundwater through the microbial activity that consumes oxygen by using N as a nutrient. Chemical N fertilizer, i.e., the source of N in peat sediment, eventually contributes to provide the reducing condition. The release of As is prompted by the reducing condition.

Thus, it was concluded that the properties of sediments, particularly peat sediment, source of the substances of the peat sediment, and groundwater parameters affect groundwater As contamination. Based on the results, the mechanism of As release from peat sediment into groundwater of wells was clarified in the villages of the Bengal Delta.

For further study, it is important to clarify the topographical conditions favorable for the formation of peat sediment, and the kinds of microorganisms living in peat sediment and their activity in terms of the release of As.

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APPENDIX: The raw data used for making figures shown in the text

Appendix Table 1. The raw data used for depicting Figure 3.2

Sl. No.	Description of the Sediments	Depth (m)	Arsenic (mg/Kg)
1	Sand	4.3	2.592
2	Sand	12.2	1.480
3	Sand	15.2	1.193
4	Sand	18.3	1.186
5	Sand	21.3	2.765
6	Sand	24.4	2.816
7	Sand	27.4	0.841
8	Sand	30.5	1.695
9	Sand	33.5	1.047
10	Sand	36.6	1.342
11	Sand	42.7	0.699
12	Sand	45.7	0.973
13	Sand	48.8	0.967
14	Sand	51.8	0.771
15	Sand	54.9	0.790
16	Sand	57.9	0.732
17	Sand	60.4	0.783
18	Silty Clay	3.0	2.978
19	Silty Clay	3.7	2.846
20	Silty Clay	29.3	3.264
21	Silty Clay	55.5	1.708
22	Clay	0.0	10.164
23	Clay	0.6	6.310
24	Clay	1.2	5.918
25	Clay	1.8	7.596
26	Clay	2.4	9.504
27	Clay	5.5	11.739
28	Clay	6.1	16.184
29	Clay	6.7	7.627
30	Clay	9.1	7.599
31	Clay	10.4	10.024
32	Clay	12.8	8.552
33	Clay	39.6	15.585
34	Peaty Clay	4.9	17.092
35	Peaty Clay	9.8	16.533
36	Peaty Clay	40.2	19.851
37	Peat	7.3	51.561
38	Peat	7.9	75.317
39	Peat	8.5	34.911

Appendix Table 2. The raw data used for depicting Figure 3.3

Sl. No.	Depth (m)	Description of the Sediments	Arsenic (mg/Kg)	Organic Mater (%C)
1	4.3	Sand	2.592	0.53
2	54.9	Sand	0.790	0.61
3	3.0	Silty Clay	2.978	0.51
4	3.7	Silty Clay	2.846	1.48
5	29.3	Silty Clay	3.264	0.44
6	55.5	Silty Clay	1.708	0.82
7	0.0	Clay	10.164	1.25
8	0.6	Clay	6.310	1.54
9	1.2	Clay	5.918	1.08
10	1.8	Clay	7.596	1.41
11	2.4	Clay	9.504	0.71
12	5.5	Clay	11.739	1.13
13	6.1	Clay	16.184	0.51
14	6.7	Clay	7.627	0.91
15	9.1	Clay	7.599	1.99
16	10.4	Clay	10.024	2.65
17	12.8	Clay	8.552	1.43
18	39.6	Clay	15.585	1.08
19	4.9	Peaty Clay	17.092	2.50
20	9.8	Peaty Clay	16.533	1.69
21	40.2	Peaty Clay	19.851	2.03
22	7.3	Peat	51.561	10.14
23	7.9	Peat	75.317	15.11
24	8.5	Peat	34.911	5.12

