# ARSENIC AND GROUNDWATER PROPERTIES OF ARAIHAZAR, BANGLADESH

By

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# Abstract

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by

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Arsenic is a highly toxic and ubiquitous metalloid dispersed throughout the earth's crust. It can be mobilized in the environment through a combination of natural processes. The mobilization of arsenic from aquifer materials usually occurs under reducing conditions and is microbially mediated. This was observed in aquifers of Araihazar, Bangladesh. There, elevated dissolved As concentrations in groundwater were found mostly in the form of inorganic arsenic as arsenite, using several analytical methods including one that uses a modified colorimetric method. However, time series data demonstrate that variations in groundwater As concentrations were considerably less in comparison to other redox-sensitive elements such as Fe, Mn and S, suggesting that there are significant decoupling between As mobilization and redox state of the aquifer. To resolve the uncertainty regarding whether mobilization of As from sediment requires reduction or not at crustal abundances, a series of laboratory microcosm experiments using a representative natural sediment sample collected from Araihazar, Bangladesh were conducted. The results show that mobilization of As does not require reduction. The mobilization and reduction of Fe and Mn are predominantly limited by availability of electron donors such as lactate. However,

the mobilization and reduction of As appears to have more limiting factors such as the type of microbes present in the system. This study also reinforced the notion that although reducing conditions are key to the mobilization of As in Bangladesh shallow aquifer, As concentrations can be significantly decoupled from Fe and P. This difference, in part, is because Fe and P concentrations are regulated by several mineral precipitation reactions. In addition to potential differences in microbial communities, there is a remarkable difference in several nutrients between the Holocene shallow aquifer and the Pleistocene deep aquifer. Future studies of the implication of the nutrient and microbial contrast on As mobility in both aquifers and viability of deep aquifer as a drinking water source are much needed.

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Chapter 2: Dhar, R. K., Y. Zheng, P. Rubenstone, and A. van Geen, 2004, A rapid colorimetric method for measuring arsenic concentration in groundwater: Analytica Chimica Acta, v. 526, p. 203-209.

Chapter 3: Dhar, R. K., Y. Zheng, M. Stute, A. van Geen, Z. Cheng, M. Shahnewaz, M. Shamsudduha, M. A. Hoque, M. W. Rahman, and K. M. Ahmed, Temporal variability of groundwater chemistry in shallow and deep aquifers in Araihazar, Bangladesh: *Geochimica Cosmochimica Acta.* ***Submitted July 2005.***

Chapter 4: Dhar, R. K., Y. Zheng, C.W. Saltikov, K. A. Radloff, B. Mailloux and A. van Geen, Microbes and arsenic mobilization in deep Bangladesh aquifer: limited roles of arsenic and iron reduction. *Not yet submitted.*

Chapter 5: Dhar, R. K., Y. Zheng, M. Stute and A. van Geen, Hydrochemistry of Shallow and Deep Aquifer in Araihazar, Bangladesh. *Not yet submitted.*

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Dedicated to Mother of Universe,
**“Ma Sarada”**
Without whom nothing,
not even arsenic geochemistry,
would make any sense.

# Chapter 1. Introduction

## *1.1 Background*

Arsenic is a highly toxic and ubiquitous metalloid (Cullen and Reimer, 1989) found in the atmosphere, soils and rocks, natural water and organisms. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities such as mining. Most arsenic problems related to drinking water exposure, however, are the result of arsenic mobilization under natural conditions. A number of large aquifers in various parts of the world have been identified with concentrations of arsenic occurring at above 10 $\mu g\ l^{-1}$, and often significantly so. Most noteworthy occurrences are in the Ganges-Brahmaputra Delta regions (parts of West Bengal, India and southern Bangladesh), Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of the USA but particularly the south-west (Smedley and Kinniburgh, 2002; Welch et al., 2000) .

In Bangladesh alone, over 35 million people are estimated to drink As contaminated groundwater that exceeds the national drinking water standard of 50 $\mu g\ l^{-1}$ of As (BGS & DPHE, 2001) and cases of arsenicosis are diagnosed (Yu et al., 2003). Additionally, USEPA (United States Environmental Protection Agency) lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 to 10 $\mu g\ l^{-1}$, effective in January 2006 (EPA, 2001). This reflects the re-evaluation of the health risks associated with ingestion of this metalloid. Because of this threat, it is critically important to understand the factors controlling arsenic migration in natural systems, both to assess risks posed by As-enriched aquifers and to design effective mitigation strategies.

Much of the aquifer system in Ganges-Brahmaputra Delta (GBD) has not been studied for sediment stratigraphy in detail, but basin wide stratigraphic reconstruction suggests that the uppermost strata with thickness ranging from 30 m to 100 m, or 100 ft to 300 ft was deposited by the meandering Ganges-Brahmaputra-Meghna river system and their tributaries during the late Quaternary or Holocene age (Goodbred and Kuehl, 2000; Mukherjee and Bhattacharya, 2001; Umitsu, 1993). This lithological succession is dominated by coarse to fine sandy deposit underlying a fine-grained silty or clayey surface floodplain deposit, with a rapid transgression of the delta during the mid-Holocene climatic optimum period (Goodbred Jr. et al., 2003). In addition to sea level changes, factors influencing the thickness of the Holocene strata, namely, tectonic activities favoring fine-grained sediment deposition and high energy fluvial events favoring coarse-grained deposits, lead to different thickness of Holocene strata in the GBD (Goodbred and Kuehl, 2000). For the most part of the GBD, regional distribution of groundwater arsenic has been shown to have a strong associate with the geomorphology (BGS & DPHE, 2001; Yu et al., 2003). In Bangladesh, Pleistocene uplifted deposits remain unaffected by low As where as moderate to strong arsenic enrichment are found in low-lying younger flood and delta plains in southern Bangladesh (Acharyya et al., 2000; Ahmed et al., 2004; BGS & DPHE, 2001). Groundwater As concentrations from the northwestern region of Bangladesh are also low (BGS & DPHE, 2001; Dhar et al., 1997).

The spatial extent of the problem and the fact that the most severely contaminated areas are in the geologically distinct low-lying flood plain, support the idea that the sediments themselves are the most likely As source. Available data for As in sediments from Bangladesh, including those bearing high-As groundwater, show the concentration of As to be largely similar to those for average sediments and are ranged from 0.4 $\text{mgkg}^{-1}$ to 16 $\text{mgkg}^{-1}$ in different parts of Bangladesh (Horneman et al., 2004; Pierce and Moore, 1982; Smedley and Kinniburgh, 2002; Zheng et al., 2005). However, the mobility of arsenic in the subsurface is influenced by a combination of the dissolved species present, minerals in aquifer solids, microbiological activity, and by ambient geochemical parameters such as Eh and pH (Smedley and Kinniburgh, 2002). Arsenic is relatively mobile at high pH (>8.5) in oxic waters or under circumneutral pH (6.5-7.5) in reducing conditions (Smedley and Kinniburgh, 2002).

To better understand the hydrological, geochemical and microbial interactions that result in enrichment of As in groundwater, this thesis investigates arsenic and groundwater properties in aquifers from central Bangladesh. The study area of ~ 25 $\text{km}^2$ is located in Araihazar, an area between a Pleistocene uplifted terrace (the Madhupur tract) to the west, and the low-lying Meghna flood plain to the east. Beneath the flood plain, the Pleistocene-Holocene unconformity quickly deepens to a depth of >90 m to the east of the study area. This geologic setting provides an unique opportunity to examine aquifers typical of the productive aquifers in Bangladesh in a small region.

## *1.2 Chapter Summaries*

### 1.2.1. Chapter 2:

The high concentrations of arsenic, found in groundwater in many parts of the world (Smedley and Kinniburgh, 2002), pose an important analytical challenge because of the large number of wells that must be tested. This is particularly true in Bangladesh where 97% population obtain their drinking water from a large number of tubewells, potentially up to 11 million (BGS & DPHE, 2001; Kinniburgh and Kosmus, 2002). Moreover, the tendency to install new tube wells does not seem to be halted even after learning of the countrywide arsenic problem (van Geen et al., 2002). Among the many options for safe water, people tend to go for pathogen free groundwater even though only one third of the wells contains <50 $\mu g\ l^{-1}$ As (BGS & DPHE, 2001; Dhar et al., 1997; McArthur et al., 2001; van Geen et al., 2003). Therefore, there is an urgent need to develop a rapid, affordable and reliable method for the arsenic-contaminated wells to be tested on site or in a laboratory for appropriate actions to be taken.

A colorimetric method (Johnson, 1971; Johnson and Pilson, 1972) was modified for arsenic detection in groundwater. The method was initially developed for analyzing seawater. The modified method is inexpensive, reliable, relatively fast, and the detection limit is below the WHO guideline value for As in drinking water of 10 $\mu g\ l^{-1}$. The method can be applied to determine the inorganic As speciation in groundwater.

### 1.2.2. Chapter 3:

Considerable spatial variability of As was observed in 6000 wells within the study area of ~25 $km^2$ in Araihazar (vanGeen et al, 2003). Such spatial variability naturally leads to the concern that shallow groundwater [As] may also change over time, especially because subsurface flow is likely to be affected by large water withdrawals for irrigation in certain areas of Bangladesh (Harvey et al., 2002; Klump et al., 2006). This understanding is urgently needed because a significant proportion of those shallow wells that presently meet the Bangladesh drinking water standard of 50 $\mu g\ l^{-1}$ are, at least temporarily, shared by villagers of Bangladesh to reduce their exposure to As (Opar et al., 2006; van Geen et al., 2002).

The temporal variability of dissolved As and other ions was assessed by bi-weekly to monthly sampling of six nests of multilevel wells consisting of a total of 37 monitoring wells installed into the shallow (5- 30 m) and deep (30- 91 m) aquifers of Araihazar, Bangladesh between 2001 and 2004. A major advantage of our current study is that sites are located to represent the geologic and hydrologic conditions representative of the Bangladesh aquifers and they have been carefully studied previously (Horneman et al., 2004; Stute et al., in review; Zheng et al., 2005). In addition, we use a highly sensitive and precise method (Cheng et al., 2004) to measure As, P, major cations (Mg, Ca, K and Na), redox sensitive elements Fe, Mn and S and ion chromatographic method to measure Cl . The chapter reports the temporal patterns of groundwater chemistry including the short term excursions of groundwater As concentration in a few shallow wells, or lack thereof in the majority of the cases for As, in both shallow and deeper aquifers. New insights on why As changes were limited became evident when the groundwater chemistry change was placed in the context of the groundwater residence time obtained by $^{3}H/^{3}He$ dating. This study demonstrated that variations in groundwater As concentrations were considerably insignificant in comparison with other redox-sensitive constituents, such as Fe, Mn and S in both the low-As deep aquifers and high-As shallow aquifers. Further, the rate of increase or decrease per year in all shallow and deep wells was examined by performing a regression analysis of As , P and other ions concentration versus time for each well over the entire period. Trends of As concentration may be linked with sediment geology and its effect on the groundwater flow regime. Groundwater associated with young (<4000 yrs) and older (6000-10,000 yrs) sediments show increase and decrease in As concentrations with time respectively which also supports the view of exhausting aqueous As due to flushing over time in older sedimentary aquifers.

### 1.2.3. Chapter 4:

Many studies have found that dissolved As concentrations in the geologically older, Pleistocene aquifers in Bangladesh, are systematically less than 10 $\mu g\ l^{-1}$ (BGS & DPHE, 2001; Cheng et al., 2005; Harvey et al., 2002; Horneman et al., 2004; van Geen et al., 2003; Zheng et al., 2005). This aquifer has been suggested as a potential source of drinking water. Considerable uncertainties remain regarding the viability of this aquifer as a long-term drinking water source. One such issue is the mobility of As in the aquifer sediment upon infiltration of shallow groundwater as a result of leakage or increasing pumping. Another motivation of the study is that reduction of As was often regarded as critical pre-requisite for As mobilization studies (Ahmann et al., 1997; Islam et al., 2004; Oremland and Stolz, 2003).

A set of incubation experiments was conducted over a period of 3 months using deep Pleistocene (orange) aquifer sands from Bangladesh which contained little Fe(II) in the acid-leachable Fe fraction (Fe(II)/Fe=0.05) and about 0.14 mg/kg phosphate-extractable As, all in the form of arsenate. The role of dissimilatory As reduction in mobilization of As was explored by comparing a wild type *Shewanella* species strain ANA-3 and its mutant type *Shewanella* species strain ANA-3 (AMR1) (Malasarn et al., 2004; Saltikov and Newman, 2003; Saltikov et al., 2005). The wild type strain ANA-3 is versatile with respect to terminal electron acceptors capable of reducing Fe(III), Mn(IV) and As(V). The mutant type strain ANA-3 (AMR1) is different, in that an As respiring gene arrA and an As detoxifying gene arsC were removed, making it less capable of reducing As. The experiments show that reduction of As may not be required to release As from oxidized Pleistocene sands of Bangladesh. More importantly, both types of *Shewanella* stains converted a significant fractions of As into a more easily mobilizable form. This suggests that microbial community studies of the Bangladesh aquifers are much needed.

### 1.2.4. Chapter 5:

Many studies have attributed As mobilization to the reductive dissolution of As-bearing iron oxyhydroxides , with evidence from Bangladesh (Nickson et al., 1998; Nickson et al., 2000; Zheng et al., 2004), Vietnam (Berg et al., 2001) and Inner Mongolia (Smedley et al., 2003). However, the conditions that lead to arsenic mobilization have not been completely understood.

A detailed hydrochemistry study of the 37 monitoring wells, same as those monitored for time series measurements (Chapter 3) was conducted on samples obtained in January, 2003. Groundwater pH is predominantly near neutral. Shallow Holocene aquifers (<30 m) associated with gray sediments showed a wide range of As (<1 to 600 μg/L) concentration. Deep Pleistocene aquifers associated with orange sediments showed low As (<10 μg/L) (Horneman et al., 2004; Zheng et al., 2005). The majority of As is determined to be As(III). Waters of Holocene aquifers are more reducing than those of deep Pleistocene aquifers. The waters in Holocene and Pleistocene aquifers are of $HCO_3^-$ type. However, Holocene aquifer water is Ca-Mg rich while Pleistocene water is Na-rich. A key finding is that a number of nutrients, including TOC, P, $NH_4^+$ and TN, displayed higher concentrations in the shallow, As-containing aquifer than in the deeper, low-As aquifers. Whether any, or a combination of these nutrients may limit microbial activities in the deep aquifer and the extent of As release warrant further study. Shallow aquifers waters were also super saturated with respect to siderite ($FeCO_3$), vivianite ($Fe_3(PO_4)_2,8H_2O$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) when PHREEQC code was used to examine precipitation reactions. These data suggest that Fe and P are released to the aquifer recently and that decoupling of As concentrations from Fe and P concentrations is not surprising.

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# Chapter 2. A rapid colorimetric method for measuring arsenic concentrations in groundwater

## *2.1. Abstract*

The arsenic content of groundwater consumed by millions of people in the developing world has become a major health concern. We report here an optimization of the colorimetric method of Johnson and Pilson (1972) to accurately measure As concentrations in the <0.03-5.3 μmole/L (<2-400 μg/L) range in groundwater containing 2-30 μmol/L dissolved phosphate. The optimization includes increases in the concentrations of potassium iodate, ascorbic acid, antimonyl tartrate used for sample pre-treatment and color development that significantly lowered the detection limit and shortened the reaction time. Mean recovery obtained for a suite of groundwater samples from Bangladesh spiked with As in the 0.13-13 μmole/L (10-1000 μg/L) range, the linear range of the method, was 97 ± 5% (n=10). The colorimetric method agrees within 10% for As concentrations up to 0.67 μmole/L (50 μg/L) and within 4% in the 0.67-5.3 μmole/L (50-400 μg/L) range with As analysis of the same Bangladesh groundwater samples by high resolution inductively coupled-plasma mass spectrometry.

## *2.2. Introduction*

Arsenic concentrations in drinking water far exceeding the guideline value of the World Health Organization (WHO) (Berg et al., 2001; Smedley and Kinniburgh, 2002) of 0.13 µmole/L (10 µg/L) are reported in many parts of the world and pose a serious health hazard to tens of millions people (BRAC, 2001; Smith et al., 2000; WHO, 2001). The most devastating case of chronic As exposure is found in Bangladesh (BGS & DPHE, 2001). Since the spatial distribution of As in aquifers of the region is highly variable (McArthur et al., 2004; van Geen et al., 2002; van Geen et al., 2003; Zheng et al., 2004), the ability to distinguish high and low As wells through rapid and reliable testing in the field is critical.

Most colorimetric methods for measuring As are based on the Gutzeit (Gutzeit, 1891) method. This classic approach is based on the generation of arsine gas by reduction of As under acid conditions following the addition of zinc powder, and quantifying the arsine by trapping it either in a silver diethyldithiocarbamate solution (Rowe et al., 1973) or on paper impregnated with mercuric bromide. The Gutzeit method suffers from difficulties in the quantitative evolution of small quantities of arsine gas (Jacob and Nagler, 1942). Several inter-comparisons with laboratory results have indicated an effective detection limit of 1.3 µmole/L (100 µg/L) As for various field kits based on this method (BRAC, 2001; Kinniburgh and Kosmus, 2002; Portmann and Riley, 1964; Rahman et al., 2002). The suppression of an interference by hydrogen sulfide in some groundwaters also requires an additional step in the procedure (BGS & DPHE, 2001). Finally, Hassam et al. (1999)

demonstrated that workers using arsine-based kits in poorly-ventilated environments can be exposed to dangerous levels of $AsH_3$, the most toxic form of As.

Johnson (1971) and Johnson and Pilson (1972) first proposed an elegant modification of the standard molybdate-based method for measuring phosphate (P) in natural waters as an alternative to the Gutzeit method. The key to Johnson and Pilson's modification is that As(V) and phosphate form a complex with reduced molybdate that strongly absorbs in the near-infrared part of the spectrum, while As(III) does not. Dissolved As can therefore be quantified from the difference in absorbance between a sample aliquot that is pre-treated to oxidize As(III) (absorbance due to P and As) and another sample aliquot pre-treated to reduce As(V) (absorbance from P only). For a seawater matrix, Johnson and Pilson (1972) showed that their method was convenient, sensitive, and precise (±1.5%) at As levels as low as ~0.013 μmole/L (1 μg/L). The method has been used widely by researchers since then, without significant modification, for analysis also of As in fresh water containing 0-10 μmole/L of phosphate (Haywood and Riley, 1976; Stauffer, 1980, 1983). Most of these recent studies report a detection limit of ~ 0.26 μmole/L (20 μg/L) and a reaction time of at least 1 hour (Lenoble et al., 2003). We report here a series of modifications to the Johnson and Pilson (1972) procedure that significantly reduce both the detection limit and the reaction time.

From the perspective of a molybdate-based method, the main difference between seawater and freshwater, and reducing groundwater in particular, is that P concentrations frequently exceed maximum seawater levels of 3 μmole/L by an order of magnitude (Lenoble et al., 2003; Stauffer, 1983; Strickland and Parsons, 1968).

Our initial tests of the original method with Bangladesh groundwater indicated a systematic 0.4-2.6 μmole/L (30-200 μg/L) underestimate in inferred As concentrations at P concentrations in the 20-80 μmole/L range. We evaluate here the performance of the optimized method in the laboratory and in the field by analyzing a set of groundwater samples from Bangladesh spanning a wide range of As and P concentrations.

## *2.3. Experimental Section*

### 2. 3.1. Instrumentation

The instrument used for most of the optimization experiments was a portable single-beam Hach DR2010 UV-Vis spectrophotometer with an absorbance display at the third decimal place. A more precise double-beam Shimadzu Pharmaspec 1700 spectrophotometer with a stable absorbance read-out at the fourth decimal place was used to determine the detection limit and to measure As concentrations for actual samples in the laboratory and in the field. Unlike previous studies (Johnson and Pilson, 1972; Pattersson and Karlberg, 1997; Stauffer, 1983) reporting different absorbance spectra for P, As, and P+As-molybdate complexes (with maxima centered at 880 nm, 850 nm, and 865 nm respectively), the absorbance spectra of arseno-molybdate and phospho-molybdate complexes formed using optimized reagent concentrations are very similar and show a broad maximum centered between 875-880 nm. Unless noted, absorbance was measured at 880 nm throughout this study.

### 2.3.2. Standards

Stock solutions of 13.3 mmole/L (1000 mg/L) As(V) and As(III) were prepared by dissolving analytical grade (Sigma) sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium *m*-arsenite ($NaAsO_2$) in deionized water. The As(V) solution was preserved with 1 mL/100 mL of concentrated HCl; the As (III) solution with 1 mg/mL of ascorbic acid (Feldman, 1979). Secondary As standards (0.13 mmole/L) were prepared by diluting the stock solutions. A stock solution of 10 mmole/L phosphate was prepared by dissolving $KH_2PO_4$ in deionized water; a secondary standard of 1 mmole/L P was prepared by further dilution.

### 2.3.3. Reagent preparation

The reagents are identical to those of Strickland and Parsons (1968). Deionized (18 MΩ) water and trace-metal grade acids were used for all reagents, standards, and blank solutions. The optimization of the method, described in subsequent sections, resulted in the following final procedure:

(1) A ~ 2 mmole/L $KIO_3$ oxidizing solution for treating one sample aliquot is prepared by dissolving 0.0425 g of potassium iodate in 100 ml deionized water containing 2% hydrochloric acid.

(2) The reducing solution (Johnson, 1971; Johnson and Pilson, 1972) for treating the other sample aliquot requires the preparation of 14% $Na_2S_2O_5$ (736 mmole/L), 1.4% $Na_2S_2O_3$ (89 mmole/L), and 10% $H_2SO_4$ (1.8 mole/L). These three solutions are then mixed in ratios of 2:2:1, respectively. The mixed reducing solution is stable for 6 hours below 30$^{o}$C.

(3) The color reagent that is added to both reduced and oxidized sample aliquots requires the preparation of 10.8% L-ascorbic acid $C_6H_8O_6$ (613 mmole/L), 3% ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (24 mmole/L), 0.56% antimony potassium tartrate $C_8H_4K_2O_{12}Sb_2\cdot 3H_2O$ (8 mmole/L), and 13.98% $H_2SO_4$ (2.5 mol/L). The preparation of these solutions follows the standard procedure (Johnson, 1971; Johnson and Pilson, 1972) with the exception of the higher concentrations of ascorbic acid and antimonyl tartrate determined from the optimization.

Mixing procedure: The solutions of ascorbic acid, ammonium molybdate solution, and potassium antimonyl tartrate are first combined. Sulfuric acid must be added to the mixed solution immediately after the addition of potassium antimonyl tartrate to avoid the generation of turbidity in the color reagent. The mixing ratios of the four reagents are 2:2:1:5, respectively. The solution is stable for 6 hours below $30^{o}$C.

### 2.3.4. Procedure: sample pre-treatment, standard additions, and blank correction

All samples were acidified to 1% HCl immediately after collection. Samples cannot be acidified with nitric acid for analysis by the molybdate method. The presence of nitrate leads to color instability (Stauffer, 1980), inhibits complex formation in the oxidized aliquot, and enhances it in the reduced aliquot. Standard reference materials that are acidified with nitric acid, such as the natural water standard NIST 1640, can therefore not reliably be analyzed by this colorimetric method.

Acidified samples are analyzed by pipetting two 5-ml aliquots into 10 ml vials (Evergreen 240-3615-060). One aliquot is treated with 0.5 ml of oxidizing reagent and the other with 0.5 ml of mixed reducing reagent. If data on As speciation is desired, 0.5 ml of a 2% HCl is added to a third aliquot. The desired redox state of As in both pre-treated aliquots is reached in 10 min and remains stable for at least 3 hours. After waiting for at least 10 minutes, 0.5 ml of color reagent is added to each vial. The color reagent is mixed thoroughly with the sample immediately after addition by shaking and allowed to react for at least 10 minutes before measuring the absorbance. The calibration slope usually was obtained by 2 or 3 replicated analyses of a series of sub-samples that were spiked with standard solutions of As(III) and As(V) to increase the total As concentration by 0.13, 0.67, 2.6, 5.2, 13.3 µmole/L (10, 50, 200, 400, 1000 µg/L) and with P standard solutions to increase concentration by 10, 20, 40 µmole/L, respectively.

One peculiarity of the formation of As-molybdate complexes encountered during this study is that samples containing very little P must be spiked to at least 2 µmole/L P (i.e. to ~0.05 absorbance for a reduced aliquot) because of a P dependence of the rate of color development for As (see sections 3.1 and 3.3). Reagent blanks were therefore also determined by analyzing acidified deionized water spiked with 2 µmole/L P with each set of analyses. A higher absorbance value was consistently observed for the reduced aliquot of spiked deionized water relative to the oxidized aliquot. Differences in absorbance between oxidized and reduced sample of this such solution averaged -0.0010 ± 0.0005 (n=5) for different batches of reagents, which is equivalent to a correction of ~.05 µmole/L (4 µg/L) in As concentration.

## *2.4. Results*

### 2.4.1. Rate of color development

The reaction rate was increased by raising the concentration of potassium antimonyl tartrate, following the suggestion of Murphy and Riley (1962).

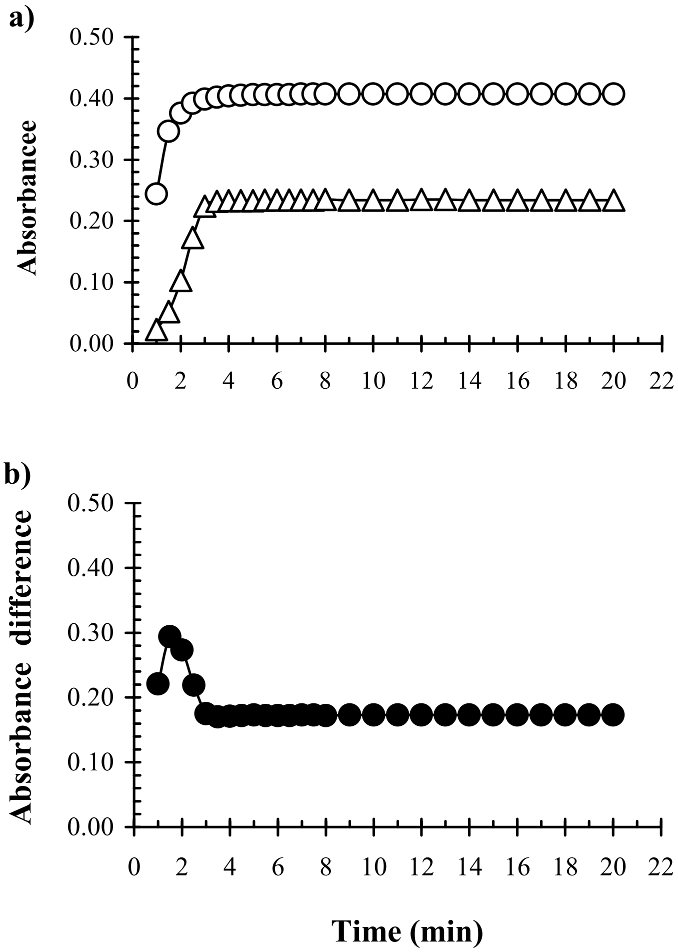

**Figure 2.1.** (a) Rate of color development and stability of the oxidized (○) and reduced (Δ) complexes under optimized conditions shown for a Bangladesh groundwater sample containing 10 µmole/L P and spiked to an As concentration of ~800 µg/L. (b) Absorbance for As (●) as shown by absorbance differences between the oxidized and reduced complexes for the same set of experiments.

The optimal Sb level was determined by spiking deionized water with 13.3 µmole/L (1000 µg/L) As, with equal proportions of As (III) and As(+V), and 20 µmole/L of phosphate, using optimized $KIO_3$ and ascorbic acid concentrations determined in parallel experiments. Potassium antimonyl tartrate concentrations in the color reagent of 0.14%, (the original conditions of Johnson and Pilson , 1972) 0.28%, 0.56% and 1.4% were compared. Based on these results, a concentration of 8 mmole/L (0.56%) was selected, 4 times the concentration used by Johnson and Pilson for the analysis of seawater.

Acidified Bangladesh groundwater containing 10 µmole/L P was spiked with As to a concentration of ~10.7 µmole/L (800 µg/L ) and analyzed using the optimal level of Sb. Maximum absorbance was reached in less than 10 minutes for both the oxidized and the reduced aliquot (Fig. 2.1a). The absorbance difference reached a stable value in 10 minutes (Fig. 2.1b) and remained constant ($\pm$0.001) for an additional hour (data not shown). However, groundwater obtained from a site in Vineland, New Jersey, that is naturally low in P (< 2 µmole/L) required ~ 45 minutes for full color development under the optimized condition. This confirmed that low-P samples must be spiked to at least 2 µmol/L P for As analysis by this method (section 2.3.4). Full color development is reached in 8 minutes for both deionized water (~3 µmol/L spiked P) and groundwater (~8.5 µmole/L P) spiked with 0.13 µmole/L (10 µg/L) As.

## 2.4.2. Oxidizing reagent

Arsenic concentrations in reducing groundwater can exceed 13 µmol/L (1000 µg/L), predominantly in the form of As(III) (Andreae, 1977; Harvey et al., 2002; Zheng et al., 2005). Experiments were therefore conducted to adjust the conditions of the oxidizing pre-treatment by varying $KIO_3$ concentrations between 0.25 mmole/L, the original conditions (Johnson and Pilson, 1972), and 3 mmole/L.

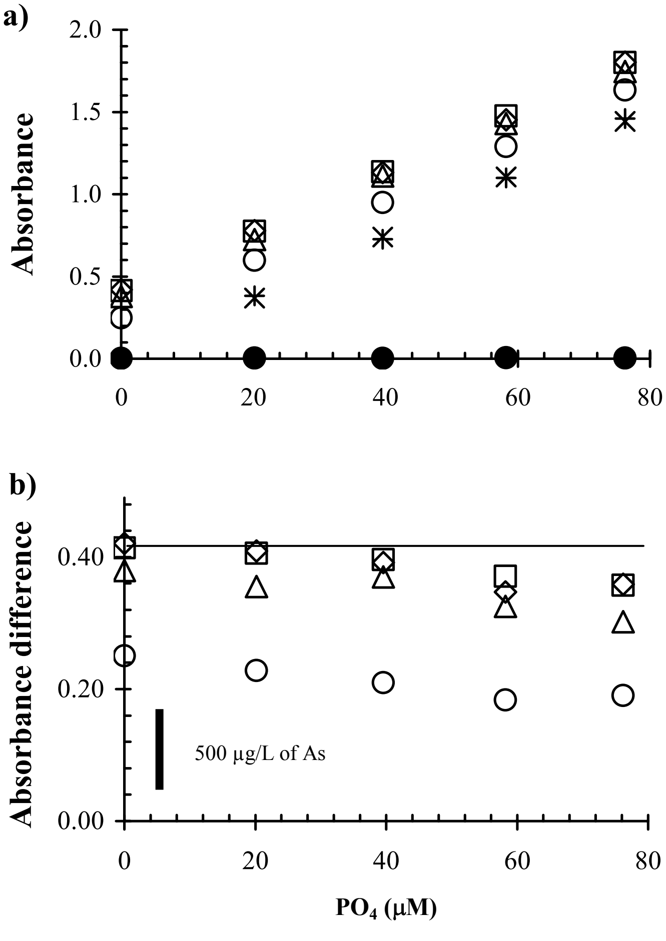

**Figure 2.2.** (a) Absorbance of oxidized and reduced complexes at various $KIO_3$ concentrations [ 3 mM (•), 2 mM (□), 1 mM (◊), 0.5 mM (Δ), 0.25 mM (○)]. The sample analyzed is deionized water spiked with 26.6 µmole/L (2000µg/L) mixed As [As(III)/As(V)-1:1] and incremental $PO_4$ (20-80 µmole/L) concentrations. An additional reduced aliquot [labeled as Red (x)] without As spike was included to compare to that with mixed As spike [labeled as Red spk (+)]. (b) Absorbance difference between oxidized and reduced complexes for the same set of experiments.

For these experiments, deionized water was spiked with 0, 20, 40, 60, and 80 μmole/L P as well as 13 μmole/L (1000 μg/L) As (V) and 13 μmole/L (1000 μg/L) As (III). Because these experiments were conducted at an early stage, absorbance was read at 865 nm instead of 880 nm, the optimal wavelength determined subsequently, and with a color reagent containing 5.4 % ascorbic acid instead of the optimal level of 10.8%. The results show maximum absorbance for an oxidized sample aliquot at a $KIO_3$ concentration of 2 mmole/L (8-fold higher than the conditions of Johnson and Pilson (Johnson and Pilson, 1972), suggesting that As(III) is entirely oxidized under these conditions (Fig. 2.2a). Absorbance differences decrease at lower $KIO_3$ concentrations, indicating incomplete oxidation of 13 μmole/L As(III) at >20 μmole/L P concentrations. The reductions in absorbance difference of 0.004 and 0.026 at 1.0 and 0.5 mmole/L $KIO_3$, respectively, relative to 2 mmole/L are equivalent to an underestimate in As concentration of 0.27 and 1.7 μmole/L (21 μg/L and 130 μg/L). No color was formed after 3 hours at a $KIO_3$ concentration of 3 mmole/L, indicating that the subsequent reduction of molybdate by the color reagent was inhibited by an excess of oxidant (Fig. 2.2a).

### 2.4.3. Elimination of P dependence

The experiments that led to an increase in the optimal concentration of potassium iodate (section 2.4.2) also showed a systematic decline in the difference in absorbance between oxidized and reduced aliquots with increasing P concentration, regardless of the $KIO_3$ concentration, and at a constant As(III+V) concentration (Fig.

2.2b). This P dependence, which to our knowledge has not been reported previously, translates into an underestimate of As concentrations of 0.4-2.7 μmole/L (30-200 μg/L) in water containing 20-80 μmole/L P. The origin of the P dependence of the absorbance difference between oxidized and reduced aliquots was investigated by measuring, in addition, color development for samples without pre-treatment.

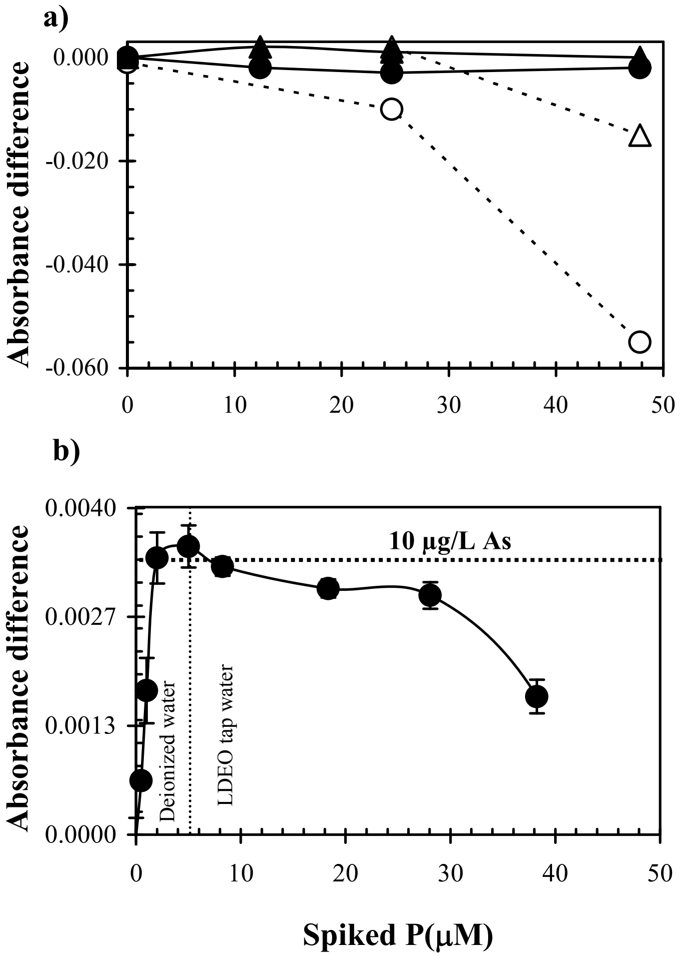

**Figure 2.3.** (a) Absorbance difference between oxidized and reduced /untreated complexes for LDEO tap water spiked at various P levels at two different concentrations of ascorbic acid in the color reagent. Open circle (○) and open triangle (Δ) show the absorbance difference between oxidized - reduced and oxidized-untreated complex respectively with 5.4% ascorbic acid. Solid circles (●) and triangles (▲) show absorbance differences for [oxidized – reduced] and [oxidized-untreated] aliquots, respectively, using 10.8% ascorbic acid . (b) Absorbance differences (●) between oxidized and reduced complexes under optimized conditions (10.8% ascorbic acid) for deionized water and LDEO (Lamont-Doherty Earth Observatory) tap water spiked at various P concentrations are also shown.

These experiments were conducted with LDEO tap water containing <0.001 µmole/L (<0.1 µg/L) As and 4 µmole/L P, and with additions of 12, 25, 48 µmole/L P. Under the initial conditions of Johnson and Pilson (Johnson and Pilson, 1972), modified by increasing the concentrations of $KIO_3$ and Sb, the reduced aliquot produced the highest absorbance, followed by the untreated and the oxidized aliquots (Fig. 2.3a). This suggested that $KIO_3$ in the oxidizing reagent suppressed the color formation and/or that $S_2O_5/S_2O_3$ in the reducing reagents enhanced color formation. Lowering the $S_2O_5/S_2O_3$ concentration led to insufficient reduction of the As(V) spike, however. Therefore, the amount of ascorbic acid in the color reagent was instead increased to compensate for the suppression caused by the higher $KIO_3$ concentration. The P dependence of the absorbance difference between oxidized and reduced or untreated aliquots was considerably reduced when the concentration of ascorbic acid in the color reagent was doubled to 10.8 %, which is close to saturation (Fig. 2.3a). As a final test, deionized water spiked with 0.13 µmole/L (10 µg/L) As and 0, 0.5, 1, 2, 5 µmole/L P and LDEO tap water spiked with 0.13 µmole/L (10 µg/L) As and 0, 10, 20, 30, 40 µmole/L P, was treated with the optimized reagents and the higher ascorbic acid concentration. Measurements with the double-beam spectrophotometer show a plateau in absorbance difference corresponding to 0.13± 0.01 µmole/L (10±1 µg/L) across the 2-30 µmole/L range in P concentrations (Fig. 2.3b). The series of experiments also confirms that samples must contain at least 2 µmole/L P to obtain accurate results.

## 2.4.4. Absorbance spectra of As-Mo and P-Mo complexes

Johnson and Pilson (1972) and Stauffer (1983) observed that the absorbance spectra for arseno-molybdate and phospho-molybdate complexes are not identical, with absorbance maxima at ~865 and ~885 nm, respectively.

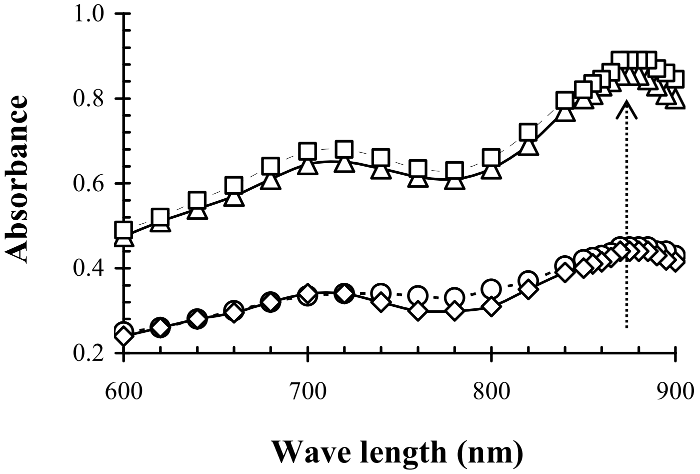

**Figure 2.4.** Absorbance spectra for samples of LDEO tap water spiked with 1500 µg/L (20 µmole/L) As (○), 20 µmole/L P (◊), 20 µmole/L of As plus 20 µmole/L P (Δ), sum (calculated) 20 µmole/L of As and 20 µmole/L P (□).

We revisited this issue by obtaining absorbance spectra using the optimized reagents for three aliquots of New York City tap water (2 µmole/L P, <0.1 µg/L As) spiked with (a) 1500 µg/L As only, (b) spiked with 20 µmole/L P only, and (c) spiked with 1500 µg/L As (i.e. 20 µmole/L As) and 20 µmole/L P. Absorbance was measured between 600 and 900 nm within 15 min using the single-beam spectrophotometer. The absorbance spectra of arseno-molybdate and phospho-molybdate complexes formed separately were very similar and showed a broad maximum centered on ~875-880 nm (Fig. 2.4). Similar results were obtained with the more precise double-beam UV/Vis- spectrophotometer. The maximum absorbance of tap water spiked with both 20 µmole/L As and 20 µmol/L P (0.890), however, was 4% lower than sum of absorbances obtained for tap water spiked with As and P separately (0.855).

### 2.4.5. Preliminary tests on arsenic speciation

Although this was not the primary focus of this study, the colorimetric method also provides a means of determining As speciation. No color complex was observed when LDEO tap water was spiked with organic species such as monomethyl arsonic acid (MMA) and dimethyl arsinic acid (DMA). As originally pointed out by Johnson and Pilson (1972), the inclusion of a third aliquot sample without pre-treatment also allows the determination of the proportion of As(III) and As(V) in a sample.

**Table-2.1.** Field inter-calibration results for As speciation in Vineland groundwater (VGW)

| **Sample Identification** | **As III+V (µg/L)** | | **AsIII (µg/L)** | | **Total As (µg/L)** | **% Org. As** |
|---|---|---|---|---|---|---|
| | **Color** | **DPCSV** | **Color** | **DPCSV** | **GFAAS** | **Calculated** |
| VGW-1 | 15 ± 0.3 | 16.2 ± 1.8 | <2 | 1.9 ± 0.5 | 23 | 35 |
| VGW-2 | 119 ± 2.6 | 127 ± 10 | 114 | 100 ± 9.1 | 124 | 4 |
| VGW-3 | 1391 ± 30.8 | 1319 ± 41 | 969 | 1173 ± 70 | 1872 | 26 |
| VGW-4 | 1078 ± 23.9 | 907 ± 45 | <2 | 3 ± 0.4 | 1193 | 10 |
| VGW-5 | 1421 ± 31.5 | 1450 ± 135 | <2 | 4.5 ± 1 | 1563 | 9 |
| VGW-6 | <2 | 2.5 ± 0.9 | <2 | N.D. | <5 | |

Variation (±) indicates std dev of mean As concentration obtained from 3 replicated tests of same sample

The method was applied to inorganic and organic arsenic containing Vineland groundwater (Vineland, NJ) on site using a sensitive differential pulse cathodic stripping voltammetry (DPCSV) method (He et al., 2004). Concentration of As(III) and As(V) determined by colorimetric method were compared with measurements by DPCSV and GFAAS (graphite furnace atomic absorption spectrophotometer) (Table-2.1). Further, the predominance of As(III) in Bangladesh groundwater previously determined by anion exchange (Zheng et al., 2004) as well as DPCSV was indeed confirmed by the colorimetric method (data not shown).

## *2.5. Discussion*

### 2.5.1. Detection limit and precision

The precision and detection limit of the colorimetric method was evaluated with repeated analyses of acidified deionized water, LDEO tap water, and acidified Bangladesh groundwater with the double-beam spectrophotometer (Table-2.2a). Replicate analyses of deionized and LDEO tap water containing <0.001 µmole/L (0.1 µg/L) As indicate a detection limit of ~ 0.026 µmole/L (2 µg/L), calculated as three times the standard deviation of replicate absorbance differences measured for each sample . This is not inconsistent with a slightly lower reproducibility of ±1-1.5 µg/L (Table 2.2a) obtained for two low-As groundwater samples containing 3 and 5 µmol/L P analyzed in the field in Bangladesh under sub-optimal conditions (i.e. under generator power and high humidity). With the single-beam spectrophotometer, the detection limit could not be lowered beyond 0.09 µmole/L (7 µg/L). This is the result of the lower precision of the single-beam instrument, possibly compounded by a display limited to the 3rd decimal place since a 0.001 absorbance difference between an oxidized and a reduced aliquot corresponds to ~0.05 µmole/L (4 µg/L) in As concentration.

**Table-2.2.** Detection limit, accuracy and precision

**a) Detection limit in the different matrices**

| Sample Identification | Phosphate (µM) | Mean absorbance Difference | Arsenic (µg/L) This method | HRICP-MS |
|---|---|---|---|---|
| Deionized water | 2 (spiked) | 0.0001 ± 0.00015 | 0.4 ± 0.7 (n=5) | <0.1 |
| LDEO tap[a] | 8.2 | 0.0000 ± 0.00013 | 0.1 ± 0.6 (n=6) | <0.1 |
| BGW-1 | 3 | 0.0001 ± 0.00023 | 0.3 ± 1.0 (n=3) | 0.6 |
| BGW-2 | 5 | -0.0004 ± 0.00036 | -1.8 ± 1.5 (n=4) | 0.1 |

**b) Recovery of arsenic in LDEO tap water**

| Sample Identification | Phosphate (µM) | Spiked As (µg/L) | Arsenic (µg/L) This method |
|---|---|---|---|
| LDEO tap | 8.2 | 0 | 0.1 ± 0.6 (n=6) |
| LDEO tap | 8.2 | 10 | 12 ±1 (n=5) |
| LDEO tap | 8.2 | 50 | 53 ± 1 (n=4) |
| LDEO tap | 8.2 | 100 | 100 ± 1 (n=4) |
| Spiked LDEO tap[b] | 45 | 320 | 314 ± 4 (n=3) |

Shimadzu UV-Vis spectrophotometer was used for all colorimetric measurements
BGW (Bangladesh Groundwater) samples were analysed in the field.

[a] LDEO tap water is groundwater

[b] Laboratory control sample (31) and measured arsenic by HRICPMS 320 ± 2 µg/L (n=26).

## 2.5.2 Accuracy based on comparison with HR ICP-MS

Arsenic concentrations determined by colorimetry were compared with measurements by high-resolution inductively coupled plasma-mass spectrometry (HR ICP-MS). This reference method requires only 0.5 mL of samples diluted 10-fold in 2% $HNO_3$ and is applicable to a wide range of matrices (Cheng et al., 2004). The selection of a resolution of 12000 eliminates the isobaric interference with As determinations from Ar-Cl. The method has a detection limit of 0.001 µmole/L (0.1

μg/L) As and a precision of ~ 2%. Samples were acidified to 1% HCl immediately after collection for HR-ICPMS analysis within 10 days of sample collection.

**Table-2.3.** Comparison of the analyses with the laboratory analyses of same samples including spikes by HR ICP-MS.

| Sample Identification | Phosphate (mM) | Arsenic (μg/L) This method | Arsenic (μg/L) HR ICP-MS |
|---|---|---|---|
| **BGW-1** | 36 | 13 ± 1 (n=5) | 13 |
| Spiked (+100 μg/L) | | 108 | 112 |
| **BGW-2** | 23 | 34 ± 1 (n=2) | 39 |
| Spiked (+100 μg/L) | | 122 | 135 |
| **BGW-3** | 24 | 41 ± 1 (n=2) | 43 |
| Spiked (+100 μg/L) | | 130 | 137 |
| **BGW-4** | 31 | 78 ± 1 (n=2) | 85 |
| Spiked (+100 μg/L) | | 166 | 180 |
| **BGW-5** | 3 | <2 ± 1 (n=3) | 1 |
| Spiked (+100 μg/L) | | 101 | 99 |
| **BGW-6** | 2 | 44 ± 1 (n=5) | 39 |
| Spiked (+100 μg/L) | | 143 | 153 |
| **BGW-7** | 5 | 67 ± 1 (n=5) | 60 |
| Spiked (+100 μg/L) | | 178 | 165 |
| **BGW-8** | 19 | 228 ± 3 (n=4) | 225 |
| Spiked (+100 μg/L) | | 322 | 333 |
| **BGW-9** | 5 | <2 ± 1 (n=4) | 0 |
| Spiked (+100 μg/L) | | 103 | |
| **BGW-10** | 33 | 223 ± 1 (n=6) | 243 |
| Spiked (+100 μg/L) | | 322 | 372 |

Bangladesh Groundwater (BGW) samples were analysed in the field.

The optimized method was used in Bangladesh to analyze in the field a representative suite of 10 groundwater samples containing 2-36 μmole/L P (Table 2.3). The same samples were also spiked with 1.3 μmole/L (100 μg/L) As. HR ICP-

MS measurements for the combined set of samples span a range of 0.001-4.9 µmole/L (0.1 to 370 µg/L) As and indicate a mean recovery of the spike of 101±5%. The colorimetry results obtained in the field are consistent with the HR ICP-MS results within 0.067 µmole/L (5 µg/L) in the <0.03-0.67 µmole/L (2-50 µg/L) As range and within 5% at higher concentrations (Table-2.3). The mean recovery calculated on the basis of the colorimetric measurements (97 ± 5%) indicates no significant matrix dependence of the response, even though the samples also spanned a wide range of Si (400-1200 µmole/L) and Fe (4-180 µmole/L) concentrations (Stauffer, 1983).

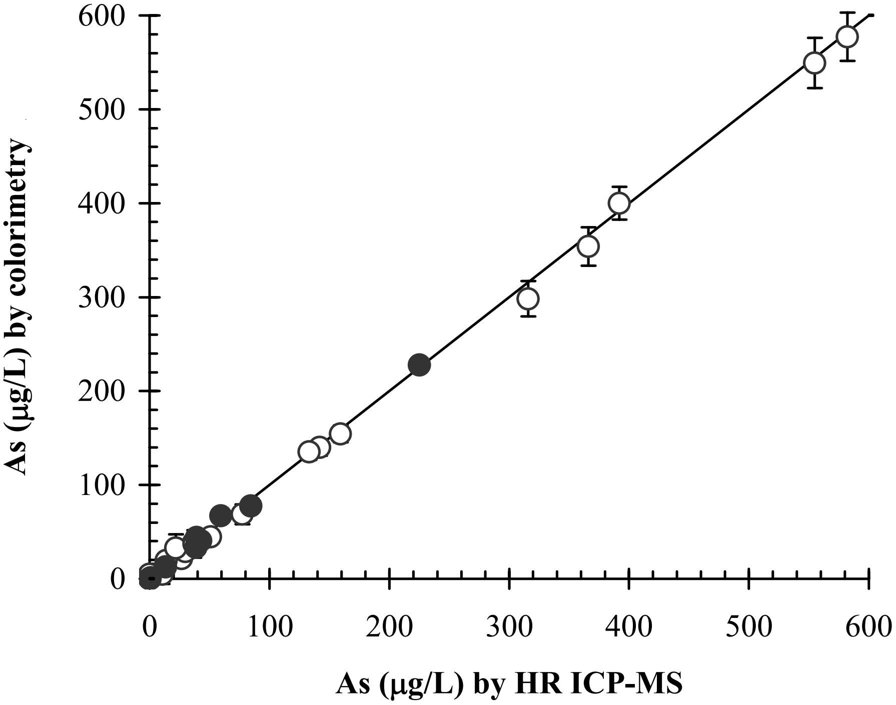

**Figure 2.5.** Comparison of As concentrations in a set of Bangladesh groundwater samples (n=10) determined with a double-beam spectrophotometer in the field and HR ICP-MS (●). Also shown is a set of measurements (n=28) with a single-beam spectrophotometer (○) . Errors bars indicate the estimate uncertainty determined by propagating the most significant digit (0.001) of readings for the single-beam instrument and absorbance underestimation (0.001) due to high P (> 40µM) and standard deviation of 3 or more replicates.

Other potential interferences were not tested, but seem unlikely given the wide range of applicability of the phosphate method itself and the good match between colorimetric and HR ICP-MS for a broad suite of groundwater samples. A larger set of Bangladesh groundwater samples (n=28) was also analyzed in the laboratory with the single-beam spectrophotometer. Although the measurements are less precise because of the limits the instrument, they are also consistent within 0.13 μmole/L (10 μg/L) for As concentrations up to 0.67 μmole/L (50 μg/L) and within 4% in the 0.67-8.0 μmole/L (50-600 μg/L) with the HR ICP-MS data (Fig. 2.5).

## *2.6. Conclusion*

The method of Johnson and Pilson (Johnson and Pilson, 1972) optimized for measuring As in groundwater offers several significant advantages over existing methods relying on arsine generation. The method is relatively fast and the detection limit is below the WHO guideline value for As in drinking water of 0.13 μmole/L (10 μg/L), even if a portable and moderately-priced single-beam spectrophotometer is used. The reagent cost is on the order of $0.01 per test at US prices. No toxic arsine is generated and no major interferences were identified across a representative range of sample matrices.

The method can also determine inorganic speciation by including a sample aliquot without pre-treatment in the analysis. Our preliminary tests also indicate that no color complex is formed with organic species such as monomethyl arsonic acid (MMA) and dimethyl arsinic acid (DMA). This suggests that the concentration of organic As species could potentially be determined by difference relative to a measurement of total As by, for instance, HR ICP-MS.

## 2.7. Acknowledgements

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# Chapter-3. Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihazar, Bangladesh

## *3.1. Abstract*

Samples were collected every 2-4 weeks from a set of 37 monitoring wells over a period of 2-3 years in Araihazar, Bangladesh, to evaluate the temporal variability of groundwater composition for As and other constituents. The monitoring wells are grouped in 6 nests and span the 5-91 m depth range. Concentrations of As, Ca, Fe, K, Mg, Mn, Na, P, and S were measured by high-resolution ICPMS with a precision of 5% or better; concentrations of Cl were measured by ion chromatography. In shallow wells <30 m deep, As and P concentrations generally varied by <±30%, whereas concentrations of the major ions (Na, K, Mg, Ca and Cl) and the redox-sensitive elements (Fe, Mn, and S) varied over time by up to ±90%. In wells >30 m deep tapping deeper aquifers, concentrations of groundwater As were much lower and varied by < ±10%. The concentrations of major cations also varied by < ±10% in these deep aquifers. In contrast, the concentration of redox-sensitive constituents Fe, S, and Mn in deep aquifers varied by up to ±97% over time. Comparison of the time series data with groundwater ages determined by $^{3}H/^{3}He$ and $^{14}C$ dating shows that large seasonal or interannual variations in major cation and chloride concentrations are restricted to shallow aquifers and groundwater recharged <5 years ago. In contrast, the monsoon cycle appears to have little impact on As

concentrations even in shallow aquifers, possibly because of chemical buffering or because the spatial distribution of As is homogeneous relative to groundwater transport over the duration of the observations. The data also indicate coupled behavior of As and P in groundwater with $^{3}$H/$^{3}$He age between 5-25 years and decoupling between variations in As and Fe concentrations. At two sites where the As content of groundwater in existing shallow wells averages 100±135 (n=118) and 270±96 (n=65) μg/L, respectively, an observed systematic long-term decline in As concentrations supports the notion that flushing may slowly deplete an aquifer of As.

## 3.2. Introduction

The spatial variability of groundwater As concentrations ([As]) at scales of $10^{1}$ to $10^{4}$ m has been well documented for Holocene (<10 kyr old) fluvial-deltaic aquifers of the Ganges-Brahmaputra Delta (GBD) region (BGS & DPHE, 2001; van Geen et al., 2003; Yu et al., 2003). There is growing evidence that at least part of this heterogeneity can be attributed to variations in local geology and its effect on shallow groundwater flow(Aziz et al., in review; Stute et al., in review; van Geen et al., 2006; Weinman et al., in review). Such spatial variability naturally leads to the concern that shallow groundwater [As] may also change over time, especially because subsurface flow is likely to be affected by large water withdrawals for irrigation in certain areas of Bangladesh (Harvey et al., 2002; Klump et al., 2006). The persisting gaps in our knowledge of the mechanisms that lead to As mobilization (Zheng et al., 2004; Polizzotto, et al., 2005), combined with pronounced seasonal fluctuations in water levels in shallow and deep aquifers linked to the monsoon, make it particularly difficult to predict variations of groundwater [As] over space or time. Yet, this understanding is urgently needed because a significant proportion of those shallow wells that presently meet the Bangladesh drinking water standard of 50 μg/L are, at least temporarily, shared by villagers of Bangladesh to reduce their exposure to As and therefore reduce the likelihood of contracting a series of debilitating diseases (Opar et al., 2006; van Geen et al., 2002).

High-quality time series data of groundwater [As] from the GBD are few (Cheng et al., 2006). With the exception of very shallow (<10 m deep) wells, the available data generally indicate little seasonality or long-term trends (BGS & DPHE, 2001; Cheng et al., 2005; van Geen et al., 2005). On a different continent, little change in [As] was also reported for 759 wells from western Nevada, USA, where concentrations ranging from <5 to 6200 μg/L were measured in the same wells over a period of 1–20 years apart (Steinmaus et al., 2005).

Other time series data indicate some degrees of As variations in groundwater, although in the case of data from GBD, they are not the most convincing due to either poor sampling resolution with time or unknown analytical quality. A striking example was the case of a highly-contaminated private well of unreported depth at Ramnagar in West Bengal, India, that was monitored biweekly between July 1992 and June 1993 and showed occasional variations of ~30% around an average of ~2700 μg/L (Chatterjee et al., 1995). The same group observed a long term rise in groundwater As concentration in a number of private wells in 23 villages out of 100 villages of West Bengal where initially low [As] (<50 μg/L) water exceeded 50 μg/L over time, although the data were not reported (Chakraborti et al., 2004; Chakraborti et al., 2002). Large seasonal variations of groundwater As levels were also reported in 5 monitoring wells at depths of 3-60 m in Samta village of Western Bangladesh (AAN, 1999), although the measurements of As were few and made by a less reliable method (silver dithiodicarbamate spectrometry) in a local laboratory. More convincing was the evidence of lower [As] in many of 68 wells sampled in May 2000 in four districts of the Red River delta in Vietnam compared to well water from the same wells collected in September and December, 1999 (Berg et al., 2001). Naturally occurring As in groundwater of Granite Falls, Washington, ranging in concentration from <10 µg/L to 14,000 µg/L also showed substantial temporal variability of 12-79 % for 15 out of 25 private drinking water monitored over 12 months (Frost et al., 1993).