Appendix Table 3. The raw data used for depicting Figure 3.4

Sl. No.	Depth (m)	Description of the Sediments	Nitrogen (%N)	Organic Mater (%C)
1	4.3	Sand	0.01	0.53
2	54.9	Sand	0.01	0.61
3	3.0	Silty Clay	0.01	0.51
4	3.7	Silty Clay	0.02	1.48
5	29.3	Silty Clay	0.02	0.44
6	0.0	Clay	0.04	1.25
7	0.6	Clay	0.02	1.54
8	1.2	Clay	0.03	1.08
9	1.8	Clay	0.02	1.41
10	2.4	Clay	0.02	0.71
11	5.5	Clay	0.04	1.13
12	6.1	Clay	0.04	0.51
13	6.7	Clay	0.04	0.91
14	9.1	Clay	0.10	1.99
15	10.4	Clay	0.16	2.65
16	12.8	Clay	0.03	1.43
17	39.6	Clay	0.07	1.08
18	4.9	Peaty Clay	0.17	2.5
19	9.8	Peaty Clay	0.09	1.69
20	40.2	Peaty Clay	0.11	2.03
21	7.3	Peat	0.70	10.14
22	7.9	Peat	0.86	15.11
23	8.5	Peat	0.30	5.12

Appendix Table 4. The raw data used for depicting Figure 4.1

Sl. No	Site	Caretaker Name	TW Depth (m)	Arsenic (mg/L)	Ammonium-N (mg/l)
1	S1	Unus Ali	33.5	0.432	4.0
2		Montaz	33.5	0.507	3.0
3		Umor Ali	39.6	0.240	3.0
4		Kuddus House	36.6	0.195	3.0
5		Anwer House	22.9	0.200	3.0
6		Observation well-1	16.8	0.223	4.0
7	S2	Abdul Mozid	36.6	0.124	1.5
8		Abdus Samad	39.6	0.130	1.5
9		Joynal Abedin	30.5	0.105	1.5
10		Abdus Salam	32.0	0.189	2.0
11		Farab	39.6	0.073	1.5
12		Observation well-2	12.2	0.569	3.0
13	S3	Kudrul	27.4	0.129	2.0
14		DW-Obs.well	45.7	0.296	3.0
15		Jalal Molla	21.3	0.410	3.0
16		Awal Hossain	27.4	0.906	4.0
17		Ser Ali	18.3	0.166	3.0
18		Observation well-3	15.2	0.187	2.0
19	S4	Robiul	33.5	0.827	4.0
20		Idris Ali	33.5	0.853	4.0
21		Laltu Gazi	39.6	0.827	4.0
22		Domser Ali	33.5	0.561	4.0
23		Kamrul	22.9	1.480	4.0
24		Observation well-4	12.8	0.077	1.2
25	S5	Mosque	35.1	0.136	2.0
26		Abul Kasem	35.1	0.352	2.0
27		Ismail Gazi	39.6	0.157	2.0
28		Mundir	27.4	0.133	2.0
29		Anser Ali	36.6	0.164	2.0
30		Observation well-5	14.0	0.104	5.0

Appendix Table 5. The raw data used for depicting Figure 4.2

Well No.	Site	Caretaker Name	TW Depth (m)	ORP (mV)	Arsenic (mg/L)
1	S1	Unus Ali	33.5	77	0.432
2		Montaz	33.5	76	0.507
3		Umor Ali	39.6	81	0.240
4		Kuddus House	36.6	95	0.195
5		Anwer House	22.9	75	0.200
6		Observation well-1	16.8	116	0.223
7	S2	Abdul Mozid	36.6	94	0.124
8		Abdus Samad	39.6	97	0.130
9		Joynal Abedin	30.5	87	0.105
10		Abdus Salam	32.0	70	0.189
11		Farab	39.6	73	0.073
12		Observation well-2	12.2	95	0.569
13	S3	Kudrul	27.4	79	0.129
14		DW-Obs.well	45.7	70	0.296
15		Jalal Molla	21.3	88	0.410
16		Awal Hossain	27.4	78	0.906
17		Ser Ali	18.3	92	0.166
18		Observation well-3	15.2	153	0.187
19	S4	Robiul	33.5	83	0.827
20		Idris Ali	33.5	86	0.853
21		Laltu Gazi	39.6	88	0.827
22		Domser Ali	33.5	85	0.561
23		Kamrul	22.9	83	1.480
24		Observation well-4	12.8	192	0.077
25	S5	Mosque	35.1	38	0.136
26		Abul Kasem	35.1	84	0.352
27		Ismail Gazi	39.6	88	0.157
28		Mundir	27.4	94	0.133
29		Anser Ali	36.6	93	0.164
30		Observation well-5	14.0	155	0.104