With the present study, we contribute to the body of groundwater monitoring data by presenting up to 3 years of bi-weekly to monthly measurements of As, P, Fe, Mg, Ca, K, Na, Mn, S, and Cl in groundwater at 6 well nests consisting of a total of 37 monitoring wells installed in Araihazar, Bangladesh. The monitoring wells tap aquifers from 5-91 m ranging over a wide range in [As] of <5 to 600 µg/L in an area where previous studies have documented a spectrum of hydrogeological conditions that is representative of much of the GBD (Horneman et al., 2004; van Geen et al., 2006; Zheng et al., 2005). In section 3, we describe the main temporal patterns in groundwater chemistry, including long-term trends, short-term excursions, and seasonal variations in both shallow and deep aquifers. The variations in groundwater major ion composition, or mostly lack thereof, are then discussed in section 4.1 in the context of groundwater ages. We focus on the decoupling between groundwater As and redox sensitive constituents in section 4.2 before discussing trends of As in our time series data in section 4.3. Section 4.4 concludes the discussion with a comparison of the behavior of As and P in shallow aquifers of Araihazar.

## 3.3. Methods

### 3.3.1. Monitoring wells

The locations of the well nests were chosen to cover the spatial patterns of groundwater As concentrations established by a previous survey of 6000 wells distributed over a ~25 $km^2$ area of Araihazar in central Bangladesh (van Geen et al., 2003). A total of 37 monitoring wells ranging from 5-91 m in depth were installed at 6 sites (Fig.3.1, Table 3.1). At each of the sites, 4 or 5 monitoring wells tapped shallow aquifers composed of Holocene alluvial deposits ranging from 15-30 m in thickness (Fig. 3.1). The sites were arranged in most figures according to increasing average concentrations of existing shallow (< 30 m) wells within the 0.16 $km^2$ area centered by each of the nest of wells: 18±26 μg/L at Site F, 19±53 μg/L at Site C, 65±69 μg/L at Site E, 94±59 μg/L at Site G, 102±135 μg/L at Site A, and 272±96 μg/L at Site B (Fig. 3.1). At all locations except for Site B, at least one monitoring well >30 m deep reached distinctly orange/brown colored sands of presumed Pleistocene age (Fig. 3.1). At site B, even the monitoring well that was installed at a depth of 91 m could only reach grey Holocene sediments (Zheng et al., 2005). At each site, one or several layers of fine-grained sediment separate the shallow aquifers that are elevated in [As] from the deep aquifer that are low in [As] (Fig. 3.1).

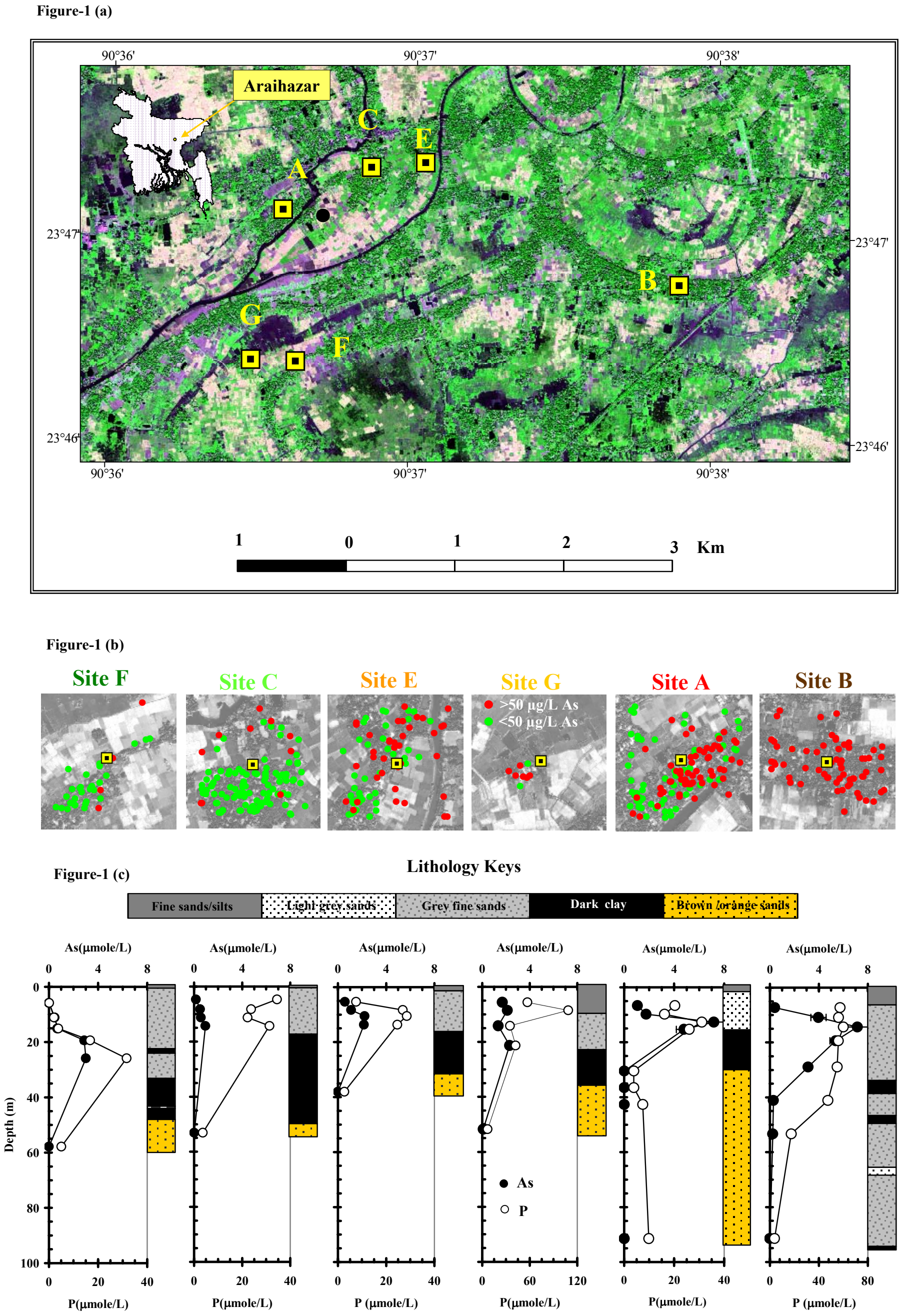

**Figure 3.1.** **(a)** Locations of six nests of wells on IKONOS image of Araihazar study area in central part of Bangladeshis (Inset). **(b)** The 400 m x 400 m squares represent an enlarged view of the spatial distribution of As in existing wells surrounding the 6 well nests. Green and red solid circles indicate the As level < 50 µg/L or greater or equal to 50 µg/L, respectively. Sites F, C, E, G, A, B are arranged from left to right and color coded with increasing average [As] concentration in the surrounding wells located in the 400 m x 400 m squares. **(c)** The depth profiles of average groundwater [As] and [P] for all sites. The scales for [P] were different for Sites G and B. A lithology sketch is placed next to the vertical profile at each site.

### 3.3.2. Sampling and field measurements

Bi-weekly to monthly groundwater samples from the monitoring wells were collected from Jan. 2001 to Feb. 2004 at Sites A and B, and from March 2002 to Feb. 2004 at Sites C, E, F and G. Each well was pumped for at least 15 minutes by a battery-driven submersible pump (Whale SuperPurger) at a rate of ~ 2 L/min. The 15 minutes of pumping allowed conductivity and temperature readings to stabilize before sampling. Samples for As, other trace elements, and major cations were collected in 30-ml or 60-ml acid-cleaned HDPE bottles and acidified to 1% HCl (Fisher Optima) immediately after collection and without filtration. We, and others before us, have shown that the standard monitoring well screens in Bangladesh are typically sufficient to exclude particles that might dissolve upon acidification, whereas filtration can produce artifacts unless carried out under nitrogen (Zheng et al., 2004). Samples for anions were collected in nanopure-washed 30-ml HDPE bottles without filtration. Starting in April, 2004, pH, Eh, temperature, and electrical conductivity of the groundwater was measured using a pH/Eh meter (Orion 210A) and a conductivity/temperature meter (Orion 105A+) with waterproof probes that were calibrated on the day of sampling. The groundwater level in each well was monitored every 1-2 weeks over the same time period using an electric water-level meter (Solinst model 101).

### 3.3.3. Laboratory measurements

Concentrations of As, P, Fe, Mn, S, Ca, Mg, K, Na and 33 other trace elements in acidified groundwater were measured at Lamont-Doherty Earth Observatory with a reproducibility typically <5% by high-resolution inductively-coupled plasma mass spectrometry (HR ICP-MS) using an Axiom single-collector instrument (Thermo Elemental, Germany) (Cheng et al., 2004). Protocols that were followed to ensure the accuracy and precision of the data included: (1) Two NIST standard reference materials (1640 & 1643E, Trace element in natural water), and an internal laboratory consistency standard (LDEO tap water spiked with analyte elements) were included with each run. Results for these standards were always within 5% of the certified values after calibration of the instrument with separate standards at the beginning and end of each run (Cheng et al., 2004); (2) Whenever possible, time-series samples from the same well were analyzed within the same run of 30 samples, which usually improved the reproducibility to <3%; (3) At least 2 samples were re-analyzed between two consecutive runs for the same well to ensure consistency between runs. Concentrations obtained for these replicates usually did not differ from each other by more than 3%.

Dissolved $Cl^-$ and $SO_4^{2-}$ concentrations in un-acidified groundwater samples were measured at Queens College by ion chromatography (IC) using a DIONEX-500 IC system, following the standard protocol of EPA method 300. Comparison of $SO_4$ data obtained by IC with total S concentrations in acidified samples obtained by HR ICP-MS showed that S quantified by HR ICP-MS was essentially all in the form of sulfate at all sites (slope of S by ICPMS versus $SO_4$ by IC is 1.0027, $R^2$: 0.9812, n=181).

In addition to measurement by HR ICP-MS, phosphate presented in groundwater was also quantified as dissolved reactive phosphate (DRP) using molybdate-blue colorimetry, modified to determine also dissolved As (Dhar et al., 2004). A comparison of colorimetric and HR ICP-MS data indicates that not all P present in groundwater reacts with molybdate. At sites A and B, total P concentrations in shallow (< 30 m) groundwater measured by HR ICP-MS were consistently higher by 30 % ($R^2 = 0.99$, n=11) than DRP concentrations for samples collected in January 2003, suggesting that a fraction of the P could be in a non-reactive organic form (Stauffer, 1980). In contrast, total P concentrations measured by HR ICP-MS were only ~ 10% and 5 % higher than DRP concentrations in shallow groundwater from Site C and Site F, respectively, for 2 sets of samples collected in Jan. 2003 and Oct. 2003 (Site C: $R^2 = 0.99$, n = 4; Site F: $R^2 = 0.99$, n = 6).

### 3.3.4. Statistical analysis

The rate of increase or decrease per year in 37 shallow and deep wells was examined by performing a regression analysis of [As], [P] and other ions concentration versus time for each well over the entire period except for C where the post summer 2003 flood period was excluded (Nov. 2003 to Feb. 2004, Fig. 3.2) because of a very large change in Na and Cl. Trends of different constituents including As, P, sum of major catios (SMC), Cl, Fe, Mn and S were considered to be statistically significant if $p$ values were <0.05. For most wells, the residuals were randomly and normally distributed around the linear trend line. The uncertainties in the rate of increase or decrease (e.g. the slope of regression) were expressed as 95% confidence intervals.

## *3.4. Results*

The temporal data of both shallow (<30 m) and deep (>30 m) groundwater As, SMC (2[Ca]+2[Mg]+[Na]+[K]) are plotted as the ratio ($C/C_{avg}$) of the concentration at the time of the sampling (C) vs. the average concentration of the entire time series ($C_{avg}$) for Sites F, C, E, G, A to B (Figs. 3.2, 3.3). Similar plots for other constituents are included as supplemental material. The depth profiles of variation in concentration of groundwater constituents including As, P, SMC, Cl, Fe, Mn and $SO_4$ are shown for both shallow and deep aquifers of all 6 sites, with the variation expressed as %RSD (Fig. 3.4). A significant temporal trend of [As] is observed for 11 out of 37 wells in both the shallow and deep Holocene aquifer (Table 3.2). A significant decrease in [As] over time is observed at 9 wells; a significant increase is recorded at only 2 wells. Correlation coefficients (R) for As trends in these wells varied from 0.5 to 0.85. The 26 wells that did not show statistically significant trends include most of the shallow and deep wells with a very low As (<10 µg/L) content (Table 3.2).

### 3.4.1. Water levels

Water levels in shallow and deep monitoring wells varied seasonally from 2-3 m above sea-level (asl) during the dry season to 6-7 m asl during the wet season in both shallow and deep monitoring wells (Figs. 3.2 and 3.3). Lack of water level data for the period July-October 2003 in both shallow (Fig. 3.2) and deep aquifers (Fig. 3.3) at low-lying Sites C, E, and G indicate that the monitoring wells were not accessible due to particularly pronounced flooding. The fluctuations in water levels tracked each other within ~0.3 m in all shallow (<30 m) monitoring wells over a period of 3 years. In contrast, the deep wells from the Pleistocene deep aquifer could be grouped in two categories, with water levels at fresh water Sites A and C remaining ~ 2 m below water levels at more saline water Sites E, F, and G throughout the seasonal cycle (Fig. 3.3).

## 3.4.2. Chemistry of shallow aquifers

### *3.4.2.1. Arsenic*

Concentrations of As in groundwater sampled from the 26 shallow (<30 m) monitoring wells spanned three orders of magnitude, from <1 μg/L at F-6 m to 600 μg/L at A-13 m and B-14 m. Groundwater [As] generally increased with depth starting from the shallowest monitoring well, peaks at ~ 15 m at Sites A, B, C and E and at ~ 20 m at Sites F and G, and then declined again towards the deeper part of the shallow aquifer (Fig. 3.1).

*3.4.2.1.1. Trends.* Overall, the temporal variability of [As] observed in the 26 shallow monitoring wells was limited (Fig. 3.2), with a relative standard deviation (RSD) <19% over a monitoring period of up to 3 years (Table 3.1). However, linear regression of [As] as a function of time indicated that there were statistically significant long-term trends ($p<0.05$) for 11 wells out of a total of 26 shallow monitoring wells (Table 3.2). The largest decreases of -19 to -41 μg/L $yr^{-1}$ were observed at Sites A, B and F for 5 wells containing > 200 μg/L [As]. In contrast, monitoring data for one well at Site E and one well at Site G, both containing ~150 μg/L [As], showed average increases of +19 and +14 μg/L $yr^{-1}$, respectively.

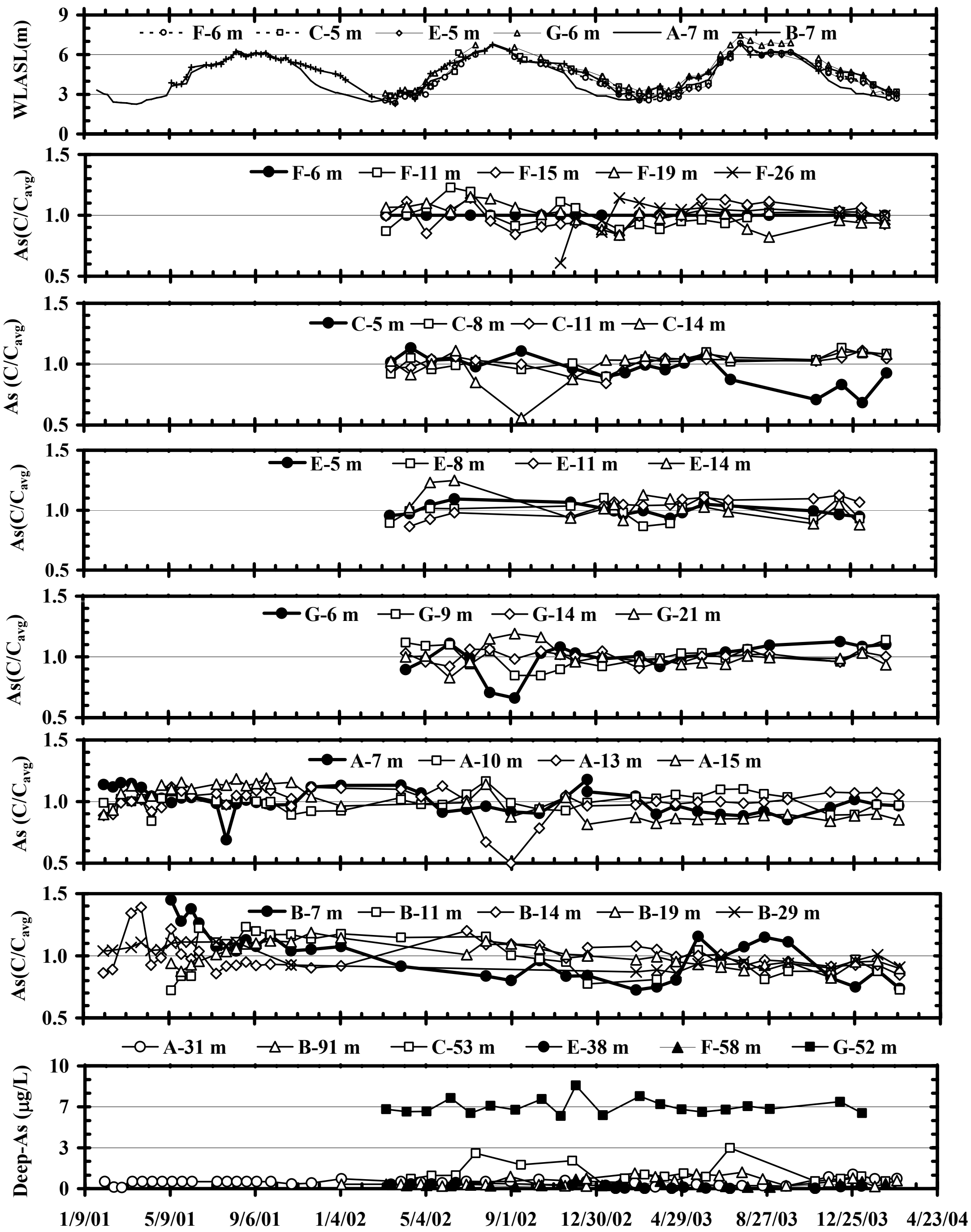

**Figure 3.2.** Water level above sea level (WLASL) spanning the entire monitoring periods from the shallowest well of each site is shown in the upper most panel. The rest of the panels from top to bottom show in sequence, the temporal variability of [As] in shallow aquifers for Sites F, C, E, G, A, B, and in the deep aquifers. Dissolved [As] are plotted as the ratio (C/C$_{avg}$) of the concentration at the time of the sampling (C) versus the average concentration of the entire time series (C$_{avg}$). In each of the shallow aquifer panel, the bold line always represents the shallowest well at a site.

*3.2.1.2. Excursions.* In addition to these long-term trends, there were noteworthy reductions of ~50% in groundwater [As] of shorter duration at three different sites starting July-August 2002: C-14 m, G-6 m and A-13 m (Fig. 3.2). By November 2002, however, [As] in all three wells had returned to within 10 µg/L of their respective long-term averages. A different situation was observed during the particularly severe flooding season of 2003 when, at well C-5 m and only in this well, a drop from 14 to ~9 µg/L in [As] was sustained over several months (Fig. 3.2).

*3.2.1.3. Seasonality.* Only a single well A-7 m, the shallowest at site A, exhibited seasonal variations in groundwater [As] that were consistent from year to year (Fig. 3.2). The amplitude of the fluctuations was on the order of ~10 % around a mean [As] of 80 µg/L, with lower concentrations corresponding to the wet season (May and October). There may also be a connection between [As] and water level at B-7 m, but it was limited to 2003 and in this case [As] concentrations were high during the wet season.

### ***3.4.2.2. Phosphorus***

As in the case of [As], concentrations of phosphorus (P) in shallow groundwater spanned three orders of magnitude: from 0.11 ± 0.07 µmole/L at F-6 m to 108 ± 23 µmole/L at G-9 m (Table 3.1). The contrast between these two monitoring wells was particularly striking because they are only 400 m apart and their depths are comparable (Fig. 3.1). Depth profiles of groundwater [P] profiles at Sites A, E. and F were broadly similar in shape to their corresponding [As] profiles, at an average atomic P:As ratio of 11±6. For at least one shallow monitoring well at Sites

B, C, and G, instead, groundwater [P] exceeded 30 µmole/L even though [As] in the same well water was no higher than ~100 µg/L, corresponding to a P:As molar ratio of 105± 92.

*3.2.2.1. Trends.* The RSD of fluctuations in groundwater [P] over time remained <32 % (Fig. 3.4), excluding F-6 m where [P] were particularly low (Table 3.1). The time series for 9 shallow wells indicated a small long-term decrease between -1 to -8 µM $yr^{-1}$. For only 3 wells (A-7 m, A-15 m and B-11 m), however, the decrease in [P] was accompanied by a detectable decline in [As]. A detectable increase in [P] over time of +7 µM $yr^{-1}$ was recorded at a single well: B-14 m (Table 3.2).

*3.2.2.2. Excursions.* Along with the [As] decreases of ~ 50% observed in A-13 m, C-14 m, and G-6 m in July-August 2002, [P] in the same shallow wells declined by up to 80% in September 2002 to then return to previous levels by November 2002. During the summer flood of 2003 that coincided with a decrease in [As] in well C-5 m, there was instead a [P] increase from 27 to 46 µmole/L that extended to the end of the monitoring period.

*3.2.2.3. Seasonality.* Seasonal fluctuations in [P] were found to be in phase with [As]. For well A-7 m, P concentrations varied between 10 and 30 µmole/L during the wet and dry season, respectively There was also a measurable increased in [P] during the wet season of 2003 in well B-7 m, again in phase with [As] in the same year. Well F-6 m displayed seasonality in [P] with higher values in the wet seasons, albeit around a low average of 0.1±0.1 µmole/L.

## Table-3.1. Composition of groundwater in aquifers from six well nests of 37 monitoring wells in Araihazar,Bangladesh.

| Depth | Age | Elevation | Sample | pH[1] | | Eh[1](mV) | | Cond.[1](mS/m) | | As (µg/L) | | P(µmole/L) | | SMC(meq/L) | | Na (meq/L) | | Cl (meq/L) | | Fe (µmole/L) | | Mn (µmole/L) | | S (µmole/L) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (m) | years[2] | (m) | No | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev | Avg | Stdev |
| **Site A ( 23.785°N, 90.603°E) - Village: Dari Satyabandi, all multlevel wells were installed in Jan. 2001** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | 3.5 | 7.47 | 43 | 6.46 | ± 0.06 | -76 | ± 12 | 54 | ± 13 | 80 | ± 8 | 20 | ± 5 | 5.6 | ± 1.0 | 1.0 | ± 0.16 | 1.2 | ± 0.13 | 413 | ± 86 | 47 | ± 13 | 374 | ± 106 |
| 10 | 10.8 | 7.47 | 43 | 6.66 | ± 0.04 | -79 | ± 13 | 39 | ± 10 | 132 | ± 8 | 16 | ± 1 | 4.2 | ± 0.6 | 0.7 | ± 0.11 | 0.7 | ± 0.08 | 159 | ± 22 | 51 | ± 7 | 135 | ± 60 |
| 13 | 20.3 | 7.43 | 42 | 6.92 | ± 0.05 | -150 | ± 17 | 51 | ± 18 | 538 | ± 64 | 31 | ± 8 | 5.4 | ± 0.4 | 0.9 | ± 0.20 | 1.3 | ± 0.12 | 262 | ± 37 | 96 | ± 6 | 25 | ± 16 |
| 15 | 31.7 | 7.40 | 38 | 7.00 | ± 0.04 | -158 | ± 14 | 63 | ± 21 | 359 | ± 45 | 26 | ± 5 | 7.0 | ± 0.3 | 2.0 | ± 0.16 | 1.0 | ± 0.07 | 334 | ± 51 | 18 | ± 2 | 6 | ± 1 |
| 30 | - | 7.53 | 41 | 6.60 | ± 0.05 | -58 | ± 17 | 34 | ± 9 | 0.5 | ± 0.03 | 4 | ± 0.3 | 3.5 | ± 0.2 | 2.5 | ± 0.14 | 0.8 | ± 0.04 | 10 | ± 5 | 2 | ± 1 | 14 | ± 12 |
| 37 | - | 7.51 | 41 | 6.52 | ± 0.06 | -45 | ± 24 | 28 | ± 7 | 0.5 | ± 0.02 | 4 | ± 0.3 | 3.7 | ± 0.2 | 2.6 | ± 0.24 | 0.8 | ± 0.02 | 10 | ± 5 | 2 | ± 1 | 15 | ± 14 |
| 43 | - | 7.48 | 41 | 6.52 | ± 0.05 | -57 | ± 25 | 28 | ± 7 | 1.0 | ± 0.03 | 7 | ± 1 | 3.0 | ± 0.2 | 1.8 | ± 0.13 | 0.9 | ± 0.06 | 52 | ± 30 | 6 | ± 3 | 18 | ± 16 |
| 91 | - | 7.50 | 21 | 6.53 | ± 0.09 | -56 | ± 27 | 32 | ± 9 | 1.3 | ± 0.04 | 10 | ± 1 | 3.8 | ± 0.3 | 1.8 | ± 0.27 | 1.4 | ± 0.05 | 224 | ± 85 | 2 | ± 1 | 29 | ± 9 |
| **Site B ( 23.780°N, 90.640°E) - Village: Baylakandi, multlevel wells were installed in Jan. and May 2001** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | 1.6 | 7.42 | 31 | 6.62 | ± 0.07 | -100 | ± 26 | 101 | ± 31 | 30 | ± 6 | 57 | ± 18 | 11.8 | ± 1.3 | 2.3 | ± 0.48 | 4.3 | ± 0.44 | 430 | ± 95 | 17 | ± 4 | 677 | ± 189 |
| 11 | 19.2 | 7.37 | 29 | 6.64 | ± 0.05 | -120 | ± 17 | 92 | ± 31 | 298 | ± 47 | 56 | ± 8 | 12.0 | ± 1.2 | 2.3 | ± 0.53 | 3.5 | ± 0.35 | 431 | ± 180 | 40 | ± 6 | 350 | ± 117 |
| 14 | 19.3 | 7.52 | 38 | 6.84 | ± 0.08 | -142 | ± 24 | 57 | ± 15 | 536 | ± 65 | 60 | ± 8 | 9.7 | ± 1.1 | 1.7 | ± 0.25 | 4.0 | ± 0.46 | 380 | ± 58 | 20 | ± 6 | 161 | ± 104 |
| 19 | 23.3 | 7.49 | 32 | 6.93 | ± 0.07 | -155 | ± 16 | 58 | ± 18 | 403 | ± 36 | 56 | ± 6 | 8.2 | ± 0.5 | 1.2 | ± 0.26 | 1.9 | ± 0.16 | 417 | ± 104 | 24 | ± 3 | 9 | ± 6 |
| 29 | - | 7.49 | 25 | 6.71 | ± 0.07 | -126 | ± 5 | 94 | ± 1 | 234 | ± 21 | 55 | ± 5 | 8.2 | ± 0.2 | 1.3 | ± 0.16 | 2.5 | ± 0.21 | 363 | ± 52 | 6 | ± 1 | 3 | ± 3 |
| 41 | - | 7.46 | 40 | 6.94 | ± 0.07 | -143 | ± 16 | 58 | ± 14 | 21 | ± 2 | 45 | ± 4 | 6.0 | ± 0.3 | 0.7 | ± 0.06 | 0.3 | ± 0.02 | 193 | ± 39 | 1 | ± 0.3 | 5 | ± 3 |
| 53 | - | 7.47 | 40 | 7.13 | ± 0.10 | -151 | ± 23 | 44 | ± 8 | 17 | ± 1 | 17 | ± 1 | 4.4 | ± 0.2 | 1.8 | ± 0.14 | 0.3 | ± 0.01 | 120 | ± 13 | 3 | ± 0.3 | 4 | ± 4 |
| 91 | - | 7.60 | 23 | 6.91 | ± 0.16 | -113 | ± 21 | 33 | ± 5 | 0.3 | ± 0.01 | 4 | ± 0.3 | 3.5 | ± 0.1 | 1.8 | ± 0.12 | 0.1 | ± 0.00 | 25 | ± 2 | 1.6 | ± 0.1 | <0.03 | ± 0.0 |
| **Site C ( 23.790°N, 90.611°E) - Village: Bhuyan Para (Satyabhandi), multlevel wells were installed in March 2002** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | 0.0 | 6.93 | 18 | 7.04 | ± 0.25 | -113 | ± 27 | 58 | ± 23 | 12 | ± 2 | 35 | ± 7 | 2.7 | ± 2.3 | 1.5 | ± 2.25 | 0.6 | ± 0.72 | 818 | ± 280 | 24 | ± 7 | 25 | ± 18 |
| 8 | 0.8 | 7.01 | 18 | 6.79 | ± 0.17 | -132 | ± 8 | 83 | ± 16 | 38 | ± 2 | 24 | ± 4 | 2.6 | ± 2.4 | 1.4 | ± 2.04 | 0.7 | ± 0.77 | 1694 | ± 704 | 63 | ± 28 | 26 | ± 16 |
| 11 | 2.6 | 7.01 | 18 | 6.46 | ± 0.11 | -111 | ± 22 | 52 | ± 9 | 42 | ± 3 | 22 | ± 2 | 1.6 | ± 0.7 | 0.6 | ± 0.50 | 0.6 | ± 0.56 | 1311 | ± 697 | 34 | ± 14 | 11 | ± 7 |
| 14 | 2.8 | 7.00 | 18 | 6.58 | ± 0.15 | -114 | ± 29 | 36 | ± 12 | 70 | ± 9 | 31 | ± 4 | 2.8 | ± 0.3 | 0.4 | ± 0.06 | 0.3 | ± 0.04 | 773 | ± 76 | 33 | ± 3 | 23 | ± 16 |
| 53 | - | 7.01 | 18 | 6.38 | ± 0.15 | -33 | ± 25 | 28 | ± 3 | 1 | ± 1 | 4 | ± 1 | 2.9 | ± 0.2 | 1.2 | ± 0.10 | 0.6 | ± 0.04 | 117 | ± 92 | 13 | ± 2 | 10 | ± 8 |
| **Site E ( 23.790°N, 90.616°E) - Village: Hatkhola Para, multlevel wells were installed in March 2002** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | 9.6 | 6.39 | 16 | 6.65 | ± 0.11 | -40 | ± 29 | 34 | ± 7 | 43 | ± 2 | 8 | ± 1 | 4.9 | ± 0.6 | 0.4 | ± 0.04 | 0.2 | ± 0.02 | 48 | ± 11 | 17 | ± 2 | 232 | ± 74 |
| 8 | - | 6.42 | 16 | 6.73 | ± 0.12 | -118 | ± 38 | 34 | ± 10 | 82 | ± 4 | 27 | ± 2 | 3.8 | ± 0.5 | 0.4 | ± 0.04 | 0.1 | ± 0.01 | 424 | ± 48 | 35 | ± 4 | 80 | ± 42 |
| 11 | 18.1 | 6.44 | 16 | 6.90 | ± 0.09 | -140 | ± 48 | 35 | ± 10 | 166 | ± 12 | 29 | ± 2 | 4.2 | ± 0.3 | 0.5 | ± 0.08 | 0.1 | ± 0.01 | 392 | ± 123 | 33 | ± 3 | 2 | ± 1 |
| 14 | - | 6.42 | 16 | 6.82 | ± 0.13 | -148 | ± 1 | 42 | ± 23 | 162 | ± 15 | 25 | ± 2 | 5.2 | ± 0.5 | 1.2 | ± 0.17 | 0.8 | ± 0.03 | 498 | ± 143 | 17 | ± 5 | 1 | ± 1 |
| 38 | - | 6.45 | 16 | 6.55 | ± 0.10 | -60 | ± 39 | 52 | ± 19 | 0.3 | ± 0.02 | 3 | ± 0.3 | 5.7 | ± 0.3 | 2.5 | ± 0.30 | 1.2 | ± 0.03 | 56 | ± 19 | 5 | ± 2 | <0.03 | ± 0.0 |
| **Site F ( 23.774°N, 90.605°E) - Village: Lashkardi (Mosque), multlevel wells were installed in March and November 2002** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | 0.8 | 7.90 | 21 | 6.18 | ± 0.12 | 95 | ± 92 | 18 | ± 2 | 0.2 | ± 0.02 | 0.1 | ± 0.1 | 1.6 | ± 0.3 | 0.2 | ± 0.06 | 0.2 | ± 0.06 | 2.4 | ± 2 | 2.6 | ± 1 | 37 | ± 25 |
| 11 | - | 7.87 | 22 | 6.23 | ± 0.10 | 10 | ± 50 | 21 | ± 8 | 35 | ± 3 | 2 | ± 1 | 1.8 | ± 0.3 | 0.1 | ± 0.02 | 0.2 | ± 0.04 | 63 | ± 22 | 31 | ± 8 | 24 | ± 15 |
| 15 | 5.3 | 7.81 | 22 | 6.73 | ± 0.23 | -47 | ± 60 | 21 | ± 3 | 51 | ± 5 | 4 | ± 1 | 2.4 | ± 0.1 | 0.1 | ± 0.01 | 0.1 | ± 0.01 | 31 | ± 18 | 27 | ± 3 | 15 | ± 9 |
| 19 | 29.1 | 7.76 | 22 | 6.88 | ± 0.11 | -63 | ± 55 | 29 | ± 6 | 215 | ± 19 | 17 | ± 3 | 3.7 | ± 0.3 | 0.3 | ± 0.02 | 0.04 | ± 0.00 | 27 | ± 16 | 42 | ± 2 | 35 | ± 4 |
| 26 | - | 7.74 | 14 | 7.00 | 0.00 | -200 | | 63 | | 225 | ± 15 | 32 | ± 4 | 5.2 | ± 0.4 | 0.5 | ± 0.03 | 0.2 | ± 0.01 | 350 | ± 22 | 35 | ± 3 | 0.3 | ± 0.02 |
| 58 | - | 7.91 | 22 | 6.95 | ± 0.08 | -63 | ± 23 | 154 | ± 8 | 0.3 | ± 0.02 | 5 | ± 0.4 | 12.5 | ± 1.0 | 11.4 | ± 0.94 | 9.7 | ± 0.74 | 5.7 | ± 2 | 9 | ± 0.4 | 9 | ± 4 |
| **Site G ( 23.774°N, 90.601°E) - Village: Lashkardi (Bilbari), multlevel wells were installed in March 2002** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | 21.4 | | 20 | 6.75 | ± 0.07 | -127 | ± 24 | 41 | ± 8 | 127 | ± 16 | 57 | ± 13 | 4.6 | ± 0.2 | 0.4 | ± 0.02 | 0.1 | ± 0.01 | 610 | ± 189 | 25 | ± 4 | 22 | ± 1 |
| 9 | 13.1 | | 20 | 6.67 | ± 0.10 | -111 | ± 38 | 45 | ± 11 | 159 | ± 13 | 108 | ± 23 | 5.2 | ± 0.3 | 0.4 | ± 0.02 | 0.1 | ± 0.01 | 501 | ± 66 | 8 | ± 2 | 6 | ± 4 |
| 14 | 26.0 | | 20 | 6.93 | ± 0.08 | -144 | ± 23 | 36 | ± 10 | 102 | ± 5 | 35 | ± 3 | 4.0 | ± 0.3 | 0.4 | ± 0.06 | 0.2 | ± 0.02 | 294 | ± 50 | 30 | ± 3 | 1 | ± 0.4 |
| 21 | - | | 20 | 7.05 | ± 0.11 | -163 | ± 31 | 42 | ± 7 | 173 | ± 15 | 42 | ± 4 | 4.2 | ± 0.3 | 0.4 | ± 0.09 | 0.6 | ± 0.06 | 194 | ± 46 | 28 | ± 2 | 2 | ± 2 |
| 52 | - | | 20 | 6.85 | ± 0.09 | -88 | ± 34 | 145 | ± 19 | 7 | ± 1 | 7 | ± 1 | 10.9 | ± 1 | 9.9 | ± 0.56 | 7.2 | ± 0.60 | 13 | ± 8 | 12 | ± 1 | 31 | ± 2 |

[1] data based on monthly measurements from March 2004 to February 2005

[2] $^3H/^3He$ age reported by Stute et al., 2006

### *3.4.2.3. Major Cations and Chloride*

Expressed in equivalents, the sum of major cations (SMC), including $Na^+$, $K^+$, $Mg^{+2}$, and $Ca^{+2}$, in shallow (<30 m) monitoring wells spanned an order of magnitude, from 1.6 ± 0.7 meq/L at C-11 m to 12 ± 1.3 meq/L at B-7 m (Table 3.1). Chloride concentrations in shallow aquifers also spanned about two orders of magnitude, from 0.040 ± 0.004 meq/L at F-19 m to 4.3 ± 0.4 meq/L at B-7 m (Table 3.1).

*3.4.2.3.1. Trends.* The temporal variability of the major ion composition of shallow well water was comparable to that of [As] and [P], with %RSDs remaining below 20%, 30% and 30% for SMC, Na and chloride concentrations, respectively (Table 3.1; Fig. 3.4). These measures of variability exclude, however, the nearly 3-fold increases in SMC and Cl concentrations in monitoring wells C-5 m, C-8 m, and C-11 m observed at the end of the wet season in 2003 (Fig. 3.3). Of the total of 26 shallows wells that were monitored, the SMC times-series indicated a significant ($p < 0.05$) decrease of -0.24 to -1.03 meq/L $yr^{-1}$ at 7 wells whereas an increase of +0.11 to +0.88 meq/L $yr^{-1}$ was observed at 8 other wells (Table 3.2).

*3.4.2.3.2. Excursions.* SMC concentrations did not vary appreciably in the 3 shallow wells where both [As] and [P] declined markedly for the period of several months centered on September 2002 (Figs. 3.2-3.3). On the other hand, a major salt pulse was observed after the summer flood of 2003 in three shallow wells at site C, with up to 3 times higher concentrations of SMC and Cl compared to the previous year (Fig. 3.3). Concentrations of SMC actually already started to rise in wells C-5 m and C-8 m in May 2003 and reached their highest level in Nov. 2003 and Jan. 2004, respectively. Concentrations of SMC also eventually rose in well C-11 m, but

**Table-3.2. Trends in groundwater chemistry from six well nests of 37 monitoring wells in Araihazar,Bangldesh.**

| Depth (m) | [1][As] µgL$^{-1}$ y-1 | [P] µmoleL$^{-1}$ y$^{-1}$ | [SMC] meqL$^{-1}$ y$^{-1}$ | [Cl] meqL$^{-1}$ y$^{-1}$ | [Fe] µmoleL$^{-1}$ y$^{-1}$ | [Mn] µmoleL$^{-1}$ y$^{-1}$ | [S] µmoleL$^{-1}$ y$^{-1}$ |
|---|---|---|---|---|---|---|---|
| **Site A** | | | | | | | |
| [2] **7** | -3 ± 2 | -2 | -0.5 | - | 35 | -9 | -62 |
| 10 | - | -1 | - | - | - | -3 | 27 |
| 13 | - | -5 | 0.3 | 0.1 | 15 | - | - |
| [2] **15** | -34 ± 10 | -3 | - | - | - | -1 | - |
| 30 | - | - | - | - | -3 | -1 | - |
| 37 | - | - | -0.7 | - | -8 | - | - |
| 43 | - | - | -1.3 | - | - | 4 | - |
| 91 | - | - | - | - | - | - | - |
| **Site B** | | | | | | | |
| 7 | -4 ± 1.8 | - | - | -0.2 | - | -2 | - |
| [2] **11** | -41 ± 11 | -5 | 0.9 | 0.3 | 171 | -4 | 65 |
| 14 | - | 7 | -1.0 | -0.5 | - | -5 | -86 |
| 19 | -19 ± 12 | - | -0.4 | -0.2 | 94 | -3 | - |
| 29 | -23 ± 8.3 | - | 0.1 | - | - | - | - |
| [2] **41** | -2 ± 0.6 | -6 | - | 0.2 | 27 | - | 2 |
| 53 | -1 ± 0.5 | - | -0.2 | - | 26 | - | -3 |
| 91 | - | - | - | - | 2 | - | - |
| **Site C** | | | | | | | |
| 5 | - | - | - | - | 270 | - | - |
| 8 | - | - | - | - | - | - | - |
| 11 | - | - | -0.3 | -0.2 | 251 | - | - |
| 14 | - | - | - | - | - | - | - |
| 53 | - | - | -0.2 | -0.1 | - | - | - |
| **Site E** | | | | | | | |
| 5 | - | - | - | -0.1 | - | -2 | - |
| 8 | - | - | - | - | - | - | - |
| 11 | 19 ± 7 | - | -0.3 | 0.0 | 169 | - | - |
| 14 | - | -8 | -0.6 | - | - | -7 | - |
| 38 | - | - | -1.2 | - | - | -3 | - |
| **Site F** | | | | | | | |
| 6 | - | - | 0.2 | - | - | - | -21 |
| 11 | - | -1 | 0.3 | - | - | - | - |
| 15 | - | - | - | - | -15 | 2 | -8 |
| 19 | -21 ± 12 | - | -0.2 | - | -17 | - | - |
| 26 | - | - | 0.6 | 0.0 | - | - | - |
| 58 | - | - | - | 0.9 | - | - | - |
| **Site G** | | | | | | | |
| [3] **6** | 14 ± 12 | - | 0.2 | - | -161 | -4 | - |
| 9 | - | - | - | - | - | - | - |
| 14 | - | -3 | - | 0.0 | -42 | - | - |
| 21 | - | -4 | 0.5 | 0.1 | - | 3 | - |
| 52 | - | - | -0.8 | 0.9 | - | -1 | -3 |

[1] **Uncertainties was shown as 95% confidence intervals**

[2] **Wells that show the decreasing trend for [As] and [P]**

[3] **Well that does not fall in normal probability plot**

only later in January 2004, whereas no marked change in SMC was observed throughout the period at well C-14 m. The increases in SMC reflected largely a rise in dissolved Na in groundwater, from ~0.3 meq/L in April 2003 to maxima ranging from 2 to 7 meq/L in subsequent months. The progression of Cl concentrations over the same period in all shallow wells at site C was similar to that of Na, although there was a gap in the Cl time series that extended from February 2002 to October 2003.

*3.4.2.3.3. Seasonality.* The concentrations of SMC in well A-7 m, where the clearest seasonal variations in [As] and [P] were also detected, were low during the wet season and high during the dry season (Fig. 3.3). In contrast to some of the other shallow wells, these changes reflected primarily changes in Ca and Mg, with the sum of their concentrations fluctuating between 1.2 and 2.2 meq/L. Although the duration of sampling was relatively short at F-6 m, SMC and Cl both appeared to be systematically elevated in this well during the dry season (Fig. 3.3), when [P] was particularly low ([As] did not change).

### *3.4.2.4 Iron, Manganese and Sulfur*

Of all the constituents of groundwater that were quantified, the concentrations of the redox-sensitive elements Fe, Mn and S varied the most spatially and temporally (Fig. 3.4). Dissolved Fe concentrations spanned nearly three orders of magnitude, from 2.4 ± 2 μmole/L at F-6 m to 1694 ± 704 μmole/L at C-8 m (Table 3.1). Dissolved S concentrations also ranged over three orders of magnitude, from 0.3 ± 0.02 μmole/L at F-26 m to 677 ± 189 μmole/L at B-7 m. Mn concentrations were not quite as variable and ranged from 2.6 ± 1 μmole/L at F-6 m to 96 ± 6 μmole/L at A-13 m.

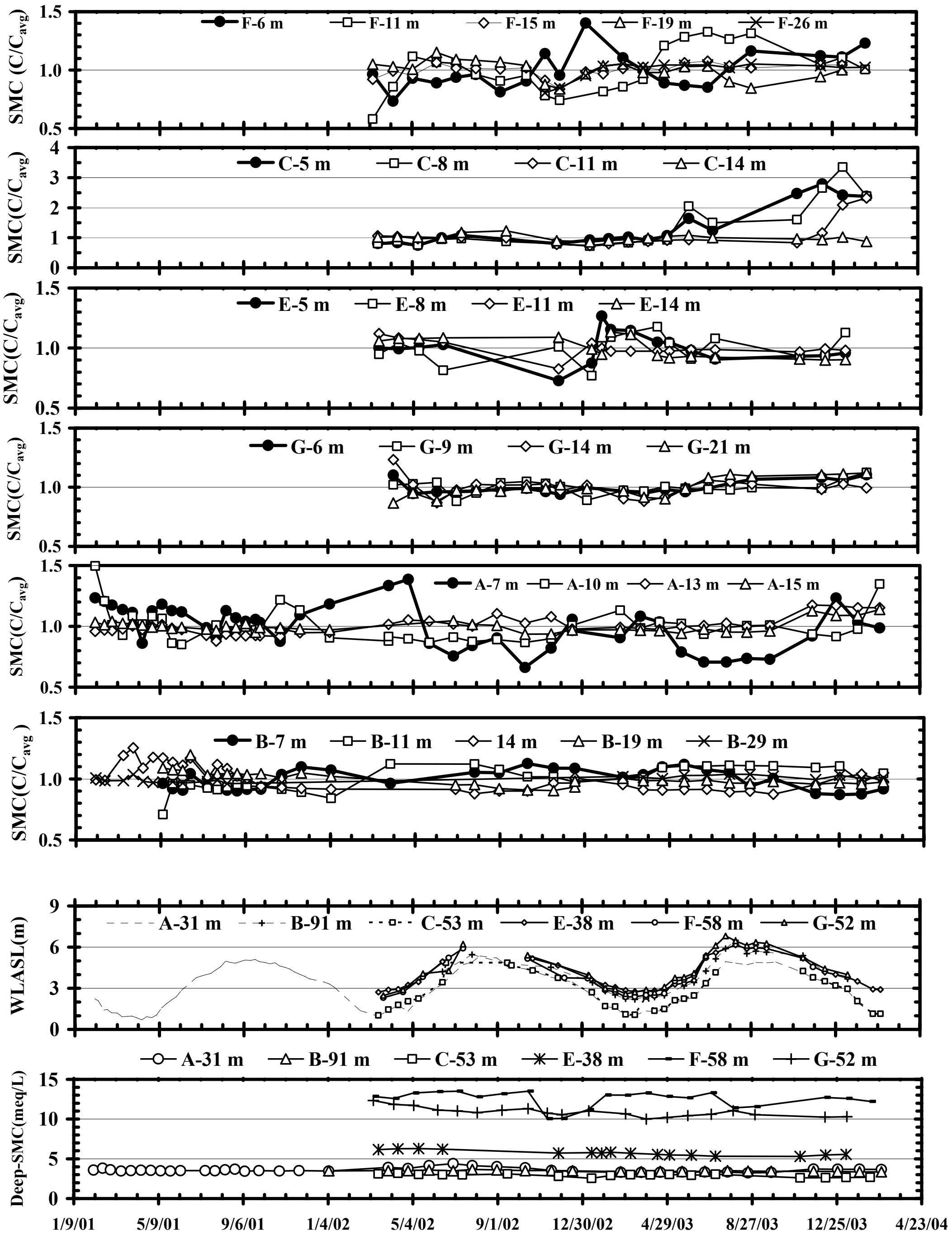

**Figure 3.3.** Temporal variability of the sum of major cations (SMC) in meq/L in shallow aquifer was shown from top to bottom in sequence for Sites F, C, E, G, A and B. Concentrations of SMC are plotted as the ratio (C/$C_{avg}$) of the concentration at the time of the sampling (C) versus the average concentration of the entire time series ($C_{avg}$). Water level above sea level (WLASL) spanning the entire monitoring periods from a deep aquifer well at each site is shown in the 2nd panel from the bottom, immediately above the panel that showed the temporal variability of SMC in deep aquifer wells. In each of the shallow aquifer panel, the bold line always represents the shallowest well at the site.

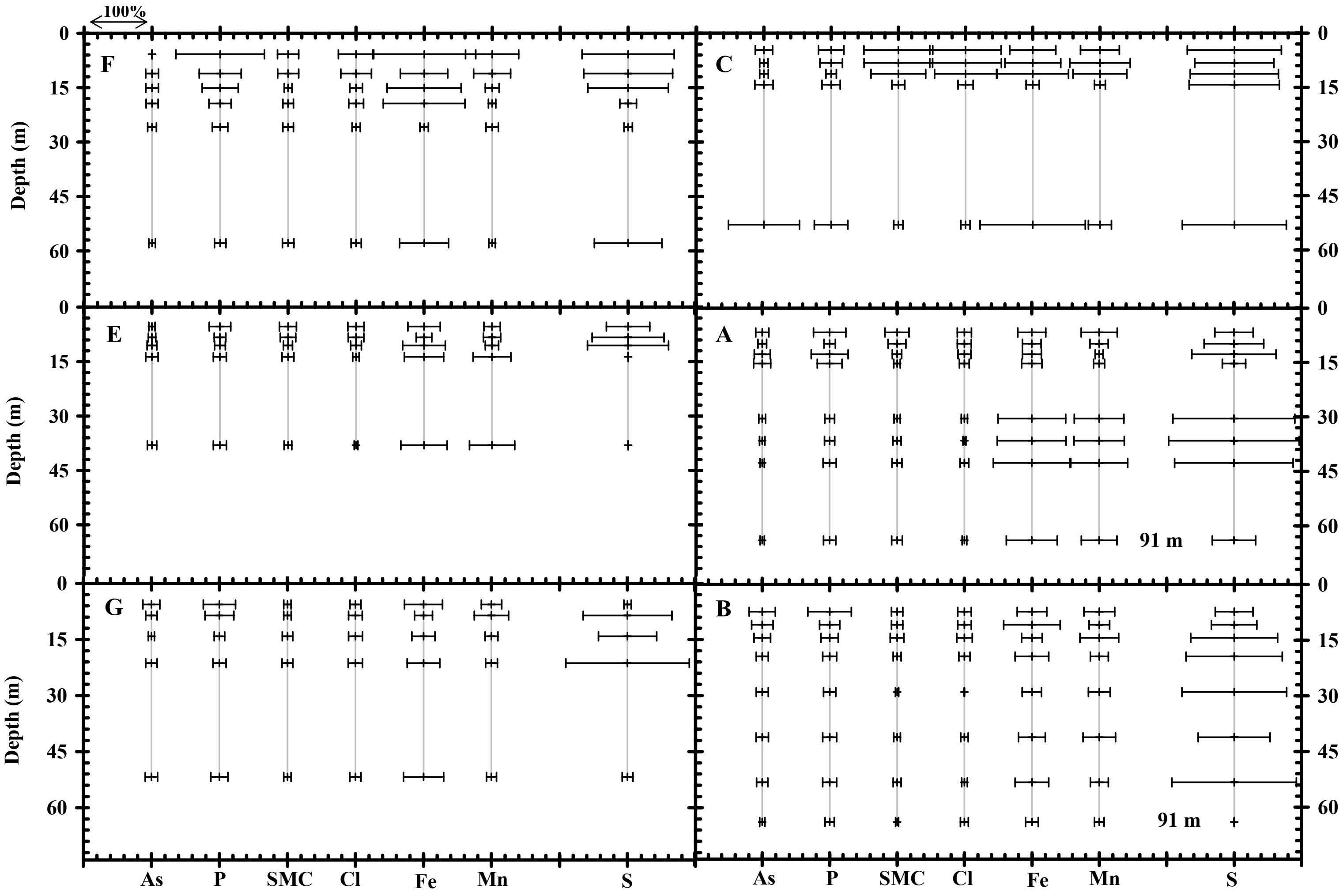

**Figure 3.4.** Variation of As, P, SMC, Cl, Fe, Mn, S in both shallow and deep aquifers of all six sites are shown as %RSD as a function of depth. The variations of the two 91m deep wells at Sites A and B are shown right below the 60 m depth and not at the actual depths of the wells.

There was no consistent relationship between depth profiles of Fe or Mn at each site with the corresponding profiles of [As] or [P]. Groundwater [S], however, generally decreased with depth at all sites.

*3.4.2.4.1. Trends.* For the 6 shallow wells at sites A and B that displayed decreasing As trends, [Fe] increased for 3 wells and did not change for the other 3 wells (Table 3.2). For the 2 shallow wells at sites E and G that showed an increasing As trends, [Fe] increased for E-11 m but decreased for G-6 m (Table 3.2). For wells at sites C and F where little change in [As] was observed (with the exception of in well F-19 m), [Fe] increased for 2 wells at Site C but decreased for two wells at site F. As in the case of Fe, there is no systematic relationship between trends in Mn, S, and As over time (Table 3.2).

*3.4.2.4.2. Excursions.* At site C, three shallow wells that were impacted by the salt pulse during the summer 2003 flood, showed an increase of [Fe] and [Mn] but a decrease of [S] after the summer (Fig. 3.5). [Fe] increased by a factor of 2 to 4; [Mn] increased by a factor of 3 (Fig. 3.5). Groundwater [S] decreased from 129, 72 and 16 μmole/L to very low values of 3, 4 and 2 μmole/L in Feb., 2004 (Fig. 3.5).

*3.4.2.4.3. Seasonality.* The seasonal fluctuations in groundwater composition observed at well A-7 m over a 3 year period were systematic for As, P, SMC, Fe and Mn. In parallel with changes in SMC, and in opposite phase to variations in As and P, concentrations of Fe and Mn rose during the dry season and dropped during the wet season. These variations were not accompanied by a consistent seasonal pattern for S in well A-7 m. In well F-6 m, a pronounced seasonality in groundwater constituents other than As was observed for Fe, Mn and P with low values found in the wet seasons. S in well F-6 m, instead, were higher in the wet seasons similar to SMC and Cl (Fig. 3.3).

### 3.4.3. Deep aquifers

In contrast to shallow aquifers of Araihazar, the overall composition of deep (>30 m) aquifers was remarkably stable over time except for Fe and $SO_4$ concentration (Fig. 3.4). In a sense, the time series data for the deep wells provide an independent measure of the quality of the data because all samples were collected, preserved, and analyzed in exactly the same fashion. At all but site B (Fig. 3.1), these deep wells tapped sandy aquifers with a characteristic orange-brown color that is typically associated with low As concentrations (Horneman et al., 2004; Zheng et al., 2005). At Sites A, C, E, F, and G, the redox potential (ORP) of groundwater was less negative than in shallow aquifers (Table 3.1). Conductivity measurements and SMC data indicated that deep groundwater was fresher than in shallow aquifers at sites A, B and C, but saltier at sites E, F and G (Table 3.1). The elevated conductivity of deep groundwater at sites E, F and G reflected primarily high concentrations of Na and Cl (Table 3.1).

The SMC concentration in the deepest well at all 6 sites was the most stable property measured over the monitoring period, with RSDs usually <9% (Table 3.1; Fig. 3.4). Concentrations of As in the deepest wells at sites A, B, C, E, F, were stable and low at 1± 0.7 μg/L. The levels of [As] were somewhat higher at B-41 m (21±2 μg/L As), B-53 m (17±1 μg/L As); and G-52 m (7±0.6 μg/L). There was a statistically significant decline in [As] over time of -2 and -1 μg/L $yr^{-1}$ at B-41 m and

B-53 m, respectively (Table 2). Concentrations of P ranged from 4 to 10 μmole/L in the deepest well from all 6 sites and varied within 30% (Fig. 3.4). Fe concentrations in the deep aquifers were generally lower than in the shallow aquifers, yet still spanned an order of magnitude: from 5.7 ± 2 (36%) μmole/L at F-58 m to 117 ± 92 (78%) μmole/L at C-53 m (Table 1). Mn concentrations were also relatively low, and ranged from 1.6 ± 0.1 (7%) μmole/L at site B-91 m to 13 ± 2 (17%) μmole/L at site C-53 m. Concentrations of S ranged more widely, from <0.002 ± 0 μmole/L at E-38 m (excluding March – April 2002) to 31 ± 2 (8%) μmole/L at G-52 m. Little systematic variation over time was observed in the deep aquifers, with the exception of a large increase in [Fe] and [S] in C-53 m that lasted from May 2002 and July 2003. In addition, there was steady rise in [S] from <0.003 to 37 μmole/L in the deep aquifer at site A over the entire monitoring period.

## *3.5. Discussion*

### 3.5.1. Fluctuations in major ion compositions and groundwater age

Groundwater ages in deep aquifers at sites A and B are 10-1000 times higher than in the corresponding shallow aquifers of Araihazar (Stute et al., in review; Zheng et al., 2005). Radiocarbon ages were recently also measured for dissolved inorganic carbon from wells C-53 m, F-58 m, and G-52 m and ranged from 3,000 to 10,000 years (Chapter 5). These observations show that the fresh and less fresh deep aquifers in Araihazar both contain groundwater that was recharged centuries to thousands of years ago.

Not surprisingly, the variability of groundwater composition for all major ion constituents that were quantified was lower (i.e., generally < 10 % for SMC and Cl; Table-3.1) than in any of the shallow aquifers. The age of deep groundwater is older and, therefore, flow lines are likely to be longer, and dispersive mixing may have smoothed out any initial temporal fluctuations.

The shallow aquifers at the 6 sites that were monitored over a period of 2-3 years were divided into 2 groups on the basis of $^3H/^3He$ ages of groundwater collected from the same set of wells (Stute et al., in review). These were, on one hand, sites C and F where groundwater $^3H/^3He$ ages remain <5 years down to a depth of ~14 m and, on the other, sites A, B, E, and G, where $^3H/^3He$ ages already exceed 20 years at the same depth. Sites C and F are also the only 2 out of a total 6 sites where the $^3H/^3He$ age of groundwater from the shallowest well was <1 year. The rapid recharge of shallow aquifers at Sites C and F indicated by the $^3H$-$^3He$ data is probably linked to the upward extension, almost to the surface, of sandy deposits at these two sites (Aziz et al., in review; van Geen et al., 2006; Weinman et al., in review). At Sites A, B, E, and G, instead, recharge appears to be limited by the presence of a thicker layer of silt or clay that capped the local sandy aquifers. These hydrogeological constraints were used to interpret the behavior of relatively conservative constituents of groundwater, i.e., SMC, $Na^+$, and $Cl^-$.