Appendix Table 6. The raw data used for depicting Figure 5.1

Well No.	Site	Caretaker Name	TW Depth (m)	ORP (mV)	Arsenic (mg/L)
31	S6	Owler Rahman	23	300	0.007
32		A. Khalek	27	261	0.007
33		A. Hamid	41	108	0.017
34		M. Motiar Rahman	23	128	0.007
35		A. Kader	38	119	0.012
36		Observation well-6	12	197	0.007
37	S7	Jahangir	30	117	0.012
38		Sohidul-A	37	110	0.011
39		Sohidul-B	76	95	0.012
40		Kobirul	27	94	0.011
41		Romjan	18	94	0.012
42		Observation well-7	12	137	0.013

Appendix Table 7. Concentrations of As and iron of the groundwater samples

Village	Site	Well No.	Caretaker Name	Depth of Wells (M)	Arsenic (mg/L)	Iron (mg/l)
Samta	S1 (Bazer para)	1	Unus Ali	34	0.432	5.67
		2	Montaz	34	0.507	6.50
		3	Umor Ali	40	0.240	5.39
		4	Kuddus House	37	0.195	5.58
		5	Anwer House	23	0.200	5.84
		6	Observation well (S1)	17	0.223	7.85
	S2 (South para)	7	Abdul Mozid	37	0.124	5.11
		8	Abdus Samad	40	0.130	5.35
		9	Joynal Abedin	30	0.105	4.94
		10	Abdus Salam	32	0.189	7.78
		11	Farab	40	0.073	6.11
		12	Observation well (S2)	12	0.569	14.26
	S3 (West para)	13	Kudrul	27	0.129	7.89
		14	DW-Obs.well	46	0.296	6.17
		15	Jalal Molla	21	0.410	10.04
		16	Awal Hossain	27	0.906	9.67
		17	Ser Ali	18	0.166	9.54
		18	Observation well (S3)	15	0.187	6.27
	S4 (Patient Para)	19	Robiul	34	0.827	7.41
		20	Idris Ali	34	0.853	7.35
		21	Laltu Gazi	40	0.827	6.79
		22	Domser Ali	34	0.561	4.42
		23	Kamrul	23	1.480	6.39
		24	Observation well (S4)	13	0.077	4.69
	S5 (Pal para)	25	Mosque	35	0.136	4.36
		26	Abul Kasem	35	0.352	5.72
		27	Ismail Gazi	40	0.157	4.32
		28	Mundir	27	0.133	4.49
		29	Anser Ali	37	0.164	5.14
		30	Observation well (S5)	14	0.104	3.67
Dhannokola	S6 (South para)	31	Owler Rahman	23	0.007	0.17
		32	A. Khalek	27	0.007	0.09
		33	A. Hamid	41	0.017	1.21
		34	M. Motiar Rahman	23	0.007	1.17
		35	A. Kader	38	0.012	1.55
		36	Observation well (S6)	12	0.007	1.00
	S7 (Council para)	37	Jahangir	30	0.012	3.81
		38	Sohidul-A	37	0.011	0.98
		39	Sohidul-B	76	0.012	1.11
		40	Kobirul	27	0.011	1.03
		41	Romjan	18	0.012	4.61
		42	Observation well (S7)	12	0.013	3.89