It is probably not a coincidence that variations in the composition of groundwater in terms of SMC, Na, and Cl are particularly pronounced (≥30% to 100%) and go deeper beyond the shallowest monitoring well at the Sites F and C where sandy deposits extend to the surface (Fig. 3.6). What is less clear is to what extent these variations reflect vertical advection of recently recharged water, lateral motion of groundwater that is heterogeneous in composition, or a combination of both. At Site C, a progressive deepening of a front containing elevated Na and Cl levels during and following the 2003 flood is consistent with at least some vertical penetration to ~ 11 m (Fig. 3.5). At present, we cannot rule out the possibility that the changes in NaCl were due to leakage of flood water along the well casings, although that seemed unlikely given the systematic pattern of the multi-elements depth profiles obtained at different time post-flood (Fig. 3.5). Elevated concentrations of NaCl have previously been linked to human waste because large quantities of salt are mobilized and added to flood water in densely populated areas where sanitation is limited to pit latrines (Ahmed et al., 2004). A sizable trench (~ 10 m wide) that presumably could collect latrine runoff is located next to Site C and separates a vegetable field from the village.

At site F, the amplitude of what appears to be a seasonal cycle of variations in Na and Cl concentrations which peaks during the dry season and is considerably muted compared to Site C and lacks the response to the 2003 flood (Fig. 3.3). Site F is located in a village that is built up to higher elevation than the surrounding area and has no such trench or pond next to it. Here again, the relative importance of vertical and lateral flow in causing the seasonal variations in major ion content at site F is difficult to determine. A detailed transect of groundwater properties in the site F area (van Geen et al., 2006) has shown that the lateral spatial variability in the major ion content of shallow groundwater in the area does not make it necessary to invoke downward transport of recharge water.

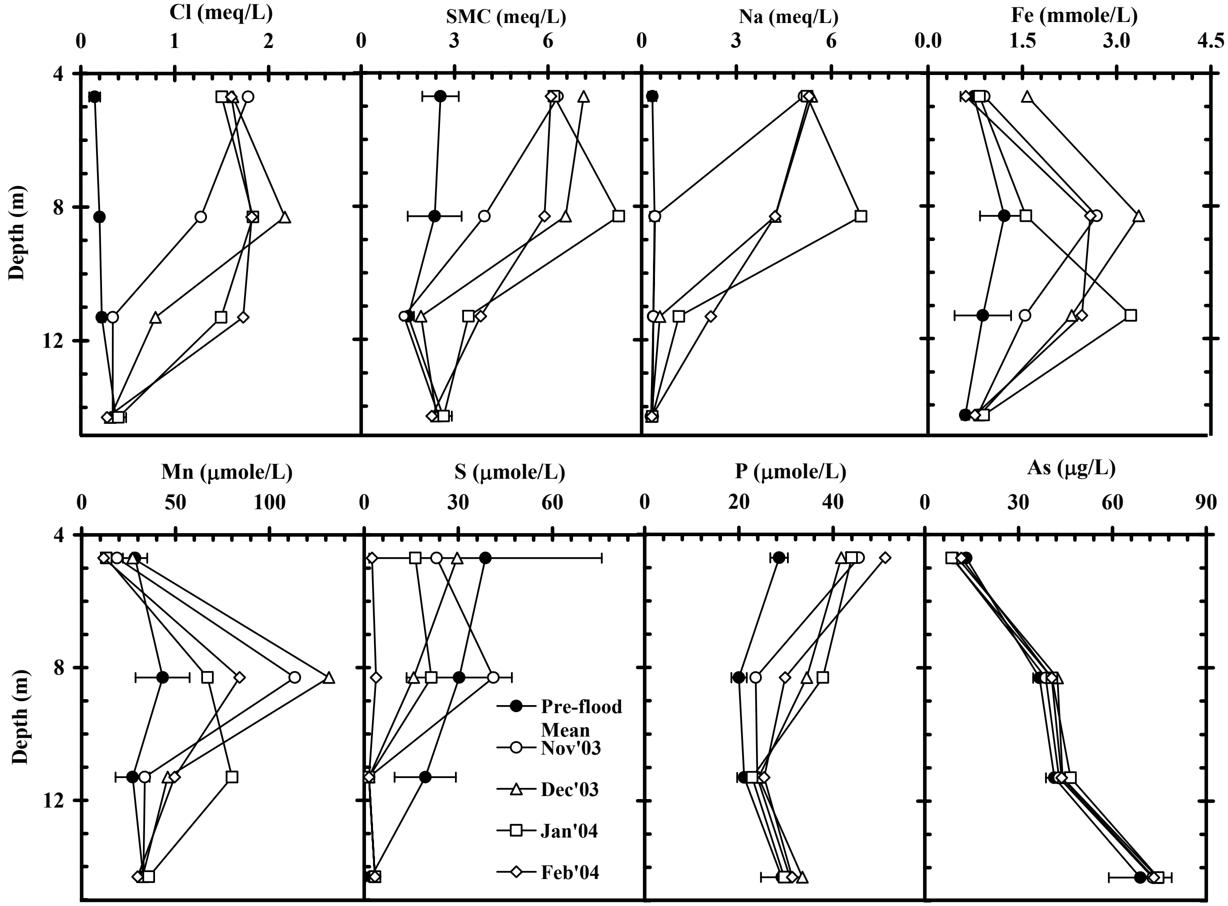

**Figure 3.5.** Depth profiles of Cl, SMC, Na, Fe, Mn, S, P and As of 4 shallow wells at Site C that compared the pre-flood profiles with 4 other times after the flood in the summer of 2003. The black solid circles indicate the average concentration prior to the 2003 flood (March 2002 to July 2003) and error bar represents the standard deviation from the average prior to the flood.

Some fluctuations in major ion concentrations were also observed at clay/silt covered sites A and B, although these were limited to the shallowest wells (Figs. 3.4 and 3.6). The $^{3}H/^{3}He$ ages of the groundwaters from shallowest wells at these sites are also <5 years, even if the groundwater age rapidly increases beyond the depth of these wells (Stute et al., in review). Given the higher ages, and the capping of shallow aquifers around Sites A and B by relatively impermeable surface sediment, it seemed more plausible to attribute the variations in groundwater composition to lateral motion of groundwater of heterogeneous composition. Seasonal patterns in major ion concentrations similar to the one observed in the shallowest well at site A, though not necessarily in phase, were previously reported for two shallow private wells in Araihazar (Cheng et al., 2005). Whereas maxima and minima in major ion concentrations for shallow wells in the area often do not coincide, the seasonal pacing of the fluctuations might still be linked to variations in water level of the nearby stream (Figs. 3.2 and 3.3).

In contrast to the shallowest wells at Sites A, B, C, and F, fluctuations in groundwater composition were limited at G-6 m (Fig. 3.3). At this location, the $^{3}H/^{3}He$ age of groundwater in even the shallowest wells is $\geq$10 years (Stute et al., in review). Variations at E-5 m, also with $^{3}H/^{3}He$ age of ~ 10 yrs, on the other hand, were comparable to Sites A and B but clearly not as stable as at G-6 m (Fig. 3.3).

In general, regardless of the actual depth of wells tapping the shallow (<30 m) aquifers, it therefore appears that the range of variations in the concentrations of major constituents decrease as the age of groundwater increases (Fig. 3.6).

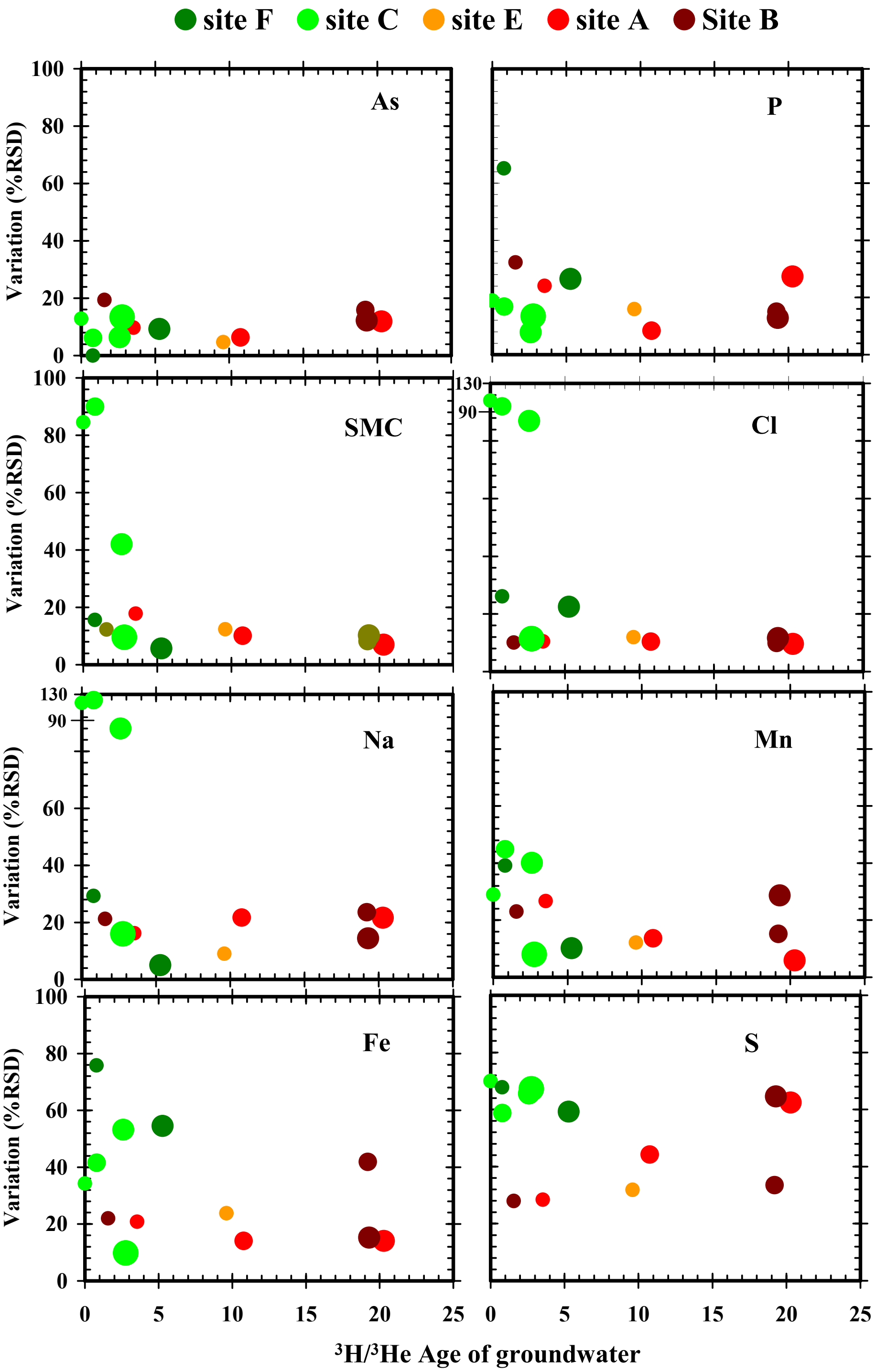

**Figure 3.6.** Variability of As and other ion concentrations expressed as %RSD as a function of $^3H/^3He$ age from the shallow (<25 m) aquifers at 5 well nests. Only water samples not affected by mixing (based on $^3H/^3He$ data) are shown (A-7 m, A-10 m, A-13 m, B-7 m, B-11 m, B-14 m, C-5 m, C- 8 m, C-11 m, C-14 m, E-5 m, F-6 m, F-15 m). Solid circles of different colors refer to the different sites. For each site indicated by a color, the size of circles increases with the depth of the well.

### 3.5.2. Decoupling between variations in redox-sensitive constituents and As

Perhaps the greatest surprise that resulted from this study is that variations in groundwater As concentrations were considerably muted in comparison with other redox-sensitive constituents, such as Fe, Mn and S in both the low-As deep aquifers and high-As shallow aquifers. Considerable variations of Fe and S, and to a lesser extent Mn, were observed in the deep aquifer where major ions and As remained stable (Fig. 3.4). In the case of deep aquifers, such decoupling is consistent with low concentrations of mobilizable As in deep aquifer sediment (Zheng et al., 2005). In such conditions, even if microbially-mediated reduction of Fe oxyhydroxides occurred, the release of Fe could be decoupled from As due to either re-adsorption (van Geen et al., 2004) or the lack of a pool of mobilizable As in the sediment (Zheng et al., 2005). Consistent with such decoupling, As concentrations changed very little over the monitoring period at F-6 m (Fig. 3.2) even though both major ion and redox-sensitive elements exhibited a strong seasonal pattern (data shown in supplementary figure).

What is more puzzling is the observation of the decoupled temporal patterns of concentrations of As, vs. Fe, Mn, and S in shallow aquifers. One example of such decoupling is the three shallow wells at sandy site C where major ion concentrations and redox-sensitive elements were strongly affected in three monitoring wells by the 2003 flood whereas the depth profile of As did not change (Fig. 3.5). Only in the shallowest well C-5 m was the concentration of As measurably affected by the flood, but in this case the result was a decrease in concentrations instead of the increase that might have been expected from the dissolution of mineral oxides suggested by the rise in Fe and Mn concentrations (Fig. 3.5). Considered as a whole, the time series data observations reinforce the notion that there may be significant decoupling between the mobilization of As and the redox state of an aquifer (Horneman et al., 2004; Polizzotto et al., 2005; van Geen et al., 2004; van Geen et al., 2006).

What is the implication of decoupling between As and the redox state of the groundwater temporally and spatially? Polizzotto et al. (2005) proposed that the decoupling between As and other redox sensitive constituents in groundwater was caused by release of As near surface followed by transport to depth. If this were the case, then one might expect more decoupling between As and other redox sensitive elements in older groundwater further down the flow-path than that of younger age at shallower depths. No evidence of more progressive decoupling is observed in our data. The groundwaters were already highly decoupled between As and other constituents of groundwater even at very shallow depths (5-7 m). While Fe, Mn and S temporal changes were internally consistent at each of these very shallow wells, there was no simple relationship to temporal patterns in [As]. Strong temporal decoupling between As and Fe, Mn and S in the shallowest wells from our sites imply that the chemical compositions of recharge water could be highly heterogeneous both spatially and temporally.

### 3.5.3. Trends in groundwater As in the shallow aquifer

Stute et al. (in review) have pointed out on the basis of paired measurement in groundwater from the same set of shallow monitoring wells (< 20 m) that there is a surprisingly linear relationship between As concentrations and groundwater age across a wide range of settings (Fig. 3.7). The simplest interpretation of this linear relationship is that the release rate of As is relatively constant at ~ 20 μg/L As in the shallow aquifers of Araihazar. This rate appears to be insensitive to, and therefore decoupled from, the redox state of the aquifer. While it is still not clear what biogeochemical processes contribute to the relatively constant rate of As release down the flow-path of recharge, it provides a useful framework for understanding the puzzling features of the spatial and temporal patterns of As and other groundwater constituents. A steady release of As under a wide range of conditions is also consistent with the observation that concentrations of major ions or redox-sensitive constituents are not necessarily linked to variations in dissolved As, both spatially and temporally. The observations also imply that the spatial heterogeneity of [As] in shallow aquifers is considerably less than that of major ions or redox-sensitive constituents in groundwater. It remains unclear if the inferred heterogeneity in major ion and redox sensitive constituents relative to As is due to reaction or to transport.

If groundwater As concentrations remain unchanged over time, then a steady state of As release (e.g. source) and discharge or immobilization (e.g. sink) is apparently reached. We recognize that our time series data span only 2 to 3 years and it may therefore be premature to draw any firm conclusions. However, an intriguing pattern emerges when these trends are linked to sedimentary geology. For Sites F and C where sandy sediment extends to surface, there is little trend in groundwater As (Table 3.2). Although F-19 m showed a decline of 21 ± 12 μg/L $\text{yr}^{-1}$ but it was below a silty layer with lower hydraulic conductivity and thus more akin to old meander environment at Sites A and B (Fig. 3.1). Sites E and G showed increase of As over

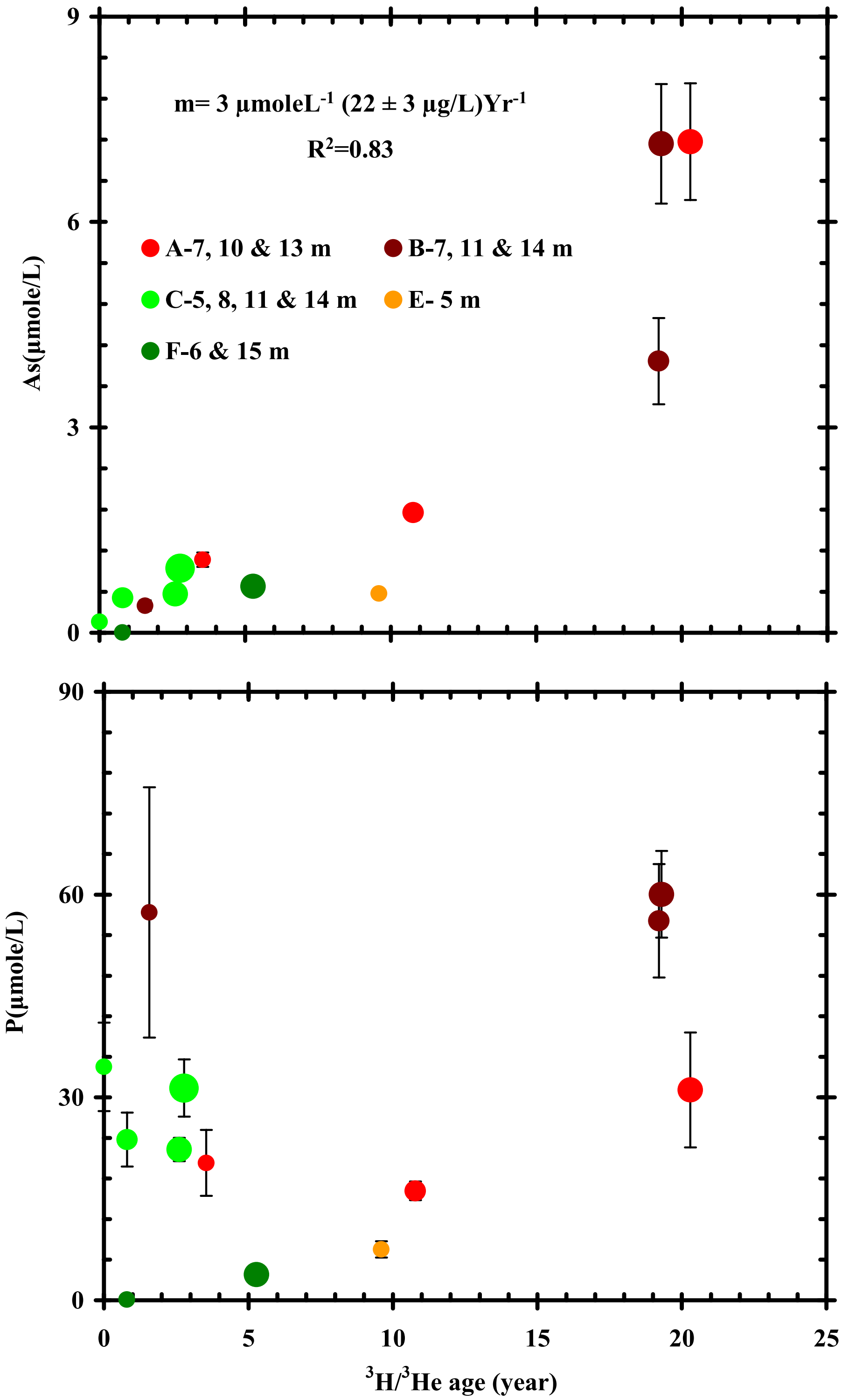

**Figure 3.7.** Average groundwater [As] (upper panel) and [P] (lower panel) as a function of $^3$H/$^3$He age for the same set of samples as in Fig. 3.6. Like Fig. 3.6, the color of the circles represents the site. The size of the circle increases with the depth of the well at each site. Error bars indicate the standard deviation of the variability.

time in 2 out of 8 shallow wells. There, groundwaters were old at very shallow depths with clay/silt surface cover but more importantly the sites were located in a young flood plain < 4000 years old (Weinman et al., in prep.). In contrast, similarly clay/silt covered sites A and B located in older meanders > 6000 yrs old (Weinman et al., in prep.) showed a systematic decline of groundwater As in 6 out of 9 shallow wells (Table 3.2). Our results suggest that if near surface mobilization and subsequent transport was what contributed to the shape of the As depth profile as proposed by Polizzotto et al. (2005), then this mechanism most likely operates today in young flood plain deposit covered by clay and silt (e.g. Sites E and G) but not those covered by sand (Sites F and C). Near-surface mobilization may have played a role in the past in older meanders with clay and silt cover (Sites A and B), but apparently not today. The data show that such settings presently experience a net loss of As over time.

### 3.5.4 Coupled and decoupled behavior of P and As

Arsenic in its oxidized form is a chemical analog for phosphate. For this reason, parallel behaviors or interactions between these two constituents are frequently invoked. Arsenic in aquifers of Araihazar, however, is predominantly present in groundwater in the As(III) form (Zheng et al., 2004). Despite the difference in redox state of the dissolved species, there appears to be a reasonable parallel to the As-age relationship for P for groundwater ages >5 years (Fig. 3.7) suggesting a similar release mechanism for As and P in these older groundwaters. Another piece of evidence supporting similar mechanism for As and P mobilization in older groundwater is the co-variance of P and As observed in time series data (Fig. 3.8). When the deviation of P from the average P concentrations over time (ΔP) was plotted over the deviation of As from the average As concentrations over time (ΔAs), a ΔP: ΔAs atomic ratio of 9.6 was found ($R^2 = 0.55$, n= 181, Fig. 3.8), nearly identical to the ratio (9.3) established independently by using P:As ratio in these wells directly (Fig. 3.8).

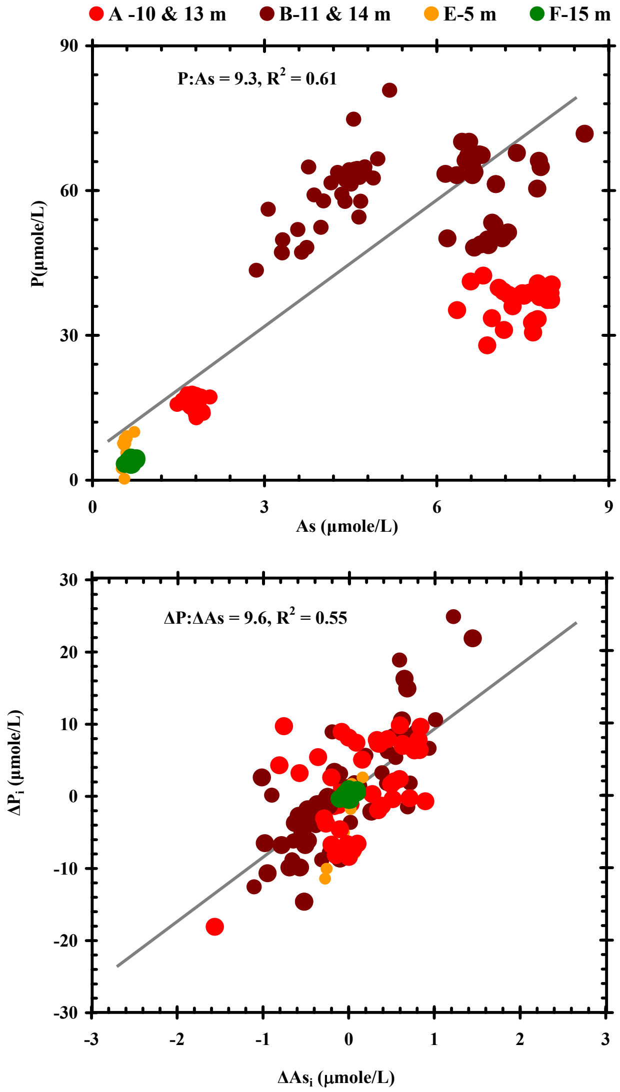

**Figure 3.8.** Concentrations of groundwater P vs. As for the shallow monitoring wells with $^3$H/$^3$He ages of > 5 years (upper panel). The data include the entire time period (2-3 yrs) for each well. The deviation of P concentration above or below the mean value ($\Delta P_i = P_i - P_{avg}$) vs. the deviation of [As] ($\Delta As_i = As_i - As_{avg}$) of the same wells as in the upper panel. . The lines in both panels represent an As:P molar ratio of ~10.

Why then is there more P relative to As in very young (< 5 yr) shallow groundwater? P concentrations are high not only in young water at sandy site C (but not F), but also in young water tapped by the shallowest well at sites A and B (Fig. 3.7). The reasons for this appears to be that P concentrations are often quite high in recharged groundwater, whereas As concentrations are not. A surface source of P that is decoupled from As is also suggested by the response to the pulse of recharge water at site C. Indeed P concentrations increased by ~20 μmole/L in both C-5 m and C-8 m after the 2003 flood, with little change detected at C-11 m (Fig. 3.6). Newly recharged water was most likely depleted in As because the shallowest well C-5 m showed a 40% decrease in As (Fig. 3.2) despite having an increase in Na, Cl, Fe and Mn (Fig. 3.6). These observations confirm that As was probably not derived from recharged surface water but that P was.

## *3.6. Conclusions*

Groundwater age is a key variable influencing the temporal variability of groundwater chemistry in shallow Holocene aquifers and deeper aquifers of Araihazar. The concentration of major ions and redox-sensitive elements are most likely to vary in shallow and young (<3.5 yr) groundwater, but the changes in As are much more muted. The decoupling between As and other elements under such conditions may reflect the greater availability of mobilizable Fe in the sediment compared to mobilizable As. The concentration of redox-sensitive ions in shallow groundwater >3.5 yrs old and deep groundwater thousands of years old in deeper aquifers is also more variable than [As]. The reason for this decoupling remains unclear.

Trends in groundwater [As] over the entire monitoring period may be governed by sediment geology and its effect on the groundwater flow regime. Aquifers underlain young flood plain sediment (< 4000 yr) show increases in [As] concentrations with time; whereas aquifers underlain older flood plain sediment (6000-10,000 yrs) indicate decreases in [As] concentrations. This supports the notion that flushing over time may gradually decrease the inventory of As in the Holocene aquifer but that process will take thousands of years if not longer (McArthur et al., 2001).

## *3.7. Acknowledgements*

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## *3.9. Supplemental materials*

Groundwater samples from six nests of 37 monitoring wells, collected bi-weekly to monthly were transported to USA and were analyzed by an Axiom Single Collector high-resolution inductively-coupled plasma mass spectrometry (HR ICP-MS) at Lamont-Doherty Earth Observatory (LDEO) of Columbia University, NY and by ion chromatography (IC) using a DIONEX-500 IC system at Queens College, NY. Unfiltered, acidified samples were run by HR ICP-MS for total concentrations of As, P, Fe, Mn, S, Ca, Mg, K, Na and 33 other trace elements, Cl was determined by ion chromatography in the unfiltered, non-acidified samples, following EPA method 300, a standard protocol for anion analyses.

### 3.9.1 Supplementary tables

Time series ions concentration for 37 monitoring wells including weekly or bi-weekly water level data are compiled in tables 1 to 43. Tables 1-9, 10-18, 19-24, 25-30, 31-37 and 38-43 represents the data for site A, B, C, E, F and G respectively.

### 3.9.2 Supplementary figures

The temporal data of shallow groundwater As, P, sum of major cations (SMC) as Na+K+2Mg+2Ca, Cl, Fe, Mn and $SO_4$ were plotted as the ratio ($C/C_{avg}$) of the concentration at the time of the sampling (C) vs. the average concentration of the entire time series ($C_{avg}$) for sites A, B, C, E, F and G in Figures 1, 2, 3, 4, 5, and 6, respectively. The temporal trends of As and other ions in deeper aquifer is described in Figure 7.

**Table-1. Time series data for As and other ions in shallow well at site A (depth - 7 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 1.21 | 30 | 1166 | 728 | 1604 | 1342 | 6.91 | 457 | 70 | 458 | 1.37 |
| 2/19/01 | 1.19 | 27 | 1106 | 750 | 1583 | 1279 | 6.75 | 447 | 67 | 544 | - |
| 3/2/01 | 1.23 | 26 | 1079 | 707 | 1567 | 1258 | 6.58 | 419 | 64 | 575 | - |
| 3/17/01 | 1.22 | 27 | 1327 | 643 | 1481 | 1138 | 6.37 | 403 | 58 | 578 | - |
| 3/31/01 | 1.19 | 25 | 1522 | 608 | 1419 | 1039 | 6.23 | 376 | 54 | 605 | - |
| 4/14/01 | 1.11 | 21 | 644 | 313 | 1402 | 1075 | 4.82 | 365 | 55 | 550 | - |
| 4/28/01 | 1.09 | 20 | 1190 | 652 | 1471 | 1174 | 6.31 | 352 | 58 | 511 | - |
| 5/12/01 | 1.06 | 15 | 1071 | 740 | 1548 | 1258 | 6.62 | 355 | 65 | 482 | - |
| 5/26/01 | 1.10 | 17 | 1068 | 679 | 1519 | 1188 | 6.32 | 318 | 61 | 448 | - |
| 6/9/01 | 1.10 | 18 | 961 | 705 | 1517 | 1187 | 6.26 | 353 | 61 | 433 | - |
| 7/14/01 | 1.05 | 23 | 968 | 588 | 1372 | 1012 | 5.54 | 327 | 52 | 411 | 1.33 |
| 7/28/01 | 0.73 | 19 | 917 | 528 | 1229 | 936 | 5.07 | 434 | 46 | 260 | 1.32 |
| 8/11/01 | 1.05 | 23 | 976 | 725 | 1504 | 1193 | 6.32 | 421 | 63 | 396 | 1.39 |
| 8/25/01 | 1.08 | 25 | 984 | 656 | 1440 | 1123 | 5.98 | 391 | 59 | 407 | 1.36 |
| 9/8/01 | 1.06 | 24 | 971 | 638 | 1395 | 1096 | 5.83 | 376 | 56 | 390 | 1.34 |
| 9/22/01 | 1.05 | 25 | 989 | 646 | 1426 | 1103 | 5.91 | 373 | 43 | 384 | - |
| 9/28/01 | 1.04 | 26 | 1026 | 627 | 1372 | 1064 | 5.78 | 365 | 55 | 380 | 1.33 |
| 10/27/01 | 1.04 | 26 | 966 | 495 | 1235 | 856 | 4.90 | 299 | 45 | 380 | 1.29 |
| 10/27/01 | 1.02 | 23 | 1138 | 382 | 1424 | 849 | 5.02 | 363 | 34 | 255 | - |
| 11/24/01 | 1.19 | 22 | 1055 | 681 | 1350 | 1181 | 6.13 | 380 | 56 | 457 | - |
| 1/5/02 | 1.21 | 21 | 1049 | 863 | 1282 | 1282 | 6.62 | 425 | 66 | 434 | 1.24 |
| 3/30/02 | 1.21 | 18 | 1265 | 1084 | 1308 | 1366 | 7.47 | 538 | 52 | 221 | 1.17 |
| 4/27/02 | 1.14 | 20 | 891 | 1279 | 1038 | 1639 | 7.77 | 560 | 48 | 217 | 1.25 |
| 5/27/02 | 0.97 | 15 | 860 | 571 | 942 | 934 | 4.81 | 350 | 30 | 254 | 1.13 |
| 6/30/02 | 1.00 | 17 | 871 | 408 | 1003 | 769 | 4.23 | 364 | 27 | 312 | 0.95 |
| 7/27/02 | 1.02 | 19 | 1009 | 499 | 1035 | 834 | 4.71 | 390 | 31 | 349 | 1.13 |
| 8/31/02 | 0.98 | 18 | 832 | 679 | 855 | 1009 | 5.06 | 390 | 32 | 308 | 1.10 |
| 10/10/02 | 0.96 | 18 | 946 | 254 | 977 | 636 | 3.70 | 271 | 24 | 205 | 0.99 |
| 11/16/02 | 1.10 | 18 | 1041 | 453 | 1067 | 791 | 4.60 | 370 | 30 | 343 | 1.17 |
| 12/16/02 | 1.26 | 19 | 1062 | 745 | 1038 | 1167 | 5.92 | 497 | 43 | 317 | 1.09 |
| 2/22/03 | 1.11 | 20 | 908 | 554 | 1043 | 1009 | 5.08 | 528 | 41 | 249 | - |
| 3/23/03 | 0.96 | 10 | 1025 | 709 | 1187 | 1216 | 6.06 | 428 | 50 | 218 | - |
| 4/19/03 | 1.03 | 15 | 967 | 659 | 1153 | 1183 | 5.80 | 581 | 46 | 220 | - |
| 5/20/03 | 0.98 | 13 | 859 | 466 | 970 | 825 | 4.41 | 407 | 40 | 363 | - |
| 6/21/03 | 0.96 | 14 | 824 | 390 | 911 | 719 | 3.95 | 335 | 34 | 342 | - |
| 7/23/03 | 0.94 | 14 | 831 | 396 | 908 | 713 | 3.96 | 357 | 34 | 344 | - |
| 8/21/03 | 0.98 | 13 | 875 | 414 | 935 | 742 | 4.12 | 347 | 35 | 324 | - |
| 9/23/03 | 0.91 | 13 | 835 | 411 | 926 | 750 | 4.08 | 341 | 35 | 325 | - |
| 11/22/03 | 1.01 | 22 | 1037 | 551 | 1204 | 908 | 5.16 | 440 | 36 | 451 | 1.29 |
| 12/26/03 | 1.08 | 24 | 1334 | 768 | 1403 | 1315 | 6.90 | 698 | 52 | 406 | 1.29 |
| 1/26/04 | 1.04 | 26 | 1147 | 618 | 1254 | 1068 | 5.77 | 547 | 45 | 297 | 1.22 |
| 2/26/04 | 1.03 | 27 | 1079 | 557 | 1299 | 1017 | 5.53 | 524 | 41 | 321 | 1.13 |

**Table-2. Time series data for As and other ions in shallow well at site A (depth - 10 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 1.74 | 18 | 955 | 1125 | 116 | 1497 | 6.32 | 211 | 50 | 142 | 0.82 |
| 2/19/01 | 1.66 | 18 | 922 | 855 | 106 | 1180 | 5.10 | 165 | 60 | 273 | - |
| 3/2/01 | 1.79 | 18 | 773 | 720 | 92 | 982 | 4.27 | 139 | 53 | 111 | - |
| 3/17/01 | 1.76 | 17 | 693 | 658 | 88 | 909 | 3.92 | 134 | 50 | 89 | - |
| 3/31/01 | 1.79 | 17 | 693 | 803 | 102 | 1091 | 4.58 | 162 | 59 | 142 | - |
| 4/14/01 | 1.48 | 16 | 689 | 737 | 92 | 1020 | 4.30 | 149 | 58 | 112 | - |
| 4/28/01 | 1.80 | 18 | 770 | 778 | 94 | 1075 | 4.57 | 183 | 63 | 107 | - |
| 5/12/01 | 1.90 | 17 | 754 | 748 | 92 | 1073 | 4.49 | 167 | 60 | 105 | - |
| 5/26/01 | 1.84 | 17 | 647 | 614 | 84 | 838 | 3.64 | 133 | 48 | 56 | - |
| 6/9/01 | 1.84 | 18 | 607 | 612 | 87 | 839 | 3.60 | 135 | 50 | 51 | 0.68 |
| 7/14/01 | 1.76 | 17 | 657 | 693 | 105 | 948 | 4.05 | 142 | 53 | 87 | 0.78 |
| 7/28/01 | 1.71 | 17 | 728 | 721 | 120 | 986 | 4.26 | 168 | 52 | 93 | 0.81 |
| 8/11/01 | 1.79 | 17 | 652 | 695 | 107 | 954 | 4.06 | 163 | 54 | 85 | 0.80 |
| 8/25/01 | 1.80 | 17 | 689 | 678 | 111 | 930 | 4.02 | 156 | 51 | 87 | 0.80 |
| 9/8/01 | 1.76 | 18 | 716 | 706 | 107 | 977 | 4.19 | 153 | 55 | 94 | 0.81 |
| 9/22/01 | 1.73 | 17 | 687 | 680 | 104 | 972 | 4.10 | 157 | 55 | 93 | 0.82 |
| 9/28/01 | 1.75 | 17 | 719 | 675 | 106 | 973 | 4.12 | 156 | 54 | 101 | 0.83 |
| 10/27/01 | 1.57 | 17 | 888 | 868 | 124 | 1196 | 5.14 | 185 | 60 | 252 | 0.73 |
| 11/24/01 | 1.62 | 16 | 816 | 794 | 128 | 1126 | 4.79 | 160 | 60 | 210 | 0.65 |
| 1/5/02 | 1.62 | 17 | 597 | 592 | 112 | 964 | 3.82 | 136 | 52 | 108 | 0.75 |
| 3/30/02 | 1.81 | 17 | 725 | 475 | 102 | 967 | 3.71 | 222 | 43 | 106 | 0.65 |
| 4/27/02 | 1.72 | 16 | 683 | 502 | 99 | 999 | 3.79 | 148 | 43 | 134 | 0.77 |
| 5/27/02 | 1.71 | 16 | 779 | 513 | 87 | 886 | 3.66 | 126 | 40 | 55 | 0.52 |
| 6/30/02 | 1.86 | 16 | 773 | 553 | 85 | 939 | 3.84 | 153 | 42 | 103 | 0.74 |
| 7/27/02 | 2.05 | 17 | 698 | 499 | 84 | 955 | 3.69 | 210 | 45 | 100 | 0.70 |
| 8/31/02 | 1.74 | 16 | 762 | 532 | 81 | 927 | 3.76 | 148 | 43 | 88 | 0.68 |
| 10/10/02 | 1.64 | 18 | 761 | 523 | 78 | 888 | 3.66 | 152 | 37 | 85 | 0.70 |
| 11/16/02 | 1.63 | 16 | 816 | 550 | 78 | 901 | 3.80 | 138 | 40 | 113 | 0.73 |
| 12/16/02 | 1.74 | 15 | 853 | 633 | 85 | 1026 | 4.26 | 153 | 45 | 225 | - |
| 2/22/03 | 1.82 | 14 | 1023 | 698 | 91 | 1133 | 4.78 | 181 | 61 | 210 | - |
| 3/23/03 | 1.80 | 14 | 914 | 608 | 80 | 972 | 4.16 | 157 | 50 | 152 | - |
| 4/19/03 | 1.85 | 14 | 935 | 647 | 83 | 1025 | 4.37 | 163 | 50 | 196 | - |
| 5/20/03 | 1.81 | 13 | 882 | 655 | 86 | 1017 | 4.31 | 151 | 50 | 198 | - |
| 6/21/03 | 1.92 | 14 | 862 | 571 | 80 | 932 | 3.95 | 148 | 52 | 148 | - |
| 7/23/03 | 1.93 | 14 | 908 | 603 | 79 | 991 | 4.18 | 159 | 48 | 171 | - |
| 8/21/03 | 1.86 | 14 | 902 | 634 | 82 | 995 | 4.24 | 165 | 47 | 177 | - |
| 9/23/03 | 1.82 | 15 | 911 | 633 | 79 | 1002 | 4.26 | 164 | 54 | 176 | - |
| 11/22/03 | 1.56 | 16 | 604 | 705 | 110 | 913 | 3.95 | 143 | 43 | 138 | 0.69 |
| 12/26/03 | 1.57 | 16 | 572 | 660 | 111 | 920 | 3.87 | 142 | 42 | 130 | 0.80 |
| 1/26/04 | 1.71 | 16 | 620 | 722 | 111 | 971 | 4.12 | 152 | 46 | 151 | 0.82 |
| 2/26/04 | 1.70 | 15 | 872 | 1000 | 124 | 1347 | 5.69 | 217 | 63 | 315 | 0.86 |

**Table-3. Time series data for As and other ions in shallow well at site A (depth - 13 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 6.37 | 35 | 866 | 737 | 97 | 1374 | 5.19 | 221 | 91 | 51 | 1.35 |
| 2/19/01 | 6.42 | 41 | 1031 | 716 | 100 | 1342 | 5.25 | 263 | 97 | 30 | - |
| 3/2/01 | 7.10 | 40 | 869 | 732 | 98 | 1393 | 5.22 | 268 | 93 | 19 | - |
| 3/17/01 | 7.18 | 39 | 848 | 755 | 96 | 1418 | 5.29 | 267 | 100 | 13 | - |
| 3/31/01 | 7.27 | 38 | 852 | 766 | 102 | 1468 | 5.43 | 279 | 96 | 12 | - |
| 4/14/01 | 6.60 | 34 | 808 | 747 | 94 | 1436 | 5.27 | 228 | 95 | 7 | - |
| 4/28/01 | 6.82 | 36 | 847 | 767 | 98 | 1461 | 5.40 | 267 | 97 | 10 | - |
| 5/12/01 | 8.02 | 41 | 884 | 776 | 100 | 1472 | 5.48 | 277 | 101 | 9 | - |
| 5/26/01 | 7.78 | 41 | 846 | 754 | 99 | 1433 | 5.32 | 273 | 102 | 19 | - |
| 6/9/01 | 7.51 | 39 | 819 | 740 | 97 | 1432 | 5.26 | 228 | 93 | 22 | 1.24 |
| 7/14/01 | 7.64 | 39 | 778 | 703 | 97 | 1362 | 5.01 | 264 | 98 | 11 | 1.22 |
| 7/28/01 | 6.98 | 34 | 720 | 655 | 91 | 1311 | 4.75 | 251 | 95 | 10 | 1.24 |
| 8/11/01 | 7.52 | 38 | 771 | 715 | 94 | 1381 | 5.06 | 265 | 95 | 14 | 1.22 |
| 8/25/01 | 7.54 | 38 | 740 | 690 | 96 | 1386 | 4.99 | 258 | 95 | 17 | 1.23 |
| 9/8/01 | 7.81 | 38 | 744 | 704 | 96 | 1372 | 4.99 | 256 | 97 | 23 | 1.25 |
| 9/22/01 | 7.99 | 39 | 743 | 690 | 94 | 1392 | 5.00 | 256 | 96 | 25 | 1.17 |
| 9/28/01 | 7.81 | 38 | 730 | 693 | 94 | 1390 | 4.99 | 257 | 96 | 29 | 1.24 |
| 10/27/01 | 7.34 | 36 | 673 | 690 | 94 | 1406 | 4.96 | 277 | 99 | 62 | 1.23 |
| 11/24/01 | 8.01 | 37 | 729 | 715 | 99 | 1433 | 5.13 | 280 | 99 | 16 | 1.25 |
| 1/5/02 | 7.95 | 37 | 719 | 712 | 101 | 1450 | 5.15 | 294 | 101 | 29 | 1.18 |
| 3/30/02 | 7.89 | 31 | 1208 | 645 | 95 | 1454 | 5.50 | 231 | 93 | 89 | 1.30 |
| 4/27/02 | 7.46 | 31 | 1316 | 735 | 89 | 1411 | 5.70 | 196 | 90 | 34 | 1.21 |
| 5/27/02 | 8.08 | 30 | 1254 | 719 | 93 | 1426 | 5.64 | 228 | 94 | 46 | 1.28 |
| 6/30/02 | 7.23 | 24 | 1211 | 678 | 88 | 1424 | 5.51 | 199 | 91 | 24 | 1.31 |
| 7/27/02 | 4.82 | 9 | 1195 | 644 | 86 | 1423 | 5.42 | 217 | 90 | 18 | 1.27 |
| 8/31/02 | 3.59 | 6 | 1440 | 799 | 87 | 1424 | 5.98 | 221 | 88 | 18 | 1.24 |
| 10/10/02 | 5.62 | 13 | 1280 | 688 | 84 | 1403 | 5.55 | 203 | 86 | 21 | 1.14 |
| 11/16/02 | 7.52 | 29 | 1326 | 745 | 88 | 1464 | 5.83 | 180 | 94 | 18 | 1.14 |
| 12/16/02 | 6.91 | 27 | 877 | 758 | 92 | 1398 | 5.28 | 233 | 93 | 19 | - |
| 2/22/03 | 6.98 | 24 | 908 | 791 | 89 | 1391 | 5.36 | 278 | 100 | 20 | - |
| 3/23/03 | 7.18 | 23 | 905 | 780 | 91 | 1388 | 5.33 | 279 | 95 | 21 | - |
| 4/19/03 | 7.03 | 23 | 896 | 762 | 88 | 1380 | 5.27 | 270 | 95 | 19 | - |
| 5/20/03 | 7.14 | 23 | 901 | 800 | 93 | 1401 | 5.40 | 288 | 95 | 29 | - |
| 6/21/03 | 7.16 | 24 | 920 | 778 | 94 | 1435 | 5.44 | 294 | 96 | 22 | - |
| 7/23/03 | 7.08 | 26 | 894 | 783 | 91 | 1498 | 5.55 | 286 | 106 | 20 | - |
| 8/21/03 | 7.13 | 24 | 906 | 794 | 88 | 1410 | 5.40 | 281 | 99 | 18 | - |
| 9/23/03 | 7.28 | 24 | 894 | 772 | 92 | 1457 | 5.45 | 280 | 98 | 18 | - |
| 11/22/03 | 7.72 | 33 | 973 | 967 | 110 | 1666 | 6.35 | 331 | 104 | 28 | 1.23 |
| 12/26/03 | 7.68 | 33 | 967 | 969 | 110 | 1657 | 6.33 | 332 | 102 | 27 | 1.64 |
| 1/26/04 | 7.69 | 31 | 954 | 927 | 111 | 1661 | 6.24 | 332 | 99 | 27 | 1.62 |
| 2/26/04 | 7.57 | 30 | 958 | 947 | 114 | 1638 | 6.24 | 337 | 98 | 28 | 1.37 |

**Table-4. Time series data for As and other ions in shallow well at site A (depth - 15 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 4.29 | 25 | 1972 | 1124 | 106 | 1457 | 7.24 | 220 | 20 | 8 | 0.97 |
| 2/19/01 | 4.46 | 23 | 1936 | 1081 | 102 | 1451 | 7.10 | 221 | 19 | 7 | - |
| 3/2/01 | 5.10 | 33 | 1993 | 1122 | 107 | 1478 | 7.30 | 310 | 20 | 8 | 0.87 |
| 3/17/01 | 5.40 | 29 | 2025 | 1100 | 100 | 1430 | 7.18 | 310 | 19 | 6 | 0.96 |
| 3/31/01 | 4.94 | 29 | 2013 | 1086 | 102 | 1436 | 7.16 | 274 | 17 | 6 | 0.94 |
| 4/14/01 | 5.01 | 27 | 1992 | 1076 | 99 | 1420 | 7.08 | 287 | 17 | 6 | 0.98 |
| 4/28/01 | 5.43 | 29 | 1947 | 1056 | 101 | 1406 | 6.97 | 320 | 19 | 6 | - |
| 5/12/01 | 5.27 | 30 | 1997 | 1051 | 99 | 1425 | 7.05 | 320 | 18 | 5 | - |
| 5/26/01 | 5.53 | 35 | 1918 | 1033 | 102 | 1407 | 6.90 | 351 | 18 | 7 | - |
| 6/9/01 | 5.28 | 30 | 1936 | 1043 | 101 | 1413 | 6.95 | 323 | 17 | 5 | 0.99 |
| 7/14/01 | 5.46 | 31 | 1795 | 1031 | 101 | 1448 | 6.85 | 359 | 17 | 6 | 1.00 |
| 7/28/01 | 5.43 | 28 | 1785 | 1021 | 98 | 1427 | 6.77 | 345 | 17 | 6 | 1.01 |
| 8/11/01 | 5.66 | 30 | 1837 | 1047 | 103 | 1491 | 7.01 | 368 | 18 | 6 | 1.03 |
| 8/25/01 | 5.41 | 30 | 1876 | 1041 | 101 | 1445 | 6.95 | 368 | 17 | 6 | 1.04 |
| 9/8/01 | 5.48 | 31 | 1844 | 1084 | 120 | 1518 | 7.17 | 524 | 20 | 7 | 1.05 |
| 9/22/01 | 5.70 | 31 | 1680 | 989 | 98 | 1457 | 6.67 | 396 | 19 | 7 | - |
| 9/28/01 | 5.48 | 35 | 1829 | 1043 | 102 | 1464 | 6.94 | 403 | 17 | 6 | 1.06 |
| 10/27/01 | 5.53 | 31 | 1857 | 1044 | 97 | 1444 | 6.93 | 387 | 18 | 6 | 1.09 |
| 11/24/01 | 4.98 | 28 | 1902 | 1023 | 100 | 1411 | 6.87 | 331 | 16 | 5 | - |
| 1/5/02 | 4.61 | 26 | 1967 | 986 | 101 | 1391 | 6.82 | 312 | 16 | 6 | 1.13 |
| 6/30/02 | 4.74 | 23 | 2108 | 1119 | 73 | 1458 | 7.33 | 339 | 19 | 6 | 0.91 |
| 7/27/02 | 5.46 | 27 | 2106 | 1156 | 65 | 1318 | 7.12 | 385 | 20 | 6 | - |
| 8/31/02 | 4.19 | 19 | 2165 | 1127 | 64 | 1296 | 7.07 | 335 | 19 | 6 | 0.86 |
| 10/10/02 | 4.53 | 24 | 1839 | 1032 | 67 | 1298 | 6.56 | 391 | 23 | 6 | 0.87 |
| 11/16/02 | 4.95 | 20 | 2007 | 1080 | 61 | 1171 | 6.57 | 339 | 21 | 6 | 0.92 |
| 12/16/02 | 3.90 | 18 | 2253 | 1057 | 61 | 1191 | 6.81 | 281 | 17 | 5 | 1.05 |
| 2/22/03 | 4.18 | 21 | 2183 | 1057 | 64 | 1225 | 6.81 | 324 | 17 | 5 | - |
| 3/23/03 | 3.94 | 18 | 2206 | 1058 | 63 | 1196 | 6.77 | 310 | 17 | 5 | - |
| 4/19/03 | 4.13 | 21 | 2101 | 1066 | 63 | 1231 | 6.76 | 322 | 17 | 5 | - |
| 5/20/03 | 4.09 | 19 | 2002 | 1046 | 60 | 1227 | 6.61 | 314 | 17 | 6 | - |
| 6/21/03 | 4.11 | 21 | 2025 | 1045 | 62 | 1339 | 6.85 | 332 | 18 | 8 | - |
| 7/23/03 | 4.12 | 21 | 1981 | 1040 | 64 | 1275 | 6.67 | 322 | 17 | 5 | - |
| 8/21/03 | 4.24 | 21 | 1995 | 1060 | 64 | 1251 | 6.68 | 344 | 17 | 6 | - |
| 9/23/03 | 4.28 | 21 | 2044 | 1060 | 64 | 1258 | 6.74 | 348 | 18 | 5 | - |
| 11/22/03 | 4.02 | 27 | 2347 | 1292 | 136 | 1416 | 7.90 | 325 | 16 | 8 | 0.92 |
| 12/26/03 | 4.23 | 28 | 2247 | 1228 | 133 | 1398 | 7.63 | 329 | 16 | 9 | 0.97 |
| 1/26/04 | 4.30 | 26 | 2254 | 1248 | 128 | 1386 | 7.65 | 326 | 16 | 9 | 1.00 |
| 2/26/04 | 4.07 | 26 | 2403 | 1296 | 133 | 1427 | 7.98 | 315 | 16 | 9 | 1.04 |

**Table-5. Time series data for As and other ions in deep well at site A (depth - 30 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 0.01 | 4 | 2275 | 233 | 55 | 393 | 3.58 | 1 | 2 | 12 | - |
| 2/19/01 | 0.01 | 4 | 2433 | 254 | 59 | 401 | 3.80 | 4 | 3 | 5 | - |
| 3/2/01 | 0.01 | 4 | 2470 | 247 | 52 | 298 | 3.61 | 9 | 3 | 0.3 | - |
| 3/17/01 | 0.01 | 4 | 2397 | 244 | 53 | 258 | 3.46 | 16 | 3 | 0.5 | - |
| 3/31/01 | 0.01 | 4 | 2476 | 244 | 50 | 246 | 3.51 | 20 | 3 | 5 | - |
| 4/14/01 | 0.01 | 4 | 2472 | 249 | 62 | 270 | 3.57 | 16 | 3 | 1 | - |
| 4/28/01 | 0.01 | 4 | 2473 | 253 | 57 | 247 | 3.53 | 15 | 3 | 0.3 | - |
| 5/12/01 | 0.01 | 4 | 2478 | 241 | 52 | 240 | 3.49 | 6 | 3 | 0.3 | - |
| 5/26/01 | 0.01 | 3 | 2437 | 243 | 51 | 246 | 3.47 | 4 | 3 | 1 | - |
| 6/9/01 | 0.01 | 4 | 2449 | 250 | 52 | 259 | 3.52 | 15 | 3 | 0.1 | - |
| 7/14/01 | 0.01 | 4 | 2480 | 250 | 53 | 240 | 3.51 | 19 | 3 | 0.3 | 0.70 |
| 7/28/01 | 0.01 | 3 | 2418 | 245 | 56 | 256 | 3.48 | 16 | 2 | 16 | 0.73 |
| 8/11/01 | 0.01 | 4 | 2546 | 251 | 55 | 255 | 3.61 | 15 | 2 | 16.4 | 0.75 |
| 8/25/01 | 0.01 | 4 | 2624 | 265 | 53 | 235 | 3.68 | 15 | 2 | 0.3 | 0.78 |
| 9/8/01 | 0.01 | 4 | 2436 | 242 | 51 | 226 | 3.42 | 15 | 2 | 12 | 0.77 |
| 9/28/01 | 0.01 | 4 | 2504 | 242 | 52 | 231 | 3.50 | 13 | 2 | 0.3 | 0.77 |
| 10/27/01 | 0.01 | 4 | 2474 | 245 | 50 | 228 | 3.47 | 13 | 2 | 0.3 | 0.76 |
| 11/24/01 | 0.01 | 4 | 2502 | 248 | 51 | 226 | 3.50 | 12 | 2 | 0.3 | 0.79 |
| 1/5/02 | 0.01 | 4 | 2474 | 240 | 50 | 227 | 3.46 | 12 | 2 | 5 | - |
| 3/30/02 | 0.01 | 4 | 2733 | 191 | 11 | 244 | 3.62 | 13 | 2 | 11 | 0.76 |
| 4/27/02 | 0.01 | 4 | 2579 | 198 | 13 | 244 | 3.48 | 8 | 1 | - | 0.77 |
| 5/27/02 | 0.01 | 4 | 2911 | 214 | 8 | 243 | 3.83 | 8 | 1 | - | 0.78 |
| 6/30/02 | 0.01 | 4 | 2742 | 221 | 57 | 272 | 3.78 | 7 | 1 | - | 0.78 |
| 7/27/02 | 0.01 | 4 | 2730 | 227 | 26 | 266 | 3.74 | 13 | 2 | 12 | 0.74 |
| 8/31/02 | 0.01 | 4 | 2763 | 216 | 12 | 257 | 3.72 | 13 | 2 | 15 | 0.83 |
| 10/10/02 | 0.01 | 4 | 2896 | 224 | 18 | 251 | 3.86 | 11 | 1 | 12 | 0.84 |
| 11/16/02 | 0.01 | 4 | 2566 | 214 | 20 | 265 | 3.54 | 14 | 2 | 13 | 0.85 |
| 12/16/02 | 0.01 | 4 | 2477 | 215 | 13 | 249 | 3.42 | 14 | 2 | 25 | - |
| 2/22/03 | 0.01 | 4 | 2392 | 204 | 16 | 245 | 3.31 | 13 | 2 | 23 | - |
| 3/23/03 | 0.01 | 4 | 2386 | 201 | 15 | 244 | 3.29 | 6 | 1 | 27 | - |
| 4/19/03 | 0.01 | 4 | 2433 | 204 | 10 | 232 | 3.32 | 5 | 1 | 26 | - |
| 5/20/03 | 0.01 | 4 | 2445 | 199 | 11 | 238 | 3.33 | 5 | 1 | 27 | - |
| 6/21/03 | 0.01 | 4 | 2441 | 205 | 11 | 234 | 3.33 | 5 | 1 | 25 | - |
| 7/23/03 | 0.01 | 4 | 2447 | 202 | 12 | 234 | 3.33 | 4 | 1 | 26 | - |
| 8/21/03 | 0.01 | 4 | 2386 | 192 | 11 | 232 | 3.24 | 4 | 1 | 30 | - |
| 9/23/03 | 0.01 | 4 | 2413 | 193 | 11 | 230 | 3.27 | 5 | 1 | 31 | - |
| 11/22/03 | 0.01 | 4 | 2567 | 289 | 32 | 262 | 3.70 | 5 | 1 | 32 | 0.79 |
| 12/26/03 | 0.01 | 4 | 2576 | 280 | 33 | 264 | 3.70 | 5 | 1 | 32 | 0.78 |
| 1/26/04 | 0.01 | 4 | 2558 | 280 | 34 | 271 | 3.69 | 5 | 1 | 35 | 0.78 |
| 2/26/04 | 0.01 | 4 | 2544 | 280 | 34 | 264 | 3.66 | 4 | 1 | 26 | 0.79 |

**Table-6. Time series data for As and other ions in deep well at site A (depth - 37 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/19/01 | 0.01 | 5 | 2510 | 239 | 27 | 417 | 3.85 | 1 | 2 | 39 | 0.81 |
| 2/6/01 | 0.01 | 4 | 2496 | 169 | 81 | 450 | 3.81 | 4 | 3 | - | - |
| 2/19/01 | 0.01 | 4 | 2624 | 172 | 11 | 446 | 3.87 | 9 | 3 | - | - |
| 3/2/01 | 0.01 | 4 | 2283 | 142 | 10 | 411 | 3.40 | 16 | 3 | - | - |
| 3/17/01 | 0.01 | 4 | 2488 | 160 | 74 | 399 | 3.68 | 20 | 3 | - | - |
| 3/31/01 | 0.01 | 4 | 2499 | 157 | 78 | 398 | 3.69 | 16 | 3 | 1 | - |
| 4/14/01 | 0.01 | 4 | 2367 | 149 | 93 | 383 | 3.52 | 15 | 3 | 1 | - |
| 4/28/01 | 0.01 | 4 | 2348 | 135 | 93 | 400 | 3.51 | 6 | 3 | 2 | - |
| 5/12/01 | 0.01 | 4 | 2551 | 176 | 96 | 392 | 3.78 | 4 | 3 | 2 | - |
| 5/26/01 | 0.01 | 3 | 2377 | 152 | 11 | 394 | 3.48 | 15 | 3 | - | - |
| 6/9/01 | 0.01 | 4 | 2281 | 139 | 91 | 387 | 3.42 | 19 | 3 | - | - |
| 7/14/01 | 0.01 | 4 | 2315 | 147 | 103 | 391 | 3.49 | 16 | 2 | - | 0.75 |
| 7/28/01 | 0.01 | 3 | 2167 | 149 | 98 | 383 | 3.33 | 15 | 2 | - | - |
| 8/11/01 | 0.01 | 4 | 2363 | 151 | 95 | 392 | 3.54 | 15 | 2 | - | 0.76 |
| 8/25/01 | 0.01 | 4 | 2514 | 158 | 93 | 376 | 3.68 | 15 | 2 | - | 0.77 |
| 9/8/01 | 0.01 | 4 | 2307 | 144 | 12 | 371 | 3.35 | 13 | 2 | 2 | 0.77 |
| 9/28/01 | 0.01 | 4 | 2388 | 149 | 101 | 377 | 3.54 | 13 | 2 | 3 | 0.76 |
| 10/27/01 | 0.01 | 4 | 2263 | 139 | 11 | 381 | 3.31 | 12 | 2 | 1 | 0.76 |
| 11/24/01 | 0.01 | 4 | 2404 | 153 | 10 | 363 | 3.44 | 12 | 2 | - | 0.76 |
| 1/5/02 | 0.01 | 4 | 2340 | 124 | 19 | 342 | 3.29 | 13 | 2 | - | 0.78 |
| 3/30/02 | 0.01 | 4 | 2766 | 157 | 18 | 384 | 3.87 | 8 | 1 | 5 | - |
| 4/27/02 | 0.01 | 4 | 2836 | 157 | 15 | 376 | 3.92 | 8 | 1 | 4 | - |
| 5/27/02 | 0.01 | 4 | 2176 | 154 | 8 | 371 | 3.23 | 7 | 1 | 4 | - |
| 6/30/02 | 0.01 | 4 | 2855 | 157 | 9 | 377 | 3.93 | 13 | 2 | 4 | - |
| 7/27/02 | 0.01 | 4 | 2898 | 159 | 8 | 368 | 3.96 | 13 | 2 | 3 | - |
| 8/31/02 | 0.01 | 4 | 2821 | 150 | 9 | 379 | 3.89 | 11 | 1 | 3 | - |
| 10/10/02 | 0.01 | 4 | 2741 | 155 | 13 | 380 | 3.82 | 14 | 2 | 2 | - |
| 11/16/02 | 0.01 | 4 | 2771 | 189 | 23 | 376 | 3.93 | 14 | 2 | 3 | - |
| 12/16/02 | 0.01 | 4 | 2883 | 161 | 14 | 367 | 3.96 | 13 | 2 | 3 | - |
| 2/22/03 | 0.01 | 4 | 2745 | 160 | 13 | 364 | 3.81 | 6 | 1 | 24 | - |
| 3/23/03 | 0.01 | 4 | 2837 | 157 | 12 | 366 | 3.89 | 5 | 1 | 25 | - |
| 4/19/03 | 0.01 | 4 | 2744 | 154 | 12 | 372 | 3.81 | 5 | 1 | 25 | - |
| 5/20/03 | 0.01 | 4 | 2787 | 155 | 12 | 365 | 3.84 | 5 | 1 | 25 | - |
| 6/21/03 | 0.01 | 4 | 2786 | 154 | 12 | 363 | 3.83 | 4 | 1 | 25 | - |
| 7/23/03 | 0.01 | 4 | 2808 | 155 | 12 | 369 | 3.87 | 4 | 1 | 24 | - |
| 8/21/03 | 0.01 | 4 | 2785 | 157 | 12 | 360 | 3.83 | 5 | 1 | 24 | - |
| 9/23/03 | 0.01 | 4 | 2863 | 146 | 13 | 359 | 3.89 | 5 | 1 | 26 | - |
| 11/22/03 | 0.01 | 4 | 2577 | 222 | 35 | 412 | 3.88 | 5 | 1 | 33 | - |
| 12/26/03 | 0.01 | 4 | 2697 | 221 | 35 | 407 | 3.99 | 5 | 1 | 37 | - |
| 1/26/04 | 0.01 | 4 | 2532 | 225 | 35 | 400 | 3.82 | 4 | 1 | 38 | - |
| 2/26/04 | 0.01 | 4 | 2698 | 223 | 36 | 402 | 3.98 | 5 | 1 | 35 | - |

**Table-7. Time series data for As and other ions in deep well at site A (depth - 43 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/19/01 | 0.01 | 6 | 2225 | 222 | 29 | 428 | 3.55 | 1 | 2 | 39 | 0.86 |
| 2/6/01 | 0.01 | 7 | 1781 | 169 | 18 | 607 | 3.35 | 9 | 2 | 69 | - |
| 2/19/01 | 0.01 | 8 | 1782 | 182 | 18 | 626 | 3.42 | 36 | 6 | 50 | - |
| 3/2/01 | 0.01 | 8 | 1827 | 187 | 20 | 639 | 3.50 | 86 | 9 | 5 | - |
| 3/17/01 | 0.01 | 8 | 1533 | 164 | 16 | 393 | 2.66 | 93 | 9 | 5 | - |
| 3/31/01 | 0.01 | 8 | 1601 | 163 | 19 | 513 | 2.97 | 94 | 9 | 5 | - |
| 4/14/01 | 0.01 | 7 | 1844 | 189 | 20 | 482 | 3.21 | 39 | 9 | 5 | - |
| 5/12/01 | 0.01 | 8 | 1810 | 175 | 19 | 484 | 3.15 | 0 | 12 | 1 | - |
| 5/26/01 | 0.01 | 8 | 1684 | 163 | 14 | 464 | 2.95 | 103 | 8 | 5 | - |
| 6/9/01 | 0.01 | 7 | 1652 | 154 | 18 | 476 | 2.93 | 101 | 8 | 1 | 0.84 |
| 7/14/01 | 0.01 | 8 | 1677 | 160 | 13 | 445 | 2.90 | 98 | 8 | 5 | 0.81 |
| 7/28/01 | 0.01 | 8 | 1723 | 156 | 18 | 431 | 2.92 | 73 | 8 | 5 | 0.84 |
| 8/11/01 | 0.01 | 7 | 1751 | 154 | 17 | 426 | 2.93 | 0 | 0 | 16 | 0.86 |
| 8/25/01 | 0.01 | 7 | 1835 | 176 | 21 | 439 | 3.08 | 72 | 7 | 5 | 0.89 |
| 9/8/01 | 0.01 | 7 | 1690 | 160 | 16 | 422 | 2.87 | 73 | 7 | 5 | 0.91 |
| 10/27/01 | 0.01 | 7 | 1755 | 160 | 16 | 402 | 2.90 | 67 | 7 | 12 | 0.93 |
| 11/24/01 | 0.01 | 7 | 1871 | 180 | 19 | 405 | 3.06 | 63 | 7 | 5 | 0.95 |
| 1/5/02 | 0.01 | 7 | 1786 | 170 | 19 | 413 | 2.97 | 65 | 7 | 5 | 0.99 |
| 1/5/02 | 0.01 | 8 | 1777 | 145 | 18 | 408 | 2.90 | 73 | 7 | 5 | - |
| 3/30/02 | 0.01 | 7 | 1895 | 150 | 15 | 392 | 3.00 | 65 | 7 | 8 | - |
| 7/27/02 | 0.01 | 8 | 1474 | 140 | 19 | 448 | 2.67 | 60 | 7 | 11 | - |
| 8/31/02 | 0.01 | 6 | 1579 | 147 | 17 | 409 | 2.71 | 61 | 6 | 12 | - |
| 10/10/02 | 0.01 | 6 | 1781 | 148 | 20 | 410 | 2.92 | 61 | 6 | 15 | - |
| 11/16/02 | 0.01 | 6 | 1771 | 143 | 14 | 379 | 2.83 | 56 | 6 | 12 | - |
| 12/16/02 | 0.01 | 6 | 1730 | 149 | 15 | 395 | 2.83 | 49 | 6 | 13 | - |
| 2/22/03 | 0.01 | 8 | 1693 | 147 | 13 | 379 | 2.76 | 32 | 5 | 25 | - |
| 3/23/03 | 0.01 | 8 | 1755 | 151 | 14 | 387 | 2.85 | 33 | 5 | 23 | - |
| 4/19/03 | 0.01 | 8 | 1775 | 215 | 22 | 467 | 3.16 | 90 | 5 | 27 | - |
| 5/20/03 | 0.01 | 8 | 1861 | 217 | 24 | 482 | 3.28 | 29 | 4 | 26 | - |
| 6/21/03 | 0.01 | 8 | 1797 | 224 | 25 | 476 | 3.22 | 28 | 4 | 27 | - |
| 7/23/03 | 0.01 | 8 | 1926 | 228 | 24 | 476 | 3.36 | 31 | 4 | 25 | - |
| 8/21/03 | 0.01 | 8 | 1792 | 210 | 21 | 453 | 3.14 | 28 | 4 | 26 | - |
| 9/23/03 | 0.01 | 7 | 1723 | 216 | 25 | 453 | 3.09 | 58 | 6 | 12 | - |
| 11/22/03 | 0.01 | 8 | 1764 | 212 | 37 | 450 | 3.12 | 26 | 3 | 34 | - |
| 12/26/03 | 0.01 | 7 | 1708 | 213 | 36 | 442 | 3.05 | 25 | 3 | 37 | - |
| 1/26/04 | 0.01 | 8 | 1723 | 212 | 36 | 444 | 3.07 | 27 | 3 | 36 | - |
| 2/26/04 | 0.01 | 8 | 1682 | 206 | 36 | 450 | 3.03 | 24 | 3 | 37 | - |

**Table-8. Time series data for As and other ions in shallow well at site A (depth - 91 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/5/02 | 0.02 | 10 | 2029 | 496 | 47 | 615 | 4.30 | - | - | - | 1.44 |
| 3/30/02 | 0.02 | 10 | 1954 | 399 | 39 | 637 | 4.07 | - | - | - | 1.44 |
| 4/27/02 | 0.02 | 9 | 2216 | 200 | 30 | 439 | 3.53 | - | 2 | - | 1.34 |
| 5/27/02 | 0.02 | 9 | 2139 | 207 | 32 | 434 | 3.45 | - | 1 | - | 1.33 |
| 6/30/02 | 0.02 | 10 | 2200 | 419 | 35 | 586 | 4.25 | 277 | 2 | - | 1.47 |
| 7/27/02 | 0.02 | 9 | 2167 | 417 | 36 | 587 | 4.21 | 211 | 2 | - | 1.47 |
| 8/31/02 | 0.02 | 11 | 1968 | 417 | 36 | 591 | 4.02 | 324 | 2 | - | 1.47 |
| 10/10/02 | 0.02 | 11 | 1997 | 423 | 33 | 552 | 3.98 | 330 | 2 | - | 1.47 |
| 11/16/02 | 0.02 | 9 | 2312 | 429 | 36 | 594 | 4.39 | 275 | 2 | - | 1.49 |
| 12/16/02 | 0.02 | 11 | 1718 | 423 | 40 | 641 | 3.89 | 301 | 3 | - | 1.50 |
| 2/22/03 | 0.02 | 11 | 1669 | 407 | 34 | 626 | 3.77 | 182 | 3 | 18 | - |
| 3/23/03 | 0.02 | 10 | 1466 | 377 | 34 | 603 | 3.46 | 130 | 3 | 24 | - |
| 4/19/03 | 0.02 | 11 | 1643 | 414 | 39 | 587 | 3.68 | 163 | 4 | 29 | - |
| 5/20/03 | 0.02 | 9 | 1702 | 417 | 30 | 612 | 3.79 | - | 3 | 27 | - |
| 6/21/03 | 0.02 | 11 | 1637 | 409 | 31 | 592 | 3.67 | 137 | 3 | 32 | - |
| 7/23/03 | 0.02 | 10 | 1681 | 433 | 31 | 586 | 3.75 | 194 | 3 | 28 | - |
| 8/21/03 | 0.02 | 10 | 1565 | 390 | 34 | 602 | 3.58 | 202 | 3 | 26 | - |
| 9/23/03 | 0.02 | 11 | 1852 | 452 | 42 | 632 | 4.06 | 341 | 3 | 8 | - |
| 11/22/03 | 0.02 | 8 | 1583 | 408 | 44 | 563 | 3.57 | 71 | 2 | 39 | 1.43 |
| 12/26/03 | 0.02 | 9 | 1549 | 390 | 43 | 568 | 3.51 | - | 2 | 36 | 1.43 |
| 1/26/04 | 0.02 | 10 | 1535 | 392 | 43 | 579 | 3.52 | - | 2 | 39 | 1.44 |
| 2/26/04 | 0.02 | 9 | 1533 | 395 | 44 | 575 | 3.52 | - | 2 | 37 | 1.44 |

**Table-9a. Time series water level data (m) for shallow and deep wells at site A (1/2001-1/2002)**

| Date of | Wells at different depths | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Measurement | 7 m | 10 m | 13 m | 15 m | 30 m | 37 m | 43 m | 91 m |
| 1/27/2001 | 3.3 | 3.2 | 3.3 | 3.2 | 2.6 | 2.6 | 2.6 | x |
| 2/6/2001 | 3.0 | 3.1 | 3.1 | 3.0 | 2.2 | 2.2 | 2.2 | x |
| 2/11/2001 | 3.0 | 3.1 | 3.0 | 2.9 | 2.1 | 2.1 | 2.1 | x |
| 2/19/2001 | 2.4 | 2.4 | 2.4 | 2.4 | 1.4 | 1.4 | 1.4 | x |
| 2/24/2001 | 2.4 | 2.4 | 2.4 | 2.4 | 1.5 | 1.5 | 1.4 | x |
| 3/2/2001 | 2.4 | 2.4 | 2.3 | 2.3 | 1.2 | 1.2 | 1.2 | x |
| 3/10/2001 | 2.3 | 2.3 | 2.3 | 2.3 | 1.2 | 1.2 | 1.2 | x |
| 3/17/2001 | 2.3 | 2.3 | 2.3 | 2.3 | 0.9 | 0.9 | 0.9 | x |
| 3/24/2001 | 2.3 | 2.3 | 2.2 | 2.2 | 1.0 | 1.0 | 0.9 | x |
| 3/31/2001 | 2.3 | 2.3 | 2.3 | 2.3 | 1.0 | 1.0 | 1.0 | x |
| 4/7/2001 | 2.6 | 2.6 | 2.6 | 2.6 | 0.9 | 0.9 | 0.8 | x |
| 4/14/2001 | 2.6 | 2.6 | 2.6 | 2.6 | 0.7 | 0.7 | 0.7 | x |
| 4/21/2001 | 2.7 | 2.7 | 2.7 | 2.7 | 0.9 | 0.9 | 0.9 | x |
| 4/28/2001 | 2.8 | 2.8 | 2.8 | 2.8 | 0.9 | 0.9 | 0.9 | x |
| 5/5/2001 | 2.9 | 2.9 | 2.9 | 2.9 | 1.1 | 1.1 | 1.1 | x |
| 5/12/2001 | 3.6 | 3.6 | 3.6 | 3.6 | 1.6 | 1.6 | 1.6 | x |
| 5/19/2001 | 3.7 | 3.7 | 3.7 | 3.7 | 1.9 | 1.9 | 1.9 | x |
| 5/26/2001 | 3.8 | 3.7 | 3.7 | 3.7 | 2.2 | 2.2 | 2.2 | x |
| 6/2/2001 | 3.8 | 3.8 | 3.8 | 3.8 | 2.4 | 2.4 | 2.4 | x |
| 6/9/2001 | 4.6 | 4.6 | 4.6 | 4.6 | 2.8 | 2.8 | 2.8 | x |
| 6/30/2001 | 5.2 | 5.2 | 5.2 | 5.2 | 3.8 | 3.8 | 3.8 | x |
| 7/7/2001 | 5.2 | 5.2 | 5.2 | 5.2 | 3.9 | 3.9 | 3.9 | x |
| 7/14/2001 | 5.3 | 5.3 | 5.3 | 5.3 | 4.0 | 4.0 | 4.0 | x |
| 7/21/2001 | 5.4 | 5.4 | 5.4 | 5.4 | 4.1 | 4.1 | 4.1 | x |
| 7/28/2001 | 5.6 | 5.6 | 5.6 | 5.6 | 4.3 | 4.3 | 4.3 | x |
| 8/4/2001 | 5.9 | 5.9 | 5.9 | 5.8 | 4.6 | 4.6 | 4.5 | x |
| 8/11/2001 | 6.3 | 6.3 | 6.3 | 6.3 | 5.0 | 5.0 | 5.0 | x |
| 8/18/2001 | 6.2 | 6.2 | 6.2 | 6.2 | 4.9 | 4.9 | 4.9 | x |
| 8/25/2001 | 6.0 | 6.0 | 6.0 | 6.0 | 4.8 | 4.8 | 4.8 | x |
| 9/1/2001 | 6.0 | 6.1 | 6.0 | 6.0 | 5.0 | 5.0 | 5.0 | x |
| 9/8/2001 | 6.2 | 6.2 | 6.2 | 6.2 | 5.1 | 5.1 | 5.1 | x |
| 9/15/2001 | 6.1 | 6.1 | 6.1 | 6.1 | 5.0 | 5.0 | 5.0 | x |
| 9/22/2001 | 6.2 | 6.2 | 6.2 | 6.2 | 5.1 | 5.1 | 5.1 | x |
| 9/28/2001 | 5.9 | 5.9 | 5.9 | 5.9 | 5.0 | 5.0 | 4.9 | x |
| 10/6/2001 | 5.7 | 5.7 | 5.7 | 5.7 | 4.9 | 4.9 | 4.9 | x |
| 10/13/2001 | 5.6 | 5.6 | 5.6 | 5.6 | 4.8 | 4.8 | 4.8 | x |
| 10/20/2001 | 5.8 | 5.8 | 5.8 | 5.8 | 4.9 | 4.9 | 4.9 | x |
| 10/27/2001 | 5.4 | 5.4 | 5.4 | 5.4 | 4.6 | 4.6 | 4.6 | x |
| 11/3/2001 | 5.2 | 5.2 | 5.1 | 5.2 | 4.5 | 4.5 | 4.5 | x |
| 11/10/2001 | 4.9 | 4.9 | 4.9 | 4.9 | 4.4 | 4.4 | 4.4 | x |
| 11/17/2001 | 4.5 | 4.5 | 4.5 | 4.5 | 4.2 | 4.2 | 4.2 | x |
| 11/24/2001 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | x |
| 12/1/2001 | 3.8 | 3.7 | 3.7 | 3.7 | 3.9 | 3.9 | 3.9 | x |
| 12/8/2001 | 3.5 | 3.5 | 3.5 | 3.5 | 3.7 | 3.7 | 3.7 | x |
| 12/29/2001 | 3.1 | 3.1 | 3.1 | 3.1 | 3.5 | 3.5 | 3.4 | x |
| 1/5/2002 | 3.1 | 3.1 | 3.1 | 3.1 | 3.3 | 3.3 | 3.3 | x |
| 1/12/2002 | 3.0 | 3.0 | 3.0 | 3.0 | 3.1 | 3.1 | 3.1 | x |

**x Well was not accessible due to public use**

**Table-9b. Time series water level data (m) for shallow and deep wells at site A (2/2002-2/2004)**

| Date of Measurement | Wells at different depths | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 7 m | 10 m | 13 m | 15 m | 30 m | 37 m | 43 m | 91 m |
| 2/18/2002 | 2.4 | 2.4 | 2.4 | 2.4 | 1.4 | 1.4 | 1.4 | x |
| 3/16/2002 | 2.6 | 2.6 | 2.6 | 2.7 | 1.0 | 1.0 | 1.0 | 1.1 |
| 3/30/2002 | 3.0 | 3.0 | 3.0 | 3.0 | 1.4 | 1.4 | 1.4 | 1.5 |
| 4/13/2002 | 3.2 | 3.2 | 3.2 | 3.2 | 1.7 | 1.7 | 1.7 | 1.5 |
| 4/27/2002 | 3.2 | 3.2 | 3.2 | 3.2 | 1.3 | 1.3 | 1.3 | 1.5 |
| 5/12/2002 | 4.0 | 4.0 | 4.0 | 4.0 | 2.2 | 2.2 | 2.2 | 2.3 |
| 5/27/2002 | 4.3 | 4.3 | 4.3 | 4.3 | 2.6 | 2.6 | 2.6 | 2.8 |
| 6/8/2002 | 4.6 | 4.6 | 4.6 | 4.6 | 3.1 | 3.1 | 3.1 | 3.2 |
| 6/15/2002 | 5.0 | 5.0 | 5.0 | 5.0 | 3.3 | 3.3 | 3.3 | 3.4 |
| 6/30/2002 | 5.8 | 5.8 | 5.8 | 5.8 | 4.1 | 4.1 | 4.1 | 4.2 |
| 7/14/2002 | 6.2 | 6.2 | 6.2 | 6.2 | 4.7 | 4.7 | 4.7 | 4.2 |
| 7/27/2002 | 6.3 | 6.3 | 6.3 | 6.3 | 4.9 | 4.9 | 4.9 | 5.0 |
| 8/7/2002 | 6.8 | 6.8 | 6.8 | 6.8 | 5.4 | 5.4 | 5.3 | 5.5 |
| 8/31/2002 | 6.4 | 6.4 | 6.4 | 6.4 | 5.2 | 5.2 | 5.2 | 5.5 |
| 9/15/2002 | 5.5 | 5.5 | 5.5 | 5.5 | 4.6 | 4.6 | 4.6 | 4.8 |
| 10/11/2002 | 5.4 | 5.4 | 5.4 | 5.4 | 4.4 | 4.4 | 4.4 | 4.4 |
| 11/16/2002 | 4.6 | 4.6 | 4.6 | 4.6 | 3.8 | 3.8 | 3.8 | 3.9 |
| 12/3/2002 | 3.5 | 3.5 | 3.5 | 3.5 | 3.6 | 3.6 | 3.6 | 3.7 |
| 12/16/2002 | 3.3 | 3.3 | 3.3 | 3.3 | 3.5 | 3.5 | 3.5 | 3.6 |
| 1/14/2003 | 2.9 | 2.9 | 2.9 | 2.9 | 2.5 | 2.5 | 2.8 | 2.7 |
| 2/1/2003 | 2.6 | 2.6 | 2.6 | 2.6 | 1.6 | 1.6 | 1.6 | 1.8 |
| 2/15/2003 | 2.6 | 2.6 | 2.6 | 2.6 | 1.6 | 1.6 | 1.6 | 1.7 |
| 3/2/2003 | 2.7 | 2.7 | 2.7 | 2.7 | 1.0 | 1.0 | 1.0 | 1.2 |
| 3/15/2003 | 2.6 | 2.6 | 2.6 | 2.6 | 1.0 | 1.0 | 1.0 | 1.1 |
| 3/31/2003 | 3.0 | 3.0 | 3.0 | 3.0 | 1.3 | 1.3 | 1.3 | 1.5 |
| 4/12/2003 | 3.2 | 3.2 | 3.2 | 3.2 | 1.3 | 1.3 | 1.3 | 1.5 |
| 4/26/2003 | 3.3 | 3.3 | 3.3 | 3.3 | 1.4 | 1.4 | 1.4 | 1.5 |
| 5/11/2003 | 3.7 | 3.7 | 3.7 | 3.7 | 2.0 | 2.0 | 2.0 | 2.1 |
| 5/24/2003 | 3.8 | 3.8 | 3.8 | 3.8 | 2.1 | 2.1 | 2.1 | 2.3 |
| 6/7/2003 | 4.1 | 4.1 | 4.1 | 4.1 | 2.4 | 2.4 | 2.4 | 2.5 |
| 6/24/2003 | 5.5 | 5.4 | 5.4 | 5.4 | 3.3 | 3.3 | 3.3 | 3.5 |
| 7/8/2003 | 6.0 | 6.0 | 6.0 | 6.0 | 4.2 | 4.2 | 4.2 | 4.3 |
| 7/22/2003 | 6.9 | 6.8 | 6.8 | 6.8 | 5.0 | 5.0 | 5.0 | 5.1 |
| 8/5/2003 | 6.5 | 6.5 | 6.5 | 6.5 | 4.8 | 4.8 | 4.8 | 5.0 |
| 8/21/2003 | 6.1 | 6.1 | 6.1 | 6.1 | 4.7 | 4.7 | 4.7 | 4.9 |
| 9/3/2003 | 6.3 | 6.3 | 6.3 | 6.3 | 4.9 | 4.9 | 4.9 | 5.0 |
| 9/18/2003 | 6.2 | 6.2 | 6.2 | 6.2 | 4.9 | 4.9 | 4.9 | 5.0 |
| 10/1/2003 | 6.3 | 6.3 | 6.3 | 6.3 | 4.9 | 4.9 | 4.9 | 5.1 |
| 10/23/2003 | 5.6 | 5.6 | 5.6 | 5.6 | 4.5 | 4.5 | 4.4 | 4.6 |
| 11/9/2003 | 4.9 | 4.9 | 4.9 | 4.9 | 4.1 | 4.1 | 4.1 | 4.3 |
| 11/23/2003 | 4.0 | 4.0 | 4.0 | 4.0 | 3.7 | 3.7 | 3.7 | 3.9 |
| 12/10/2003 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.6 |
| 12/25/2003 | 3.4 | 3.4 | 3.4 | 3.4 | 3.2 | 3.2 | 3.2 | 3.3 |
| 1/1/2004 | 3.0 | 3.0 | 3.0 | 3.0 | 2.8 | 2.8 | 2.8 | 3.0 |
| 1/25/2004 | 2.9 | 2.9 | 2.9 | 2.9 | 2.0 | 2.0 | 2.0 | 2.1 |
| 2/16/2004 | 2.7 | 2.7 | 2.7 | 2.7 | 1.1 | 1.1 | 1.1 | 1.2 |
| 2/27/2004 | 2.7 | 2.7 | 2.7 | 2.7 | 1.1 | 1.1 | 1.1 | 1.2 |

**x Well was not accessible due to public use**

**Table-10. Time series data for As and other ions in shallow well at site B (depth - 7 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/12/01 | 0.57 | 106 | 2725 | 1563 | 219 | 2688 | 11.45 | 690 | 19 | 633 | - |
| 5/26/01 | 0.50 | 76 | 2236 | 1650 | 195 | 2590 | 10.91 | 411 | 31 | 576 | - |
| 6/9/01 | 0.54 | 96 | 2419 | 1429 | 137 | 2584 | 10.58 | 363 | 21 | 531 | - |
| 6/20/01 | 0.50 | 91 | 3070 | 1799 | 152 | 2778 | 12.38 | 234 | 9 | 463 | 4.64 |
| 7/14/01 | 0.42 | 55 | 2017 | 2085 | 186 | 2368 | 11.11 | 388 | 22 | 561 | 3.91 |
| 8/11/01 | 0.41 | 46 | 1634 | 1976 | 185 | 2499 | 10.77 | 348 | 19 | 633 | 3.99 |
| 8/25/01 | 0.44 | 50 | 1611 | 1946 | 184 | 2506 | 10.70 | 361 | 20 | 654 | 4.06 |
| 9/8/01 | 0.42 | 49 | 1657 | 2046 | 187 | 2456 | 10.85 | 370 | 18 | 641 | 4.16 |
| 9/28/01 | 0.46 | 45 | 1659 | 2010 | 192 | 2499 | 10.87 | 374 | 18 | 715 | 4.24 |
| 10/27/01 | 0.41 | 44 | 1766 | 2289 | 198 | 2882 | 12.31 | 375 | 18 | 957 | 5.11 |
| 11/24/01 | 0.41 | 48 | 2129 | 2499 | 199 | 3360 | 14.04 | 379 | 20 | 990 | 5.28 |
| 1/5/02 | 0.42 | 53 | 2003 | 2272 | 191 | 2995 | 12.73 | 386 | 21 | 1073 | 4.61 |
| 3/30/02 | 0.36 | 37 | 2227 | 1871 | 150 | 2809 | 11.74 | 386 | 14 | 1164 | 4.66 |
| 7/27/02 | 0.33 | 42 | 2471 | 1993 | 153 | 3098 | 12.81 | 564 | 18 | 910 | 4.27 |
| 8/31/02 | 0.31 | 39 | 2485 | 2108 | 143 | 2818 | 12.48 | 561 | 18 | 828 | 4.41 |
| 10/10/02 | 0.38 | 43 | 2472 | 2328 | 150 | 3293 | 13.86 | 597 | 20 | 802 | 4.69 |
| 11/16/02 | 0.33 | 39 | 2299 | 2222 | 150 | 3319 | 13.53 | 587 | 20 | 827 | 4.60 |
| 12/16/02 | 0.33 | 45 | 2234 | 2439 | 198 | 2793 | 12.90 | 464 | 16 | 673 | 4.60 |
| 2/22/03 | 0.28 | 46 | 2160 | 2255 | 184 | 2585 | 12.03 | 407 | 15 | 591 | 4.47 |
| 3/23/03 | 0.29 | 39 | 2169 | 2281 | 194 | 2674 | 12.27 | 401 | 14 | 722 | 4.26 |
| 4/19/03 | 0.32 | 56 | 3171 | 2112 | 200 | 2720 | 13.03 | 417 | 15 | 607 | 4.13 |
| 5/20/03 | 0.45 | 82 | 3040 | 2121 | 196 | 3047 | 13.57 | 532 | 15 | 659 | - |
| 6/21/03 | 0.39 | 76 | 2937 | 2049 | 176 | 2781 | 12.77 | 470 | 17 | 570 | - |
| 7/23/03 | 0.42 | 75 | 2829 | 2005 | 181 | 2746 | 12.51 | 478 | 18 | 566 | - |
| 8/21/03 | 0.45 | 64 | 2462 | 1794 | 169 | 2462 | 11.14 | 409 | 17 | 470 | - |
| 9/23/03 | 0.44 | 73 | 2810 | 1913 | 182 | 2551 | 11.92 | 450 | 13 | 510 | - |
| 11/22/03 | 0.32 | 48 | 1284 | 1863 | 180 | 2125 | 9.44 | 370 | 13 | 542 | 3.73 |
| 12/26/03 | 0.29 | 56 | 1155 | 1861 | 181 | 2199 | 9.46 | 375 | 13 | 424 | 3.58 |
| 1/26/04 | 0.35 | 53 | 1153 | 1862 | 188 | 2172 | 9.41 | 371 | 13 | 481 | 3.63 |
| 2/26/04 | 0.29 | 49 | 1279 | 2017 | 193 | 2193 | 9.89 | 374 | 14 | 528 | 4.16 |

**Table-11. Time series data for As and other ions in shallow well at site B (depth - 11 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/12/01 | 2.88 | 38 | 1856 | 1218 | 167 | 1983 | 8.42 | 233 | 31 | 257 | - |
| 5/26/01 | 3.33 | 41 | 1741 | 1751 | 179 | 2995 | 11.41 | 211 | 48 | 299 | - |
| 6/9/01 | 3.34 | 44 | 1520 | 1739 | 173 | 3059 | 11.29 | 229 | 48 | 245 | - |
| 6/20/01 | 4.87 | 42 | 1520 | 1739 | 173 | 3059 | 11.29 | 153 | 39 | 239 | 3.00 |
| 7/14/01 | 4.42 | 52 | 1671 | 1644 | 150 | 2942 | 10.99 | 252 | 45 | 281 | 3.27 |
| 7/28/01 | 4.37 | 54 | 1619 | 1565 | 151 | 2973 | 10.84 | 244 | 47 | 281 | 3.23 |
| 8/11/01 | 4.43 | 57 | 1765 | 1630 | 147 | 2945 | 11.06 | 267 | 48 | 299 | 3.31 |
| 8/25/01 | 4.92 | 57 | 1819 | 1660 | 148 | 3021 | 11.33 | 253 | 50 | 333 | 3.39 |
| 9/8/01 | 4.78 | 58 | 1821 | 1638 | 146 | 2983 | 11.21 | 268 | 49 | 321 | 3.34 |
| 9/28/01 | 4.67 | 49 | 1818 | 1634 | 145 | 2936 | 11.10 | 278 | 47 | 281 | 3.27 |
| 10/27/01 | 4.67 | 57 | 1683 | 1601 | 141 | 2922 | 10.87 | 264 | 47 | 262 | 3.25 |
| 11/24/01 | 4.53 | 56 | 1584 | 1584 | 137 | 2846 | 10.58 | 265 | 46 | 231 | 2.99 |
| 1/5/02 | 4.70 | 52 | 1375 | 1528 | 130 | 2723 | 10.01 | 256 | 42 | 188 | 2.92 |
| 3/30/02 | 4.57 | 69 | 2844 | 1726 | 186 | 3430 | 13.34 | 724 | 36 | 427 | 3.26 |
| 7/27/02 | 4.60 | 75 | 2714 | 1798 | 183 | 3414 | 13.32 | 758 | 37 | 420 | 4.01 |
| 8/31/02 | 4.00 | 47 | 2816 | 1681 | 178 | 3216 | 12.79 | 675 | 36 | 369 | 4.06 |
| 10/10/02 | 3.88 | 54 | 2637 | 1738 | 162 | 2903 | 12.08 | 689 | 34 | 341 | 4.00 |
| 11/16/02 | 3.79 | 59 | 2611 | 1659 | 163 | 2997 | 12.08 | 566 | 35 | 259 | 3.84 |
| 12/16/02 | 3.08 | 51 | 2460 | 1599 | 166 | 2868 | 11.56 | 546 | 32 | 201 | 3.46 |
| 3/23/03 | 3.23 | 54 | 2362 | 1703 | 164 | 3051 | 12.03 | 562 | 35 | 412 | 3.65 |
| 4/19/03 | 3.86 | 60 | 2825 | 1774 | 170 | 3217 | 12.98 | 503 | 39 | 568 | 3.82 |
| 5/20/03 | 4.17 | 58 | 2795 | 1825 | 171 | 3256 | 13.13 | 517 | 38 | 542 | 4.03 |
| 6/21/03 | 3.71 | 59 | 2715 | 1811 | 172 | 3301 | 13.11 | 551 | 38 | 579 | - |
| 7/23/03 | 3.73 | 60 | 2718 | 1785 | 177 | 3370 | 13.21 | 543 | 38 | 566 | - |
| 8/21/03 | 3.23 | 65 | 2710 | 1787 | 176 | 3349 | 13.16 | 618 | 37 | 513 | - |
| 9/23/03 | 3.49 | 61 | 2835 | 1789 | 171 | 3273 | 13.13 | 519 | 37 | 497 | - |
| 11/22/03 | 3.49 | 65 | 2831 | 1795 | 168 | 3197 | 12.98 | 563 | 37 | 391 | 4.05 |
| 12/26/03 | 3.87 | 62 | 2638 | 1724 | 168 | 3434 | 13.12 | 450 | 36 | 325 | 3.72 |
| 1/26/04 | 3.49 | 62 | 2554 | 1553 | 162 | 2864 | 11.55 | 451 | 33 | 216 | 3.35 |
| 2/26/04 | 2.89 | 64 | 2729 | 1726 | 162 | 3034 | 12.41 | 526 | 31 | 353 | 3.52 |

**Table-12. Time series data for As and other ions in shallow well at site B (depth - 14 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 6.16 | 42 | 1335 | 1263 | 129 | 2854 | 9.70 | 340 | 30 | 199 | - |
| 2/19/01 | 6.35 | 42 | 1342 | 1267 | 126 | 2830 | 9.66 | 328 | 30 | 156 | - |
| 3/17/01 | 9.59 | 50 | 1495 | 1463 | 123 | 3552 | 11.65 | 470 | 34 | 343 | - |
| 3/31/01 | 9.93 | 56 | 1612 | 1554 | 123 | 3707 | 12.26 | 496 | 34 | 415 | - |
| 4/14/01 | 6.61 | 34 | 1311 | 1407 | 119 | 3192 | 10.63 | 336 | 26 | 263 | - |
| 4/28/01 | 7.03 | 40 | 1600 | 1551 | 125 | 3336 | 11.50 | 353 | 26 | 297 | - |
| 5/12/01 | 8.68 | 54 | 1747 | 1533 | 122 | 3262 | 11.46 | 463 | 25 | 340 | - |
| 5/26/01 | 7.24 | 50 | 1578 | 1451 | 125 | 3243 | 11.09 | 432 | 24 | 326 | - |
| 6/9/01 | 6.97 | 52 | 1629 | 1411 | 126 | 3149 | 10.87 | 412 | 23 | 273 | - |
| 6/20/01 | 7.40 | 47 | 2033 | 1666 | 151 | 2959 | 11.44 | 257 | 23 | 207 | 3.66 |
| 7/14/01 | 6.12 | 51 | 1610 | 1217 | 122 | 2827 | 9.82 | 344 | 21 | 168 | 3.67 |
| 7/28/01 | 6.55 | 46 | 1620 | 1405 | 130 | 3183 | 10.93 | 386 | 24 | 281 | 4.24 |
| 8/11/01 | 6.60 | 45 | 1726 | 1435 | 123 | 2939 | 10.60 | 362 | 23 | 264 | 4.31 |
| 8/25/01 | 6.78 | 46 | 1612 | 1310 | 126 | 2827 | 10.01 | 346 | 22 | 246 | 4.21 |
| 9/8/01 | 6.59 | 45 | 1609 | 1287 | 127 | 2752 | 9.82 | 336 | 20 | 226 | 4.22 |
| 9/28/01 | 6.66 | 43 | 1565 | 1178 | 123 | 2572 | 9.19 | 323 | 20 | 185 | 4.16 |
| 10/27/01 | 6.63 | 42 | 1505 | 1204 | 126 | 2537 | 9.11 | 312 | 20 | 133 | 4.15 |
| 11/24/01 | 6.44 | 39 | 1524 | 1184 | 127 | 2501 | 9.02 | 303 | 21 | 116 | 4.35 |
| 1/5/02 | 6.57 | 39 | 2430 | 1516 | 83 | 2400 | 10.34 | 359 | 24 | 194 | 5.45 |
| 6/30/02 | 8.58 | 71 | 1914 | 1039 | 122 | 2413 | 8.94 | 494 | 16 | 88 | 3.56 |
| 7/27/02 | 7.78 | 65 | 1862 | 1012 | 115 | 2690 | 8.58 | 473 | 16 | 78 | 3.64 |
| 8/31/02 | 7.82 | 64 | 1876 | 988 | 119 | 2714 | 8.80 | 451 | 16 | 73 | 3.70 |
| 10/10/02 | 7.76 | 59 | 1887 | 1022 | 120 | 2676 | 8.80 | 432 | 17 | 74 | 3.89 |
| 11/16/02 | 7.01 | 52 | 1986 | 1100 | 131 | 2861 | 9.44 | 432 | 19 | 143 | 4.36 |
| 12/16/02 | 7.14 | 50 | 2035 | 1109 | 129 | 2828 | 9.44 | 457 | 20 | 139 | 4.67 |
| 2/22/03 | 7.69 | 62 | 2106 | 1113 | 145 | 2717 | 9.91 | 409 | 16 | 136 | 4.11 |
| 3/23/03 | 7.50 | 61 | 1900 | 1010 | 143 | 2718 | 9.50 | 355 | 15 | 84 | 3.70 |
| 4/19/03 | 7.10 | 66 | 1657 | 963 | 130 | 2477 | 8.67 | 336 | 13 | 42 | - |
| 5/20/03 | 7.16 | 66 | 1726 | 944 | 134 | 2488 | 8.72 | 349 | 13 | 47 | - |
| 6/21/03 | 7.23 | 66 | 1653 | 924 | 136 | 2447 | 8.53 | 355 | 13 | 50 | - |
| 7/23/03 | 6.57 | 65 | 1608 | 938 | 132 | 2456 | 8.53 | 347 | 13 | 40 | - |
| 8/21/03 | 6.90 | 64 | 1573 | 942 | 135 | 2494 | 8.58 | 352 | 13 | 37 | - |
| 9/23/03 | 6.82 | 64 | 1495 | 911 | 128 | 2455 | 8.35 | 345 | 13 | 35 | - |
| 11/22/03 | 6.52 | 61 | 1732 | 987 | 141 | 2536 | 8.92 | 371 | 15 | 60 | 3.60 |
| 12/26/03 | 6.61 | 58 | 1951 | 1049 | 149 | 2548 | 9.29 | 380 | 16 | 93 | 3.58 |
| 1/26/04 | 6.61 | 57 | 2123 | 1078 | 147 | 2563 | 9.55 | 384 | 16 | 112 | 3.38 |
| 2/26/04 | 6.04 | 66 | 1487 | 936 | 132 | 2535 | 8.56 | 335 | 13 | 18 | 3.35 |

**Table-13. Time series data for As and other ions in shallow well at site B (depth - 19 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/12/01 | 5.06 | 47 | 1904 | 1170 | 129 | 2284 | 8.94 | 221 | 26 | 28 | - |
| 5/26/01 | 4.71 | 47 | 1747 | 1147 | 112 | 2334 | 8.82 | 222 | 28 | 7 | - |
| 6/9/01 | 4.99 | 52 | 1574 | 1152 | 103 | 2398 | 8.78 | 231 | 31 | 4 | - |
| 6/20/01 | 5.15 | 48 | 1762 | 1426 | 121 | 2546 | 9.83 | 210 | 26 | 3 | 2.08 |
| 7/14/01 | 5.44 | 58 | 1372 | 1116 | 95 | 2382 | 8.46 | 337 | 27 | 2 | 1.94 |
| 7/28/01 | 5.57 | 62 | 1393 | 1129 | 93 | 2404 | 8.55 | 312 | 28 | 3 | 2.02 |
| 8/11/01 | 5.68 | 64 | 1365 | 1120 | 92 | 2429 | 8.56 | 303 | 28 | 3 | 1.93 |
| 8/25/01 | 5.89 | 64 | 1367 | 1136 | 95 | 2418 | 8.57 | 315 | 29 | 3 | 1.93 |
| 9/8/01 | 5.92 | 64 | 1375 | 1118 | 91 | 2395 | 8.49 | 337 | 28 | 2 | 1.88 |
| 9/28/01 | 6.03 | 65 | 1370 | 1131 | 91 | 2412 | 8.55 | 349 | 28 | 2 | 1.85 |
| 10/27/01 | 5.98 | 64 | 1286 | 1114 | 90 | 2334 | 8.27 | 351 | 28 | 2 | 1.72 |
| 11/24/01 | 6.38 | 66 | 1402 | 1135 | 93 | 2422 | 8.61 | 377 | 28 | 2 | 1.79 |
| 1/5/02 | 6.16 | 65 | 1414 | 1088 | 89 | 2352 | 8.38 | 381 | 26 | 2 | 2.16 |
| 6/30/02 | 5.43 | 48 | 1115 | 1037 | 92 | 2259 | 7.80 | 477 | 22 | 20 | 1.80 |
| 7/27/02 | 6.02 | 54 | 1048 | 994 | 92 | 2348 | 7.82 | 499 | 22 | 13 | 1.74 |
| 8/31/02 | 5.89 | 56 | 1081 | 1027 | 86 | 2171 | 7.56 | 529 | 22 | 20 | 1.81 |
| 10/10/02 | 5.68 | 60 | 1053 | 1009 | 90 | 2153 | 7.47 | 523 | 22 | 13 | 1.71 |
| 11/16/02 | 5.44 | 55 | 1053 | 1000 | 93 | 2135 | 7.42 | 497 | 21 | 13 | 1.72 |
| 12/16/02 | 5.40 | 54 | 1093 | 1003 | 89 | 2239 | 7.66 | 487 | 20 | 12 | 1.73 |
| 2/22/03 | 5.21 | 58 | 1085 | 1098 | 118 | 2424 | 8.25 | 493 | 21 | 14 | 2.14 |
| 3/23/03 | 5.34 | 53 | 1033 | 1069 | 114 | 2397 | 8.08 | 492 | 22 | 13 | 2.00 |
| 4/19/03 | 5.13 | 56 | 1065 | 1069 | 114 | 2395 | 8.11 | 484 | 22 | 13 | - |
| 5/20/03 | 5.00 | 55 | 925 | 1049 | 118 | 2440 | 8.02 | 498 | 22 | 13 | - |
| 6/21/03 | 4.89 | 54 | 962 | 1068 | 118 | 2454 | 8.12 | 491 | 22 | 12 | - |
| 7/23/03 | 4.74 | 52 | 936 | 1030 | 112 | 2415 | 7.94 | 497 | 22 | 10 | - |
| 8/21/03 | 4.98 | 53 | 963 | 1075 | 111 | 2345 | 7.91 | 515 | 21 | 10 | - |
| 9/23/03 | 5.11 | 55 | 947 | 1029 | 116 | 2453 | 8.03 | 500 | 22 | 12 | - |
| 11/22/03 | 4.42 | 45 | 992 | 1038 | 123 | 2329 | 7.85 | 447 | 21 | 7 | 1.77 |
| 12/26/03 | 5.11 | 55 | 1041 | 1049 | 122 | 2340 | 7.94 | 497 | 21 | 7 | 1.74 |
| 1/26/04 | 5.14 | 55 | 1041 | 1059 | 118 | 2296 | 7.87 | 516 | 22 | 7 | 1.74 |
| 2/26/04 | 4.83 | 51 | 987 | 1056 | 123 | 2388 | 8.00 | 489 | 21 | 6 | 1.65 |

**Table-14. Time series data for As and other ions in shallow well at site B (depth - 29 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 3.23 | 54 | 1064 | 1084 | 121 | 2446 | 8.25 | 329 | 8 | 5 | - |
| 2/19/01 | 3.26 | 56 | 1030 | 1039 | 122 | 2419 | 8.07 | 348 | 7 | 4 | - |
| 3/17/01 | 3.32 | 62 | 1094 | 1024 | 138 | 2398 | 8.08 | 414 | 7 | 1.7 | - |
| 3/31/01 | 3.45 | 61 | 1167 | 1071 | 143 | 2513 | 8.48 | 403 | 6 | 1.6 | - |
| 4/14/01 | 3.25 | 58 | 1144 | 990 | 136 | 2383 | 8.03 | 368 | 6 | 2 | - |
| 4/28/01 | 3.27 | 58 | 1165 | 974 | 134 | 2347 | 7.94 | 366 | 6 | 1 | - |
| 5/12/01 | 3.43 | 62 | 1192 | 970 | 131 | 2356 | 7.98 | 399 | 7 | 0.9 | - |
| 5/26/01 | 3.47 | 53 | 1149 | 969 | 129 | 2389 | 7.99 | 368 | 7 | 0.2 | - |
| 6/9/01 | 3.46 | 52 | 1084 | 968 | 125 | 2387 | 7.92 | 354 | 7 | 2 | - |
| 7/14/01 | 3.46 | 50 | 1092 | 977 | 131 | 2418 | 8.01 | 347 | 7 | 2.5 | 2.64 |
| 7/28/01 | 3.38 | 50 | 1142 | 1034 | 131 | 2382 | 8.10 | 345 | 7 | 3.5 | 2.64 |
| 8/11/01 | 3.46 | 51 | 1097 | 979 | 124 | 2350 | 7.88 | 368 | 7 | 0 | 2.64 |
| 10/27/01 | 2.98 | 38 | 1136 | 986 | 127 | 2350 | 7.93 | 300 | 7 | 0.9 | 2.24 |
| 2/22/03 | 2.91 | 48 | 1436 | 1073 | 167 | 2299 | 8.35 | 333 | 5 | 6.7 | - |
| 3/23/03 | 2.86 | 56 | 1455 | 1088 | 159 | 2242 | 8.27 | 369 | 5 | 3 | - |
| 4/19/03 | 2.69 | 41 | 1475 | 1078 | 157 | 2212 | 8.21 | 304 | 5 | 5.2 | - |
| 5/20/03 | 2.92 | 56 | 1431 | 1117 | 152 | 2300 | 8.42 | 412 | 5 | 2.5 | - |
| 6/21/03 | 3.08 | 62 | 1369 | 1078 | 158 | 2372 | 8.43 | 417 | 5 | 1.3 | - |
| 7/23/03 | 2.96 | 60 | 1379 | 1137 | 155 | 2346 | 8.50 | 410 | 5 | 3 | - |
| 8/21/03 | 2.75 | 57 | 1420 | 1119 | 157 | 2340 | 8.49 | 397 | 5 | 3 | - |
| 9/23/03 | 2.93 | 58 | 1367 | 1101 | 156 | 2324 | 8.37 | 413 | 6 | 3 | - |
| 11/22/03 | 2.95 | 53 | 1383 | 1189 | 159 | 2112 | 8.14 | 387 | 5 | 10 | - |
| 12/26/03 | 2.99 | 35 | 1408 | 1092 | 162 | 2335 | 8.42 | 269 | 5 | 7 | - |
| 1/26/04 | 3.14 | 62 | 1420 | 1064 | 165 | 2255 | 8.22 | 444 | 5 | 5 | - |
| 2/26/04 | 2.33 | 29 | 1410 | 1072 | 163 | 2274 | 8.26 | 213 | 6 | 10 | - |

**Table-15. Time series data for As and other ions in deep well at site B (depth - 41 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 0.24 | 43 | 785 | 1490 | 127 | 946 | 5.78 | 135 | 1.0 | 4 | - |
| 2/19/01 | 0.24 | 37 | 720 | 1402 | 113 | 909 | 5.45 | 135 | 1.2 | 8 | - |
| 3/17/01 | 0.27 | 39 | 709 | 1320 | 107 | 890 | 5.24 | 156 | 1.8 | 8 | - |
| 4/14/01 | 0.26 | 40 | 708 | 1374 | 115 | 958 | 5.49 | 153 | 1.8 | 8 | - |
| 4/28/01 | 0.25 | 39 | 682 | 1344 | 113 | 933 | 5.35 | 149 | 1.7 | 8 | - |
| 5/12/01 | 0.27 | 43 | 712 | 1426 | 108 | 879 | 5.43 | 171 | 1.7 | 8 | - |
| 5/26/01 | 0.26 | 44 | 711 | 1393 | 112 | 933 | 5.47 | 173 | 1.6 | 8 | - |
| 6/9/01 | 0.25 | 44 | 720 | 1398 | 114 | 928 | 5.49 | 169 | 1.6 | 8 | - |
| 6/20/01 | 0.30 | 43 | 1009 | 1565 | 146 | 1035 | 6.35 | 111 | 1.7 | 2 | 0.31 |
| 7/14/01 | 0.24 | 44 | 697 | 1443 | 112 | 938 | 5.57 | 155 | 1.5 | 8 | 0.30 |
| 7/28/01 | 0.24 | 44 | 706 | 1418 | 115 | 952 | 5.56 | 158 | 1.4 | 8 | 0.30 |
| 8/11/01 | 0.25 | 43 | 712 | 1407 | 112 | 947 | 5.53 | 158 | 1.3 | 8 | 0.30 |
| 8/25/01 | 0.25 | 45 | 691 | 1413 | 117 | 963 | 5.56 | 160 | 1.3 | 8 | 0.30 |
| 9/8/01 | 0.24 | 43 | 712 | 1451 | 115 | 943 | 5.62 | 155 | 1.3 | 8 | 0.31 |
| 9/28/01 | 0.26 | 42 | 681 | 1424 | 112 | 961 | 5.56 | 158 | 1.3 | 8 | 0.34 |
| 10/27/01 | 0.25 | 41 | 723 | 1498 | 111 | 963 | 5.76 | 168 | 1.3 | 8 | 0.33 |
| 11/24/01 | 0.27 | 41 | 725 | 1475 | 115 | 983 | 5.76 | 162 | 1.4 | 9 | 0.34 |
| 1/5/02 | 0.29 | 45 | 754 | 1521 | 114 | 1010 | 5.93 | 215 | 1.5 | 3 | - |
| 3/30/02 | 0.26 | 46 | 766 | 1547 | 110 | 970 | 5.91 | 204 | 1.0 | 3 | - |
| 4/27/02 | 0.26 | 42 | 800 | 1607 | 120 | 1021 | 6.18 | 191 | 1.1 | 3 | - |
| 5/27/02 | 0.30 | 56 | 831 | 1662 | 119 | 1069 | 6.41 | 244 | 1.1 | 3 | - |
| 6/30/02 | 0.32 | 54 | 811 | 1660 | 120 | 1064 | 6.38 | 239 | 1.2 | 3 | - |
| 7/27/02 | 0.32 | 53 | 790 | 1609 | 115 | 1038 | 6.20 | 253 | 1.1 | 2 | - |
| 8/31/02 | 0.32 | 52 | 787 | 1591 | 116 | 1022 | 6.13 | 247 | 1.1 | 3 | - |
| 10/10/02 | 0.33 | 51 | 782 | 1636 | 114 | 1011 | 6.19 | 244 | 1.2 | 3 | - |
| 11/16/02 | 0.31 | 48 | 764 | 1627 | 116 | 1002 | 6.14 | 240 | 1.1 | 3 | - |
| 12/16/02 | 0.30 | 43 | 768 | 1590 | 111 | 995 | 6.05 | 214 | 1.4 | 3 | - |
| 2/22/03 | 0.27 | 48 | 729 | 1679 | 148 | 1079 | 6.39 | 213 | 1.0 | 2 | - |
| 3/23/03 | 0.30 | 48 | 723 | 1690 | 147 | 1074 | 6.40 | 207 | 1.0 | 3 | - |
| 4/19/03 | 0.28 | 48 | 729 | 1675 | 148 | 1069 | 6.36 | 207 | 0.9 | 3 | - |
| 5/20/03 | 0.31 | 49 | 729 | 1803 | 152 | 1119 | 6.72 | 212 | 1.0 | 3 | - |
| 6/21/03 | 0.26 | 48 | 738 | 1763 | 152 | 1115 | 6.64 | 208 | 0.9 | 3 | - |
| 7/23/03 | 0.29 | 48 | 735 | 1820 | 154 | 1159 | 6.85 | 227 | 0.8 | 3 | - |
| 8/21/03 | 0.26 | 48 | 722 | 1823 | 153 | 1141 | 6.80 | 223 | 0.8 | 3 | - |
| 9/23/03 | 0.26 | 49 | 719 | 1831 | 159 | 1157 | 6.86 | 216 | 0.9 | 3 | - |
| 11/22/03 | 0.28 | 47 | 727 | 1749 | 149 | 1123 | 6.62 | 224 | 0.9 | 6 | - |
| 12/26/03 | 0.28 | 45 | 694 | 1734 | 148 | 1129 | 6.57 | 228 | 0.9 | 5 | - |
| 1/26/04 | 0.28 | 47 | 721 | 1744 | 162 | 1137 | 6.64 | 230 | 0.9 | 6 | - |
| 2/26/04 | 0.28 | 45 | 716 | 1768 | 154 | 1117 | 6.64 | 218 | 0.9 | 6 | - |

**Table-16. Time series data for As and other ions in deep well at site B (depth - 53 m)**

| **Date of Sampling** | **As** (µmoleL$^{-1}$) | **P** (µmoleL$^{-1}$) | **Na** (µmoleL$^{-1}$) | **Mg** (µmoleL$^{-1}$) | **K** (µmoleL$^{-1}$) | **Ca** (µmoleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** (µmoleL$^{-1}$) | **Mn** (µmoleL$^{-1}$) | **S** (µmoleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/6/01 | 0.24 | 16 | 1705 | 501 | 51 | 764 | 4.29 | 100 | 3 | 10 | - |
| 2/19/01 | 0.24 | 16 | 1714 | 498 | 52 | 755 | 4.27 | 101 | 3 | 8 | - |
| 3/17/01 | 0.25 | 17 | 1796 | 509 | 50 | 759 | 4.38 | 109 | 4 | 8 | - |
| 3/31/01 | 0.23 | 17 | 1741 | 490 | 51 | 744 | 4.26 | 104 | 4 | 8 | - |
| 4/14/01 | 0.23 | 17 | 1720 | 475 | 49 | 773 | 4.26 | 105 | 4 | 8 | - |
| 4/28/01 | 0.24 | 18 | 1803 | 490 | 48 | 743 | 4.32 | 111 | 4 | 8 | - |
| 5/12/01 | 0.25 | 19 | 1757 | 480 | 48 | 745 | 4.26 | 122 | 4 | 9 | - |
| 5/26/01 | 0.25 | 18 | 1819 | 471 | 48 | 737 | 4.28 | 117 | 4 | 9 | - |
| 6/9/01 | 0.24 | 18 | 1803 | 479 | 45 | 731 | 4.27 | 119 | 4 | 8 | - |
| 6/20/01 | 0.19 | 16 | 2038 | 706 | 57 | 727 | 5.26 | 61 | 3 | <0.003 | 0.33 |
| 7/14/01 | 0.25 | 18 | 1730 | 468 | 43 | 746 | 4.20 | 121 | 3 | 8 | 0.31 |
| 7/28/01 | 0.24 | 18 | 1757 | 480 | 44 | 740 | 4.24 | 117 | 3 | 8 | 0.30 |
| 8/11/01 | 0.24 | 18 | 1780 | 468 | 43 | 726 | 4.21 | 115 | 4 | 8 | 0.32 |
| 8/25/01 | 0.24 | 18 | 1783 | 471 | 45 | 746 | 4.26 | 119 | 3 | 8 | 0.30 |
| 9/8/01 | 0.25 | 18 | 1747 | 448 | 45 | 748 | 4.18 | 122 | 4 | 8 | 0.32 |
| 9/28/01 | 0.24 | 18 | 1772 | 473 | 44 | 732 | 4.23 | 117 | 3 | 8 | 0.32 |
| 10/27/01 | 0.24 | 18 | 1791 | 474 | 44 | 735 | 4.25 | 118 | 3 | 8 | 0.34 |
| 11/24/01 | 0.25 | 18 | 1793 | 481 | 45 | 759 | 4.32 | 124 | 4 | 8 | 0.33 |
| 1/5/02 | 0.21 | 18 | 2003 | 516 | 49 | 679 | 4.44 | 130 | 3 | <0.003 | - |
| 3/30/02 | 0.21 | 18 | 1939 | 537 | 49 | 696 | 4.45 | 123 | 3 | <0.003 | - |
| 4/27/02 | 0.20 | 16 | 1946 | 530 | 50 | 723 | 4.50 | 118 | 3 | <0.003 | - |
| 5/27/02 | 0.23 | 17 | 2070 | 538 | 46 | 673 | 4.54 | 127 | 3 | <0.003 | - |
| 6/30/02 | 0.22 | 17 | 2075 | 547 | 44 | 632 | 4.48 | 119 | 3 | <0.003 | - |
| 7/27/02 | 0.22 | 17 | 1947 | 511 | 46 | 679 | 4.37 | 128 | 3 | <0.003 | - |
| 8/31/02 | 0.24 | 18 | 2067 | 526 | 47 | 671 | 4.51 | 132 | 3 | <0.003 | - |
| 10/10/02 | 0.22 | 18 | 1978 | 515 | 49 | 697 | 4.45 | 132 | 3 | <0.003 | - |
| 11/16/02 | 0.21 | 17 | 2028 | 522 | 49 | 682 | 4.49 | 124 | 3 | <0.003 | - |
| 12/16/02 | 0.24 | 16 | 1968 | 505 | 47 | 662 | 4.35 | 130 | 3 | <0.003 | - |
| 2/22/03 | 0.21 | 17 | 1802 | 590 | 61 | 788 | 4.62 | 134 | 3 | <0.003 | - |
| 3/23/03 | 0.24 | 17 | 1779 | 589 | 60 | 778 | 4.57 | 128 | 3 | <0.003 | - |
| 4/19/03 | 0.24 | 17 | 1721 | 578 | 59 | 763 | 4.46 | 120 | 3 | <0.003 | - |
| 5/20/03 | 0.25 | 17 | 1787 | 586 | 62 | 780 | 4.58 | 126 | 3 | <0.003 | - |
| 6/21/03 | 0.23 | 18 | 1738 | 571 | 59 | 768 | 4.48 | 135 | 3 | <0.003 | - |
| 7/23/03 | 0.23 | 17 | 1771 | 566 | 59 | 770 | 4.50 | 130 | 3 | <0.003 | - |
| 8/21/03 | 0.22 | 17 | 1759 | 557 | 58 | 749 | 4.43 | 133 | 3 | <0.003 | - |
| 9/23/03 | 0.22 | 17 | 1697 | 560 | 60 | 775 | 4.43 | 132 | 3 | <0.003 | - |
| 11/22/03 | 0.19 | 18 | 1778 | 536 | 77 | 762 | 4.45 | 131 | 3 | 7 | - |
| 12/26/03 | 0.22 | 19 | 1789 | 552 | 75 | 749 | 4.47 | 125 | 3 | 7 | - |
| 1/26/04 | 0.23 | 16 | 1795 | 542 | 66 | 773 | 4.49 | 128 | 3 | 7 | - |
| 2/26/04 | 0.20 | 16 | 1826 | 521 | 63 | 740 | 4.41 | 125 | 3 | 7 | - |

**Table-17. Time series data for As and other ions in deep well at site B (depth - 91 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/5/02 | 0.004 | 4 | 2079 | 304 | 40 | 380 | 3.49 | 22 | 1 | <.003 | - |
| 3/30/02 | 0.004 | 3 | 1955 | 344 | 43 | 406 | 3.50 | 23 | 2 | <.003 | 0.07 |
| 4/27/02 | 0.004 | 4 | 1875 | 378 | 42 | 415 | 3.50 | 25 | 2 | <.003 | 0.07 |
| 5/27/02 | 0.004 | 4 | 1846 | 369 | 47 | 478 | 3.59 | 23 | 1 | <.003 | 0.07 |
| 6/30/02 | 0.004 | 4 | 1959 | 372 | 45 | 364 | 3.48 | 23 | 2 | <.003 | 0.07 |
| 7/27/02 | 0.004 | 3 | 1852 | 350 | 44 | 532 | 3.66 | 29 | 2 | <.003 | 0.07 |
| 8/31/02 | 0.004 | 4 | 1639 | 459 | 49 | 502 | 3.61 | 22 | 2 | <.003 | 0.07 |
| 10/10/02 | 0.004 | 4 | 1959 | 361 | 47 | 397 | 3.52 | 24 | 2 | <.003 | - |
| 11/16/02 | 0.004 | 4 | 1931 | 363 | 40 | 419 | 3.54 | 26 | 2 | <.003 | 0.08 |
| 12/16/02 | 0.004 | 4 | 1777 | 374 | 46 | 456 | 3.48 | 25 | 2 | <.003 | 0.08 |
| 2/22/03 | 0.004 | 4 | 1845 | 357 | 44 | 395 | 3.39 | 24 | 2 | <.003 | - |
| 3/23/03 | 0.004 | 4 | 1807 | 341 | 42 | 425 | 3.38 | 21 | 2 | <.003 | - |
| 4/19/03 | 0.004 | 4 | 1815 | 335 | 44 | 442 | 3.41 | 27 | 2 | <.003 | - |
| 5/20/03 | 0.004 | 4 | 1718 | 371 | 44 | 458 | 3.42 | 26 | 2 | <.003 | - |
| 6/21/03 | 0.004 | 4 | 1741 | 365 | 44 | 460 | 3.44 | 29 | 2 | <.003 | - |
| 7/23/03 | 0.004 | 4 | 1508 | 427 | 45 | 557 | 3.52 | 27 | 2 | <.003 | - |
| 8/21/03 | 0.004 | 4 | 1852 | 370 | 44 | 405 | 3.45 | 27 | 2 | <.003 | - |
| 9/23/03 | 0.004 | 4 | 1815 | 352 | 43 | 442 | 3.45 | 25 | 2 | <.003 | - |
| 11/22/03 | 0.004 | 4 | 1751 | 368 | 43 | 450 | 3.43 | 25 | 2 | <.003 | 0.08 |
| 12/26/03 | 0.004 | 4 | 1877 | 333 | 48 | 411 | 3.41 | 25 | 2 | <.003 | 0.08 |
| 1/26/04 | 0.004 | 4 | 1860 | 330 | 48 | 399 | 3.37 | 27 | 2 | <.003 | 0.08 |
| 2/26/04 | 0.004 | 4 | 1714 | 349 | 47 | 453 | 3.37 | 30 | 2 | <.003 | 0.08 |

**Table-18a. Time series water level data (m) for shallow and deep wells at site B (5/2001-5/2002)**

| Date of | Wells at different depths | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Measurement | 7 m | 11 m | 14 m | 19 m | 29m | 41 m | 53 m | 91 m |
| 05/12/01 | 3.9 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.0 | - |
| 05/19/01 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.2 | - |
| 05/26/01 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.3 | - |
| 06/02/01 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 3.6 | - |
| 06/09/01 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 4.0 | - |
| 06/30/01 | 5.2 | 5.2 | 5.2 | 5.2 | 5.2 | 5.2 | 4.8 | - |
| 07/07/01 | 5.1 | 5.2 | 5.2 | 5.2 | 5.2 | 5.3 | 4.8 | - |
| 07/14/01 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 4.9 | - |
| 07/21/01 | 5.3 | 5.3 | 5.2 | 5.0 | 5.3 | 5.5 | 5.4 | - |
| 07/28/01 | 5.7 | 5.6 | 5.6 | 5.2 | 5.6 | 5.7 | 5.8 | - |
| 08/04/01 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.5 | - |
| 08/11/01 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | 5.9 | - |
| 08/18/01 | 6.0 | 6.0 | 6.1 | 6.0 | 6.1 | 6.1 | 5.8 | - |
| 08/25/01 | 5.9 | 5.9 | 5.9 | 5.9 | 5.9 | 5.9 | 5.6 | - |
| 09/01/01 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 5.7 | - |
| 09/08/01 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 5.9 | - |
| 09/15/01 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 5.8 | - |
| 9/22/2001 | 6.0 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 5.9 | - |
| 09/28/01 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.6 | - |
| 10/06/01 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.5 | - |
| 10/13/01 | 5.6 | 5.6 | 5.6 | 5.6 | 5.6 | 5.6 | 5.4 | - |
| 10/20/01 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.7 | 5.5 | - |
| 10/27/01 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.3 | - |
| 11/03/01 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.5 | 5.2 | - |
| 11/10/01 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.1 | - |
| 11/17/01 | 5.2 | 5.2 | 5.2 | 5.2 | 5.2 | 5.2 | 4.9 | - |
| 11/24/01 | 5.0 | 5.1 | 5.1 | 5.1 | 5.1 | 5.0 | 4.8 | - |
| 12/01/01 | 4.9 | 4.9 | 4.9 | 4.9 | 4.9 | 4.9 | 4.6 | - |
| 12/08/01 | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 4.5 | - |
| 12/29/01 | 4.5 | 4.6 | 4.5 | 4.5 | 4.5 | 4.5 | 4.2 | - |
| 01/05/02 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.1 | - |
| 01/12/02 | 4.1 | 4.0 | 4.0 | 3.9 | 4.0 | 4.2 | 4.2 | - |
| 02/18/02 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.9 | 2.8 | - |
| 03/16/02 | 2.4 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.4 | - |
| 03/23/02 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.4 | 2.3 | - |
| 03/30/02 | 3.3 | 3.3 | 3.3 | 3.3 | 3.3 | 3.3 | 2.9 | - |
| 04/13/02 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 | - |
| 04/20/02 | 2.7 | 2.7 | 2.7 | 2.7 | 2.7 | 2.7 | 2.6 | - |
| 04/27/02 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 2.7 | - |
| 05/12/02 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 | 4.5 | 3.8 | - |

**- Well was not installed**

**Table-18b. Time series water level data (m) for shallow and deep wells at site B (5/2002-2/2004)**

| Date of Measurement | Wells at different depths | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 7 m | 11 m | 14 m | 19 m | 29m | 41 m | 53 m | 91 m |
| 05/27/02 | 4.9 | 4.9 | 4.8 | 4.9 | 4.9 | 4.9 | 4.1 | - |
| 06/08/02 | 5.4 | 5.4 | 5.4 | 5.4 | 5.2 | 5.4 | 4.6 | - |
| 06/15/02 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.3 | 5.4 | 4.2 |
| 06/30/02 | 5.7 | 5.6 | 5.7 | 5.7 | 5.7 | 5.8 | 5.7 | x |
| 07/14/02 | 6.1 | 6.1 | 6.2 | 6.2 | 6.1 | 6.1 | 5.8 | x |
| 07/27/02 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | 6.0 | 5.5 |
| 08/07/02 | 6.7 | 6.7 | 6.7 | 6.7 | 6.7 | 6.7 | 6.4 | x |
| 08/31/02 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 | 6.1 | x |
| 09/15/02 | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 | 5.4 | 4.8 |
| 10/11/02 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.2 | x |
| 11/16/02 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 4.8 | 4.5 |
| 12/03/02 | 4.7 | 4.8 | 4.7 | 4.7 | 4.7 | 4.7 | 4.4 | x |
| 12/16/02 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 | 4.3 | x |
| 01/14/03 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.9 | 3.7 | 3.4 |
| 02/01/03 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.1 | 3.0 | 2.8 |
| 02/15/03 | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 | 3.2 | 2.9 | 2.5 |
| 03/02/03 | 2.6 | 2.6 | 2.6 | 2.6 | 2.6 | 2.6 | 2.5 | 2.2 |
| 03/15/03 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 3.3 | 2.6 | 2.2 |
| 03/31/03 | 3.6 | 3.6 | 3.6 | 3.6 | 3.6 | 3.6 | 2.8 | 2.4 |
| 04/12/03 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.9 | 2.6 | 2.4 |
| 04/26/03 | 3.3 | 3.3 | 3.3 | 3.3 | 3.3 | 3.4 | 2.9 | 2.5 |
| 05/11/03 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 3.6 | x |
| 05/24/03 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 3.1 | 4.2 | 3.2 |
| 06/07/03 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 3.3 | 4.6 | 3.4 |
| 06/24/03 | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 | 4.2 | 5.4 | 4.3 |
| 07/08/03 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 5.1 | 6.0 | 5.2 |
| 07/22/03 | 6.8 | 6.8 | 6.8 | 6.8 | 6.8 | 6.7 | 6.3 | 5.9 |
| 08/05/03 | 6.0 | 6.3 | 6.4 | 6.4 | 6.4 | 5.7 | 6.3 | 6.5 |
| 08/21/03 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 5.7 | 5.5 |
| 09/03/03 | 6.2 | 6.2 | 6.2 | 6.2 | 5.6 | 6.0 | 5.9 | 5.7 |
| 09/18/03 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 5.8 | 5.6 |
| 10/01/03 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | 5.9 | x |
| 11/09/03 | 4.8 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.0 | 5.4 |
| 11/23/03 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 4.7 | x |
| 12/10/03 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.4 | 4.2 |
| 12/25/03 | 4.6 | 4.7 | 4.7 | 4.7 | 4.7 | 4.6 | 4.2 | x |
| 01/11/04 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.0 | 3.7 |
| 01/25/04 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.5 | x |
| 02/16/04 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 2.7 | x |
| 02/27/04 | 2.9 | 2.9 | 2.9 | 2.9 | 2.9 | 2.9 | 2.6 | x |

**x Well was not accessible due to public use**

**Table-19. Time series data for As and other ions in shallow well at site C (depth - 5 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.17 | 32 | 226 | 188 | 60 | 293 | 1.25 | 466 | 22 | 5 | 0.11 |
| 4/13/02 | 0.19 | 33 | 234 | 190 | 59 | 308 | 1.29 | 487 | 22 | 4 | 0.11 |
| 5/12/02 | 0.17 | 34 | 237 | 156 | 50 | 276 | 1.15 | 598 | 24 | 8 | 0.11 |
| 6/15/02 | 0.18 | 31 | 396 | 190 | 57 | 350 | 1.54 | 796 | 28 | 33 | 0.16 |
| 7/13/02 | 0.16 | 32 | 434 | 217 | 61 | 374 | 1.68 | 795 | 28 | 45 | 0.17 |
| 9/15/02 | 0.19 | 31 | 347 | 194 | 50 | 341 | 1.47 | 676 | 23 | 23 | 0.14 |
| 11/26/02 | 0.16 | 32 | 278 | 182 | 64 | 270 | 1.25 | 614 | 19 | 16 | 0.10 |
| 1/12/03 | 0.15 | 31 | 276 | 206 | 74 | 330 | 1.42 | 688 | 22 | 21 | 0.28 |
| 2/8/03 | 0.16 | 31 | 346 | 202 | 55 | 348 | 1.50 | 795 | 26 | 24 | - |
| 3/8/03 | 0.17 | 27 | 327 | 209 | 69 | 382 | 1.58 | 883 | 30 | 75 | - |
| 4/5/03 | 0.16 | 35 | 325 | 197 | 74 | 319 | 1.43 | 804 | 25 | 31 | - |
| 5/2/03 | 0.17 | 29 | 357 | 211 | 80 | 395 | 1.65 | 913 | 32 | 26 | - |
| 6/2/03 | 0.18 | 29 | 658 | 329 | 85 | 573 | 2.55 | 1378 | 44 | 45 | - |
| 7/6/03 | 0.15 | 33 | 645 | 228 | 61 | 382 | 1.93 | 929 | 26 | 29 | - |
| 11/3/03 | 0.12 | 45 | 5479 | 235 | 120 | 341 | 6.75 | 898 | 19 | 23 | 1.78 |
| 12/9/03 | 0.14 | 42 | 5738 | 369 | 121 | 511 | 7.62 | 1578 | 27 | 30 | 1.62 |
| 1/7/04 | 0.12 | 44 | 5584 | 207 | 93 | 255 | 6.60 | 819 | 13 | 16 | 1.50 |
| 2/10/04 | 0.16 | 51 | 5646 | 159 | 84 | 223 | 6.49 | 600 | 12 | 3 | 1.60 |

**Table-20. Time series data for As and other ions in shallow well at site C (depth - 8 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.46 | 24 | 436 | 135 | 146 | 251 | 1.25 | 1316 | 44 | 27 | 0.21 |
| 4/13/02 | 0.52 | 19 | 353 | 157 | 144 | 284 | 1.38 | 1300 | 47 | 21 | 0.18 |
| 5/12/02 | 0.48 | 23 | 433 | 121 | 128 | 235 | 1.17 | 1250 | 43 | 27 | 0.20 |
| 6/15/02 | 0.49 | 20 | 514 | 143 | 145 | 264 | 1.47 | 1267 | 47 | 39 | 0.25 |
| 7/13/02 | 0.51 | 24 | 515 | 146 | 140 | 280 | 1.51 | 1367 | 48 | 39 | 0.25 |
| 9/15/02 | 0.48 | 21 | 456 | 136 | 100 | 264 | 1.36 | 1099 | 50 | 21 | 0.19 |
| 11/26/02 | 0.50 | 24 | 491 | 125 | 105 | 246 | 1.24 | 1113 | 48 | 7 | 0.18 |
| 1/12/03 | 0.45 | 24 | 543 | 113 | 129 | 228 | 1.12 | 1159 | 43 | 17 | 0.16 |
| 3/8/03 | 0.52 | 23 | 526 | 139 | 153 | 268 | 1.29 | 1391 | 44 | 22 | - |
| 4/5/03 | 0.51 | 23 | 362 | 154 | 167 | 282 | 1.40 | 1377 | 44 | 25 | - |
| 5/2/03 | 0.51 | 21 | 382 | 149 | 168 | 295 | 1.44 | 1310 | 44 | 29 | - |
| 6/2/03 | 0.55 | 20 | 831 | 326 | 266 | 711 | 3.17 | 2823 | 103 | 24 | - |
| 7/6/03 | 0.51 | 20 | 600 | 250 | 171 | 529 | 2.33 | 1851 | 75 | 72 | - |
| 11/3/03 | 0.52 | 24 | 452 | 333 | 168 | 599 | 2.48 | 2681 | 114 | 41 | 1.29 |
| 12/9/03 | 0.57 | 31 | 4510 | 397 | 191 | 749 | 6.99 | 3352 | 132 | 16 | 2.10 |
| 1/7/04 | 0.54 | 33 | 7399 | 229 | 155 | 403 | 8.82 | 1557 | 67 | 21 | 1.88 |
| 2/10/04 | 0.54 | 30 | 4504 | 289 | 175 | 509 | 6.27 | 2580 | 84 | 4 | 1.61 |

**Table-21. Time series data for As and other ions in shallow well at site C (depth - 11 m)**

| **Date of Sampling** | **As** (μmoleL$^{-1}$) | **P** (μmoleL$^{-1}$) | **Na** (μmoleL$^{-1}$) | **Mg** (μmoleL$^{-1}$) | **K** (μmoleL$^{-1}$) | **Ca** (μmoleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** (μmoleL$^{-1}$) | **Mn** (μmoleL$^{-1}$) | **S** (μmoleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.54 | 21 | 416 | 180 | 158 | 308 | 1.55 | 684 | 28 | 17 | 0.35 |
| 4/13/02 | 0.54 | 22 | 463 | 163 | 150 | 288 | 1.52 | 783 | 28 | 17 | 0.36 |
| 5/12/02 | 0.58 | 22 | 469 | 140 | 145 | 258 | 1.41 | 1069 | 32 | 16 | 0.35 |
| 6/15/02 | 0.59 | 23 | 450 | 153 | 149 | 266 | 1.44 | 798 | 31 | 16 | 0.38 |
| 7/13/02 | 0.58 | 23 | 485 | 160 | 147 | 269 | 1.49 | 838 | 30 | 16 | 0.38 |
| 9/15/02 | 0.56 | 19 | 469 | 150 | 143 | 269 | 1.45 | 987 | 30 | 16 | 0.38 |
| 11/26/02 | 0.50 | 21 | 345 | 123 | 123 | 213 | 1.14 | 1196 | 26 | 2 | 0.40 |
| 1/12/03 | 0.47 | 25 | 287 | 116 | 133 | 213 | 1.08 | 988 | 25 | 2 | 0.39 |
| 2/8/03 | 0.56 | 22 | 320 | 133 | 132 | 223 | 1.17 | 969 | 24 | 16 | - |
| 3/8/03 | 0.56 | 22 | 340 | 143 | 138 | 239 | 1.24 | 893 | 25 | 16 | - |
| 4/5/03 | 0.59 | 23 | 344 | 148 | 137 | 251 | 1.28 | 1044 | 28 | 16 | - |
| 5/2/03 | 0.58 | 21 | 352 | 156 | 139 | 264 | 1.33 | 1179 | 31 | 16 | - |
| 6/2/03 | 0.58 | 20 | 372 | 151 | 136 | 276 | 1.36 | 1358 | 33 | 15 | - |
| 11/3/03 | 0.57 | 24 | 406 | 312 | 197 | 554 | 2.94 | 1543 | 34 | 2 | 0.39 |
| 12/9/03 | 0.59 | 24 | 620 | 170 | 162 | 278 | 1.47 | 2284 | 46 | 2 | 0.77 |
| 1/7/04 | 0.62 | 23 | 1263 | 238 | 177 | 387 | 2.05 | 3227 | 80 | 2 | 2.13 |
| 2/10/04 | 0.58 | 25 | 2335 | 389 | 234 | 699 | 3.67 | 2446 | 50 | 2 | 1.39 |

**Table-22. Time series data for As and other ions in shallow well at site C (depth - 14 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.96 | 34 | 361 | 504 | 105 | 671 | 2.82 | 828 | 36 | 36 | 0.32 |
| 4/13/02 | 0.86 | 28 | 375 | 501 | 100 | 699 | 2.88 | 741 | 35 | 40 | 0.34 |
| 5/12/02 | 0.94 | 34 | 360 | 500 | 99 | 683 | 2.82 | 827 | 35 | 36 | 0.35 |
| 6/15/02 | 1.04 | 36 | 349 | 485 | 93 | 677 | 2.77 | 820 | 35 | 34 | 0.33 |
| 7/13/02 | 0.80 | 24 | 538 | 532 | 96 | 774 | 3.25 | 705 | 32 | 3 | 0.35 |
| 9/15/02 | 0.52 | 19 | 518 | 509 | 100 | 875 | 3.39 | 637 | 31 | 3 | 0.36 |
| 11/26/02 | 0.82 | 31 | 357 | 413 | 115 | 594 | 2.49 | 790 | 31 | 41 | 0.32 |
| 1/12/03 | 0.97 | 33 | 313 | 372 | 115 | 605 | 2.38 | 622 | 27 | 38 | 0.25 |
| 2/8/03 | 0.97 | 34 | 393 | 407 | 115 | 591 | 2.50 | 756 | 30 | 39 | - |
| 3/8/03 | 1.00 | 34 | 386 | 430 | 99 | 623 | 2.59 | 676 | 29 | 41 | - |
| 4/5/03 | 0.98 | 33 | 359 | 464 | 106 | 666 | 2.73 | 773 | 33 | 28 | - |
| 5/2/03 | 0.98 | 32 | 361 | 507 | 107 | 709 | 2.90 | 877 | 36 | 25 | - |
| 6/2/03 | 1.02 | 32 | 361 | 521 | 98 | 740 | 2.98 | 770 | 35 | 22 | - |
| 7/6/03 | 0.99 | 35 | 335 | 495 | 96 | 670 | 2.76 | 852 | 33 | 21 | - |
| 11/3/03 | 0.97 | 31 | 323 | 421 | 127 | 683 | 2.66 | 787 | 33 | 3 | 0.34 |
| 12/9/03 | 0.99 | 33 | 334 | 418 | 129 | 639 | 2.58 | 820 | 32 | 3 | 0.31 |
| 1/7/04 | 1.00 | 30 | 363 | 459 | 131 | 708 | 2.83 | 887 | 36 | 3 | 0.40 |
| 2/10/04 | 0.98 | 31 | 341 | 391 | 124 | 588 | 2.42 | 747 | 30 | 3 | 0.28 |

**Table-23. Time series data for As and other ions in deep well at site C (depth - 53 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.015 | 4 | 1254 | 352 | 31 | 560 | 3.11 | 47 | 12 | 3 | 0.59 |
| 4/13/02 | 0.012 | 2 | 1325 | 372 | 23 | 542 | 3.18 | 27 | 6 | 3 | 0.61 |
| 5/12/02 | 0.015 | 3 | 1266 | 351 | 30 | 515 | 3.03 | 53 | 14 | 5 | 0.62 |
| 6/15/02 | 0.014 | 2 | 1267 | 342 | 28 | 507 | 2.99 | 37 | 15 | 8 | 0.63 |
| 7/13/02 | 0.038 | 4 | 1310 | 348 | 25 | 476 | 2.98 | 67 | 16 | 18 | 0.64 |
| 9/15/02 | 0.026 | 5 | 1328 | 418 | 39 | 455 | 3.11 | 195 | 16 | 22 | 0.65 |
| 11/26/02 | 0.030 | 3 | 1206 | 334 | 40 | 439 | 2.79 | 72 | 15 | 11 | 0.64 |
| 1/12/03 | 0.012 | 4 | 1024 | 320 | 46 | 422 | 2.55 | 158 | 14 | 17 | 0.53 |
| 2/8/03 | 0.012 | 4 | 1246 | 375 | 29 | 442 | 2.91 | 196 | 14 | 15 | - |
| 3/8/03 | 0.015 | 5 | 1293 | 390 | 32 | 451 | 3.01 | 240 | 14 | 17 | - |
| 4/5/03 | 0.013 | 5 | 1283 | 391 | 33 | 440 | 2.98 | 274 | 14 | 18 | - |
| 5/2/03 | 0.017 | 5 | 1285 | 400 | 36 | 456 | 3.03 | 288 | 14 | 17 | - |
| 6/2/03 | 0.013 | 4 | 1258 | 381 | 32 | 435 | 2.92 | 203 | 13 | 15 | - |
| 7/6/03 | 0.044 | 4 | 1338 | 366 | 27 | 475 | 3.05 | 60 | 14 | 8 | - |
| 11/3/03 | 0.012 | 3 | 1110 | 340 | 34 | 391 | 2.61 | 28 | 12 | 0 | 0.54 |
| 12/9/03 | 0.014 | 3 | 1082 | 340 | 35 | 413 | 2.62 | 32 | 12 | 0 | 0.55 |
| 1/7/04 | 0.013 | 3 | 1095 | 344 | 36 | 411 | 2.64 | 34 | 12 | 0 | 0.55 |
| 2/10/04 | 0.012 | 4 | 1093 | 357 | 41 | 410 | 2.67 | 102 | 12 | 0 | 0.56 |

**Table-24. Time series water level data (m) for shallow and deep wells at site C**

| Date of Measurement | Wells at different depths<br>5 m | 8 m | 11 m | 14 m | 53 m |
|---|---|---|---|---|---|
| 3/16/2002 | 2.9 | 2.9 | 2.9 | 2.9 | 1.0 |
| 3/30/2002 | 3.0 | 3.0 | 3.0 | 3.0 | 1.5 |
| 4/13/2002 | 3.1 | 3.1 | 3.1 | 3.1 | 1.8 |
| 4/27/2002 | 3.3 | 3.3 | 3.3 | 3.3 | 2.0 |
| 5/12/2002 | 3.6 | 3.6 | 3.6 | 3.6 | 2.3 |
| 6/15/2002 | 4.7 | 4.7 | 4.7 | 4.7 | 3.4 |
| 6/20/2002 | 6.1 | 6.1 | 6.1 | 6.1 | 4.9 |
| 9/15/2002 | 5.9 | 5.9 | 5.9 | 5.9 | 4.9 |
| 9/21/2002 | 5.6 | 5.6 | 5.6 | 5.6 | 4.7 |
| 10/21/2002 | 5.4 | 5.4 | 5.4 | 5.4 | 4.3 |
| 11/26/2002 | 4.9 | 4.9 | 4.9 | 4.9 | 3.8 |
| 1/13/2003 | 3.9 | 3.9 | 3.9 | 3.9 | 2.7 |
| 2/1/2003 | 3.6 | 3.6 | 3.6 | 3.6 | 1.7 |
| 2/15/2003 | 3.3 | 3.3 | 3.3 | 3.3 | 1.7 |
| 3/2/2003 | 3.1 | 3.1 | 3.1 | 3.1 | 1.1 |
| 3/15/2003 | 3.0 | 3.0 | 3.0 | 3.0 | 1.1 |
| 3/31/2003 | 3.2 | 3.2 | 3.2 | 3.2 | 2.4 |
| 4/12/2003 | 3.1 | 3.1 | 3.0 | 3.0 | 1.4 |
| 4/26/2003 | 3.1 | 3.1 | 3.1 | 3.2 | 1.5 |
| 5/11/2003 | 3.5 | 3.5 | 3.5 | 3.5 | 2.1 |
| 5/24/2003 | 3.6 | 3.6 | 3.6 | 3.6 | 2.2 |
| 6/7/2003 | 3.8 | 3.8 | 3.8 | 3.8 | 2.5 |
| 6/24/2003 | 5.6 | 5.6 | 5.6 | 5.6 | 3.4 |
| 7/8/2003 | 5.8 | 5.8 | 5.8 | 5.8 | 4.2 |
| 7/22/2003 | + | + | + | + | + |
| 8/5/2003 | + | + | + | + | + |
| 8/21/2003 | + | + | + | + | + |
| 9/3/2003 | + | + | + | + | + |
| 9/18/2003 | + | + | + | + | + |
| 10/1/2003 | + | + | + | + | + |
| 10/23/2003 | + | + | + | + | + |
| 11/9/2003 | 5.4 | 5.4 | 5.4 | 5.4 | 4.3 |
| 11/23/2003 | 4.9 | 4.9 | 4.9 | 4.9 | 3.8 |
| 12/10/2003 | 4.4 | 4.4 | 4.4 | 4.4 | 3.5 |
| 12/25/2003 | 4.2 | 4.2 | 4.2 | 4.2 | 3.2 |
| 1/11/2004 | 4.0 | 4.0 | 4.0 | 4.0 | 3.0 |
| 1/25/2004 | 3.7 | 3.7 | 3.7 | 3.7 | 2.1 |
| 2/16/2004 | 3.2 | 3.2 | 3.2 | 3.2 | 1.1 |
| 2/27/2004 | 3.2 | 3.1 | 3.1 | 3.1 | 1.1 |

**+ Wells were not accessible due to monsoonal flood**

**Table-25. Time series data for As and other ions in shallow well at site E (depth - 5 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.55 | 7 | 413 | 1033 | 81 | 1184 | 4.93 | 67 | 19 | 206 | 0.18 |
| 4/13/02 | 0.56 | 7 | 418 | 1040 | 76 | 1162 | 4.90 | 31 | 17 | 209 | 0.19 |
| 5/12/02 | 0.60 | 7 | 408 | 1044 | 76 | 1190 | 4.95 | 35 | 19 | 266 | 0.15 |
| 6/15/02 | 0.63 | 8 | 451 | 1052 | 80 | 1216 | 5.07 | 46 | 20 | 236 | 0.16 |
| 11/26/02 | 0.61 | 4 | 364 | 751 | 65 | 825 | 3.58 | 72 | 13 | 149 | 0.15 |
| 1/12/03 | 0.58 | 8 | 379 | 837 | 72 | 1093 | 4.31 | 49 | 18 | 183 | 0.17 |
| 1/26/03 | 0.57 | 8 | 502 | 1357 | 82 | 1472 | 6.24 | 45 | 21 | 443 | - |
| 2/8/03 | 0.55 | 7 | 485 | 1242 | 79 | 1321 | 5.69 | 46 | 19 | 312 | - |
| 3/8/03 | 0.57 | 8 | 490 | 1220 | 78 | 1319 | 5.65 | 45 | 18 | 313 | - |
| 4/15/03 | 0.53 | 8 | 464 | 1110 | 75 | 1204 | 5.17 | 40 | 17 | 238 | - |
| 5/2/03 | 0.56 | 9 | 456 | 1120 | 76 | 1196 | 5.17 | 57 | 18 | 237 | - |
| 6/2/03 | 0.60 | 9 | 419 | 1037 | 74 | 1132 | 4.83 | 59 | 18 | 199 | - |
| 7/6/03 | 0.59 | 9 | 413 | 943 | 71 | 1055 | 4.48 | 46 | 18 | 164 | - |
| 11/3/03 | 0.57 | 8 | 421 | 988 | 74 | 1059 | 4.59 | 50 | 16 | 177 | 0.14 |
| 12/9/03 | 0.55 | 7 | 422 | 980 | 72 | 1080 | 4.61 | 31 | 15 | 180 | 0.14 |
| 1/7/04 | 0.54 | 7 | 425 | 990 | 74 | 1123 | 4.72 | 46 | 14 | 198 | 0.15 |

**Table-26. Time series data for As and other ions in shallow well at site E (depth - 8 m)**

| **Date of Sampling** | **As** (µmoleL$^{-1}$) | **P** (µmoleL$^{-1}$) | **Na** (µmoleL$^{-1}$) | **Mg** (µmoleL$^{-1}$) | **K** (µmoleL$^{-1}$) | **Ca** (µmoleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** (µmoleL$^{-1}$) | **Mn** (µmoleL$^{-1}$) | **S** (µmoleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.98 | 24 | 386 | 775 | 75 | 811 | 3.63 | 333 | 35 | 108 | 0.13 |
| 4/13/02 | 1.09 | 27 | 421 | 876 | 77 | 870 | 3.99 | 453 | 39 | 132 | 0.13 |
| 5/12/02 | 1.11 | 26 | 398 | 806 | 76 | 826 | 3.74 | 375 | 35 | 86 | 0.13 |
| 6/15/02 | 1.11 | 29 | 362 | 646 | 71 | 698 | 3.12 | 378 | 29 | 15 | 0.11 |
| 11/26/02 | 1.13 | 28 | 335 | 571 | 58 | 568 | 2.67 | 460 | 26 | 44 | 0.10 |
| 1/12/03 | 1.21 | 27 | 323 | 581 | 69 | 695 | 2.95 | 347 | 29 | 22 | 0.12 |
| 1/26/03 | 1.09 | 28 | 417 | 850 | 74 | 851 | 3.89 | 426 | 35 | 75 | - |
| 2/8/03 | 1.07 | 25 | 431 | 932 | 75 | 902 | 4.17 | 443 | 37 | 115 | - |
| 3/8/03 | 1.05 | 25 | 435 | 963 | 76 | 949 | 4.34 | 454 | 40 | 138 | - |
| 4/15/03 | 1.07 | 23 | 447 | 987 | 78 | 1003 | 4.50 | 466 | 41 | 140 | - |
| 5/2/03 | 1.12 | 28 | 429 | 882 | 76 | 860 | 3.99 | 460 | 36 | 85 | - |
| 6/2/03 | 1.14 | 30 | 400 | 715 | 73 | 786 | 3.48 | 409 | 32 | 38 | - |
| 7/6/03 | 1.13 | 29 | 429 | 866 | 79 | 947 | 4.13 | 506 | 39 | 89 | - |
| 11/3/03 | 1.00 | 31 | 417 | 717 | 75 | 820 | 3.57 | 410 | 32 | 37 | 0.12 |
| 12/9/03 | 1.15 | 27 | 419 | 745 | 73 | 800 | 3.58 | 405 | 33 | 43 | 0.10 |
| 1/7/04 | 1.02 | 24 | 441 | 941 | 75 | 961 | 4.32 | 464 | 40 | 116 | 0.10 |

**Table-27. Time series data for As and other ions in shallow well at site E (depth - 11 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 2.25 | 29 | 701 | 809 | 110 | 1136 | 4.70 | 89 | 31 | 3 | 0.08 |
| 4/13/02 | 1.85 | 27 | 554 | 786 | 107 | 1154 | 4.54 | 196 | 36 | 4 | 0.08 |
| 5/12/02 | 1.98 | 30 | 521 | 788 | 109 | 1140 | 4.49 | 249 | 39 | <0.03 | 0.08 |
| 6/15/02 | 2.10 | 35 | 507 | 762 | 109 | 1133 | 4.41 | 329 | 37 | <0.03 | 0.07 |
| 11/26/02 | 2.02 | 30 | 372 | 603 | 86 | 900 | 3.46 | 312 | 26 | 2 | 0.07 |
| 1/12/03 | 2.21 | 30 | 690 | 702 | 103 | 1083 | 4.36 | 545 | 27 | 1 | 0.07 |
| 1/26/03 | 2.29 | 28 | 493 | 729 | 107 | 1065 | 4.19 | 458 | 34 | 1 | - |
| 2/8/03 | 2.24 | 26 | 467 | 698 | 107 | 1056 | 4.08 | 430 | 33 | 2 | - |
| 3/8/03 | 2.22 | 28 | 467 | 704 | 106 | 1048 | 4.08 | 455 | 33 | 1 | - |
| 4/15/03 | 2.23 | 27 | 466 | 725 | 106 | 1032 | 4.08 | 439 | 32 | 1 | - |
| 5/2/03 | 2.34 | 28 | 476 | 717 | 107 | 1032 | 4.08 | 463 | 32 | 1 | - |
| 6/2/03 | 2.37 | 28 | 460 | 719 | 107 | 1068 | 4.14 | 478 | 33 | 2 | - |
| 7/6/03 | 2.32 | 29 | 471 | 713 | 108 | 1067 | 4.14 | 452 | 32 | 1 | - |
| 11/3/03 | 2.34 | 28 | 462 | 696 | 109 | 1048 | 4.06 | 474 | 33 | 1 | 0.07 |
| 12/9/03 | 2.41 | 26 | 480 | 716 | 108 | 1073 | 4.17 | 463 | 32 | 1 | 0.07 |
| 1/7/04 | 2.29 | 28 | 461 | 708 | 108 | 1067 | 4.12 | 447 | 31 | <0.03 | 0.07 |

**Table-28. Time series data for As and other ions in shallow well at site E (depth - 14 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 2.20 | 22 | 1244 | 821 | 90 | 1247 | 5.47 | 206 | 21 | 3 | 0.82 |
| 4/13/02 | 2.12 | 25 | 1245 | 814 | 91 | 1309 | 5.58 | 357 | 26 | 3 | 0.79 |
| 5/12/02 | 2.55 | 28 | 1226 | 805 | 87 | 1331 | 5.58 | 367 | 26 | 1 | 0.77 |
| 6/15/02 | 2.59 | 30 | 1268 | 820 | 87 | 1307 | 5.61 | 470 | 23 | 1 | 0.76 |
| 11/26/02 | 1.99 | 22 | 1665 | 711 | 101 | 1226 | 5.64 | 552 | 14 | 1 | 0.83 |
| 1/12/03 | 2.10 | 25 | 1172 | 739 | 67 | 1205 | 5.13 | 474 | 15 | 1 | 0.81 |
| 1/26/03 | 2.17 | 26 | 1102 | 693 | 72 | 1170 | 4.90 | 528 | 15 | 1 | - |
| 2/8/03 | 2.00 | 22 | 1117 | 1063 | 126 | 1245 | 5.86 |  | 22 | 2 | - |
| 3/8/03 | 2.34 | 27 | 1152 | 990 | 115 | 1255 | 5.76 | 855 | 20 | 2 | - |
| 4/15/03 | 2.27 | 26 | 1071 | 700 | 79 | 1152 | 4.85 | 591 | 14 | 1 | - |
| 5/2/03 | 2.10 | 24 | 1010 | 677 | 68 | 1158 | 4.75 | 455 | 14 | 1 | - |
| 6/2/03 | 2.13 | 25 | 1033 | 703 | 74 | 1153 | 4.82 | 578 | 14 | 1 | - |
| 7/6/03 | 2.05 | 24 | 1037 | 677 | 70 | 1156 | 4.77 | 591 | 13 | 1 | - |
| 11/3/03 | 1.94 | 23 | 1039 | 667 | 67 | 1125 | 4.69 | 459 | 13 | 1 | 0.75 |
| 12/9/03 | 2.18 | 23 | 1005 | 656 | 66 | 1132 | 4.65 | 538 | 13 | 1 | 0.76 |
| 1/7/04 | 1.92 | 22 | 1023 | 671 | 65 | 1122 | 4.67 | 441 | 13 | 1 | 0.75 |

**Table-29. Time series data for As and other ions in deep well at site E (depth - 38 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/16/02 | 0.005 | 3 | 2748 | 843 | 80 | 821 | 6.16 | 60 | 7 | <0.03 | 1.21 |
| 4/13/02 | 0.005 | 3 | 2849 | 842 | 80 | 831 | 6.27 | 40 | 9 | <0.03 | 1.22 |
| 5/12/02 | 0.005 | 3 | 3056 | 801 | 73 | 772 | 6.28 | 60 | 8 | <0.03 | 1.21 |
| 6/15/02 | 0.005 | 3 | 3114 | 770 | 70 | 745 | 6.21 | 86 | 8 | <0.03 | 1.20 |
| 11/26/02 | 0.004 | 3 | 2370 | 588 | 59 | 1062 | 5.73 | 66 | 6 | <0.03 | 1.16 |
| 1/12/03 | 0.005 | 2 | 2572 | 609 | 49 | 974 | 5.79 | 53 | 6 | <0.03 | 1.24 |
| 1/26/03 | 0.004 | 2 | 2478 | 609 | 49 | 998 | 5.74 | 38 | 4 | <0.03 | - |
| 2/8/03 | 0.005 | 3 | 2449 | 619 | 50 | 1043 | 5.82 | 29 | 4 | <0.03 | - |
| 3/8/03 | 0.004 | 3 | 2412 | 620 | 48 | 1002 | 5.70 | 42 | 4 | <0.03 | - |
| 4/15/03 | 0.004 | 3 | 2320 | 604 | 49 | 988 | 5.55 | 43 | 4 | <0.03 | - |
| 5/2/03 | 0.004 | 3 | 2276 | 598 | 49 | 985 | 5.49 | 46 | 4 | <0.03 | - |
| 6/2/03 | 0.005 | 3 | 2273 | 606 | 47 | 965 | 5.46 | 33 | 4 | <0.03 | - |
| 7/6/03 | 0.004 | 3 | 2216 | 587 | 46 | 951 | 5.34 | 94 | 4 | <0.03 | - |
| 11/3/03 | 0.004 | 3 | 2144 | 586 | 55 | 968 | 5.31 | 76 | 4 | <0.03 | 1.19 |
| 12/9/03 | 0.005 | 3 | 2231 | 607 | 45 | 997 | 5.48 | 67 | 4 | <0.03 | 1.25 |
| 1/7/04 | 0.004 |  | 2235 | 620 | 109 | 989 | 5.56 | 71 | 4 | <0.03 | 1.26 |

**Table-30. Time series water level data (m) for shallow and deep wells at site E**

| Date of Measurement | Wells at different depths 5 m | 8 m | 11 m | 14 m | 38 m |
|---|---|---|---|---|---|
| 3/16/2002 | 2.9 | 2.9 | 2.9 | 2.9 | 2.7 |
| 3/30/2002 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 |
| 4/13/2002 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 |
| 4/27/2002 | 3.3 | 3.3 | 3.3 | 3.3 | 3.2 |
| 5/12/2002 | 3.6 | 3.6 | 3.6 | 3.5 | 3.5 |
| 6/15/2002 | 5.1 | 5.1 | 5.1 | 5.1 | 5.0 |
| 10/21/2002 | 5.3 | 5.3 | 5.3 | 5.2 | 5.2 |
| 11/26/2002 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 |
| 1/12/2003 | 3.8 | 3.8 | 3.8 | 3.8 | 3.7 |
| 2/1/2003 | 3.3 | 3.3 | 3.3 | 3.3 | 3.2 |
| 2/15/2003 | 3.2 | 3.2 | 3.2 | 3.2 | 3.1 |
| 3/2/2003 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 |
| 3/15/2003 | 2.9 | 2.9 | 2.9 | 2.9 | 2.8 |
| 3/31/2003 | 2.9 | 2.9 | 2.9 | 2.9 | 2.8 |
| 4/12/2003 | 3.0 | 3.0 | 3.0 | 3.0 | 2.8 |
| 4/26/2003 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 |
| 5/11/2003 | 3.4 | 3.4 | 3.4 | 3.4 | 3.3 |
| 5/24/2003 | 3.4 | 3.4 | 3.5 | 3.4 | 3.4 |
| 6/7/2003 | 3.7 | 3.7 | 3.7 | 3.6 | 3.6 |
| 6/24/2003 | 5.6 | 5.6 | 5.6 | 5.6 | 5.4 |
| 7/8/2003 | 5.7 | 5.7 | 5.7 | 5.7 | 5.6 |
| 7/22/2003 | + | + | + | + | + |
| 8/5/2003 | 6.3 | 6.3 | 6.3 | 6.2 | 6.2 |
| 8/21/2003 | 6.0 | 6.0 | 6.0 | 6.0 | 5.9 |
| 9/3/2003 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| 9/18/2003 | 6.0 | 6.0 | 6.0 | 6.0 | 5.9 |
| 11/9/2003 | 5.3 | 5.3 | 5.3 | 5.2 | 5.2 |
| 11/23/2003 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 |
| 12/10/2003 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |
| 12/25/2003 | 4.0 | 4.1 | 4.1 | 4.0 | 4.0 |
| 1/11/2004 | 3.9 | 3.9 | 3.9 | 3.8 | 3.8 |
| 1/25/2004 | 3.6 | 3.6 | 3.6 | 3.6 | 3.5 |
| 2/16/2004 | 3.1 | 3.1 | 3.1 | 3.1 | 2.9 |
| 2/27/2004 | 3.1 | 3.1 | 3.1 | 3.0 | 2.9 |

**+ Well was not accessible due to monsoonal flood**

**Table-31. Time series data for As and other ions in shallow well at site F (depth - 6 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 0.00 | 0 | 218 | 315 | 51 | 334 | 1.57 | 1 | <0.002 | 111 | 0.22 |
| 4/7/02 | 0.00 | 0 | 237 | 235 | 42 | 222 | 1.19 | 2 | <0.002 | 38 | 0.16 |
| 5/5/02 | 0.00 | 0 | 180 | 302 | 52 | 338 | 1.51 | 1 | <0.002 | 64 | 0.18 |
| 6/8/02 | 0.00 | 0 | 179 | 284 | 49 | 326 | 1.45 | 2 | 4 | 38 | 0.19 |
| 7/6/02 | 0.00 | 0 | 142 | 323 | 43 | 348 | 1.53 | 4 | 6 | 27 | 0.19 |
| 8/3/02 | 0.00 | 0 | 154 | 321 | 46 | 362 | 1.57 | 4 | 5 | 24 | 0.17 |
| 9/7/02 | 0.00 | 0 | 159 | 290 | 43 | 271 | 1.32 | 5 | 4 | 21 | 0.17 |
| 10/14/02 | 0.00 | 0 | 172 | 293 | 47 | 334 | 1.47 | 1 | 3 | 29 | 0.24 |
| 11/10/02 | 0.00 | 0 | 261 | 400 | 52 | 371 | 1.86 | 5 | 2 | 63 | 0.31 |
| 12/1/02 | 0.00 | 0 | 161 | 351 | 51 | 320 | 1.55 | 4 | 2 | 41 | 0.29 |
| 1/7/03 | 0.00 | 0 | 324 | 438 | 62 | 511 | 2.28 |  | <0.002 | 60 | 0.34 |
| 3/1/03 | 0.00 | 0 | 278 | 330 | 52 | 404 | 1.80 | 3 | <0.002 | 65 | 0.42 |
| 3/30/03 | 0.00 | 0 | 210 | 314 | 49 | 368 | 1.62 |  | <0.002 | 60 | 0.30 |
| 4/29/03 | 0.00 | 0 | 127 | 295 | 49 | 341 | 1.45 | 1 | <0.002 | 16 | 0.22 |
| 5/28/03 | 0.00 | 0 | 118 | 293 | 46 | 332 | 1.41 | 0 | 3 | 14 | 0.23 |
| 6/30/03 | 0.00 | 0 | 117 | 294 | 45 | 317 | 1.39 | 1 | 5 | 16 | 0.24 |
| 7/31/03 | 0.00 | 0 | 133 | 347 | 48 | 395 | 1.66 | 0 | 6 | 5 | 0.24 |
| 8/31/03 | 0.00 | 0 | 141 | 400 | 51 | 451 | 1.89 | 7 | 5 | 13 | 0.23 |
| 12/8/03 | 0.00 | 0 | 215 | 367 | 65 | 407 | 1.83 | 6 | 3 | 33 | 0.26 |
| 1/8/04 | 0.00 | 0 | 191 | 367 | 62 | 411 | 1.81 | 2 | 2 | 17 | 0.25 |
| 2/10/04 | 0.00 | 0 | 318 | 381 | 65 | 428 | 2.00 | 3 | <0.002 | 30 | 0.28 |

**Table-32. Time series data for As and other ions in shallow well at site F (depth - 11 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 0.41 | 2 | 109 | 209 | 51 | 222 | 1.02 | 25 | 15 | 6 | 0.06 |
| 4/7/02 | 0.47 | 2 | 126 | 328 | 61 | 334 | 1.51 | 39 | 27 | 46 | 0.17 |
| 5/5/02 | 0.50 | 2 | 148 | 417 | 69 | 459 | 1.97 | 76 | 38 | 36 | 0.22 |
| 6/8/02 | 0.58 | 2 | 150 | 394 | 71 | 436 | 1.88 | 63 | 39 | 45 | 0.23 |
| 7/6/02 | 0.56 | 4 | 150 | 385 | 68 | 437 | 1.86 | 85 | 30 | 26 | 0.22 |
| 8/3/02 | 0.47 | 3 | 150 | 352 | 66 | 388 | 1.70 | 120 | 28 | 33 | 0.24 |
| 9/7/02 | 0.43 | 3 | 126 | 334 | 57 | 375 | 1.60 | 91 | 24 | 14 | 0.22 |
| 10/14/02 | 0.45 | 3 | 132 | 350 | 59 | 394 | 1.68 | 96 | 26 | 15 | 0.23 |
| 11/10/02 | 0.52 | 2 | 116 | 306 | 52 | 298 | 1.38 | 50 | 23 | 26 | 0.16 |
| 12/1/02 | 0.50 | 2 | 114 | 287 | 50 | 285 | 1.31 | 42 | 21 | 24 | 0.16 |
| 2/1/03 | 0.41 | 2 | 133 | 311 | 56 | 314 | 1.44 | 49 | 22 | 13 | 0.20 |
| 3/1/03 | 0.43 | 2 | 119 | 317 | 59 | 350 | 1.51 | 51 | 23 | 14 | 0.20 |
| 3/30/03 | 0.42 | 2 | 125 | 333 | 62 | 386 | 1.62 | 43 | 26 | 21 | 0.12 |
| 4/29/03 | 0.45 | 2 | 137 | 373 | 63 | 594 | 2.13 | 58 | 40 | 34 | 0.19 |
| 5/28/03 | 0.45 | 1 | 171 | 467 | 70 | 493 | 2.16 | 55 | 41 | 39 | 0.19 |
| 6/30/03 | 0.44 | 1 | 174 | 494 | 74 | 452 | 2.14 | 61 | 48 | 60 | 0.22 |
| 7/31/03 | 0.46 | 2 | 171 | 520 | 70 | 424 | 2.13 | 65 | 41 | 10 | 0.24 |
| 8/31/03 | 0.48 | 2 | 149 | 485 | 60 | 469 | 2.12 | 78 | 38 | 7 | 0.24 |
| 12/8/03 | 0.48 | 2 | 157 | 502 | 61 | 312 | 1.84 | 62 | 33 | 17 | 0.17 |
| 1/8/04 | 0.48 | 2 | 155 | 383 | 72 | 478 | 1.95 | 63 | 35 | 10 | 0.18 |
| 2/10/04 | 0.46 | 2 | 162 | 406 | 74 | 362 | 1.77 | 51 | 30 | 0 | 0.23 |

**Table-33. Time series data for As and other ions in shallow well at site F (depth - 15 m)**

| **Date of Sampling** | **As** ($\mu$moleL$^{-1}$) | **P** ($\mu$moleL$^{-1}$) | **Na** ($\mu$moleL$^{-1}$) | **Mg** ($\mu$moleL$^{-1}$) | **K** ($\mu$moleL$^{-1}$) | **Ca** ($\mu$moleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** ($\mu$moleL$^{-1}$) | **Mn** ($\mu$moleL$^{-1}$) | **S** ($\mu$moleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 0.68 | 4 | 159 | 422 | 47 | 574 | 2.20 | 16 | 22 | 37 | 0.07 |
| 4/7/02 | 0.76 | 4 | 151 | 458 | 46 | 628 | 2.37 | 21 | 24 | 23 | 0.07 |
| 5/5/02 | 0.58 | 3 | 155 | 445 | 47 | 593 | 2.28 | 38 | 22 | 24 | 0.06 |
| 6/8/02 | 0.71 | 3 | 144 | 476 | 41 | 703 | 2.54 | 42 | 30 | 13 | 0.08 |
| 7/6/02 | 0.78 | 6 | 142 | 477 | 49 | 640 | 2.43 | 68 | 27 | 16 | 0.06 |
| 8/3/02 | 0.65 | 5 | 142 | 479 | 48 | 637 | 2.42 | 71 | 27 | 15 | 0.07 |
| 9/7/02 | 0.58 | 4 | 145 | 489 | 49 | 618 | 2.41 | 61 | 27 | 12 | 0.06 |
| 10/14/02 | 0.62 | 4 | 148 | 491 | 49 | 627 | 2.43 | 51 | 28 | 10 | 0.06 |
| 11/10/02 | 0.63 | 2 | 143 | 471 | 53 | 520 | 2.18 | 27 | 23 | 15 | 0.06 |
| 12/1/02 | 0.64 | 1 | 139 | 424 | 49 | 481 | 2.00 | 43 | 24 | 18 | 0.07 |
| 1/7/03 | 0.62 | 4 | 130 | 459 | 52 | 626 | 2.35 | 10 | 26 | 15 | 0.06 |
| 2/1/03 | 0.57 | 3 | 146 | 461 | 47 | 599 | 2.31 | 20 | 28 | 15 | 0.06 |
| 3/1/03 | 0.68 | 4 | 149 | 473 | 49 | 639 | 2.42 | 21 | 29 | 22 | 0.07 |
| 3/30/03 | 0.68 | 4 | 154 | 495 | 49 | 625 | 2.44 | 24 | 30 | 34 | 0.07 |
| 4/29/03 | 0.68 | 5 | 146 | 475 | 48 | 621 | 2.39 | 21 | 28 | 19 | 0.07 |
| 5/28/03 | 0.75 | 4 | 152 | 491 | 48 | 678 | 2.54 | 23 | 30 | 0 | 0.07 |
| 6/30/03 | 0.75 | 5 | 150 | 492 | 48 | 694 | 2.57 | 22 | 30 | 5 | 0.07 |
| 7/31/03 | 0.72 | 4 | 147 | 471 | 49 | 669 | 2.48 | 20 | 30 | 5 | 0.07 |
| 8/31/03 | 0.74 | 4 | 143 | 469 | 49 | 653 | 2.44 | 26 | 31 | 6 | 0.07 |
| 12/8/03 | 0.71 | 4 | 161 | 475 | 65 | 660 | 2.50 | 26 | 29 | 8 | 0.06 |
| 1/8/04 | 0.72 | 4 | 166 | 468 | 65 | 663 | 2.49 | 21 | 30 | 11 | 0.06 |
| 2/10/04 | 0.63 | 4 | 151 | 390 | 62 | 544 | 2.08 | 11 | 24 | 14 | 0.08 |

**Table-34. Time series data for As and other ions in shallow well at site F (depth - 19 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 3.06 | 18 | 353 | 662 | 58 | 1066 | 3.87 | 17 | 42 | 42 | 0.04 |
| 4/7/02 | 3.07 | 18 | 359 | 655 | 57 | 1035 | 3.79 | 23 | 43 | 32 | 0.03 |
| 5/5/02 | 3.16 | 19 | 347 | 623 | 57 | 1029 | 3.71 | 55 | 41 | 38 | 0.03 |
| 6/8/02 | 2.95 | 18 | 380 | 721 | 72 | 1172 | 4.24 | 32 | 39 | 30 | 0.04 |
| 7/6/02 | 3.31 | 20 | 364 | 683 | 58 | 1116 | 4.02 | 54 | 43 | 36 | 0.03 |
| 8/3/02 | 3.26 | 20 | 362 | 685 | 56 | 1099 | 3.99 | 60 | 42 | 34 | 0.03 |
| 9/7/02 | 3.06 | 18 | 361 | 671 | 57 | 1089 | 3.94 | 48 | 41 | 35 | 0.03 |
| 10/14/02 | 2.89 | 17 | 347 | 657 | 55 | 1053 | 3.82 | 51 | 41 | 36 | 0.03 |
| 11/10/02 | 2.96 | 11 | 322 | 595 | 69 | 825 | 3.23 | 22 | 41 | 35 | 0.03 |
| 12/1/02 | 2.77 | 9 | 315 | 573 | 66 | 782 | 3.09 | 34 | 38 | 31 | 0.04 |
| 1/7/03 | 2.54 | 17 | 330 | 613 | 71 | 973 | 3.57 | 16 | 47 | 39 | 0.04 |
| 2/1/03 | 2.41 | 15 | 350 | 647 | 55 | 1059 | 3.82 | 7 | 43 | 42 | 0.04 |
| 3/1/03 | 2.93 | 18 | 355 | 664 | 56 | 1067 | 3.87 | 18 | 45 | 41 | 0.04 |
| 3/30/03 | 2.79 | 17 | 339 | 615 | 53 | 994 | 3.61 | 13 | 41 | 39 | 0.04 |
| 4/29/03 | 2.89 | 18 | 338 | 610 | 53 | 999 | 3.61 | 18 | 43 | 38 | 0.04 |
| 5/28/03 | 2.99 | 18 | 347 | 635 | 54 | 1061 | 3.79 | 18 | 40 | 36 | 0.04 |
| 6/30/03 | 2.91 | 19 | 346 | 632 | 55 | 1074 | 3.81 | 18 | 40 | 38 | 0.03 |
| 7/31/03 | 2.54 | 15 | 299 | 552 | 45 | 935 | 3.32 | 18 | 40 | 31 | 0.04 |
| 8/31/03 | 2.36 | 14 | 279 | 519 | 41 | 928 | 3.22 | 16 | 38 | 25 | 0.04 |
| 12/8/03 | 2.75 | 18 | 319 | 546 | 80 | 993 | 3.48 | 17 | 45 | 30 | 0.04 |
| 1/8/04 | 2.69 | 17 | 335 | 587 | 81 | 1049 | 3.69 | 16 | 45 | 33 | 0.04 |
| 2/10/04 | 2.69 | 16 | 333 | 573 | 79 | 997 | 3.55 | 11 | 44 | 37 | 0.04 |

**Table-35. Time series data for As and other ions in shallow well at site F (depth - 26 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/10/02 | 1.78 | 30 | 454 | 647 | 111 | 1168 | 4.19 | 292 | 28 | 0.28 | 0.21 |
| 12/1/02 | 2.85 | 28 | 516 | 594 | 97 | 1304 | 4.41 | 330 | 28 | 0.29 | 0.21 |
| 1/7/03 | 2.51 | 21 | 432 | 454 | 95 | 1758 | 4.95 | 339 | 35 | 0.35 | 0.21 |
| 2/1/03 | 3.33 | 34 | 478 | 718 | 77 | 1692 | 5.37 | 382 | 37 | 0.35 | 0.19 |
| 3/1/03 | 3.21 | 34 | 482 | 724 | 78 | 1741 | 5.49 | 376 | 38 | 0.32 | 0.23 |
| 3/30/03 | 3.09 | 34 | 478 | 722 | 75 | 1666 | 5.33 | 358 | 37 | 0.33 | 0.20 |
| 4/29/03 | 3.05 | 34 | 482 | 725 | 75 | 1710 | 5.43 | 350 | 37 | 0.33 | 0.21 |
| 5/28/03 | 3.09 | 33 | 451 | 697 | 76 | 1754 | 5.43 | 354 | 37 | 0.34 | 0.21 |
| 6/30/03 | 3.05 | 33 | 472 | 708 | 76 | 1735 | 5.43 | 355 | 37 | 0.33 | 0.22 |
| 7/31/03 | 3.02 | 33 | 473 | 709 | 71 | 1672 | 5.31 | 358 | 35 | 0.31 | 0.22 |
| 8/31/03 | 3.07 | 35 | 499 | 753 | 74 | 1698 | 5.48 | 359 | 36 | 0.31 | 0.23 |
| 12/8/03 | 2.97 | 31 | 447 | 655 | 107 | 1767 | 5.40 | 368 | 36 | 0.31 | 0.23 |
| 1/8/04 | 2.90 | 30 | 436 | 646 | 104 | 1740 | 5.31 | 341 | 36 | 0.31 | 0.24 |
| 2/10/04 | 2.91 | 31 | 432 | 651 | 103 | 1746 | 5.33 | 346 | 36 | 0.31 | 0.23 |

**Table-36. Time series data for As and other ions in deep well at site F (depth - 58 m)**

| **Date of Sampling** | **As** (µmoleL$^{-1}$) | **P** (µmoleL$^{-1}$) | **Na** (µmoleL$^{-1}$) | **Mg** (µmoleL$^{-1}$) | **K** (µmoleL$^{-1}$) | **Ca** (µmoleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** (µmoleL$^{-1}$) | **Mn** (µmoleL$^{-1}$) | **S** (µmoleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 0.004 | 6 | 11672 | 295 | 35 | 278 | 12.85 | 7 | 9 | 4 | 8.94 |
| 4/7/02 | 0.004 | 5 | 11450 | 271 | 36 | 285 | 12.60 | 3 | 9 | 4 | 7.79 |
| 5/5/02 | 0.004 | 5 | 12073 | 302 | 35 | 281 | 13.27 | 6 | 9 | 5 | 9.17 |
| 6/8/02 | 0.004 | 5 | 12253 | 294 | 38 | 293 | 13.46 | 4 | 9 | 6 | 9.19 |
| 7/6/02 | 0.004 | 5 | 12276 | 312 | 35 | 288 | 13.51 | 7 | 9 | 7 | 9.38 |
| 8/3/02 | 0.004 | 5 | 11611 | 286 | 35 | 293 | 12.80 | 4 | 9 | 7 | 9.04 |
| 9/7/02 | 0.004 | 5 | 11982 | 292 | 35 | 294 | 13.19 | 5 | 10 | 11 | 9.82 |
| 10/14/02 | 0.003 | 5 | 12254 | 307 | 36 | 303 | 13.51 | 5 | 9 | 12 | 10.07 |
| 11/10/02 | 0.004 | 4 | 9024 | 255 | 32 | 245 | 10.06 | 3 | 8 | 12 | 10.21 |
| 12/1/02 | 0.004 | 4 | 9017 | 267 | 33 | 253 | 10.09 | 4 | 8 | 12 | 10.30 |
| 1/7/03 | 0.004 | 5 | 10640 | 234 | 32 | 28 | 11.20 | 8 | 9 | 13 | 10.16 |
| 2/1/03 | 0.004 | 5 | 11806 | 297 | 37 | 300 | 13.04 | 9 | 9 | 12 | 10.02 |
| 3/1/03 | 0.004 | 5 | 11770 | 307 | 35 | 294 | 13.01 | 7 | 9 | 13 | 9.89 |
| 3/30/03 | 0.004 | 5 | 12062 | 306 | 34 | 288 | 13.28 | 7 | 10 | 12 | 9.76 |
| 4/29/03 | 0.004 | 5 | 11654 | 285 | 35 | 292 | 12.84 | 5 | 9 | 12 | 9.85 |
| 5/28/03 | 0.004 | 5 | 11562 | 263 | 33 | 273 | 12.67 | 5 | 9 | 11 | 9.32 |
| 6/30/03 | 0.004 | 5 | 12140 | 276 | 35 | 287 | 13.30 | 5 | 9 | 11 | 9.53 |
| 7/31/03 | 0.004 | 5 | 10321 | 237 | 34 | 295 | 11.42 | 3 | 9 | 0.1 | 9.24 |
| 8/31/03 | 0.004 | 5 | 10452 | 235 | 34 | 301 | 11.56 | 4 | 9 | 1 | 9.75 |
| 12/8/03 | 0.004 | 5 | 11459 | 305 | 42 | 311 | 12.73 | 9 | 9 | 14 | 10.66 |
| 1/8/04 | 0.004 | 5 | 11371 | 294 | 39 | 302 | 12.60 | 9 | 8 | 10 | 11.48 |
| 2/10/04 | 0.004 | 5 | 11062 | 275 | 38 | 287 | 12.22 | 4 | 8 | 9 | 10.69 |

**Table-37. Time series water level data (m) for shallow and deep wells at site F**

| Date of<br>Measureme | Wells at different depths<br>6 m | 11 m | 15 m | 19 m | 26m | 58 m |
|---|---|---|---|---|---|---|
| 03/09/02 | 2.5 | 2.5 | 2.5 | 2.5 | - | x |
| 03/23/02 | 2.3 | 2.3 | 2.3 | 2.3 | - | 2.3 |
| 04/06/02 | 2.8 | 2.8 | 2.8 | 2.8 | - | x |
| 04/20/02 | 2.8 | 2.7 | 2.7 | 2.7 | - | 2.7 |
| 05/05/02 | 3.0 | 3.0 | 3.0 | 3.0 | - | x |
| 05/18/02 | 3.8 | 3.8 | 3.8 | 3.8 | - | 3.8 |
| 06/01/02 | 4.3 | 4.3 | 4.2 | 4.3 | - | x |
| 06/24/02 | 5.3 | 5.3 | 5.3 | 5.2 | - | 5.2 |
| 07/14/02 | 6.0 | 6.0 | 6.0 | 6.0 | - | 5.9 |
| 09/07/02 | 5.8 | 5.8 | 5.8 | 5.8 | - | x |
| 10/14/02 | 5.3 | 5.3 | 5.3 | 5.3 | - | 5.2 |
| 11/10/02 | 4.5 | 4.5 | 4.4 | 4.4 | 4.5 | x |
| 12/16/02 | 4.3 | 4.2 | 4.2 | 4.2 | 4.3 | x |
| 01/05/03 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 |
| 01/07/03 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.7 |
| 02/01/03 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 |
| 02/15/03 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |
| 03/02/03 | 2.6 | 2.6 | 2.6 | 2.5 | 2.7 | 2.4 |
| 03/15/03 | 2.6 | 2.6 | 2.6 | 2.6 | 2.8 | 2.4 |
| 03/31/03 | 2.7 | 2.7 | 2.7 | 2.7 | 2.9 | 2.5 |
| 04/12/03 | 2.7 | 2.6 | 2.6 | 2.6 | 2.8 | 2.5 |
| 04/26/03 | 2.8 | 2.8 | 2.8 | 2.8 | 3.0 | 2.6 |
| 05/11/03 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 |
| 05/24/03 | 3.6 | 3.6 | 3.6 | 3.6 | 3.6 | 3.6 |
| 06/07/03 | 3.9 | 3.9 | 3.9 | 3.9 | 3.9 | 3.9 |
| 06/24/03 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.2 |
| 07/08/03 | 6.1 | 6.1 | 6.0 | 6.0 | 6.1 | x |
| 07/22/03 | 6.9 | 6.7 | 6.7 | 6.7 | 6.7 | x |
| 08/05/03 | 6.4 | 6.3 | 6.3 | 6.3 | 6.3 | x |
| 08/21/03 | 6.0 | 5.9 | 5.9 | 5.9 | 5.9 | x |
| 09/03/03 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | x |
| 09/18/03 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | x |
| 10/01/03 | 6.2 | 6.2 | 6.1 | 6.2 | 6.2 | x |
| 11/09/03 | 5.1 | 5.0 | 5.0 | 5.0 | 5.0 | x |
| 11/23/03 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 |
| 12/10/03 | 4.3 | 4.4 | 4.3 | 4.3 | 4.3 | x |
| 12/25/03 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | x |
| 01/11/04 | 3.9 | 3.9 | 3.9 | 3.9 | 3.9 | x |
| 01/25/04 | 3.7 | 3.6 | 3.6 | 3.6 | 3.6 | x |
| 02/16/04 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | x |
| 02/27/04 | 2.7 | 2.7 | 2.7 | 2.7 | 2.7 | x |

**- Well was not installed    x Wells were not accessible due to public use**

**Table-38. Time series data for As and other ions in shallow well at site G (depth - 6 m)**

| Date of Sampling | As (μmoleL$^{-1}$) | P (μmoleL$^{-1}$) | Na (μmoleL$^{-1}$) | Mg (μmoleL$^{-1}$) | K (μmoleL$^{-1}$) | Ca (μmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (μmoleL$^{-1}$) | Mn (μmoleL$^{-1}$) | S (μmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4/7/02 | 1.53 | 66 | 405 | 952 | 115 | 1300 | 5.02 | 1049 | 29 | 24 | 0.11 |
| 5/5/02 | 1.67 | 60 | 358 | 700 | 69 | 1242 | 4.31 | 487 | 25 | 22 | 0.11 |
| 6/8/02 | 1.89 | 62 | 364 | 726 | 69 | 1247 | 4.38 | 523 | 26 | 22 | 0.11 |
| 7/6/02 | 1.69 | 47 | 377 | 728 | 67 | 1245 | 4.39 | 655 | 30 | 21 | 0.12 |
| 8/3/02 | 1.20 | 27 | 363 | 715 | 70 | 1272 | 4.41 | 999 | 34 | 24 | 0.13 |
| 9/7/02 | 1.13 | 17 | 374 | 721 | 67 | 1304 | 4.49 | 1022 | 31 | 24 | 0.12 |
| 10/14/02 | 1.76 | 55 | 359 | 703 | 74 | 1335 | 4.51 | 750 | 25 | 23 | 0.12 |
| 11/10/02 | 1.84 | 66 | 361 | 682 | 71 | 1296 | 4.39 | 552 | 21 | 22 | 0.12 |
| 12/1/02 | 1.76 | 65 | 361 | 664 | 71 | 1261 | 4.28 | 498 | 22 | 22 | 0.12 |
| 1/8/03 | 1.68 | 59 | 336 | 689 | 91 | 1365 | 4.54 | 515 | 23 | 20 | - |
| 3/1/03 | 1.72 | 62 | 356 | 722 | 69 | 1271 | 4.41 | 478 | 23 | 21 | - |
| 3/30/03 | 1.57 | 53 | 366 | 736 | 66 | 1210 | 4.32 | 450 | 23 | 21 | 0.11 |
| 4/29/03 | 1.70 | 60 | 369 | 765 | 67 | 1252 | 4.47 | 491 | 23 | 21 | 0.11 |
| 5/28/03 | 1.73 | 59 | 359 | 748 | 65 | 1231 | 4.38 | 491 | 22 | 21 | 0.11 |
| 6/30/03 | 1.77 | 55 | 372 | 770 | 67 | 1269 | 4.52 | 532 | 23 | 21 | - |
| 7/31/03 | 1.81 | 64 | 368 | 780 | 73 | 1351 | 4.70 | 520 | 23 | 21 | 0.11 |
| 8/31/03 | 1.87 | 65 | 369 | 801 | 75 | 1406 | 4.86 | 543 | 24 | 21 | 0.11 |
| 12/8/03 | 1.92 | 69 | 369 | 800 | 73 | 1442 | 4.93 | 564 | 22 | 22 | 0.14 |
| 1/8/04 | 1.85 | 72 | 397 | 758 | 76 | 1414 | 4.82 | 513 | 18 | 22 | 0.14 |
| 2/10/04 | 1.88 | 60 | 380 | 861 | 75 | 1430 | 5.04 | 573 | 25 | 21 | 0.12 |

**Table-39. Time series data for As and other ions in shallow well at site G (depth - 9 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4/7/02 | 2.36 | 150 | 384 | 740 | 96 | 1683 | 5.33 | 483 | 6 | 9 | 0.10 |
| 5/5/02 | 2.31 | 135 | 384 | 744 | 97 | 1697 | 5.36 | 447 | 6 | 14 | 0.10 |
| 6/8/02 | 2.33 | 138 | 364 | 735 | 93 | 1753 | 5.43 | 523 | 7 | 5 | 0.09 |
| 7/6/02 | 1.98 | 86 | 360 | 681 | 87 | 1394 | 4.60 | 460 | 10 | 6 | 0.11 |
| 8/3/02 | 2.21 | 105 | 361 | 692 | 92 | 1560 | 4.96 | 551 | 12 | 14 | 0.11 |
| 9/7/02 | 1.79 | 65 | 404 | 746 | 87 | 1712 | 5.41 | 616 | 15 | <0.03 | 0.12 |
| 10/14/02 | 1.79 | 69 | 380 | 727 | 91 | 1770 | 5.46 | 649 | 9 | <0.03 | 0.12 |
| 11/10/02 | 1.90 | 90 | 373 | 727 | 90 | 1730 | 5.38 | 587 | 9 | 9 | 0.11 |
| 12/1/02 | 2.04 | 146 | 365 | 705 | 92 | 1682 | 5.23 | 578 | 10 | 7 | 0.10 |
| 1/8/03 | 1.95 | 84 | 347 | 629 | 90 | 1473 | 4.64 | 400 | 9 | 2 | - |
| 3/1/03 | 2.07 | 104 | 332 | 630 | 102 | 1692 | 5.08 | 449 | 7 | 3 | - |
| 3/30/03 | 2.09 | 109 | 352 | 683 | 90 | 1615 | 5.04 | 424 | 7 | 2 | 0.09 |
| 4/29/03 | 2.18 | 116 | 352 | 703 | 92 | 1697 | 5.24 | 446 | 6 | 3 | 0.10 |
| 5/28/03 | 2.18 | 109 | 364 | 732 | 90 | 1625 | 5.17 | 478 | 8 | 3 | - |
| 6/30/03 | 2.10 | 108 | 350 | 712 | 86 | 1628 | 5.12 | 465 | 8 | 3 | - |
| 7/31/03 | 2.25 | 111 | 348 | 693 | 92 | 1640 | 5.11 | 459 | 8 | 3 | 0.11 |
| 8/31/03 | 2.11 | 110 | 354 | 726 | 95 | 1649 | 5.20 | 481 | 7 | 7 | 0.12 |
| 12/8/03 | 2.03 | 98 | 336 | 680 | 93 | 1694 | 5.18 | 537 | 7 | 4 | 0.10 |
| 1/8/04 | 2.26 | 119 | 367 | 772 | 95 | 1786 | 5.58 | 489 | 7 | 5 | 0.11 |
| 2/10/04 | 2.42 | 117 | 407 | 822 | 97 | 1856 | 5.86 | 492 | 7 | 3 | 0.11 |

**Table-40. Time series data for As and other ions in shallow well at site G (depth - 14 m)**

| Date of Sampling | As (µmoleL$^{-1}$) | P (µmoleL$^{-1}$) | Na (µmoleL$^{-1}$) | Mg (µmoleL$^{-1}$) | K (µmoleL$^{-1}$) | Ca (µmoleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe (µmoleL$^{-1}$) | Mn (µmoleL$^{-1}$) | S (µmoleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4/7/02 | 1.39 | 36 | 424 | 706 | 82 | 1490 | 4.90 | 356 | 39 | 2.6 | 0.18 |
| 5/5/02 | 1.30 | 36 | 365 | 586 | 76 | 1225 | 4.06 | 293 | 33 | 1.8 | 0.16 |
| 6/8/02 | 1.25 | 33 | 335 | 491 | 70 | 1033 | 3.45 | 229 | 26 | 1.0 | 0.17 |
| 7/6/02 | 1.44 | 40 | 342 | 530 | 73 | 1203 | 3.88 | 327 | 30 | 1.0 | 0.17 |
| 8/3/02 | 1.44 | 40 | 344 | 564 | 72 | 1263 | 4.07 | 304 | 30 | 1.4 | 0.19 |
| 9/7/02 | 1.33 | 38 | 353 | 564 | 72 | 1243 | 4.04 | 438 | 29 | 1.0 | 0.20 |
| 10/14/02 | 1.42 | 38 | 345 | 551 | 74 | 1267 | 4.05 | 313 | 29 | 1.4 | 0.21 |
| 11/10/02 | 1.38 | 39 | 349 | 552 | 73 | 1280 | 4.09 | 291 | 29 | 1.4 | 0.22 |
| 12/1/02 | 1.36 | 37 | 593 | 936 | 72 | 659 | 3.86 | 334 | 29 | 1.0 | 0.20 |
| 1/8/03 | 1.42 | 36 | 340 | 554 | 72 | 1259 | 4.04 | 357 | 29 | 1.0 | 0.19 |
| 3/1/03 | 1.22 | 31 | 287 | 449 | 68 | 1167 | 3.59 | 246 | 29 | 1.4 | 0.18 |
| 3/30/03 | 1.30 | 34 | 328 | 506 | 70 | 1047 | 3.50 | 248 | 26 | 1.0 | 0.18 |
| 4/29/03 | 1.29 | 36 | 358 | 517 | 81 | 1087 | 3.65 | 248 | 27 | 1.0 | 0.16 |
| 5/28/03 | 1.36 | 33 | 270 | 507 | 75 | 1301 | 3.96 | 290 | 32 | 1.0 | 0.20 |
| 6/30/03 | 1.36 | 34 | 350 | 568 | 76 | 1320 | 4.20 | 293 | 31 | 1.0 | - |
| 7/31/03 | 1.38 | 33 | 337 | 563 | 76 | 1309 | 4.16 | 276 | 30 | 1.0 | 0.21 |
| 8/31/03 | 1.39 | 33 | 342 | 552 | 75 | 1277 | 4.08 | 259 | 29 | 1.0 | 0.22 |
| 12/8/03 | 1.29 | 33 | 341 | 548 | 71 | 1197 | 3.90 | 248 | 28 | 1.0 | 0.21 |
| 1/8/04 | 1.41 | 33 | 338 | 565 | 74 | 1269 | 4.08 | 271 | 31 | 1.0 | 0.22 |
| 2/10/04 | 1.36 | 32 | 337 | 539 | 73 | 1230 | 3.95 | 256 | 29 | 1.4 | 0.17 |

**Table-41. Time series data for As and other ions in shallow well at site G (depth - 21 m)**

| Date of Sampling | As ($\mu$moleL$^{-1}$) | P ($\mu$moleL$^{-1}$) | Na ($\mu$moleL$^{-1}$) | Mg ($\mu$moleL$^{-1}$) | K ($\mu$moleL$^{-1}$) | Ca ($\mu$moleL$^{-1}$) | SMC (meqL$^{-1}$) | Fe ($\mu$moleL$^{-1}$) | Mn ($\mu$moleL$^{-1}$) | S ($\mu$moleL$^{-1}$) | Cl (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4/7/02 | 2.30 | 43 | 330 | 490 | 80 | 1122 | 3.63 | 195 | 23 | 7.0 | 0.45 |
| 5/5/02 | 2.32 | 45 | 372 | 565 | 98 | 1197 | 3.99 | 369 | 27 | 6.4 | 0.46 |
| 6/8/02 | 1.91 | 41 | 332 | 476 | 75 | 1172 | 3.70 | 151 | 25 | 5.9 | 0.45 |
| 7/6/02 | 2.21 | 44 | 365 | 525 | 79 | 1288 | 4.07 | 148 | 26 | 1.9 | 0.51 |
| 8/3/02 | 2.65 | 51 | 352 | 518 | 78 | 1314 | 4.09 | 189 | 28 | 0.9 | 0.53 |
| 9/7/02 | 2.75 | 47 | 354 | 522 | 78 | 1288 | 4.05 | 222 | 28 | 2.3 | 0.53 |
| 10/14/02 | 2.68 | 51 | 370 | 526 | 79 | 1337 | 4.18 | 202 | 29 | 1.0 | 0.55 |
| 11/10/02 | 2.36 | 44 | 373 | 525 | 81 | 1324 | 4.15 | 179 | 27 | 0.9 | 0.58 |
| 12/1/02 | 2.21 | 44 | 433 | 566 | 87 | 1314 | 4.28 | 190 | 28 | 3.2 | 0.57 |
| 1/8/03 | 2.31 | 37 | 398 | 545 | 79 | 1287 | 4.14 | 192 | 30 | 1.0 | 0.57 |
| 3/1/03 | 2.23 | 43 | 390 | 472 | 97 | 1313 | 4.06 | 200 | 29 | 1.0 | 0.58 |
| 3/30/03 | 2.26 | 41 | 346 | 480 | 79 | 1225 | 3.84 | 164 | 25 | 5.6 | 0.55 |
| 4/29/03 | 2.16 | 39 | 345 | 475 | 78 | 1205 | 3.78 | 149 | 26 | 4.8 | 0.56 |
| 5/28/03 | 2.19 | 39 | 383 | 527 | 78 | 1313 | 4.14 | 156 | 27 | 1.6 | 0.56 |
| 6/30/03 | 2.16 | 38 | 439 | 592 | 80 | 1413 | 4.53 | 183 | 31 | 1.1 | - |
| 7/31/03 | 2.32 | 39 | 501 | 585 | 84 | 1447 | 4.65 | 195 | 31 | 0.8 | 0.56 |
| 8/31/03 | 2.29 | 40 | 521 | 572 | 87 | 1415 | 4.58 | 205 | 30 | 1.0 | 0.57 |
| 12/8/03 | 2.28 | 39 | 562 | 588 | 86 | 1406 | 4.63 | 201 | 32 | 0.7 | 0.57 |
| 1/8/04 | 2.38 | 45 | 561 | 589 | 82 | 1422 | 4.67 | 213 | 31 | 0.8 | 0.68 |
| 2/10/04 | 2.15 | 37 | 620 | 591 | 85 | 1406 | 4.70 | 183 | 29 | 0.7 | 0.66 |

**Table-42. Time series data for As and other ions in deep well at site G (depth - 52 m)**

| **Date of Sampling** | **As** (µmoleL$^{-1}$) | **P** (µmoleL$^{-1}$) | **Na** (µmoleL$^{-1}$) | **Mg** (µmoleL$^{-1}$) | **K** (µmoleL$^{-1}$) | **Ca** (µmoleL$^{-1}$) | **SMC** (meqL$^{-1}$) | **Fe** (µmoleL$^{-1}$) | **Mn** (µmoleL$^{-1}$) | **S** (µmoleL$^{-1}$) | **Cl** (mmoleL$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/9/02 | 6.473 | 8 | 11279 | 230 | 42 | 282 | 12.34 | 17 | 14 | 34 | 6.84 |
| 4/7/02 | 6.270 | 8 | 10772 | 223 | 61 | 279 | 11.84 | 14 | 13 | 32 | 6.19 |
| 5/5/02 | 6.284 | 7 | 10704 | 214 | 41 | 278 | 11.73 | 8 | 13 | 34 | 5.98 |
| 6/8/02 | 7.369 | 8 | 10130 | 208 | 40 | 275 | 11.14 | 9 | 12 | 35 | 6.68 |
| 7/6/02 | 6.152 | 8 | 10020 | 202 | 40 | 282 | 11.03 | 12 | 11 | 32 | 6.81 |
| 8/3/02 | 6.751 | 6 | 9848 | 201 | 36 | 263 | 10.81 | 10 | 12 | 33 | 7.04 |
| 9/7/02 | 6.426 | 7 | 10093 | 213 | 39 | 273 | 11.10 | 9 | 12 | 29 | 6.47 |
| 10/14/02 | 7.294 | 6 | 10303 | 214 | 40 | 266 | 11.30 | 10 | 12 | 32 | 7.72 |
| 11/10/02 | 5.919 | 7 | 9772 | 200 | 40 | 267 | 10.75 | 9 | 11 | 30 | 7.85 |
| 12/1/02 | 8.405 | 7 | 9619 | 196 | 38 | 248 | 10.54 | 18 | 11 | 30 | 6.72 |
| 1/8/03 | 5.980 | 9 | 9998 | 197 | 45 | 298 | 11.03 | 11 | 12 | 30 | 7.49 |
| 3/1/03 | 7.523 | 6 | 9686 | 205 | 38 | 256 | 10.65 | 35 | 12 | 30 | 7.65 |
| 3/30/03 | 6.875 | 6 | 9083 | 193 | 36 | 247 | 10.00 | 36 | 12 | 32 | 7.14 |
| 4/29/03 | 6.454 | 6 | 9315 | 191 | 36 | 234 | 10.20 | 15 | 11 | 31 | 7.43 |
| 5/28/03 | 6.233 | 6 | 9457 | 202 | 37 | 263 | 10.42 | 9 | 11 | 30 | 7.48 |
| 6/30/03 | 6.440 | 6 | 9695 | 199 | 35 | 243 | 10.61 | 8 | 11 | 30 | - |
| 7/31/03 | 6.714 | 7 | 10071 | 214 | 38 | 259 | 11.06 | 8 | 11 | 29 | 7.78 |
| 8/31/03 | 6.482 | 6 | 9622 | 204 | 36 | 239 | 10.54 | 7 | 11 | 28 | 7.69 |
| 12/8/03 | 7.073 | 7 | 9291 | 201 | 39 | 259 | 10.25 | 12 | 11 | 25 | 7.87 |
| 1/8/04 | 6.157 | 7 | 9364 | 198 | 36 | 259 | 10.31 | 8 | 11 | 27 | 7.83 |
| 2/10/04 | 6.464 | 6 | 9246 | 194 | 36 | 252 | 10.17 | 15 | 12 | 28 | 7.72 |

**Table-43. Time series water level data (m) for shallow and deep wells at site G**

| Date of Measurement | Wells at different depths | | | | |
|---|---|---|---|---|---|
| | 6 m | 9 m | 14 m | 21 m | 52 m |
| 3/9/2002 | 3.1 | 3.0 | 2.9 | 2.9 | x |
| 3/23/2002 | 2.9 | 2.9 | 2.9 | 2.8 | 2.5 |
| 4/6/2002 | 3.4 | 3.3 | 3.3 | 3.2 | x |
| 4/20/2002 | 3.3 | 3.2 | 3.2 | 3.9 | 2.9 |
| 5/5/2002 | 3.9 | 3.9 | 3.9 | 3.8 | x |
| 5/18/2002 | 4.6 | 4.5 | 4.5 | 4.4 | 4.1 |
| 6/1/2002 | 5.1 | 5.0 | 5.0 | 4.9 | x |
| 6/24/2002 | 6.0 | 6.0 | 5.9 | 5.7 | 4.3 |
| 7/14/2002 | 6.7 | 6.7 | 6.6 | 6.6 | 6.2 |
| 9/7/2002 | 6.6 | 6.5 | 6.5 | 6.4 | x |
| 10/14/2002 | 5.8 | 5.2 | 5.9 | 5.8 | 5.4 |
| 11/10/2002 | 5.1 | 5.1 | 5.0 | 4.9 | x |
| 12/16/2002 | 4.8 | 4.8 | 4.7 | 4.6 | x |
| 1/8/2003 | 4.4 | 4.3 | 4.3 | 4.2 | 4.0 |
| 1/9/2003 | 4.4 | 4.3 | 4.3 | 4.2 | 3.9 |
| 2/1/2003 | 3.5 | 3.4 | 3.4 | 3.3 | 3.0 |
| 2/15/2003 | 3.5 | 3.5 | 3.4 | 3.4 | 2.9 |
| 3/2/2003 | 3.3 | 3.2 | 3.2 | 3.1 | 2.6 |
| 3/15/2003 | 3.4 | 3.3 | 3.3 | 3.2 | 2.7 |
| 3/31/2003 | 3.6 | 3.5 | 3.5 | 3.4 | 2.9 |
| 4/12/2003 | 3.3 | 3.2 | 3.2 | 3.1 | 2.7 |
| 4/26/2003 | 3.7 | 3.7 | 3.6 | 3.5 | 3.1 |
| 5/11/2003 | 4.4 | 4.4 | 4.3 | 4.2 | 3.8 |
| 5/24/2003 | 4.4 | 4.3 | 4.3 | 4.2 | 3.8 |
| 6/7/2003 | 4.7 | 4.7 | 4.6 | 4.5 | 4.1 |
| 6/24/2003 | 6.0 | 6.0 | 5.9 | 5.8 | 5.4 |
| 7/8/2003 | 6.7 | 6.7 | 6.6 | 6.6 | 6.1 |
| 7/22/2003 | 7.5 | 7.4 | 7.4 | 7.3 | 6.8 |
| 8/5/2003 | 7.1 | 7.0 | 7.0 | 6.9 | 6.5 |
| 8/21/2003 | 6.7 | 6.6 | 6.6 | 6.5 | 6.1 |
| 9/3/2003 | 6.9 | 6.8 | 6.8 | 6.7 | 6.4 |
| 9/18/2003 | 6.8 | 6.8 | 6.7 | 6.7 | 6.3 |
| 10/1/2003 | 6.9 | 6.8 | 6.8 | 6.7 | x |
| 11/9/2003 | 5.7 | 5.7 | 5.6 | 5.6 | 5.2 |
| 11/23/2003 | 5.2 | 5.2 | 5.1 | 5.1 | x |
| 12/10/2003 | 4.8 | 4.8 | 4.7 | 4.7 | 4.4 |
| 12/25/2003 | 4.7 | 4.6 | 4.6 | 4.5 | x |
| 1/11/2004 | 4.5 | 4.4 | 4.4 | 4.3 | 4.0 |
| 1/25/2004 | 3.1 | 3.0 | 3.0 | 2.9 | x |
| 2/16/2004 | 3.4 | 3.3 | 3.3 | 3.2 | x |
| 2/27/2004 | 3.1 | 3.1 | 3.0 | 2.9 | x |

**x Well was not accessible due to public use**

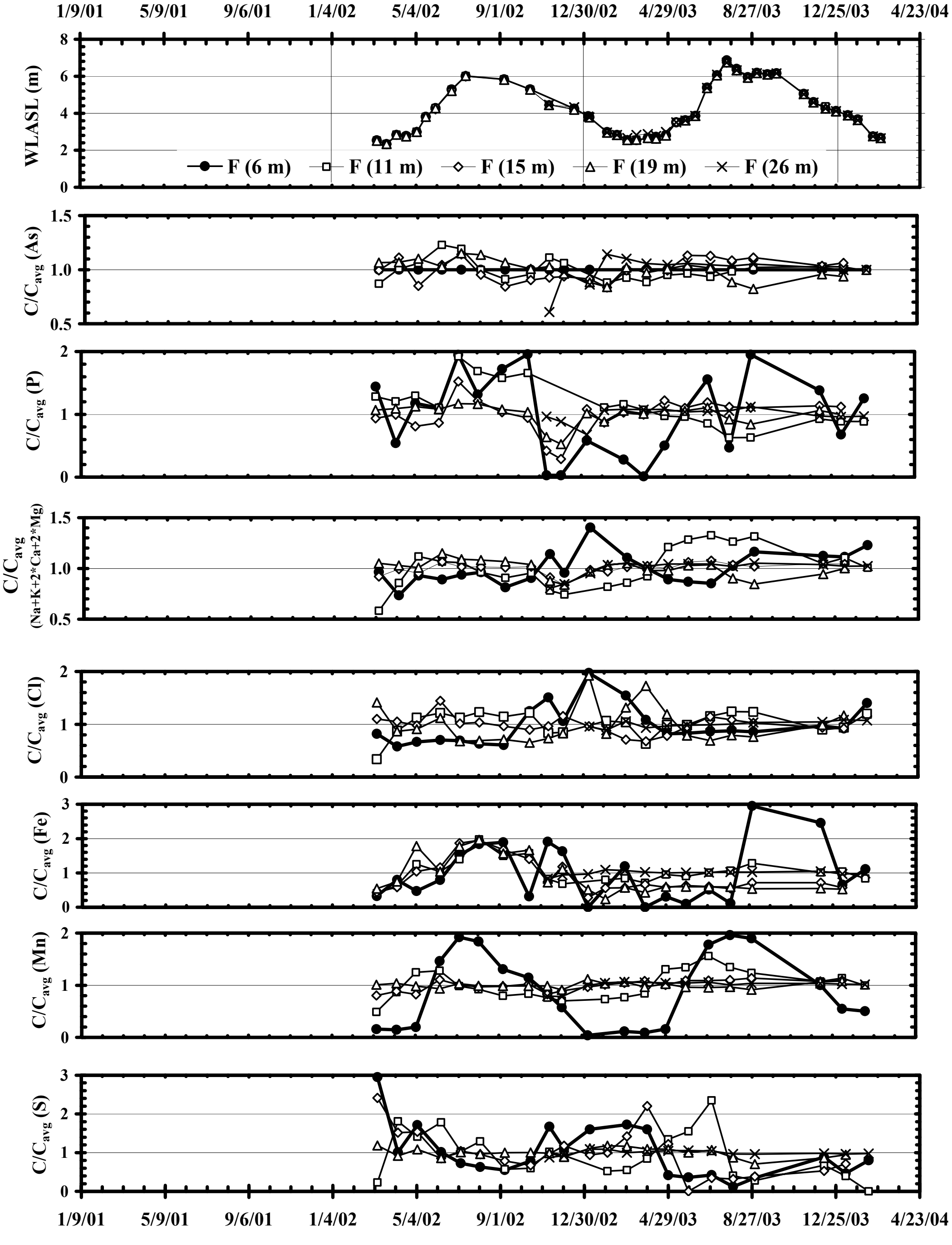

**Figure 1** Temporal variation in As and other ions concentrations in shallow aquifers of site A. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (80, 132, 538, 359 μg/L), P (20, 16, 31, 27 μmole/L ), SMC (5.6, 4.2, 5.4, 7 meq/L), Cl (1.3, 0.8, 1.2, 1.0 meq/L), S (374, 145, 16, 6 μmole/L), Fe (413, 158, 265, 332 μmole/L), Mn (47, 51, 96, 18 μmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

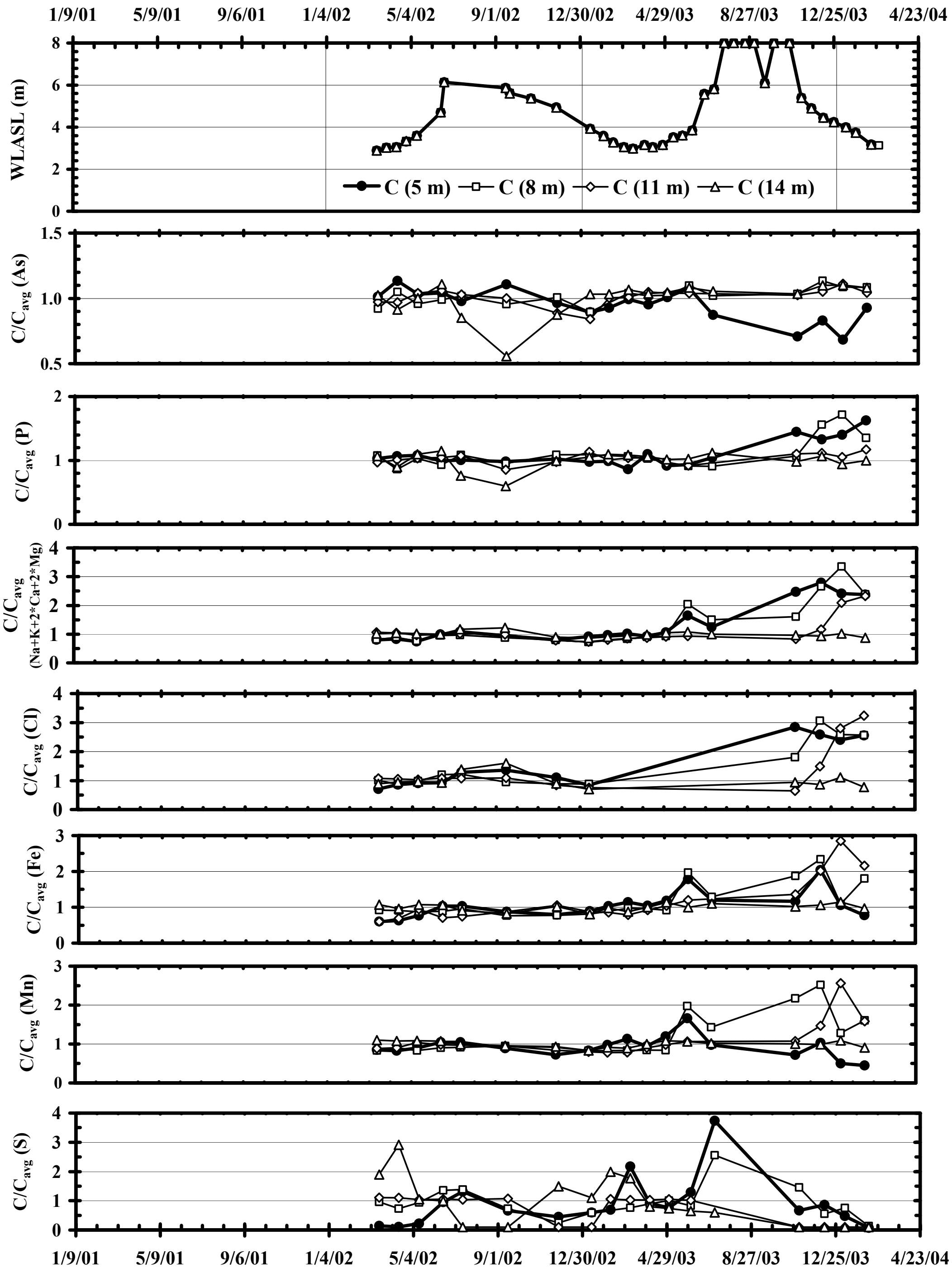

**Figure 2** Temporal variation in As and other ions concentrations in shallow aquifers of site B. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (29, 299, 536, 403, 225 μg/L), P (56, 56, 54, 56, 53 μmole/L), SMC (13.9, 11.9, 9.5, 8.2, 8.2 meq/L), Cl (4.3, 3.5, 4.1, 2.1, 2.5 meq/L), S (684, 350, 161, 9, 3 μmole/L), Fe (445, 431, 380, 417, 363 μmole/L), Mn ( 18, 40, 20, 24, 6 μmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

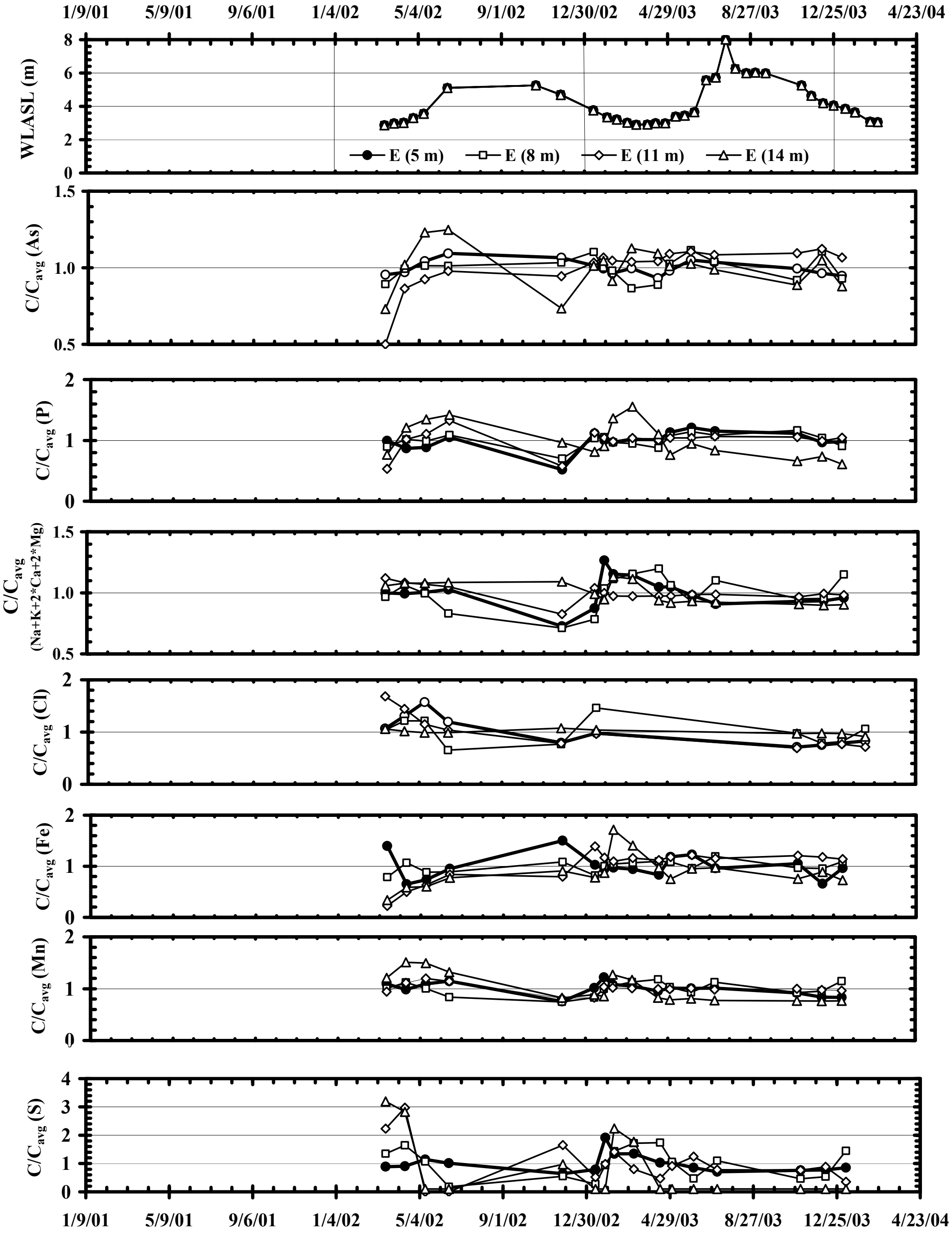

**Figure 3** Temporal variation in As and other ions concentrations in shallow aquifers of site C. Well were installed in March 2002. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (13, 37, 42, 71 μg/L), P (31, 22, 22, 29 μmole/L), SMC (2.7, 1.3, 1.3, 2.8 meq/L), Cl (0.6, 0.7, 0.5, 0.3 meq/L), S (35, 28, 15, 2 μmole/L), Fe (773, 1433, 1132, 601 μmole/L), Mn (26, 52, 31, 33 μmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

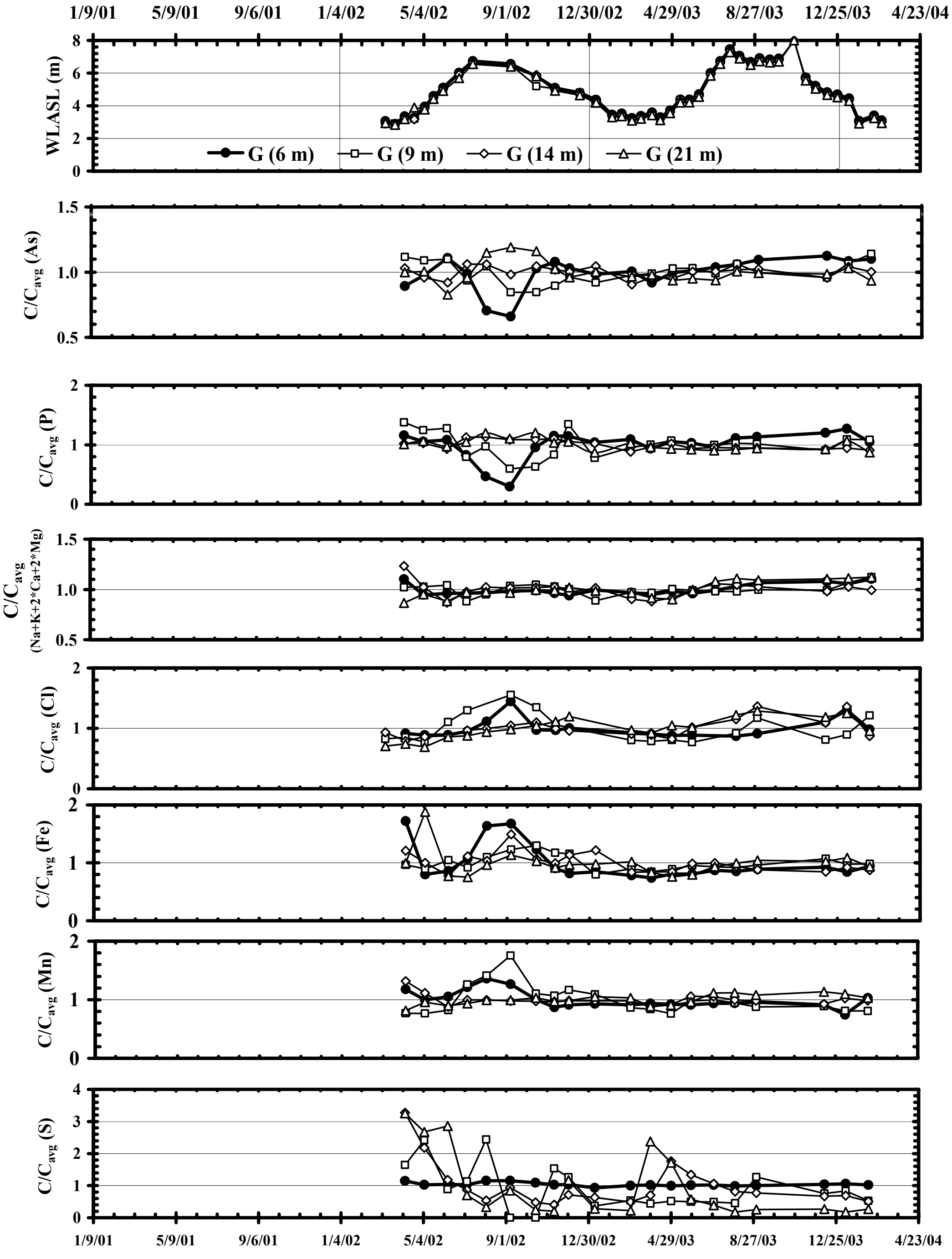

**Figure 4** Temporal variation in As and other ions concentrations in shallow aquifers of site E. Well were installed in March 2002. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (43, 82, 166, 153 µg/L), P (8, 26, 27, 29 µmole/L), SMC (4.9, 3.8, 4.2, 5.1 meq/L), Cl (0.2, 0.1, 0.1, 0.8 meq/L), S (232, 80, 15, 2 µmole/L), Fe (48, 424, 392, 608 µmole/L), Mn (17, 35, 33, 17 µmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

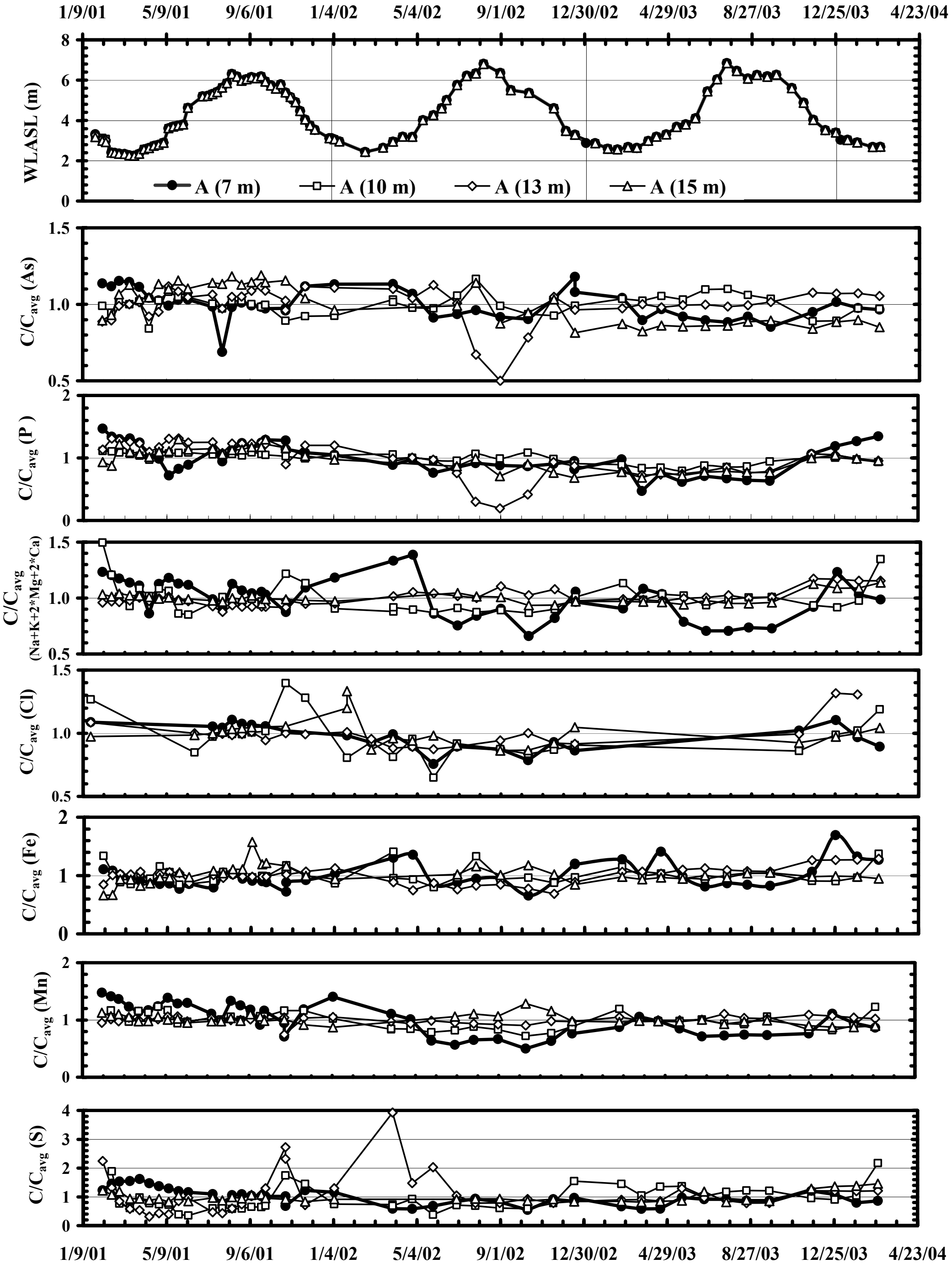

**Figure 5** Temporal variation in As and other ions concentrations in shallow aquifers of site F. Well were installed in March 2002. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (0.2, 35, 51, 215, 219 µg/L), P (0.1, 2, 4, 17, 32 µmole/L), SMC (1.6, 1.8, 2.4, 3.7, 5.2 meq/L), Cl (0.3, 0.2, 0.1, 0.05, 0.2 meq/L), S (40, 24, 19, 35, 0.3 µmole/L), Fe (2.4, 60, 23, 30, 350 µmole/L), Mn (3, 31, 27, 42, 35 µmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

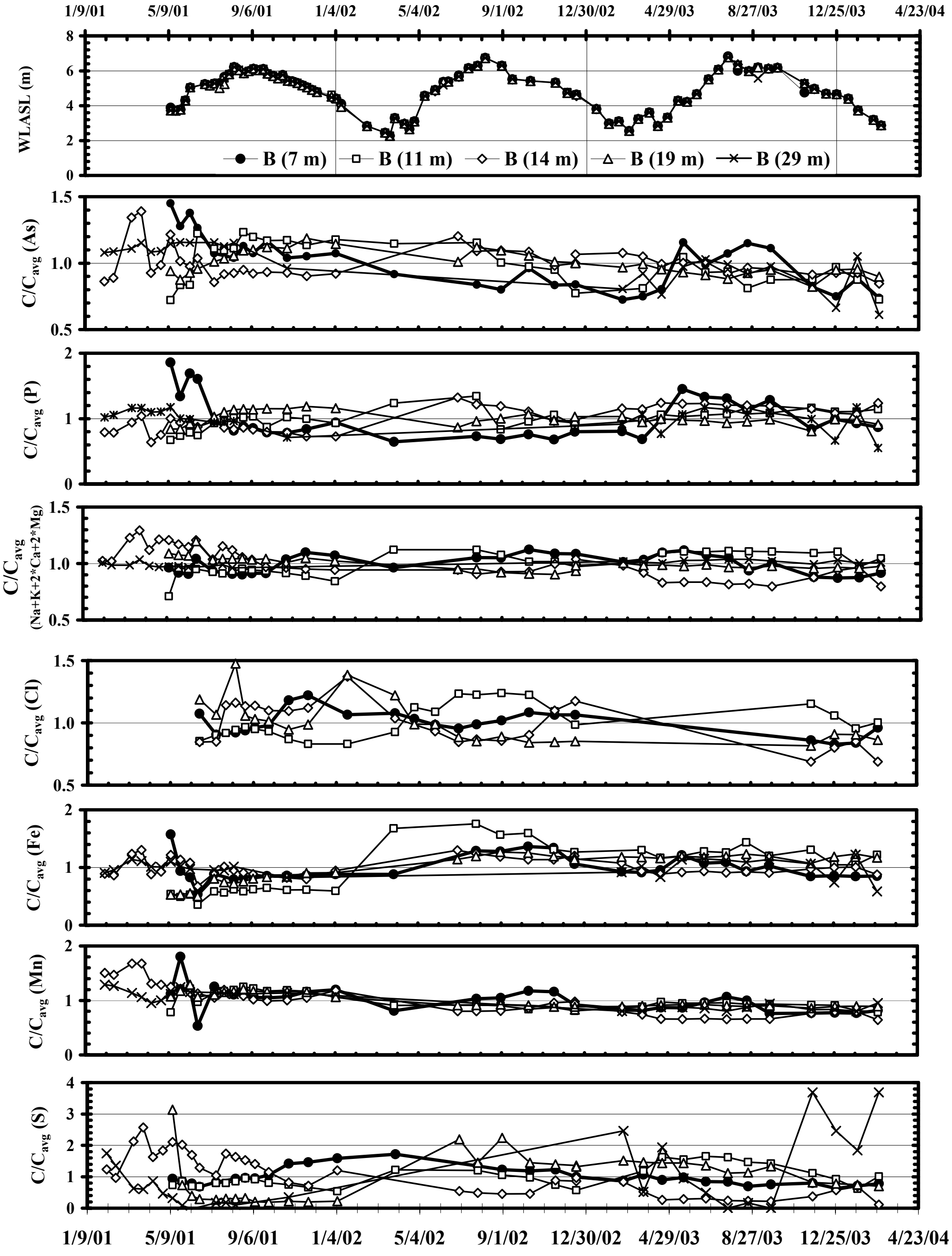

**Figure 6** Temporal variation in As and other ions concentrations in shallow aquifers of site G. Well were installed in March 2002. The average concentration of dissolved ions including As from shallowest to deepest depths are summarized here: As (129, 158, 101, 173 µg/L), P (57, 106, 35, 42 µmole/L), SMC (4.6, 5.2, 4.0, 4.2 meq/L), Cl (0.1, 0.1, 0.2, 0.6 meq/L), S (21, 5, 1, 2 µmole/L), Fe (610, 497, 290, 195 µmole/L), Mn (25, 8, 29, 28 µmole/L). The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

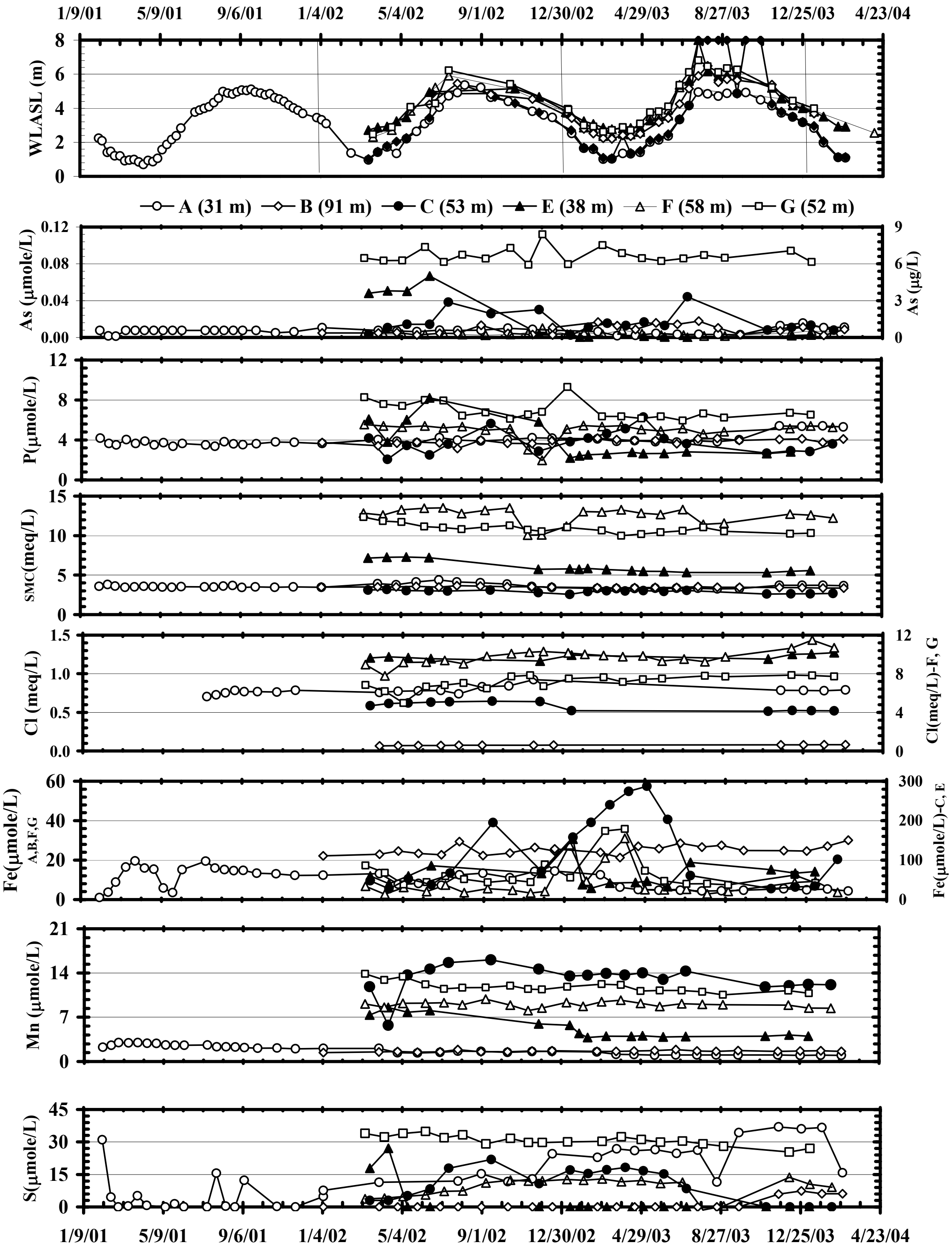

**Figure 7** Temporal variation in As and other ions concentrations in deep aquifers of all six sites. Different scale was used in right Y-axes to show higher level of Cl at site F, G and high level of Fe at sites C and E. The uppermost panel shows the water table fluctuation as water level above sea level (WLASL) with time.

# Chapter 4. Microbes and arsenic mobilization in Pleistocene deep aquifer of Araihazar, Bangladesh: limited roles of arsenic and iron reduction

## *4.1. Abstract*

The role of microbial arsenate and iron reduction in the mobilization of As can be difficult to distinguish. In a setting of great practical importance, a set of incubation experiments was conducted over a period of 3 months using deep Pleistocene aquifer orange sands from Bangladesh that are typically associated with low groundwater As concentrations. Aliquots of 5 g of orange sands collected in 2001 and resuspended in 2005 in 10 ml of anaerobic artificial groundwater (Agw) were inoculated with wild-type *Shewanella* sp. ANA-3 and a mutant *Shewanella* sp. ANA-3 (AMR1). The wild-type ANA-3 can use Fe(III), Mn(IV), or As(V) as terminal electron acceptors. The AMR1 strain is deficient in As(V) reduction due to deletions of genes for As-respiration (*arrA*) and As-detoxification (*arsC*). The Pleistocene sands initially contained little Fe(II) in the acid-leachable Fe fraction (Fe(II)/total Fe=0.05) and about 0.14 μg $g^{-1}$ phosphate-extractable As, all as arsenate. Aqueous As speciation in solution and in the P-extract was assayed by a voltammetric method that selectively detects arsenite with a detection limit of ~ 0.2 μg/L. Anaerobic incubations were conducted with and without additions of 0.02 M lactate or kanamycin. Kanamycin was used in an attempt to suppress the activity of indigenous microbes (both *Shewanella* strains contained plasmids with kanamycin-resistant genes).

Surprisingly, wild-type and mutant strains of *Shewanella* mobilized As and Fe to a similar extent in the presence of lactate. The equivalent of 0.035 and 0.031 µg $g^{-1}$ sediment of As was mobilized on day 23 of the incubations with the wild and mutant strains, respectively. However, 97% of the aqueous As was arsenite in the wild incubation, whereas only 37% of the aqueous As was arsenite in the mutant incubation. The solid phase in both inoculations contained the equivalent of <0.004 mg/kg As(III) on day 23. The controls with or without lactate and without either strain of *Shewanella* all released less than the equivalent of 0.003 mg/kg As from the solid phase. We conclude that reduction of As may not be required to release As from oxidized Pleistocene sands of Bangladesh. Furthermore, wild-type and mutant strains of *Shewanella* converted the tightly bound As to a mobilzable form by 92 days, with higher concentrations (0.3 µg $g^{-1}$) with lactate than without (0.1 µg $g^{-1}$). Microbial processes responsible for this conversion may therefore be the critical process to evaluate to assess the vulnerability of Pleistocene aquifers of Bangladesh.

## ***4.2. Introduction***

Reduction of arsenic directly by As-reducing microbes through dissimilatory reduction of arsenate (As(V)) by which microbes gain energy for growth (Ahmann et al., 1997; Stolz and Oremland, 1999) is often invoked as a potential mechanism for As mobilization in aquifer systems (McArthur et al., 2004; Oremland et al., 2005; Zobrist et al., 2000). Growing evidence of dissimilatory arsenate reduction, especially in anoxic sediments (Dowdle et al., 1996; Zobrist et al., 2000) and high-As saline lakes (Oremland and Stolz, 2003), has generated significant interest in investigating how this mechanism may influence biogeochemical As transformation and the molecular biology of this transformation (Croal et al., 2004; Newman et al., 1998; Silver and Phung, 2005). In microcosm experiments, reduction of As and Fe either occur simultaneously or closely follow each other (Islam et al., 2004; Langner and Inskeep, 2000; van Geen et al., 2004), contributing to the widely-held view that elevated concentrations of As in groundwater is related to the activity of anaerobic metal-reducing bacteria in aquifers such as those in Bangladesh (Akai et al., 2004; Gault et al., 2005) that may reduce both As and Fe. Microbial community analysis has indeed identified Fe(III)-reducing bacteria, e.g., *Geobacter*, in the Ganges Delta (Islam et al., 2005)and in Maine (Weldon and MacRae, 2006). These findings underscore the role that Fe(III)-reducing bacteria may play in As mobilization indirectly either upon reduction of As-bearing Fe-oxyhydroxide (McArthur et al., 2004; Nickson et al., 1998; Swartz et al., 2004; Zheng et al., 2004) or by reducing As(V) via microbially generated Fe(II) (Islam et al., 2004).

Considerable uncertainty remains regarding the need for As reduction for mobilization, especially for sediment containing As concentrations at crustal abundances of 1-10 mg/kg (Cullen and Reimer, 1989) as opposed to highly contaminated sediment. On one hand, arsenic in anaerobic groundwater or pore water has been found to exist mainly as arsenite (Peterson and Carpenter, 1986; Yan et al., 2000; Zheng et al., 2004). There are few reliable data of arsenic speciation in sediment, but when gray colored, fresh aquifer sediment from a shallow (<30 m) aquifer of Bangladesh was anaerobically leached by a near neutral phosphate solution and subsequently analyzed for arsenite by voltammetry (Jung and Zheng, 2006), most of the arsenic was found to be present as arsenite (Zheng et al., in prep.). This suggests that reduction of arsenic may not be required for As mobilization to groundwater. Indeed, microcosm studies have found that mobilization of As can take place by the activity of dissimilatory Fe-reducing bacteria without As reduction. No reduction of As(V) to As(III) was found when *Geobacter* metallireducens was inoculated to As(V)-loaded synthetic ferrihydrite contaning ~2400 mg/kg As even when on average 10% of the Fe(III) was reduced (Tadanier et al., 2005). Incubation experiments of sediment from Lake Coeur d'Alene, Idaho, that was allowed to oxidize in air and then was artificially spiked with 100 mM As(V) and inoculated with a Fe(III)-reducing bacterium *Shewanella alga* strain BrY, also showed that reduction of As(V) was not needed for mobilization (Cummings et al., 1999). Both studies, however, used concentrations of As much higher than crustal levels.

For the present study, we incubated orange colored Pleistocene deep sediment from Bangladesh to examine the role of microbial As(V) reduction in mobilization of As. Recently, an arsenate-reduction deficient mutant of *Shewanella* sp. strain ANA-3 that is still capable of reducing Fe(III) and Mn(IV) was created by deleting two As(V) reducing genes (respiratory: *arrA* and detoxifying: *arsC)*. The result was the so-called "double knock-out" *Shewanella* sp. ANA-3 (AMR1) (Malasarn et al., 2004; Saltikov et al., 2003; Saltikov and Newman, 2003; Saltikov et al., 2005). Because of its properties, *Shewanella* sp. ANA-3 (AMR1) created a new opportunity to determine if dissimilatory As reduction was required for mobilization of As in sediment. The present study also builds on recent analytical advances that made it possible to determine electrochemically the speciation of As at low concentrations in both the aqueous and the solid phase (He et al., 2004; Jung and Zheng, 2006). Although *Geobacter* and *Shewanella* species have been identified in diverse environments around the world (Coates et al., 1996; Venkateswaran et al., 1999), *Shewanella* species are more versatile with respect to terminal electron acceptors (Croal et al., 2004). To our knowledge, a mutant *Geobacter* that does not reduce As is not available. The study also has practical implication for the sustainability of the low-As Pleistocene deep aquifers as a drinking water source in Bangladesh (Zheng et al., 2005).

## *4.3. Experimental*

### 4.3.1. Collection and preservation of aquifer sediment

Aliquots of a section of sediment core from depth 43.3-43.9 m from Dari Satyabandi village (23.785$^o$N, 90.603$^o$E) in Araihazar, Bangladesh, was used in all experiments after the entire section was manually homogenized inside a anaerobic chamber containing 95% $N_2$/5% $H_2$ (Coy Lab. Prod. Inc., AALC). The sediment was collected in January 2001 and had the characteristic orange color of Pleistocene aquifers in Bangladesh (Horneman et al., 2004). Both ends of the PVC liner containing the core were wax-sealed on site immediately after collection. The cores were shipped at ambient temperature and stored at 4°C upon their arrival at Lamont-Doherty's core repository in May, 2001. The sediment was still wet and orange when the liner was opened in July 2005 inside the anaerobic chamber. The diffuse spectral reflectance of the sediment and a Fe(II)/Fe ratio 0.052 ± 0.001 in the acid-leachable fraction of the sediment were consistent with previous field or laboratory analyses of Pleistocene sediment from Araihazar (Horneman et al., 2004; Zheng et al., 2005).

### 4.3.2. Culturing of *Shewanella*

The wild-type *Shewanella* sp. strain ANA-3 was initially isolated from an As-treated wooden pier pilling in Woods Hole, Massachusetts. The mutant-type *Shewanella* sp. strain AMR1 was obtained after deletion of the arrA and arsC genes (Saltikov et al., 2003; Saltikov and Newman, 2003; Saltikov et al., 2005). Both wild and mutant types of ANA-3 strains were initially grown aerobically and then anaerobically in Techniques in Microbial Ecology (TME) media at 28-30°C on an incubator shaker (250 rpm) for 24 hours and 72 hours respectively. The TME media is prepared by adding 1.5 g of $NH_4Cl$, 0.6 g of $NaH_2PO_4$, 0.1 g of KCl, 50 ml of 10 g $l^{-1}$ yeast extract (sterilized by autoclaving), 20 ml of 1 mole $l^{-1}$ Na-lactate (sterilized by autoclaving), and 10 ml trace metal solution (Kostka and Nealson, 1998) to 1 liter of nanopure water. The pH of the media was adjusted to 7 by adding 1 g of Na-HEPES to 1 liter of the media ( 4 mmole $l^{-1}$). The final TME media is prepared by adding two different electron acceptors for wild and mutant type growth, respectively. To two 500 ml aliquots of media, 1.56 g of $Na_2HAsO_4$, $7H_2O$ (10 mmole $l^{-1}$) and 1.56 g of Na-fumarate (20 mmole $l^{-1}$) were added for mutant- and wild-type cultures, respectively (Saltikov et al., 2005).

### 4.3.3. Incubations

Pleistocene sediment from Bangladesh was incubated anaerobically for 3 months with seven types of amendments. In all incubations, approximately 5 g of sediment sample was added to a sterile 17-ml culture tube (Hungate 2047-16125) with ~ 10 ml of artificial groundwater, bubbled with pure $N_2$ for 2 hours prior to incubation. Three sets of controls were incubated without the addition of microbes: the first, labeled $C^-$, contained only sediment and artificial groundwater; the second ($C^+$) was amended with lactate (Fisher, syrup 60% w/w) to a concentration of 0.02 mole $l^{-1}$; the third ($C^{+k}$) was amended with lactate and the antibiotic kanamycin to a concentration of 50 mg $l^{-1}$. The four sets of inoculated incubations were all amended with the same amount of kanamycin. Two sets were inoculated with wild-type *Shewanella* sp. ANA-3, one with lactate ($W^{+k}$) and one without ($W^{-k}$). The other two sets were inoculated with the mutant *Shewanella* sp. ANA-3 (AMR1), again one with lactate ($M^{+k}$) and one without ($M^{-k}$). Both wild and mutant types of *Shewanella* strains contained plasmids with kanamycin resistance genes (Saltikov et al., 2003; Saltikov and Newman, 2003). The purpose of the kanamycin addition was to isolate the effect of the inoculation of the two *Shewanella* strains whose properties are known from that of the complex natural assemblage of micro-organisms present in the sediment that would have responded to the lactate addition.

Artificial groundwater of composition similar to that of groundwater associated with the Pleistocene aquifer (Zheng et al., 2005) was prepared by adding salts of Na, Ca, K, Mg, Cl, $HCO_3$, $PO_4$ and $SO_4$ to ultra-pure water (Millipore MQ system) at concentrations of 2.0, 0.06, 0.045, 0.29, 0.53, 3, 0.005 and xxx mM followed by filtration through a disposable sterile system (Corning, 09-761). The optical density of *Shewanella* cultures was measured prior to addition to each tube, and were 0.053 ± 0.001 for the wild-type *Shewanella* sp. ANA-3 and 0.090 ± 0.001 for the mutant *Shewanella* sp. ANA-3 (AMR1). The culture tubes were wrapped in black plastic and set horizontally on a rocking shaker (Cole-Parmer, 51401-15) rotating at 50-75 rpm.

Each set of incubations started with 7 replicates that were sampled in sacrificial mode on the 23rd, 42nd and 92nd day in 3, 2 and 2 replicates, respectively. The sampling intervals were chosen by monitoring the color change of the suspensions. After measuring the pH (Orion, model 260A), the supernatant from each sampled tube was filtered in the anaerobic chamber through a 0.45 µm filter (Whatman syringe filter, Cat. No.6790-2504). Before acidification of the filtered supernatant to 1% HCl (Fisher, Optima), aliquots were taken for As(III) and Fe(II) determinations immediately.

### 4.3.4. Sediment reflectance

Changes in the color of the sediment over the course of the incubations were recorded with a Minolta CM2500D diffuse spectral reflectance spectrophotometer through the round bottom of the glass tubes. The difference in reflectance (ΔR) between wavelengths of 520 nm and 530 nm was used as a measure of conversion of Fe(III) to Fe(II) in the solid phase (Horneman et al., 2004).

### 4.3.5. Analysis of As, As(III), Fe, and Fe(II)

After opening each tube, a ~0.5 g aliquot of wet sediment was leached in 10 ml of 1.2 M HCl at 80°C for up to 24 hours. This leachate was analyzed by ferrozine colorimetry to determine the proportion of Fe(II) and Fe(III) in the solid phase that is relatively mobile (Viollier et al., 2000) and by high resolution inductively coupled plasma spectrometry (HR ICP-MS) to measure the As, total Fe, and Mn content of the same phase (Cheng et al., 2004). A second ~0.5 g of wet sediment from each tube was leached in 10 mL of 1 M $Na_2HPO_4$ (pH 5) and 0.1 M L-ascorbic acid, at room temperature and in the anaerobic chamber, for 24 hours and then another 16 hours (Jung and Zheng, 2006). The concentration of As(III) in the phosphate leachate was measured by differential pulse cathodic stripping voltammetry (DPCSV) (He et al., 2004) and the concentration of total As by HR ICP-MS.

The concentrations of As(III), Fe(II), and total Fe in the filtered, non-acidified supernatant were also determined by DPCSV and ferrozine colorimetry respectively. The concentrations of total As, Fe and Mn in the acidified supernatant were analyzed by HR ICP-MS.

## *4.4. Results*

### 4.4.1. Aqueous Phase As, Fe and Mn

The largest increases in dissolved As concentrations of 16 ± 3 $\mu g\ l^{-1}$ and 14 ± 2 $\mu g\ l^{-1}$ that are equivalent (eqv.) to mobilization of 0.035 $\mu g\ g^{-1}$ and 0.031 $\mu g\ g^{-1}$ As from sediment were observed between day 1 and 23 in the two incubations amended with lactate and inoculated with either type of *Shewanella* sp. strain ANA-3 ($W^{+k}$, $M^{+k}$, Fig. 4.1a). The increases in dissolved As were smaller but easily detectable by HR ICP-MS over the same period for the two inoculated incubations without lactate; 2.3 ± 0.04 μg $l^{-1}$ (eqv. 0.005 μg $g^{-1}$) and 2.9 ± 0.11 μg $l^{-1}$ (eqv. 0.007 μg $g^{-1}$) in $W^{-k}$ and $M^{-k}$, respectively (Fig. 4.1a). No significant increase in dissolved As was observed on day 23 in the supernatant of the three incubations that were not inoculated ($C^{+}$, $C^{-}$, $C^{+k}$).

Essentially all dissolved As in the supernatant of incubation ($W^{+k}$) amended with lactate and inoculated with the wild-type *Shewanella* sp. ANA-3 was in the form of As(III) on day 23 ($W^{+k}$, Fig. 4.1b). On the other hand, only one third of dissolved As released in incubation amended with lactate and inoculated with the mutant-type *Shewanella* sp. ANA-3 (AMR1) was in the form of As(III) ($M^{+k}$, Fig. 4.1b). The proportion of AsIII in the incubations with wild type *Shewanella* ($W^{-k}$) and mutant-type *Shewanella* sp. ANA-3 (AMR1) without lactate ($M^{-k}$) was not detectable (< 2 μg $l^{-1}$) in this period (Fig. 4.1b). There were no further increases in dissolved As concentrations or changes in As speciation after day 23 for 3 out of the 4 inoculated incubations ($W^{-k}$, $W^{+k}$, $M^{+k}$, Fig. 4.1a, b). For incubations with the mutant-type *Shewanella* sp. ANA-3 (AMR1) without lactate ($M^{-k}$ ), maximum aqueous As release was 6.0 ± 0.3 μg $l^{-1}$ on the 42nd day that is equivalent to mobilization of 0.015 μg $g^{-1}$ As from sediment (Fig. 4.1a, Table-4.1 ) and the percentage of As(III) was about 45% (Fig. 4.1b).

**Table 4.1. Incubation experiments and As, Fe, Mn release**

| | **Seds (Before incub.)** | **Without Microbial inoculation(control)** | | | **Shewanella ANA-3 (wild)** | | **Shewanella ANA-3 (mutant)** | |
|---|---|---|---|---|---|---|---|---|
| | **BI** | **C $^{-}$** | **C $^{+}$** | **C $^{+k}$** | **W $^{-k}$** | **W $^{+k}$** | **M $^{-k}$** | **M $^{+k}$** |
| As (µg kg$^{-1}$) | 137.0 ± 30.4 | nd | 3.4 ± 0.15 | 2.6 ± 0.01 | 5.3 ± 0.02 | 34.6 ± 7.4 | 15.3 ± 1.15 | 30.8 ± 7.4 |
| Fe (µg g$^{-1}$) | 10.6 ± 1.2 | nd | 34.9 ± 0.1 | 30.9 ± 0.5 | 0.9 ± 0.08 | 48.4 ± 11.1 | 1.4 ± 0.04 | 44.3 ± 2.1 |
| Mn (µg g$^{-1}$) | 284.0 ± 17.9 | nd | 34.7 ± 0.4 | 32.0 ± 0.2 | 1.8 ± 0.19 | 35.8 ± 3.7 | 6.4 ± 0.21 | 34.5 ± 0.2 |
| $P^{H}$ | | 8.06 ± 0.16 | 7.25 ± 0.31 | 7.14 ± 0.29 | 7.82 ± 0.07 | 7.13 ± 0.23 | 7.79 ± 0.07 | 7.25 ± 0.14 |
| As/Fe (mmole/mole) | | | 0.1 | 0.1 | 5.9 | 2.2 | 11.1 | 1.5 |
| As/Mn (mmole/mole) | | | 0.1 | 0.1 | 4.1 | 1.0 | 2.4 | 0.9 |

Aqueous As was not detectable (< 0.1 μg $l^{-1}$) in the control without amendment ($C^{-}$, Fig. 1a) over three months whereas in the control amended by lactate, without or with kanamycin mobilized 1.5 ± 0.2 μg $l^{-1}$ As (eqv. 0.003 μg $g^{-1}$) ($C^{+}$, $C^{+k}$, Fig. 1a, Table-4.1).

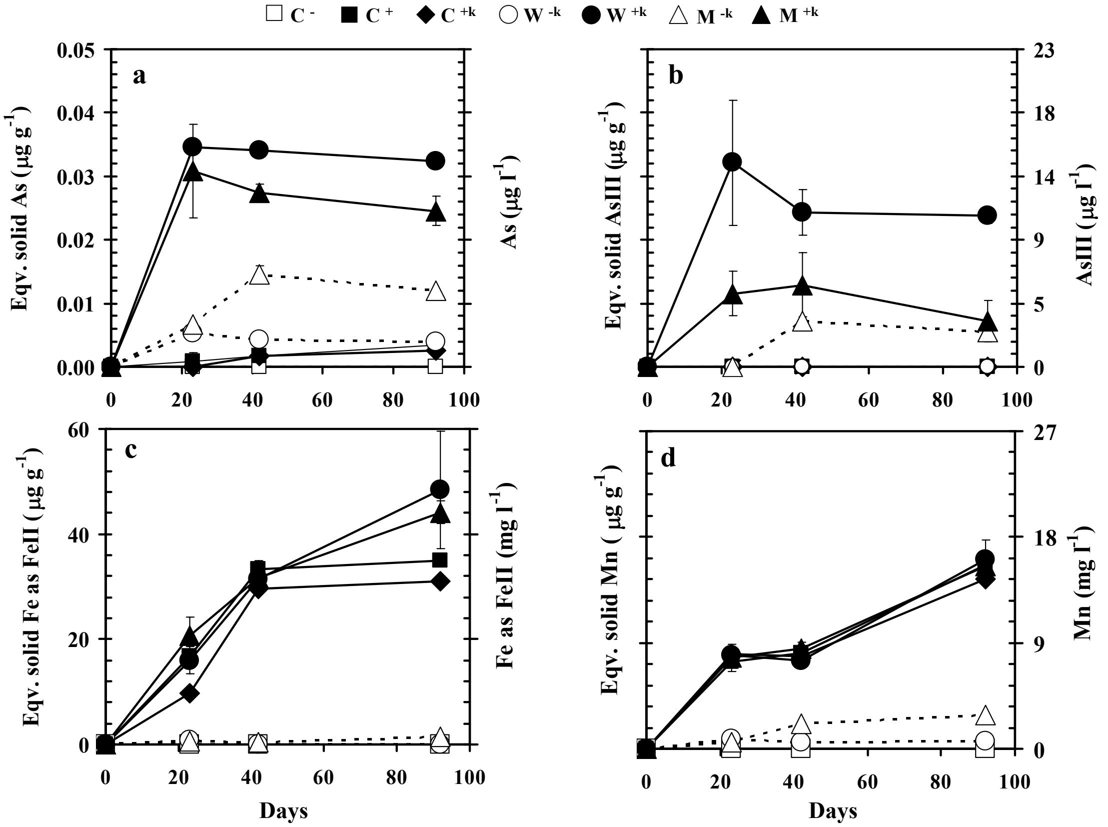

**Figure-4.1.** Release of (a) As, (b) As(III), (c) Fe as ~100% Fe(II), (d) Mn in artificial groundwater (Agw) from Pleistocene deep aquifers orange sediments in different incubation types as shown by different symbols for seven manipulations : control without lactate ($C^{-}$), control with lactate ($C^{+}$), control with lactate, kanamycin ($C^{+k}$), Shewanella wild type strain ANA-3 without lactate, kanamycin ($W^{-k}$) and with lactate, kanamycin ($W^{+k}$), Shewanella mutant type strain ANA-3 without lactate, kanamycin ($M^{-k}$) and with lactate, kanamycin ($M^{+k}$). Concentrations are expressed as equivalent to solid content by normalizing with sediments weights (left y-axes) and solution concentration are shown in right y-axes. Error bars indicate the standard deviation of 3 replicates.

Experiments with lactate amendment ($C^+$, $C^{+k}$, $W^{+k}$, $M^{+k}$) showed consistently higher concentrations of $[Fe]_{aq}$ than those without lactate ($C^-$, $W^{-k}$, $M^{-k}$) by 23 and 42 days (Fig. 4.1c). Sediment incubated with the addition of either wild ($W^{+k}$) or mutant type ($M^{+k}$) Fe-reducer *Shewanella* in the presence of lactate continued to release Fe up to 92 days, equivalent to mobilization of 48 and 44 μg $g^{-1}$ Fe from sediment, respectively (Table 4.1). Only in the control incubation without lactate and microbes the $[Fe]_{aq}$ was not detectable (< 30 μg $l^{-1}$, $C^-$, Fig. 4.1, Table-4.1), a small but detectable amount of Fe, or equivalent to ~ 1 μg $g^{-1}$ from sediment, was measured in $W^{-k}$ and $M^{-k}$ incubations (Table 4.1). The patterns of Mn release were similar to those of Fe (Fig. 4.1d; Table 4.1).

## 4.4.2. Sediment As, Fe and Mn

The Pleistocene sediment amended with lactate ($C^+$, $C^{+k}$, $W^{+k}$, $M^{+k}$) visibly started to turn grey on day 17 of the incubations. This is detected by the onset of a divergence in the reflectance data between sediment amended with lactate and sediment without lactate ($C^-$, $W^{-k}$, $M^{-k}$, Fig. 4.2f). The difference in diffuse reflectance at 530 and 520 nm reached a steady value by day 50 for the incubations amended with lactate. There was no detectable change in the reflectance for two of the incubations without acetate ($C^-$, $W^{-k}$) over the entire 3 month duration of the experiment. The reflectance data indicate, however, that the color of Pleistocene sediment inoculated with mutant *Shewanella* sp. ANA-3 (AMR1) without lactate ($M^{-k}$) also evolved towards that of the sediment amended with lactate, without ever turning as intensely grey (Fig. 4.2f).

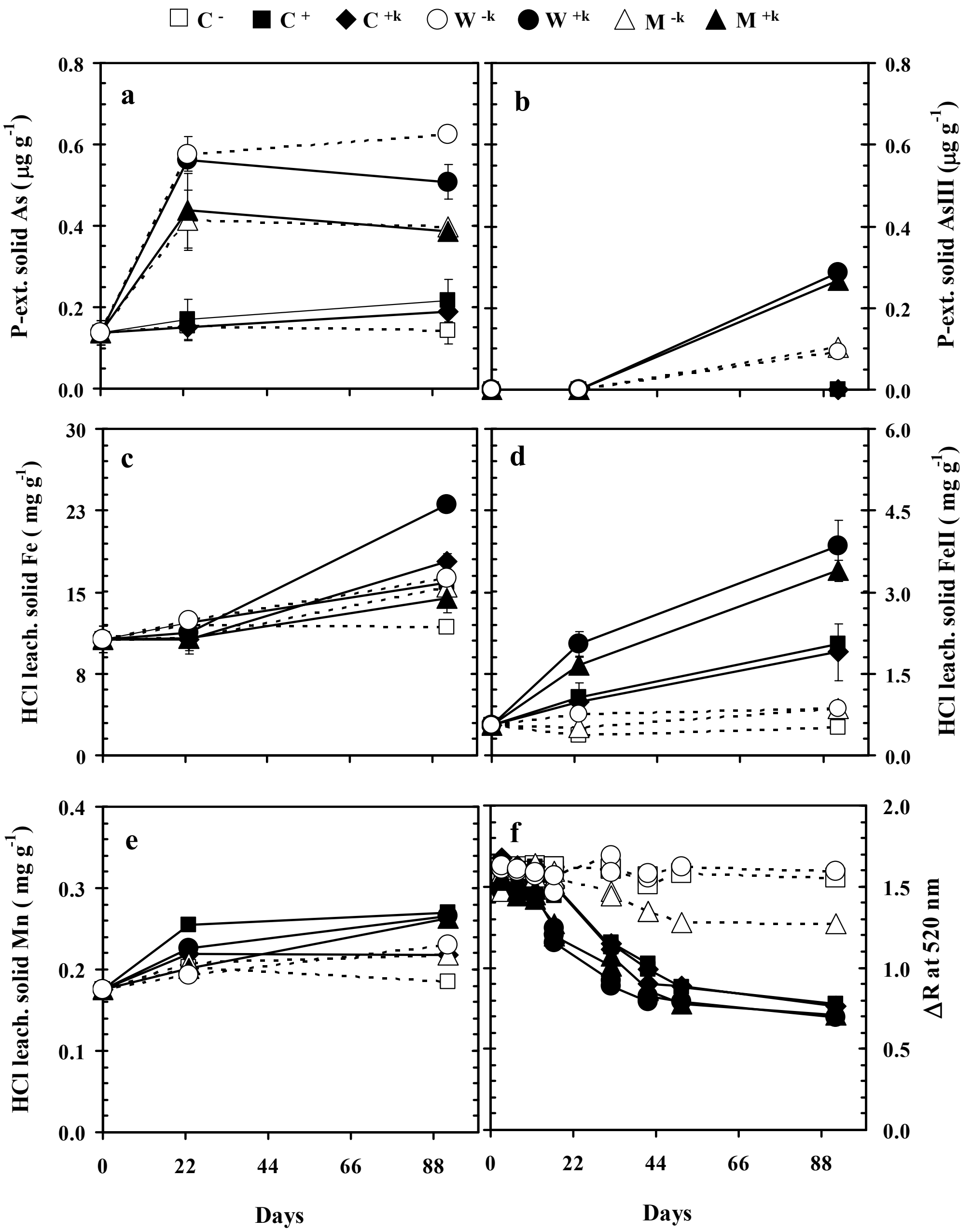

**Figure-4.2.** Solid phase characterization of not incubated (0 days) and post-incubated sediments used in different manipulation types as shown by different symbols for seven manipulations : control without lactate ($C^-$), control with lactate ($C^+$), control with lactate, kanamycin ($C^{+k}$), Shewanella wild type strain ANA-3 without lactate, kanamycin ($W^{-k}$) and with lactate, kanamycin ($W^{+k}$), Shewanella mutant type strain ANA-3 without lactate, kanamycin ($M^{-k}$) and with lactate, kanamycin ($M^{+k}$). The sum of 24 hrs and 16 hrs P-extractable As and As(III) are shown in panel (a) and (b) respectively using same y-axes scale. 24 hours hot HCl leachable total Fe and Fe (II) are shown in panel (c) and (d) respectively with different y-axes scale; Fe(II) scale is 5 times less than total Fe scale. 24 hours hot HCl leachable Mn is shown in panel (e) and sediment color in terms of reflectance difference (ΔR) is shown in panel (f). Error bars indicate the standard deviation of 3 replicates.

The initial P-extractable As concentration in the sediment was 0.13 ± 0.03 μg $g^{-1}$, primarily in the form of As(V) (Figs. 4.2a and 4.2b), consistent with previous analyses of orange-colored sediment samples from the Pleistocene aquifer at the same site but different depth (Zheng et al., 2005). The P-extractions on day 23 indicate a 3 to 4-fold increase in mobilizable As in the solid phase for all four inoculated incubations, and no significant change for the incubations that were not inoculated (Fig. 4.2a). The quantity of As extracted from the solid phase in the four inoculated incubations after 23 days was about 20-fold greater than the total released to the supernatant over the same period. Whereas As in the dissolved phase was primarily and partially in the form of As(III) for inoculated incubations with lactate $W^{+k}$, $M^{+k}$ respectively, the P-extractions of the sediment in the inoculated incubations contain no detectable As(III) on day 23. The amount of the P-extractable As on the solid phase did not increase significantly after day 23, but the proportion of As(III) in the mobilizable phase did rise to about ~50% at the end of 3 months for the two inoculated incubations with lactate ($W^{+k}$, $M^{+k}$), and to about half that much for the inoculated incubations without lactate ($W^{-k}$, $M^{-k}$) (Fig. 4.2b).

The amount of HCl-leachable Fe from sediments remained relatively unchanged in incubations without lactate ($C^{-}$, $W^{-k}$, $M^{-k}$, Fig. 4.2c) and increased slightly in those with lactate by 92 days ($C^{+}$, $C^{+k}$, $W^{+k}$, $M^{+k}$, Fig. 4.2c). The proportion of FeII in the sediment did not increase in the three incubations without lactate ($C^{-}$, $W^{-k}$, $M^{-k}$, Fig. 4.2d). However, not only the proportion of FeII in the sediment increased significantly in those with lactate, this increase of FeII was already evident for all four incubations with lactate as early as the 23rd day ($C^{+}$, $C^{+k}$, $W^{+k}$, $M^{+k}$, Fig. 4.2d).

The amount of HCl-leachable Mn from sediments showed relatively little changes in all incubations, although the 3 incubations with lactate had slightly higher Mn ($C^{+}$, $W^{+k}$, $M^{+k}$, Fig. 4.2e).

## *4.5. Discussion*

### 4.5.1. The limited role of As Reduction

The interpretation of the results first focuses on changes from initial conditions to day 23 of the incubations of Pleistocene sediment from Bangladesh. The absence of detectable As(III) in the P-extractable phase of the 4 incubations inoculated with either type of *Shewanella* sp. strain and only a modest proportion of As(III) in solution in the incubation amended with lactate and inoculated with mutant-type *Shewanella* sp. ANA-3 (AMR1) is a clear indication that As reduction is not a requirement for transfer to of As to the dissolved phase. The comparable total amounts of As released by the incubations amended with lactate and inoculated with wild-type *Shewanella* sp. ANA-3 and mutant-type *Shewanella* sp. ANA-3 (AMR1) provides additional evidence that As reduction is not a crucial step for the potential mobilization of As from Pleistocene sediments of Bangladesh.

The detection of any As(III) in the incubation amended with lactate inoculated with mutant-type *Shewanella* sp. ANA-3 (AMR1) is somewhat surprising given the extensive evidence that the organism has entirely lost its capability to reduce As(V).

Abiotic reduction of As(V) by Fe(II) is unlikely because in the controls with lactate ($C^+$ and $C^{+k}$), FeII concentrations were very similar to those of mutant incubations ($M^{-k}$ and $M^{+k}$). However, there were no detectable As(III) in both the dissolved or solid phase in these controls (Fig. 4.1b and 4.2b). One possibility is that mutant-type *Shewanella* sp. ANA-3 (AMR1) cultured for the experiment either mutated back or not entirely mutated to begin with.

## 4.5.2. The limited role of Fe Reduction

All four amendments of Pleistocene sediment with lactate led to significant reduction and release of Fe(II) to solution, including the two incubations that were not inoculated with *Shewanella* sp. strain ANA-3 ($C^+$, $C^{+k}$), one which was amended with kanamycin. The observation is consistent with the well-established requirement of an abundant supply of electron donors to induce microbial Fe reduction (Lovley, 1991), but also suggests that kanamycin was not effective in inhibiting Fe reduction by the endogenous population of micro-organisms. As an alternative explanation for Fe reduction in the incubation amended with lactate and kanamycin only ($C^{+k}$), the possibility of abiotic Fe reduction by lactate cannot be excluded although this has, to our knowledge, not been reported previously.

Two features of the series of incubations suggest that Fe reduction *per se* may not be a critical step for the mobilization of As from Pleistocene sediment of Bangladesh. The first is that most of the As mobilization from the sediment amended with lactate and inoculated with either *Shewanella* sp. strain took place before day 23, whereas Fe (II) levels continued to build up in the solid and dissolved phase over 3 months. Even more telling, however, is that dissolved As concentrations had already increased significantly by day 23 in the incubations without lactate inoculated with either type of *Shewanella* sp. strain ($W^{-k}$, $M^{-k}$). This release of As from Pleistocene sediment occurred in the absence of any detectable Fe reduction.

### 4.5.3. The importance of micro-organisms

With or without amendment with lactate and, consequently, with or without significant Fe reduction, the addition of either *Shewanella* sp. strain clearly had a strong effect on As contained in Pleistocene sediments of Bangladesh (Fig. 4.2a). All four inoculations rapidly generated large quantities of P-extractable As on the solid phase within the first 23 days of the incubations. The conversion of As to a more mobile form is the one property that most closely relates to the level and evolution of As present in solution over the duration of the experiments. Interestingly, the amendment with lactate did not measurably affect the conversion of As to a more mobilizable form in the solid phase, even if the corresponding concentrations of As in the dissolved were lower for the incubation without lactate ($W^{-k}$, $M^{-k}$). It may be at this level that the partial reduction of Fe oxydroxides plays a detectable though secondary role by reducing the availability of Fe (III) sites for which both As(III) and As(V) have a strong binding affinity (Dixit and Hering, 2003) and therefore modulating the concentration of As in solution for a given amount of mobilizable As in the solid phase. The key finding, however, is that the addition of *Shewanella* sp. strain systematically converted As into a mobilizable form on the solid phase. The mechanism of this conversion is presently not known and requires further investigation.

In addition to converting As to a more mobilizable form in the sediment, *Shewallena* sp. strain mediated reduction of As because significant proportion of As(III) was detected in phosphate-extractable As on the 92nd day of the 4 incubations with *Shewallena* sp. strains. The reduction of As in this case, appears to depend on whether electron donors were made available rather than whether the *Shewallena* is wild or mutant type. The proportion of P-extractable As(III) were 51% for both $W^{+k}$ and $M^{+k}$ . The proportion of P-extractable As(III) were lower at 16% and 25% for $W^{-k}$ and $M^{-k}$, respectively. The indigenous microbes in the sediment seem to be capable of neither mediating reduction of As (Fig. 4.2b) nor promoting formation of more easily mobilizable As (Fig. 4.2a).

It is worth noting that microbes without lactate resulted in little Fe reduction ($W^{-k}$ and $M^{-k}$, Fig. 4.2d), contrary to the As reduction evident on sediment. The reason for this is unclear.

### 4.5.4. Decoupling between As and Fe, Mn

The decoupling between As and Fe, and also between As and Mn becomes easier to understand because the mobilizations of Fe and Mn are limited by electron donors whereas the mobilization of As is more complicated and may be limited by microbes. The very low As/Fe and As/Mn ratios in the $C^{+}$ and $C^{+k}$ amendments (Table 4.1) resulted from low aqueous As due to microbial limitation on As mobilization and high aqueous Fe concentrations due to abundant electron donors.

The intermediate As/Fe and As/Mn ratios in the $W^{+k}$ and $M^{+k}$ incubations (Table 4.1) resulted from high aqueous As and high aqueous Fe concentrations, corresponding to abundant electron donors and Fe(III) reducing bacteria. The high As/Fe and As/Mn ratios in the $W^{-k}$ and $M^{-k}$ (Table 4.1) resulted from medium aqueous As due to abundant Fe(III) reducing bacteria but low aqueous Fe concentrations due to lack of electron donors. Therefore, the wide range of As/Fe and As/Mn ratios observed in the groundwater system (BGS & DPHE, 2001) is expected because a single sediment yielded ratios spanning 2 orders of magnitude by varying availability of electron donors and a single metal-reducing bacterium *Shewanella* sp. strain.

### 4.5.5. Implications for Pleistocene aquifers of Bangladesh

Concerns about the long-term viability of withdrawals from Pleistocene aquifers in Bangladesh have been raised primarily on the basis of hydrological and biogeochemical considerations (Harvey et al., 2002; Islam et al., 2004; van Geen et al., 2004). With respect to the volume of pumping, Zheng et al. (2005) pointed out that withdrawal for human consumption using hand pumps is unlikely to draw a significant amount of shallow groundwater elevated in As into deep aquifers. Instead, pumping for irrigation at a much larger volume, which is presently not tapping the deeper aquifers in Bangladesh, remains an issue of great concern for the sustainability of the deep aquifer as a drinking water source (Zheng et al., 2005). A problem that presently is more likely than whole-aquifer contamination is the penetration of shallow water elevated in As around the pipe of improperly installed wells (van Geen et al., 2004).

The nature of the biogeochemical interactions for arsenic mobilization illustrated by this set of controlled laboratory experiments using representative aquifer material shed new light on mobility of As, should shallow groundwater elevated in As penetrate Pleistocene aquifers in Bangladesh. Considering first purely abiotic processes, As from shallow groundwater is likely to adsorb significantly to Pleistocene aquifer material because the adsorptive capacity of the orange Pleistocene aquifers sands had been determined in a column experiment to be 15-20 mg of As per g of Fe(III) surfaces (Stollenwerk et al., 2003). The potential conversion of (orange) Fe(III) oxyhydroxides to more reduced (grey) Fe phases because shallow groundwater containing somewhat labile organic matter stimulates the activity of Fe-reducing bacteria is not likely to result in a significant reduction of adsorption sites for As. This is because sorption capacity of Fe(III) and mixed Fe(II)-Fe(III) oxyhydroxide were similar for As(V) and As(III) (Dixit and Hering, 2003). Our experiments indicate that the real concern may be the conversion of the abundant quantities of As that are presently tightly bound to Pleistocene sediment to a reduced and more mobilizable form. Very few studies of the microbial population of Bengal delta, or similarly affected aquifers, have been hitherto conducted (Oremland et al., 2005). It is therefore not known if the bacterial population of shallow aquifers is fundamentally different from that of deeper Pleistocene aquifers. The question raised by our demonstration using the model organism *Shewanella* sp. strain ANA-3, which may or may not be present in Pleistocene aquifers, is whether the entrainment of certain micro-organisms capable of converting As from a tightly bound form to a loosely bound form.

## *4.6. Conclusions*

Microcosm experiments of a natural sediment sample using an As reduction deficient mutant bacterium *Shewanella* sp. strain ANA-3 (AMR1) capable of reducing Fe(III) show convincingly that mobilization of As does not require reduction. The *Shewanella* sp. strain ANA-3, as well as its double knock-out mutant AMR1 promote reduction of As in sediment whereas the indigenous microbes do not under our experimental conditions. Reduction does not appear to enhance As release. The mobilization and reduction of Fe and Mn are predominantly limited by availability of electron donors such as lactate. However, the mobilization and reduction of As appears to have more limiting factors such as the type of microbes present in the system. This difference in response to electron donor availability with or without metal reducing bacteria helps to understand why groundwater aquifer has a wide range of As/Fe and As/Mn ratios. The important role of microbes in converting arsenic to a more mobilizable form in the Pleistocene sediment calls for careful investigation of microbial community in this aquifer and upon anthropogenic perturbation.

## *4.7. Acknowledgements*

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## *4.8. References*

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# Chapter 5. Hydrochemistry of Shallow and Deep Aquifers in Araihazar, Bangladesh

## *5.1. Abstract*

A hydrogeochemical study was conducted in Araihazar, Bangladesh to compare and contrast groundwater compositions in the shallow, As containing Holocene aquifer (5-30 m) and deep, low-As aquifers (30 – 91 m) that are of Holocene and Pleistocene strata. Groundwaters from 37 monitoring wells from 6 nests, as well as 21 existing private wells were sampled in January, 2003 and January 2001 respectively. In addition to parameters measured in the field such as ORP, pH, alkalinity, dissolved oxygen, ammonia, As(III) was separated from total As by anion exchange resin on site. Other parameters quantified are major cations, anions, trace elements, and nutrients (P, total organic carbon and total nitrogen).

Groundwater is $HCO_3$ type, although the shallow aquifer water is Ca-Mg rich while the deep Pleistocene water is Na rich. Shallow wells with elevated As concentrations (> 50 μg/L) are all reducing with negative ORP values between -50 mV and -200 mV, with predominantly As(III). PHREEQC calculations show that Fe and P are super-saturated with respect to siderite, vivianite and hydroxyapatite in shallow groundwaters from 5 sites except one that is influenced by irrigation pumping (Site F). In general, shallow aquifer waters contain much higher nutrients (TOC, TN, $NH_4$ and P) than the deep aquifer waters. This suggests that the role of nutrients on

the microbial activity and the mobility of As in both aquifers warrant further investigation.

## *5.2. Introduction*

The occurrence of elevated As concentrations in groundwater has been linked to reducing groundwaters (BGS & DPHE, 2001; Harvey et al., 2002; McArthur et al., 2001; Nickson et al., 1998; Nickson et al., 2000; Swartz et al., 2004; Zheng et al., 2004). However, detailed hydrogeochemical processes that contribute to mobilization of As (and Fe) remain elusive. Mobilization of As caused by the reduction of As-bearing Fe-oxyhydroxdes is a widely accepted explanation for enrichment of As in groundwater of Bangladesh. Yet, what processes lead to the reducing conditions in Bangladesh aquifers remain unclear. Organic matter that derived either from decomposition of peat layers (McArthur et al., 2004) or from inflow of surfacial organic carbon resulted from hydrologic drawdown caused by irrigation (Harvey et al., 2002) have both been proposed to explain the reducing conditions encountered in the aquifers there.

A detailed hydrogeochemical study was conducted on groundwaters from six nests of monitoring wells installed in Araihazar, Bangladesh that capture nearly the entire dynamic range of groundwater As concentrations encountered in Bangladesh. Wells are installed to Holocene shallow aquifer (5-30 m), Holocene deep aquifer (> 30 m) and Pleistocene deep aquifer (> 30 m) that are typical of high yielding aquifers used throughout Bangladesh. A wide range of hydrochemical parameters were measured in these representative samples to examine the systematics of As mobilization with major components of the groundwater, as well as redox conditions and nutrient characteristics in the shallow aquifer and deep aquifers, respectively.

## 5.3. Study area

The study area, approximately 25 km$^2$, is located in Araihazar thana in the central part of Bangladesh (Fig. 5.1), where the Columbia University Superfund Basic Research Program has conducted research in health and earth sciences (van Geen et al., 2002; van Geen et al., 2003; Zheng et al., 2005). Araihazar straddles the Holocene Meghna fluvial floodplain to the east and a much older Pleistocene deposit, known as Madhupur tract, to the west (Goodbred Jr. et al., 2003). This transition results in thickening of the sequence of Holocene deposits from western part to the eastern part of the study area. Therefore, existing wells are installed to the Holocene alluvial deposits at shallow depth (6m -30 m) and to the Pleistocene aquifer at deeper depth, usually below 30 m in the western part of the study area. However, existing wells do not reach the Pleistocene aquifer at 90 m and tap the shallow (5 m – 30 m) and deep Holocene aquifer (30 m – 91 m) in the eastern part of the study area (Zheng et al., 2005). The surficial sediment in the study area is mostly composed of silty-clay, with limited exposure of sand at surface (Weinman et al., in review). Both shallow and deep Holocene aquifers are mostly composed of gray sand. Usually below formations of finer grain size of variable thickness, the Pleistocene aquifer is observed and is composed of orange/light brown sands, as in other parts of Bangladesh (Harvey et al., 2002).

The three aquifers, shallow Holocene, deep Holocene, deep Pleistocene, are very distinct in terms of dissolved and solid phase As distribution. Groundwater As concentrations in the shallow Holocene aquifer contain elevated As, with 75% of private wells at >50 µg/L (van Geen et al., 2003). Groundwater in the deep Holocene aquifer are significantly lower, but still display As concentrations between 11 µg/L to 22 µg/L (Zheng et al., 2005). The deep Pleistocene aquifers consistently show low As (<10 µg/L) (Horneman et al., 2004; Stute et al., in review; van Geen et al., 2003; Zheng et al., 2005). An order of magnitude higher P-extractable As (up to 6 mg/kg) was found in shallow Holocene aquifer sands than in the deep Holocene and Pleistocene aquifer sands (Zheng et al., 2005).

## *5.4. Methods*

### 5.4.1. Locations of the nests of monitoring wells

A total of 6 nests of 37 monitoring wells (5-91 m) (Table 5.1) were installed in the study area to capture the spectrum of both spatial and vertical variation in groundwater As from <1 to 600 µg/L (Dhar et al., Submitted). The spatial and depth distribution of groundwater was established based on testing of 6000 existing private wells (van Geen et al., 2003) (Fig. 5.1). Two nests of monitoring wells were installed in January 2001 in two villages where the existing wells displayed high average As concentrations. However Site A (Dari Satyabandi, 23.785°N, 90.603°E) displayed a range of As from low (<0.1 µg/L) to high (582 µg/L) but Site B (Bailarkandi, 23.780°N, 90.639°E) displayed a narrower range from from low (11 µg/L) to high (555 µg/L) (Zheng el, al., 2005).

**Table-5.1. Monitoring wells depth and dates of installation**

| Site name | Village name | Latitude (°N) | Longitude (°E) | Depth Range (m) | Installation Date | Sampling Date |
|---|---|---|---|---|---|---|
| **A** | Dari Satyabandi | 23.78534 | 90.6032 | 7 - 91 | Jan-01 | 01/14/03 |
| **B** | Baylakandi | 23.78036 | 90.6386 | 7 - 91 | Jan-01 | 01/17/03 |
| **C** | Bhuyan Para (Satyabandi) | 23.78955 | 90.6111 | 5 - 53 | Mar-02 | 01/13/03 |
| **E** | Hatkhola Para | 23.78999 | 90.6159 | 5 - 38 | Mar-02 | 01/12/03 |
| **F** | Lashkardi (Mosque) | 23.77364 | 90.6045 | 6 - 58 | Mar-02 | 01/06/03 |
| **G** | Lashkardi (Bilbari) | 23.77376 | 90.6007 | 6 - 52 | Mar-02 | 01/08/03 |

Four additional nests of monitoring wells were installed in March 2002 (Dhar et al., Submitted). Site C (Bhuyan para-Satyabandi, 23.790°N, 90.611°E) is located in a sandy area with a low As containing upper aquifer. Site E (Hatkhola para, 23.790°N, 90.616°E) represents a mixed As environment surrounded by both low and high As containing shallow aquifers. Both sites F (Lashkardi Mosque, 23.774°N, 90.605°E) and G (Bilbari-Lashkardi, 23.774°N, 90.601°E) are located where the lands are intensively cultivated. Techniques used to install all wells were previously described but for most wells involved manual drilling (van Geen et al., 2003; Zheng et al., 2005).

At all sites but Site B, shallow Holocene aquifer composed mostly of grey sand is separated from the deep Pleistocene aquifer composed of orange/light brown sand aquifer by at least one fine sediment layer of clay or silty clay. The thickness of each section varies considerably from site to site (Dhar et al., Submitted).

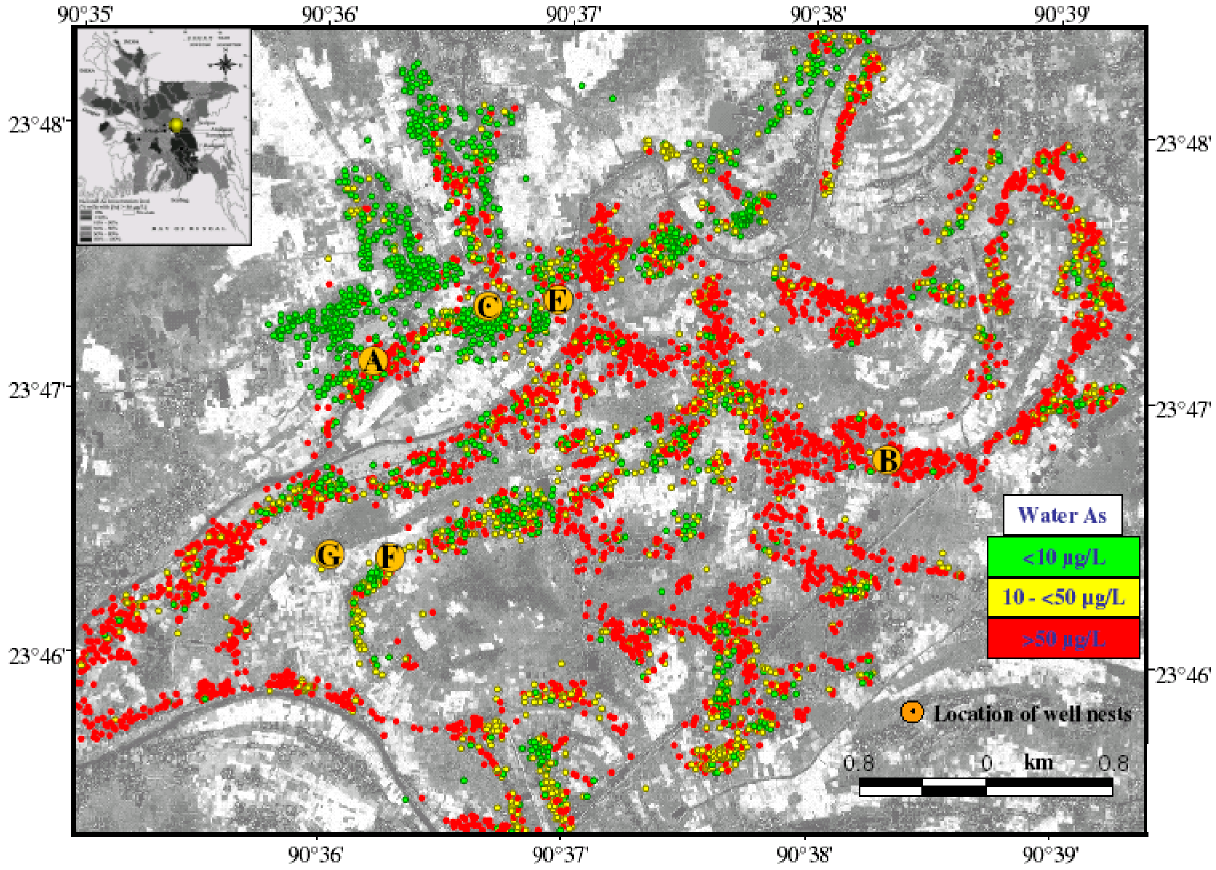

**Figure-5.1**. IKONOS image of study area in Araihazar, Bangladesh with a wide range of As distribution as indicated by respective colors;green: within WHO limit (10 µg/L), green and yellow within Bangladesh national standard(50 µg/L), red above Bangladesh limit (50 µg/L). The location of the well nests were marked with respective letters for site A, B, C, E, F and G.

### 5.4.2. Sampling protocols and on-site measurements

Groundwaters were sampled from monitoring wells at Sites A and B (Zheng et al., 2005) in January 2001 and from all six sites for detailed hydrochemical analyses in January 2003. Each well was pumped by a battery-driven submersible pump (Whale SuperPurger) at a rate of ~ 2 L/min to remove all standing water from the well before sampling. Usually, 15-30 minutes of pumping allowed conductivity, temperature, pH and ORP readings to stabilize in a flow cell equipped with waterproof probes of a conductivity-temperature meter (Orion 105A+) and a pH - Eh meter (Orion 210A). Selected existing private wells at Site A spanning a range of As concentrations from <5 μg/L to 860 μg/L (van Geen et al., 2003), were also sampled similarly by removing the heads of the wells in January, 2001.

A set of 4 samples, not filtered-acidified, filtered-acidified, filtered-not acidified, not filtered-not acidified, were collected in 60-ml or 30-ml acid-cleaned (for acidified sample) and nanopure-washed (for not acidified sample) HPDE bottles. Samples were filtered using a vacuum filter unit (Nalgene) connected to a hand-vacuum pump (Nalgene) to avoid the iron precipitation (Zheng et al., 2004; Zheng et al., 2005). Trace metals and major ions were measured in filtered-acidified samples and dissolved anions were measured on filtered-not acidified samples. For acidification, concentrated HCl (Fisher Optima) was used to acidify samples to 1% HCl. Samples for analyses of $^{13}C/^{12}C$ and $^{14}C/^{12}C$ in dissolved inorganic carbon were collected in 250-mL glass bottles with Polyseal caps and were poisoned with 0.2 mL of saturated $HgCl_2$ (Fisher Scientific) solution (Zheng et al., 2005).

Samples for TOC (dissolved organic carbon) analyses were collected in 20-ml glass bottles (height: 8.8 cm, dia.: 2.3 cm) (Wheaton, cat. 2247228) with blue polyseal caps. For each well, two replicates of water samples were collected and acidified to 1% HCl (Fisher, optima grade).

Dissolved $O_2$, alkalinity, dissolved Fe(II) and dissolved $NH_4^+$ were measured on site by CHEMet kit for 0-100 ppb oxygen detection (Cole-Parmer), Gran titration (Gran, 1952), Ferrozine colorimetry (stookey, 1970) and methylene blue colorimetry (Sorzano, 1969) respectively. Inorganic As species separation was conducted on site by a modified anion exchange columns (Ficklin, 1983) (Zheng et al., 2004). Inorganic arsenic speciation were also conducted on site using voltammetry (He et al., 2004) and molybdenum blue colorimetry (Dhar et al., 2004)

## 5.4.3. Laboratory analyses

Concentrations of 33 dissolved trace metals and major ions including As, P, Fe, Mn, S, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $SiO_2$ were measured in filtered-acidified groundwater by high-resolution inductively-coupled plasma mass spectrometry (HR ICP-MS) at Lamont-Doherty Earth Observatory with a reproducibility typically <5% (Cheng et al., 2004). For accuracy and precision, two NIST standard reference materials (1640 & 1643E, Trace elements in natural water), and an internal laboratory consistency standard (LDEO tap water spiked with analyte elements) were included in each run. Laboratory results were within 5% of certified values after calibrating instrument with separate standard series at the beginning and end of each run (Cheng et al., 2004). Separated As(III) in acidified eluted samples from the field were also measured by HR ICP-MS.

Dissolved $F^-$, $Cl^-$, $Br^-$, $NO_2^-$, $NO_3^-$, $SO_4^{2-}$ concentrations in filtered-not acidified groundwater samples were measured at Queens College by ion chromatography (IC) using a DIONEX-500 IC system, following the standard protocol of EPA method 300.

Dissolved reactive phosphate (DRP) was determined using the classic molybdate-blue colorimetric method, modified also to determine As (Dhar et al., 2004). A comparison of dissolved reactive phosphate with total P concentrations obtained by HR ICP-MS indicates the not all total P are $PO_4$ (Dhar et al., Submitted).

The TOC- $V_{CPH}$/TOC-$V_{CPN}$ (TOC-V) instrument (Shimadzu) was used to measure total organic carbon (TOC) and total water-borne nitrogen (TN). TN is measured with an optional TN unit installed with TOC-V using the principles of "oxidative combustion-chemiluminescence". Not-filtered and acidified Bangladesh groundwater water samples were collected as sample volume size in 24 ml vials (Wheaton) were directly placed in the auto-sampler unit (ASI-V) for measurements after acidification and purging to remove dissolved inorganic carbon. A standard series of mixed TOC and TN solution were prepared from stock solutions of TOC and TN standard. The stock solution,1000 mgC/L of TOC was prepared by adding 2.125g of reagent grade potassium hydrogen phthalate (($HOCOC_6H_4COOK$) that was previously dried at 105-120°C for about 1 hour into 1 L nanopure water (Shimadzu, 2001). The stock solution,1000 mg/L of TN was prepared by adding 7.129g of special reagent grade potassium nitrate ($KNO_3$) that was previously dried at 105-110oC for about 3 hour into 1 L nanopure water (Shimadzu, 2001).

### 5.4.4. Geochemical Calculation

PHREEQC (version 2.32) was used to investigate precipitation reactions based on groundwater chemical composition data of all monitoring wells. For comparison and validation, MINTEQA (version 2.0), another geochemical modeling tool, was also used to calculate saturation indices for 11 common minerals including siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), vivianite ($Fe_3(PO_4)_2$, $8H_2O$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Saturation index SI is defined as:

$$SI = \text{Log}\ (IAP/K_{sp}) \qquad (1)$$

where IAP is the ion activity product and $K_{sp}$ is the solubility product for a given temperature. When SI is zero, or $IAP=K_{sp}$, the water is at equilibrium with respect to a mineral. The positive values of SI indicate supersaturation whereas the negative values of SI suggest undersaturation.

The PHREEQC code also calculates the anion/cation balance for each water composition. The anion/cation balance is calculated using the equation

$$\text{Anion/Cation Balance (\%)} = \frac{[\text{Cations(eq/L)}-\text{Anions (eq/L)}]}{[\text{Cations(eq/L)}+\text{Anions (eq/L)}]} \times 100 \qquad (2)$$

For simple groundwater compositions the anion/cation balance should not exceed a few percent .

For the purpose of water classification, a Piper diagram was constructed as the graphical representation of water chemistry. The normalized cation and anion concentrations are plotted in their appropriate triangle (Fig. 5.2). The data plotted on each triangle are then projected into the quadrilateral by drawing a line from the point on the cation triangle parallel to Mg axis into the quadrilateral and by drawing a line from the point in the anion triangle parallel to the $SO_4$ axis into the quadrilateral. The intersection of these two lines marks the location of the point to be plotted on the quadrilateral (Fig. 5.2).

## *5.5. Results*

### 5.5.1. Radiocarbon Age of Dissolved Inorganic Carbon

The deep Pleistocene aquifer (depth > 30 m) at Site A displayed much older than $^{14}$C-DIC age of the deep Holocene aquifers (depth> 30 m) at Site B (Table 5.2). The $^{14}$C-DIC ages of deep groundwaters from the Pleistocene aquifers at Sites C, F, G were 10700, 6240, and 3620 years, respectively. The result from Site C compares well with the ages of deep waters at Site A (Table 5.2), and these two sites also display similar hydrographs (Chapter 3). Radiocarbon ages of 450 and 390 years were measured for F-26 m and G-21 m (Table 5.2). These two wells were separated from the shallower wells at each site by a thin silty formation (Chapter 3). This separation was observed at Site B, where B-41 m also yielded $^{14}$C-DIC age of 540 years (Table 5.2).

Shallow waters from Sites A and B contained bomb radio carbon (Table 5.2). However, shallow waters at site F displayed a $^{14}$C-DIC age of 45 years. This may be a result of extensive irrigation at Site F.

**Table-5.2. Dissolved inorganic carbon $^{14}$C ages**

| MW* ID | Depth (m) | NOSAMS Accession # | δ13C-DIC (%PDB) | $^{14}$C-DIC (FM) | Fm Error | $^{14}$C Age (year) | Age Error (year) | $\delta^{14}$C | Data source |
|---|---|---|---|---|---|---|---|---|---|
| **A-1** | 7 | | -13.9 | 1.136 | | >Mod. | | | Zheng et al., 2005 |
| **A-2** | 10 | | - | - | | - | | | |
| **A-3** | 13 | | -16.2 | 1.054 | | >Mod. | | | Zheng et al., 2005 |
| **A-4** | 15 | | - | - | | - | | | |
| **A-5** | 30 | | -19.2 | 0.301 | | 9660 | | | Zheng et al., 2005 |
| **A-6** | 37 | | - | - | | - | | | |
| **A-7** | 43 | | -19.0 | 0.284 | | 10100 | | | Zheng et al., 2005 |
| **A-8** | 91 | | -19.1 | 0.284 | | 10100 | | | Zheng et al., 2005 |
| **B-7** | 7 | | - | - | | - | | | |
| **B-8** | 11 | | - | 1.090 | | >Mod. | | | Zheng et al., 2005 |
| **B-3** | 14 | | - | - | | - | | | |
| **B-9** | 19 | | - | - | | - | | | |
| **B-4** | 29 | | - | - | | - | | | |
| **B-5** | 41 | | - | 0.890 | | 540 | | | Zheng et al., 2005 |
| **B-6** | 53 | | - | 0.840 | | 1018 | | | Zheng et al., 2005 |
| **BCW** | 91 | | - | 0.930 | | 176 | | | Zheng et al., 2005 |
| **C-1** | 5 | | - | - | | - | | | |
| **C-2** | 8 | | - | - | | - | | | |
| **C-3** | 11 | | - | - | | - | | | |
| **C-4** | 14 | | - | - | | - | | | |
| **C-5** | 53 | OS- 41278 | -17.6 | 0.2631 | 0.0018 | 10700 | 55 | -738.5 | this study |
| **E-1** | 5 | | - | - | | - | | | |
| **E-2** | 8 | | - | - | | - | | | |
| **E-3** | 11 | | - | - | | - | | | |
| **E-4** | 14 | | - | - | | - | | | |
| **E-5** | 38 | | - | - | | - | | | |
| **F-1** | 6 | OS- 41274 | -18.7 | 0.9941 | 0.0036 | 45 | 30 | -12.3 | this study |
| **F-2** | 11 | | - | - | | - | | | |
| **F-3** | 15 | | - | - | | - | | | |
| **F-4** | 19 | | - | - | | - | | | |
| **F-6** | 26 | OS- 41279 | -15.8 | 0.9454 | 0.0030 | 450 | 25 | -60.7 | this study |
| **F-5** | 58 | OS- 41275 | -25.9 | 0.4596 | 0.0019 | 6240 | 30 | -593.4 | this study |
| **G-1** | 6 | | - | - | | - | | | |
| **G-2** | 9 | | - | - | | - | | | |
| **G-3** | 14 | | - | - | | - | | | |
| **G-4** | 21 | OS- 41277 | -14.7 | 0.9523 | 0.0035 | 390 | 30 | -53.8 | this study |
| **G-5** | 52 | OS- 41276 | -21.6 | 0.6373 | 0.0026 | 3620 | 35 | -366.8 | this study |

## 5.5.2. Chemistry of Shallow Aquifer Water

### 5.5.2.1. Conductivity

Conductivities of shallow aquifer groundwaters did not show obvious depth trends at most sites. Average conductivity of the groundwater increased in the sequence of C, F, E, G, A to B by a factor of ~ 4, with values of 27±5 mS/m, 38±17 mS/m, 51±11 mS/m, 55±7 mS/m, 68±18 mS/m, and 112±24 mS/m (Table 5.3).

## Table-5.3. Chemistry data of monitoring wells

| MW* | Depth | Temp. | cond. | Eh | pH | Alkalinity | DO | NH$_4$ | As$_{tot}$ | As(III) | F | Cl | NO$_2$ | Br | NO$_3$ | SO$_4$ | Na | Mg | K | Ca | Si | P | Fe$_{tot}$ | Mn | Zn | Se | Sr | Mo | Sb | Ba | Pb | U | TOC | TN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ID | (m) | ($^{o}$C) | (mS/m) | (mV) | | (meq/L) | (µg/L) | (mg/L) | (µg/L) | (µg/L) | (mg/L) | (meq/L) | (mg/L) | (mg/L) | (mg/L) | (µmole/L) | (meq/L) | (meq/L) | (meq/L) | (meq/L) | (meq/L) | (µmole/L) | (µmole/L) | (µmole/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (mg/L) | (mg/L) |
| | | Orion meter and probe | | | | Gran. Titration | CHEMet | Colorimetry | HR ICP-MS | | Ion Chromatography | | | | | | HR ICP-MS | | | | | | | | | | | | | | | | | |
| **A-1** | 7 | 26.1 | 86 | -88 | 6.17 | 6.64 ± 0.09 | <10 | 18.9 | 81 | 73 | <0.1 | 0.8 | <0.1 | <0.1 | 21.6 | 281 | 1.2 | 0.46 | 1.46 | 1.0 | 4 | 18 | 381 | 38 | 372 | 2.2 | 22 | 2.1 | <0.1 | 27 | <0.1 | <0.1 | 15.2 | - |
| **A-2** | 10 | 26 | 46 | -86 | 6.38 | 3.33 ± 0.05 | <10 | 0.7 | 103 | 94 | <0.1 | 0.6 | <0.1 | <0.1 | 1.2 | 209 | 0.8 | 0.54 | 0.13 | 1.1 | 4 | 12 | 118 | 41 | 70 | 1.8 | 6 | 1.1 | <0.1 | 2 | <0.1 | <0.1 | 13.0 | - |
| **A-3** | 13 | 26.1 | 61 | -159 | 6.56 | 5.41 ± 0.06 | <10 | 7.3 | 517 | 520 | <0.1 | 0.6 | <0.1 | <0.1 | 8.5 | 4 | 1.2 | 0.76 | 0.15 | 1.4 | 5 | 26 | 310 | 64 | 108 | 1.1 | 187 | 3.7 | <0.1 | 57 | <0.1 | <0.1 | 9.8 | - |
| **A-4** | 15 | 26.3 | 78 | -182 | 6.79 | 7.29 ± 0.07 | <10 | 4.8 | 286 | 289 | <0.1 | 0.9 | <0.1 | <0.1 | 4.2 | 5 | 2.9 | 0.95 | 0.14 | 1.2 | 5 | 20 | 310 | 11 | 93 | 1.6 | 33 | 3.9 | <0.1 | 14 | <0.1 | <0.1 | 10.6 | - |
| **A-5** | 30 | 26.1 | 42 | -100 | 6.31 | 2.98 ± 0.07 | <10 | <0.1 | 1.8 | <0.1 | <0.1 | 0.8 | <0.1 | <0.1 | <0.1 | 13 | 3.5 | 0.30 | 0.05 | 0.2 | 5 | 6 | 55 | 4 | 48 | 1.7 | 13 | 16.7 | <0.1 | 2 | 1.9 | <0.1 | - | - |
| **A-6** | 37 | 26.1 | 36 | -45 | 6.19 | 2.98 ± 0.09 | <10 | <0.1 | 1.9 | <0.1 | <0.1 | 0.5 | <0.1 | <0.1 | <0.1 | 5 | 2.6 | 0.22 | 0.05 | 0.4 | 6 | 5 | 52 | 2 | 127 | 2.3 | 44 | 0.3 | <0.1 | 4 | 1.0 | <0.1 | - | - |
| **A-7** | 43 | 26.1 | 35 | -19 | 6.23 | 2.55 ± 0.10 | <10 | <0.1 | 1.8 | <0.1 | <0.1 | 0.5 | <0.1 | <0.1 | <0.1 | 13 | 2.4 | 0.19 | 0.05 | 0.4 | 6 | 7 | 40 | 5 | 69 | 2.5 | 65 | 0.4 | <0.1 | 9 | <0.1 | <0.1 | - | - |
| **A-8** | 91 | 26.2 | 41 | 26 | 6.17 | 2.40 ± 0.06 | - | <0.1 | 0.9 | <0.1 | <0.1 | 0.9 | <0.1 | <0.1 | <0.1 | 24 | 2.4 | 0.18 | 0.05 | 0.6 | 6 | 6 | 2 | 2 | 46 | 1.6 | 69 | 0.5 | <0.1 | 8 | <0.1 | <0.1 | - | - |
| **B-7** | 7 | 25.8 | 149 | -144 | 6.66 | 9.77 ± 0.02 | <10 | 0.3 | 25 | 24 | <0.1 | 2.9 | <0.1 | <0.1 | <0.1 | 643 | 3.4 | 1.57 | 0.19 | 0.7 | 5 | 42 | 268 | 13 | 71 | 1.1 | 69 | 2.2 | <0.1 | 47 | <0.1 | 0.11 | 13.3 | - |
| **B-8** | 11 | 25.7 | 116 | -148 | 6.7 | 7.57 ± 0.00 | <10 | 1.6 | 293 | 301 | <0.1 | 2.4 | <0.1 | <0.1 | <0.1 | 136 | 2.6 | 0.84 | 0.16 | 0.6 | 6 | 44 | 289 | 32 | 48 | 1.9 | 98 | 4.3 | <0.1 | 34 | <0.1 | <0.1 | 11.9 | - |
| **B-3** | 14 | 25.8 | 113 | -171 | 6.86 | 8.44 ± 0.02 | <10 | 1.4 | 458 | 460 | <0.1 | 2.5 | <0.1 | <0.1 | <0.1 | 110 | 2.8 | 0.98 | 0.16 | 1.7 | 5 | 71 | 347 | 17 | 14 | 2.1 | 271 | 1.8 | <0.1 | 101 | <0.1 | <0.1 | 17.5 | - |
| **B-9** | 19 | 25.8 | 92 | -171 | 6.87 | 8.99 ± 0.05 | <10 | 2.0 | 383 | 385 | <0.1 | 1.0 | <0.1 | <0.1 | 2.6 | 5 | 1.5 | 0.56 | 0.13 | 0.2 | 6 | 47 | 396 | 21 | 97 | 1.9 | 24 | 1.6 | <0.1 | 11 | <0.1 | <0.1 | 14.9 | - |
| **B-4** | 29 | 25.8 | 90 | -178 | 6.94 | - | - | 12.6 | 197 | <0.1 | - | - | - | - | - | - | 1.8 | 1.00 | 0.16 | 1.9 | 6 | 43 | 320 | 5 | 139 | 1.6 | 302 | 2.2 | <0.1 | 133 | <0.1 | <0.1 | - | - |
| **B-5** | 41 | 26 | 70 | -157 | 6.94 | 6.68 ± 0.00 | <10 | 9.2 | 21 | 21 | <0.1 | 0.3 | <0.1 | <0.1 | 12.7 | 3 | 1.0 | 1.10 | 0.15 | 0.1 | 6 | 40 | 162 | 1.0 | 140 | 1.7 | 18 | 1.1 | <0.1 | 2 | 20.7 | <0.1 | - | - |
| **B-6** | 53 | 25.9 | 52 | -155 | 7.15 | 5.12 ± 0.04 | <10 | 0.4 | 15 | 16 | <0.1 | 0.2 | <0.1 | <0.1 | 0.9 | 3 | 2.6 | 0.42 | 0.08 | 0.0 | 6 | 14 | 88 | 3.2 | 242 | 2.3 | 13 | 2.3 | <0.1 | 2 | 6.4 | <0.1 | - | - |
| **BCW** | 91 | 26.2 | 38 | -134 | 6.94 | 4.07 ± 0.04 | - | <0.1 | 0.8 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 | <0.1 | 3 | 2.4 | 0.30 | 0.06 | 0.0 | 6 | 3 | 16 | 1.6 | 27 | 1.3 | 32 | 0.6 | <0.1 | 3 | 4.0 | <0.1 | - | - |
| **C-1** | 5 | 26.4 | 25 | -113 | 6.37 | 2.15 ± 0.03 | <10 | 0.3 | 13 | 10 | <0.1 | 0.3 | <0.1 | <0.1 | <0.1 | 22 | 0.4 | 0.24 | 0.09 | 0.3 | 3 | 23 | 670 | 23 | 83 | 3.0 | 48 | 0.3 | <0.1 | 89 | <0.1 | <0.1 | 0.8 | 0.2 |
| **C-2** | 8 | 26.2 | 26 | -144 | 6.54 | 2.31 ± 0.03 | <10 | 0.8 | 34 | 31 | <0.1 | 0.2 | <0.1 | <0.1 | <0.1 | 16 | 0.5 | 0.15 | 0.15 | 0.2 | 1 | 20 | 994 | 34 | 22 | 2.6 | 42 | 0.7 | <0.1 | 109 | <0.1 | <0.1 | 1.7 | 0.7 |
| **C-3** | 11 | 25.8 | 23 | -155 | 6.62 | 2.06 ± 0.01 | <10 | 0.9 | 36 | 27 | <0.1 | 0.2 | <0.1 | <0.1 | <0.1 | <1 | 0.4 | 0.15 | 0.15 | 0.2 | 1 | 21 | 706 | 19 | 27 | 3.7 | 34 | 0.7 | <0.1 | 122 | <0.1 | <0.1 | 2.4 | 0.9 |
| **C-4** | 14 | 25.7 | 34 | -156 | 6.75 | 3.01 ± 0.02 | <10 | 1.0 | 73 | 51 | <0.1 | 0.3 | <0.1 | <0.1 | <0.1 | <1 | 0.4 | 0.42 | 0.13 | 0.6 | 1 | 26 | 480 | 26 | 252 | 2.9 | 96 | 0.6 | <0.1 | 83 | <0.1 | <0.1 | 2.8 | 1.0 |
| **C-5** | 53 | 26.2 | 34 | -3 | 6.37 | 1.14 ± 0.00 | <10 | 0.1 | 1.9 | <0.1 | <0.1 | 0.52 | <0.1 | <0.1 | <0.1 | 15 | 1.4 | 0.39 | 0.06 | 0.4 | 1 | 3.4 | 173 | 14 | 790 | 3.3 | 130 | 0.6 | <0.1 | 33 | <0.1 | 0.23 | 0.7 | 0.2 |
| **E-1** | 5 | 26.5 | 51 | -78 | 6.67 | 4.53 ± 0.02 | <10 | 0.1 | 57 | 37 | <0.1 | 0.12 | <0.1 | <0.1 | <0.1 | 190 | 0.6 | 1.07 | 0.09 | 1.2 | 1 | 8 | 64 | 21 | 133 | 3.0 | 126 | 1.2 | <0.1 | 88 | <0.1 | 0.66 | 0.4 | 0.2 |
| **E-2** | 8 | 26.5 | 39 | -160 | 6.78 | 3.93 ± 0.02 | <10 | 0.5 | 91 | 72 | <0.1 | 0.11 | <0.1 | <0.1 | <0.1 | 19 | 0.5 | 0.69 | 0.09 | 0.8 | 0.5 | 25 | 347 | 27 | 32 | 1.8 | 93 | 1.5 | <0.1 | 78 | <0.1 | <0.1 | 1.1 | 0.6 |
| **E-3** | 11 | 26.5 | 50 | -187 | 6.97 | 5.06 ± 0.03 | <10 | 1.5 | 160 | 127 | <0.1 | 0.08 | <0.1 | <0.1 | 1.6 | <1 | 0.6 | 0.77 | 0.12 | 1.2 | 0.4 | 23 | 414 | 31 | 85 | 2.3 | 158 | 2.8 | <0.1 | 128 | 33.4 | <0.1 | 1.3 | 1.6 |
| **E-4** | 14 | 26.4 | 65 | -180 | 6.84 | 5.89 ± 0.02 | <10 | 3.6 | 161 | 146 | <0.1 | 0.68 | <0.1 | <0.1 | 2.8 | <1 | 1.4 | 0.81 | 0.12 | 1.2 | 0.9 | 31 | 748 | 16 | 83 | 1.2 | 276 | 2.2 | <0.1 | 158 | <0.1 | 0.39 | 2.5 | 3.0 |
| **E-5** | 38 | 26.1 | 79 | -94 | 6.61 | 6.55 ± 0.04 | <10 | 2.8 | 1.9 | 3 | <0.1 | 1.17 | <0.1 | <0.1 | 0.10 | <1 | 3.4 | 0.73 | 0.07 | 1.1 | 0.7 | 5.3 | 62 | 5.2 | 36 | 1.0 | 309 | 0.4 | <0.1 | 75 | <0.1 | 0.71 | 1.8 | 3.4 |
| **F-1** | 6 | 26.3 | 34 | 112 | 6.3 | 1.56 ± 0.04 | <10 | 0.1 | 0.5 | <0.1 | <0.1 | 0.65 | <0.1 | <0.1 | <0.1 | 58 | 0.5 | 0.52 | 0.07 | 0.5 | 0.5 | 0.2 | 0.1 | 0.1 | 11 | 3.1 | 55 | 0.1 | <0.1 | 38 | <0.1 | 0.16 | 0.5 | 0.4 |
| **F-2** | 11 | 26 | 18 | -20 | 6.34 | 0.72 ± 0.07 | <10 | 0.1 | 22 | 21 | <0.1 | 0.14 | <0.1 | <0.1 | <0.1 | 35 | 0.2 | 0.36 | 0.07 | 0.3 | 0.5 | 0.2 | 0.3 | 21 | 6 | 3.4 | 42 | 0.2 | <0.1 | 22 | <0.1 | <0.1 | 0.7 | 0.1 |
| **F-3** | 15 | 26.1 | 27 | -71 | 6.83 | 2.51 ± 0.03 | <10 | 0.3 | 42 | 43 | <0.1 | 0.06 | <0.1 | <0.1 | <0.1 | 14 | 0.2 | 0.36 | 0.07 | 0.02 | 4 | 4 | 9 | 22 | 5 | 3.6 | 12 | 1.0 | <0.1 | 1 | <0.1 | 0.14 | 0.7 | 0.4 |
| **F-4** | 19 | 26.1 | 46 | -96 | 6.92 | 4.34 ± 0.05 | <10 | 0.7 | 183 | 188 | <0.1 | 0.09 | <0.1 | <0.1 | <0.1 | 31 | 0.4 | 0.42 | 0.09 | 0.03 | 6 | 14 | 15 | 42 | 9 | 4.1 | 5 | 1.6 | <0.1 | 1 | <0.1 | 1.02 | 0.9 | 0.7 |
| **F-6** | 26 | 26.2 | 63 | -200 | 7 | 5.83 ± 0.02 | <10 | 2.7 | 203 | 203 | <0.1 | 0.13 | <0.1 | <0.1 | <0.1 | <1 | 0.6 | 0.55 | 0.11 | 0.8 | 7 | 29 | 294 | 31 | 24 | 4.3 | 120 | 3.1 | <0.1 | 50 | <0.1 | <0.1 | 2.3 | 2.3 |
| **F-5** | 58 | 26.2 | 188 | -40 | 6.94 | 6.74 ± 0.03 | <10 | 0.6 | 1.0 | 0 | <0.1 | 8.90 | <0.1 | <0.1 | 0.5 | 10 | 13.9 | 0.28 | 0.05 | 0.0 | 7 | 4.2 | 28 | 9 | 33 | 4.5 | 33 | 1.3 | <0.1 | 1 | <0.1 | 1.52 | 1.1 | 0.6 |
| **G-1** | 6 | 25.9 | 58 | -171 | 6.77 | 6.64 ± 0.04 | <10 | 4.1 | 123 | 118 | <0.1 | 0.08 | <0.1 | <0.1 | <0.1 | 5 | 0.5 | 0.84 | 0.11 | 1.5 | 1 | 53 | 532 | 22 | 45 | 3.2 | 235 | 52.9 | <0.1 | 118 | <0.1 | <0.1 | 4.2 | 2.9 |
| **G-2** | 9 | 26 | 63 | -176 | 6.69 | 6.58 ± 0.04 | <10 | 7.0 | 151 | 135 | <0.1 | 0.06 | <0.1 | <0.1 | 6.9 | 6 | 0.5 | 0.78 | 0.12 | 1.8 | 1 | 90 | 425 | 7 | 1598 | 2.5 | 324 | 0.9 | <0.1 | 132 | <0.1 | 0.21 | 6.1 | 5.6 |
| **G-3** | 14 | 26 | 47 | -200 | 7.08 | 6.29 ± 0.04 | <10 | 1.2 | 98 | 78 | <0.1 | 0.28 | <0.1 | <0.1 | <0.1 | 4 | 0.4 | 0.56 | 0.09 | 1.3 | 1 | 29 | 259 | 29 | 12 | 2.5 | 167 | 2.4 | <0.1 | 106 | 6.7 | <0.1 | 1.7 | 1.0 |
| **G-4** | 21 | 26.1 | 53 | -209 | 7.21 | 5.95 ± 0.02 | <10 | 2.4 | 181 | 139 | <0.1 | 0.54 | <0.1 | <0.1 | 0.7 | <1 | 0.6 | 0.63 | 0.12 | 1.5 | 0.5 | 72 | 215 | 29 | 133 | 2.1 | 214 | 3.3 | <0.1 | 108 | <0.1 | <0.1 | 1.3 | 2.1 |
| **G-5** | 52 | 26.4 | 176 | -51 | 6.8 | 7.70 ± 0.04 | <10 | 0.6 | 7 | 7 | <0.1 | 8.39 | <0.1 | <0.1 | 0.5 | 34 | 13.9 | 0.25 | 0.06 | 0.3 | 1 | 8.0 | 11 | 11 | 26 | 1.8 | 88 | 1.2 | <0.1 | 72 | <0.1 | 0.28 | 0.6 | 0.6 |

***MW: multilevel wells in different sites A, B, C, E, F, G.**

The concentrations of As in the shallow monitoring wells increased by a factor of ~ 7 in the same order from Site C, F, E, G, A to B, averaging 40 ± 25 µg/L, 90 ± 95 µg/L, 117 ± 52 µg/L, 138 ± 36 µg/L, 247 ± 202 µg/L, and 271 ± 169 µg/L, respectively (Table 5.3). In the following, the average concentrations of the monitoring wells from each site are described in this order of increasing As concentration and conductivity.

#### 5.5.2.2. Major Ions

Approximately 25 to 50% of the major cations in most shallow groundwaters are Ca or Mg (Fig. 5.2a), although there are clearly exceptions such as two wells from Site F and three wells from Site B that contain < 20% of Ca. Concentrations of Ca were about 3 times lower at Sites C and F than the other sites, averaging 0.4 ± 0.2 meq/L and 0.3 ± 0.3 meq/L, respectively. Concentrations were higher for Sites E, G, A and B, averaging 1.1 ± 0.4 meq/L, 1.5 ± 0.2 meq/L, 1.2 ± 0.16 meq/L, 1.0 ± 0.85 meq/L, respectively (Table 5.3). The concentrations of Mg were lower also by as much as a factor of 4 at Site C (0.2 ± 0.1 meq/L) than that of Site B (1.0 ± 0.4 meq/L). Concentrations of Mg were higher for Sites F, E, G, and A, averaging 0.4 ± 0.1 meq/L, 0.8 ± 0.2 meq/L, 0.7 ± 0.1 meq/L, and 0.7 ± 0.2 meq/L, respectively (Table. 5.3). Concentrations of Na for Sites C, F, E, G, A and B were 0.4 ± 0.03 meq/L, 0.4 ± 0.2 meq/L, 0.8 ± 0.45 meq/L, 0.5 ± 0.08 meq/L, 1.5 ± 0.9 meq/L, 2.4 ± 0.8 meq/L, respectively (Table 5.3). Concentrations of K for Sites C, F, E, G, A and B showed the least difference among these sites, and were 0.1 ± 0.03 meq/L, 0.1 ± 0.02 meq/L, 0.1 ± 0.02 meq/L, 0.1 ± 0.02 meq/L, 0.5± 0.7 meq/L and 0.2 ± 0.02 meq/L, respectively (Table 5.3).

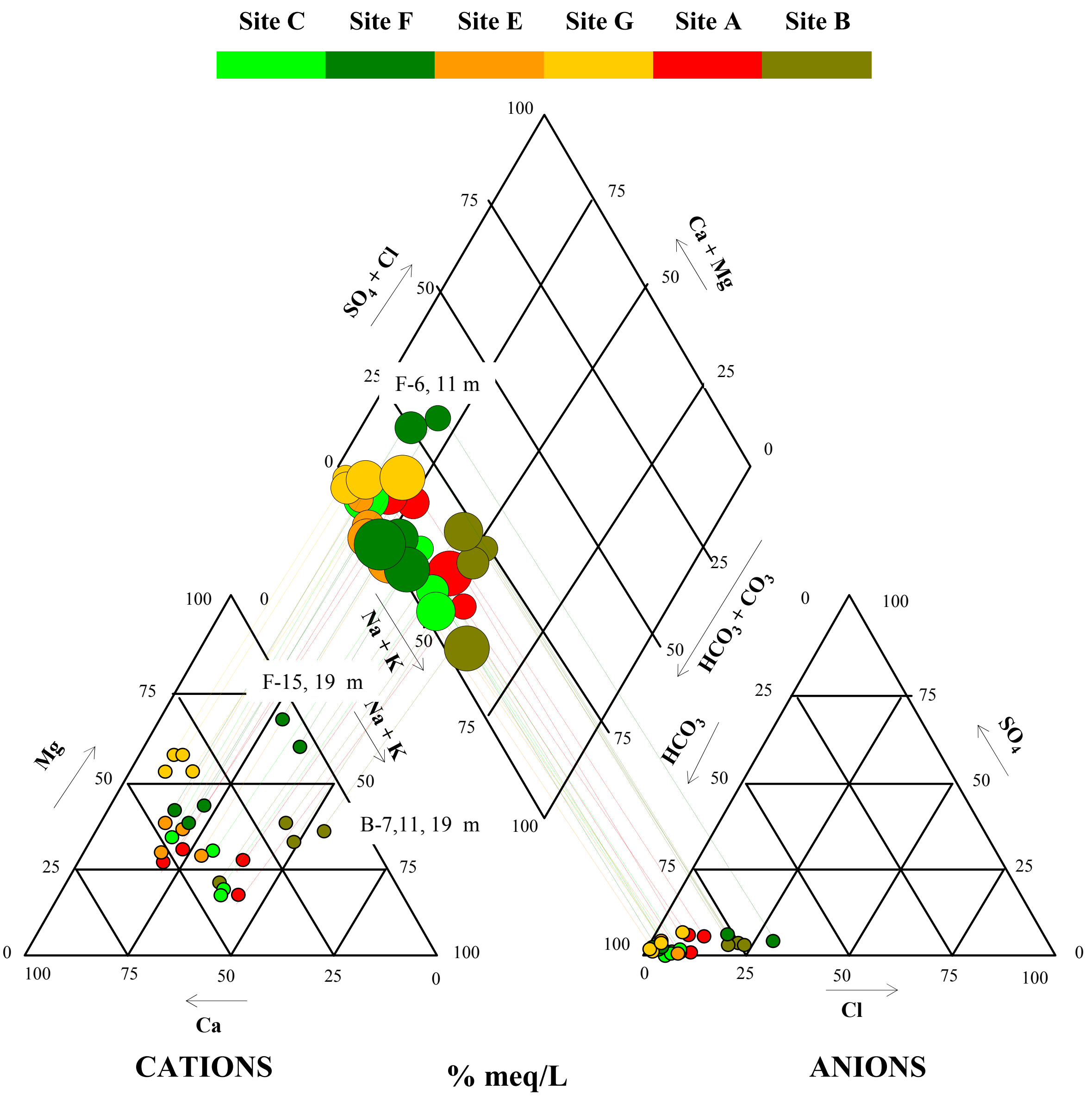

**Figure-5.2. (a)** Piper diagram illustrating the main hydrochemical features of the groundwaters of shallow Holocene aquifers at Sites A, B, C, E, F and G. The size of the symbols indicates the depth of wells and symbol size in the quadrilateral increases with increasing depth. Groundwaters at different sites represented by solid circles filled with different colors for different sites.

The most important anion in the shallow groundwater is $HCO_3^-$, accounting for 70% or more of the anions (Fig. 5.2a). Groundwater were nearly neutral, with average pH values of 6.56 ± 0.16, 6.68 ± 0.33, 6.82 ± 0.13, 6.94 ± 0.25, 6.48 ± 0.26 and 6.87 ± 0.12 for Sites C, F, E, G, A and B respectively (Table 5.3). The groundwater therefore is distinctly $HCO_3^-$ type, with the wells with higher proportions of Na (and lower proportions of Ca) also displaying up to ~ 25% Cl (Fig. 5.2a). Concentrations of $HCO_3^-$ for Sites C, F, E, G, A and B were 2.4 ± 0.4 meq/L, 3.0 ± 2.1 meq/L, 4.9 ± 0.8 meq/L, 6.4 ± 0.3 meq/L, 5.7 ± 1.7 meq/L and 8.7 ± 0.9 meq/L, respectively (Table 5.3). Concentrations of $Cl^-$ were lower at Sites C, F, E and G, averaging 0.2 ± 0.07 meq/L, 0.2 ± 0.24 meq/L, 0.1 ± 0.02 meq/L (excluding E-4), and 0.2 ± 0.2 meq/L, respectively. Concentrations of Cl were higher at site A and B and were 0.7 ± 0.2 meq/L and 2.2 ± 0.9 meq/L, respectively (Table 5.3).

Perhaps the most significant feature is that all shallow waters are depleted in $SO_4^{2-}$ (Fig. 5.2a). Despite of low proportion of $SO_4^{2-}$ at all sites, sulfate concentrations decreased systematically with depth (Table 5.3), and were higher from Sites A, B and E than those of Sites C, F and G. Nitrate concentrations also decreased with depth in the shallow aquifer at Site A, from 21.6 to 4.2 mg/L. Nitrate is largely undetectable in most wells, but appeared at small concentrations (< 3 mg/L) in a number of wells at various depths (B-19 m, E-11 m, E-14 m, G-21 m, except G-9 m; 6.9 mg/L, Table 5.3).

Concentrations of $SiO_2$ for Sites C, F, E, G, A and B were 1.2 ± 0.9 meq/L, 3.7 ± 3 meq/L, 0.6 ± 0.2 meq/L, 0.6 ± 0.1 meq/L, 4.4 ± 0.7 meq/L and 5.6 ± 0.3

meq/L, respectively (Table 5.3). The concentrations of $F^-$, $NO_2^-$, $Br^-$ were not detectable (<0.1 mg/L).

### 5.5.2.3. Arsenic Species

Consistent with negative ORP values from all shallow monitoring wells except F-6 m, most of the As is in the form of As(III) determined by anion exchange separation. The proportion of As(III) generally increase with depths and approached 100% at Sites F, A and B. At Site E, the proportion of As(III) increased from 64 to 90% with depth (Table 5.3). . At Sites C and G, the proportion of As(III) decreased from >90% to ~ 70% as depth increased (Table 5.3). At Site C, on site speciation analyses by differential pulse cathodic stripping voltammetry (He et al., 2004) and molybdenum colorimetry ((Dhar et al., 2004) showed that %As(III) decreased from >95% to ~71% with depth. These measurements suggest that As(V) is present at some sites. However, it has been shown recently that negatively charged As(III)-sulfide (thioarsenite) species, important at sulfide concentrations >10 μmole/L, also bind to the anion exchange resins, and therefore might be interpreted incorrectly as As(V) (Jay et al., 2004). Whether this or other As species may have been mistakenly identified as As(V) for C-11 m, C-14 m, G-9 m, G-14 m and G-139 m remain to be resolved, although the dissolved sulfide concentrations never exceeded 0.1 μM in all our monitoring wells (Zheng, unpublished results).

### 5.5.2.4. Groundwater Fe and Mn

Concentrations of Fe and Mn are characterized more by the differences among the sites than the gradient with depth at any individual site. Concentrations of Fe for Sites C, F, E, G, A and B were 713 ± 212 μmole/L, 64 ± 129 μmole/L (except F-26 m; 6.3 ± 7.4 µmole/L), 393 ± 281 µmole/L, 358 ± 147 µmole/L, 280 ± 113 µmole/L and 324 ± 50 µmole/L, respectively (Table 5.3). Concentrations of Mn for Sites C, F, E, G, A and B were 25 ± 6 µmole/L, 23 ± 15 µmole/L, 24 ± 7 µmole/L, 22 ± 10 µmole/L, 39 ± 22 µmole/L and 18 ± 10 µmole/L, respectively (Table 5.3).

#### 5.5.2.5. Total organic carbon, total nitrogen, ammonia and P

Total organic cabon (TOC), total nitrogen (TN), $NH_4^+$ and P generally increase with depth, and sometimes the profiles resemble that of As (Fig. 5.3). Concentrations of TOC for Sites C, F, E, G, A and B were 1.9 ± 88 mg/L, 1.0 ± 0.73 mg/L, 1.3 ± 0.88 mg/L, 3.3 ± 2.3 mg/L, 12.1 ± 2.4 mg/L and 14.4 ± 2.4 mg/L, respectively (Table 5.3). Concentrations of TN were measured for the waters from four sites. The concentrations of TN for Sites C, F, E and G were 0.7 ± 0.33 mg/L, 0.8 ± 0.87 mg/L, 1.3 ± 1.2 mg/L, 2.9 ± 2.0 mg/L, respectively (Table 5.3). Concentrations of $NH_4^+$ for Sites C, F, E, G, A and B were 0.7 ± 0.31 mg/L, 0.8 ± 1.1 mg/L, 1.4 ± 1.6 mg/L, 3.7 ± 2.5 mg/L, 4.2 ± 3.3 mg/L (except A-7 m; 18.9 mg/L), and 3.6 ± 5.1 mg/L, respectively (Table 5.3). Therefore, most of the total nitrogen is ammonia N. Concentrations of P for Sites C, F, E, G, A and B were 22 ± 2.6 µmole/L, 9.4 ± 12.3 µmole/L, 22 ± 9.8 µmole/L, 61 ± 26 µmole/L, 19 ± 6 µmole/L and 50 ± 12 µmole/L, respectively (Table 5.3).

### 5.5.3. Chemistry of Deep Aquifer Water

#### 5.5.3.1. Conductivity

Compared to the shallow aquifer at each site, the conductivities of deep aquifer water were ~ 50% lower at Sites A (38 ± 3 mS/m) and B (53 ± 17 mS/m); were about the same at Sites C (34 mS/m) and E (79 mS/m); and were ~ 3 times higher at Sites F (188 mS/m) and G (176 mS/m). Groundwater As in the deep wells drilled to the Pleistocene aquifers were all < 10 µg/L, with values clearly detectable and were 1, 2, 2, 1 and 7 µg/L for Sites A, C, E, F and G.

### 5.5.3.2. Major Ions

Groundwater from Holocene deep aquifer from Site B (Fig. 5.2b) is Ca-poor (<5%), with the proportion of Na increasing and the proportion of Mg decreasing as the groundwater As level decreased from 21 µg/L (41 m), to 15 µg/L (53 m) and finally to 1 µg/L (91 m). The concentrations of 2.0 ± 0.84 meq/L, 0.1 ± 0.05 meq/L, 0.04 ± 0.02 mg/L and 0.61 ± 0.43 meq/L were measured for $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ respectively (Table 5.3).

Ground waters from Pleistocene deep aquifers from the other sites are Na-rich. At Sites F and G, the major cation is overwhelmingly Na (~ 13.9 meq/L), with much lower concentrations of $K^+$, $Ca^{2+}$, $Mg^{2+}$. At Sites A, C and E, Na is still dominant, accounting for 50% to 75% of the major cations (Fig. 5.2c) because $K^+$ concentrations were nearly the same at only ~ 0.05 meq/L. In comparison, $Na^+$ concentrations of 2.7 ± 0.55 meq/L, 1.4 meq/L, 3.4 meq/L, were measured for Sites A, C, and E, respectively (Table 5.3). Ca and Mg accounted for no more than 30% of the major cations, with waters from Sites C and E containing more Mg than waters from Site A (Fig. 5.2c).

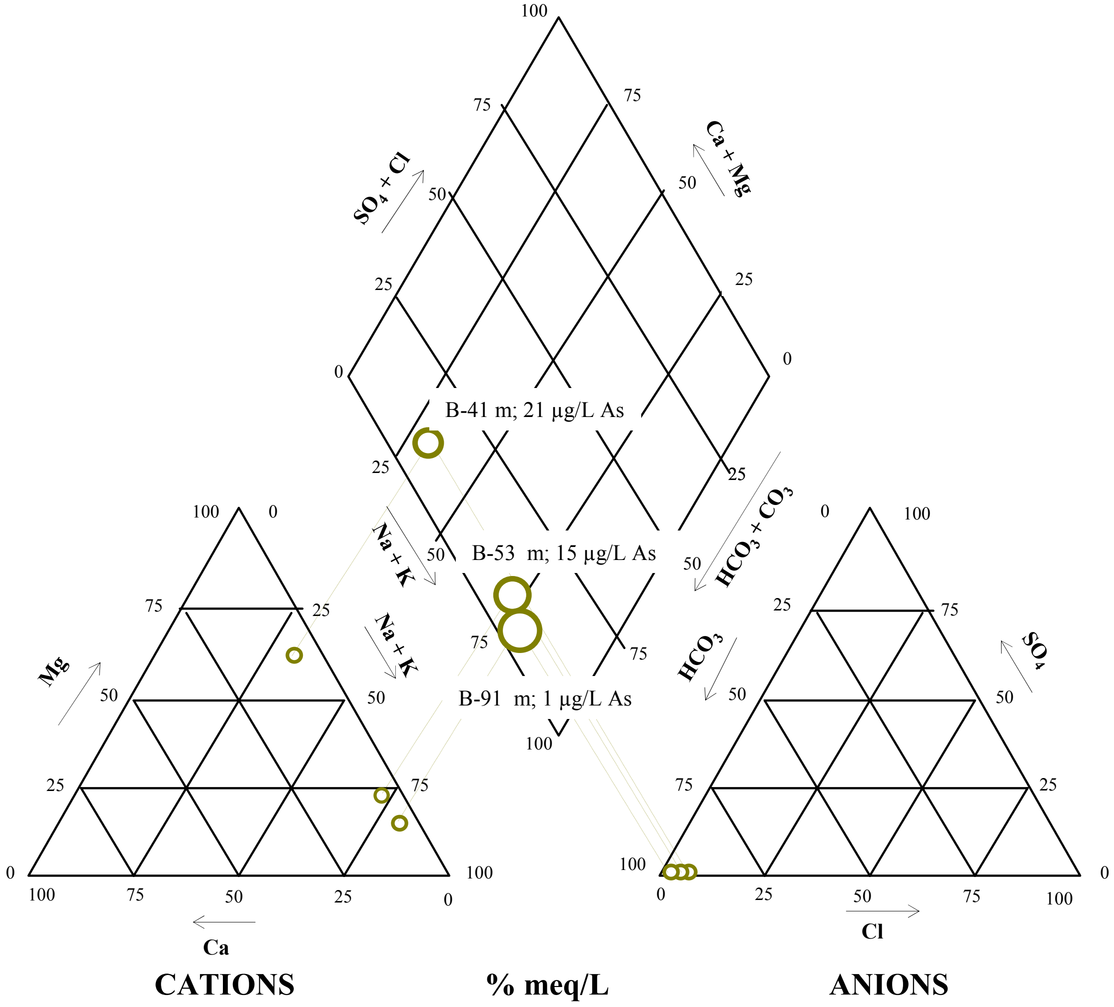

**Figure-5.2. (b)** Piper diagram illustrating the main hydrochemical features of the groundwaters of deep Holocene aquifers at site B. The size of the symbols indicates the depth of wells and symbol size in the quadrilateral increases with increasing depth.

The anion in the 3 wells from the Holocene deep aquifer at Site B is overwhelmingly dominated by $HCO_3^-$, averaging 5.3 ± 1.3 meq/L (Fig. 5.2b). The waters of deep Holocene aquifers at site B are neutral, with pH of 7.01 ± 0.12. There is very little $Cl^-$ and $SO_4^{2-}$, with concentrations of 0.2 ± 0.1 meq/L and 3.2 ± 0.3

µmole/L, respectively. $NO_3^-$ concentrations of 12.7, 0.9, <0.1 mg/L were measured at B-41 m, B-53 m, B-91 m respectively.

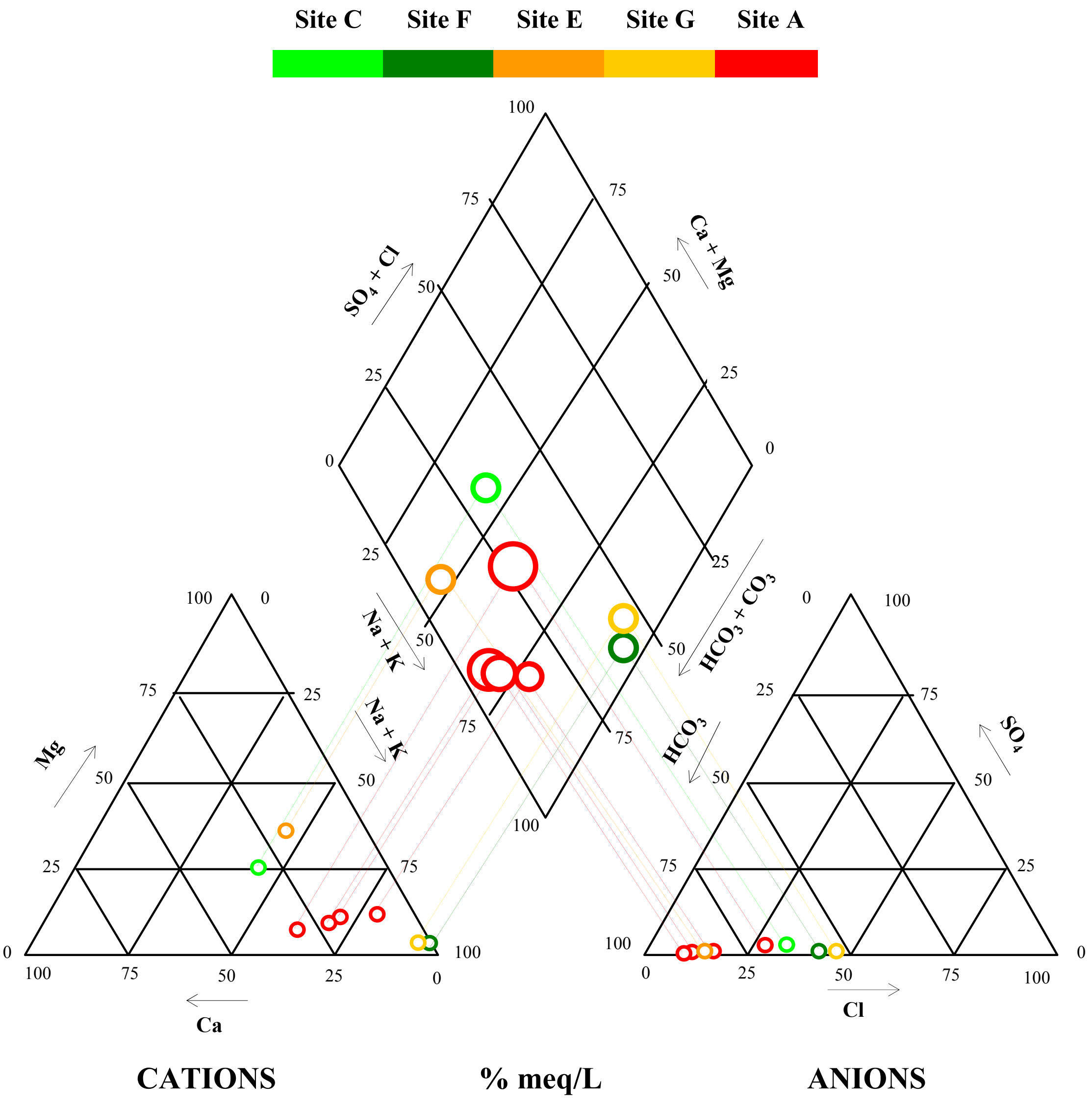

**Figure-5.2. (c)** Piper diagram illustrating the main hydrochemical features of the groundwaters of deep Pleistocene aquifers at site A, C, E, F and G. The size of the symbols indicates the depth of wells and symbol size increases with increasing depth. Groundwater from deep Pleistocene aquifers at different sites represented by open circles outlined with respective colors as indicated on color bar.

The Pleistocene deep aquifer waters from other sites are still dominated by $HCO_3^-$ and again is nearly depleted in $SO_4^{2-}$ (Fig. 5.2c), although at Sites F and G the proportions of Cl were close to 50%. The pH values of the waters ranged from 6.17 at A-91 m to 6.94 at F-58 m (Table 5.3). Concentrations of $HCO_3^-$ were 2.73 ± 0.3 meq/L, 1.14 meq/L , 6.55 meq/L , 6.74 meq/L and 7.7 meq/L for Sites A, C, E, F and G respectively. The concentrations of Cl were 0.68 ± 0.2 meq/L, 0.52 meq/L, 1.17 meq/L, 8.9 meq/L and 8.4 meq/L for Sites A, C, E, F and G respectively (Table 5.3). Small amounts of $SO_4^{2-}$ were detected at all sites except at Site E. The concentrations of $SO_4^{2-}$ were 13 ± 7.8 µmole/L, 15 µmole/L, <1 µmole/L, 10 µmole/L and 34 µmole/L were for Sites A, C, E, F and G respectively (Table 5.3). Trace but easily detectable amounts of $NO_3^-$ were observed at Sites E, F, and G.

### 5.5.3.3. Arsenic Species

Consistent with the negative ORP values of about -160 mV for the 2 deep Holocene aquifer wells at Site B, arsenic is nearly 100% As(III) for B-41 m and B-53 m. The deepest well, B-91 m, also with a negative ORP value of -134 mV, has no detectable As(III) but the total As was only 1 µg/L.

The ORP values of waters from Pleistocene aquifers are relatively less negative, especially as A-91 m, with values reaching +26 mV (Table 5.3). At Sites A, C, F with < 2 µg/L total As, As(III) was not detectable (< 0.1 µg/L). However, As(III) was detectable Sites G and E, with all of the As in the form of As(III) (Table 5.3).

### 5.5.3.4. Groundwater Fe and Mn

The concentrations of Fe in the deep aquifers are generally several times lower than those of the shallow aquifer at each site. Concentrations of Fe were 162, 88, 16 µmole/L for the Holocene deep aquifer wells B-41 m, B-53 m, B- 91 m, respectively (Table 5.3). Other than Site C deep water with ~ 173 µmole/L Fe, other Pleistocene deep aquifer waters contained 2 to 62 µmole/L Fe at Sites A, E, F and G.

Although Mn concentrations were generally lower by about an order of magnitude than those of shallow aquifers at each site, they still exceed the Bangladesh standard of 0.1 mg/L (1.8 µmole/L) and WHO guideline values of 0.4 mg/L (7 µmole/L) for many wells. Interestingly, Holocene deep aquifer waters at Site B yielded consistently low Mn water (Table 5.3). But at least one well from other 5 sites of the Pleistocene deep aquifer yielded water > 4.5 µmole/L, although the highest level reached was 14 µmole/L at Site C.

#### 5.5.3.5. Total organic carbon, total nitrogen, ammonia and P

The concentrations of TOC in the deep Pleistocene aquifers are generally lower than those of the shallow aquifer at Sites C, E, F and G (Table 5.3; Fig. 5.3). Concentrations of TOC were 0.7, 1.8, 0.1 and 0.6 mg/L for the Pleistocene deep aquifer waters contained at Sites A, C, E, F and G, respectively.

The concentrations of TN in the deep Pleistocene aquifers are much lower than those of the shallow aquifer at Sites C, F and G, but are slightly higher than that of the shallow waters at Site E (Table 5.3). The concentrations of TN were 0.2, 3.4, 0.6 and 0.6 mg/L for the Pleistocene deep aquifer waters at Sites C, E, F and G, respectively. Again, total N is composed primarily of ammonia N.

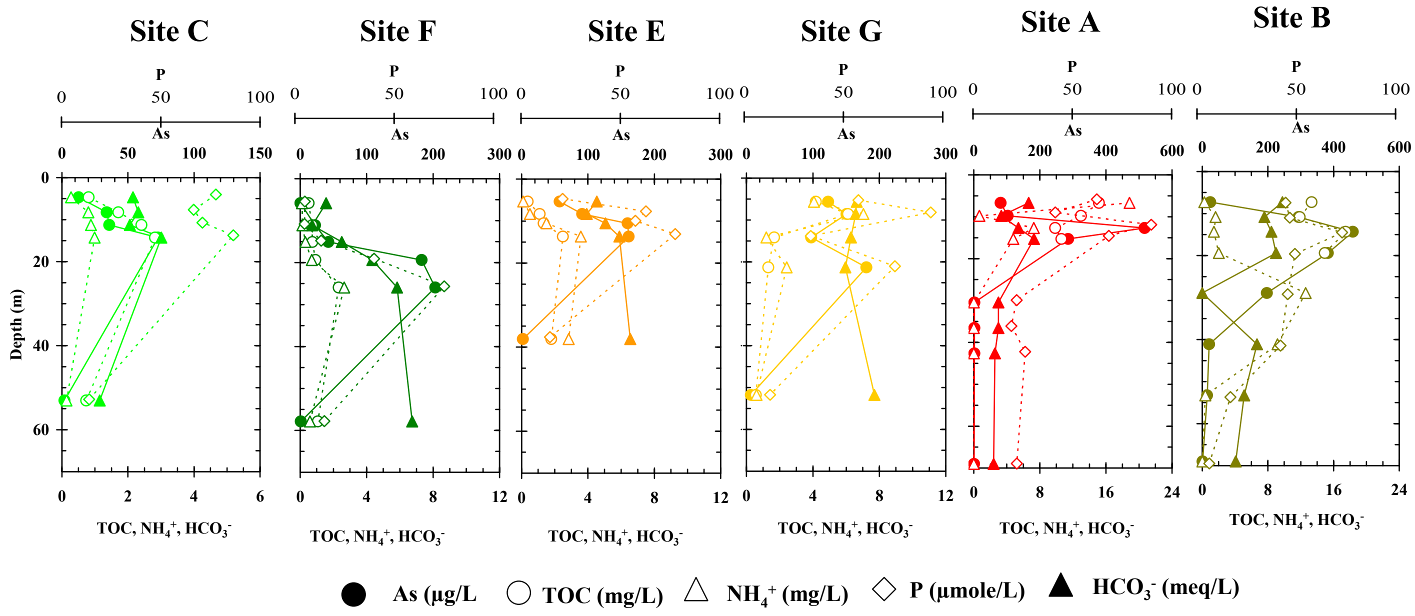

**Figure-5.3.** Depth profiles of As, TOC, P, $NH_4^+$, $HCO_3^-$ of groundwaters from shallow and deep aquifers at Sites C, F, E, G, A and B arranged as the their average As concentration from left to right. Scales for As and (TOC,$NH_4^+$, $HCO_3^-$ ) vary from site to site. Scale for P was shown above As scale for all sites. Different symbols are used to indicate different constituent as listed in the legend; solid circle (As), open circle(TOC), open triangle ($NH_4^+$), open diamond (P), solid triangle ($HCO_3^-$) with respective colors for different sites as indicated on color bar. Note that in Sites A and B, the depth just immediate below the 60 m represents the much larger depth; 91 m, as shown along the Y-axis for these two sites.

$NH_4^+$ concentrations were also generally an order of magnitude lower than those of shallow aquifers at each site except Site E (Table-5.3; Fig. 5.3). Concentrations of $NH_4^+$ were 9.2, 0.4, and <0.1 mg/L for the Holocene deep aquifer wells B-41 m, B-53 m, B-91 m, respectively (Table 5.3). $NH_4^+$ concentrations of <0.1 mg/L, 0.1 mg/L, 2.8 mg/L, 0.6 mg/L and 0.6 mg/L were measured for site A, C, E, F and G respectively (Table-5.3).

P concentrations were also generally lower by about an order of magnitude than those of shallow aquifers at each site. Concentrations of P were 40, 14, and 3 µmole/L for the Holocene deep aquifer wells B-41 m, B-53 m, B-91 m, respectively (Table 5.3). P concentrations of 5.9 ± 0.9 µmole/L, 3.4 µmole/L, 5.3 µmole/L, 4.2 µmole/L and 8 µmole/L were measured for Sites A, C, E, F and G respectively.

## 5.5.4. Chemistry of existing well water

Concentrations of As in the existing wells from the villages, like monitoring nests of Sites A, B were mostly elevated in the shallow Holocene aquifers (<30 m) but were low with detectable As from 0.3 to 6 µg/L in the deep Pleistocene aquifers (>30 m). The pH values of the groundwater were 6.54 ± 0.12 and 6.34 ± 0.13 for shallow and deep aquifers, respectively (Table 5.4). Groundwater were reducing in shallow waters (n=14), with ORP values ranging from -32 mV to -166 mV except W4068 with an ORP value of + 58 mV and As of 9 µg/L; (Table 5.4) Deep groundwaters, all from the vicinity of Site A, showed positive ORP values(n=6) from +24 to + 75 mV.

# Table-5.4. Chemistry data of existing wells

| Sample | Village | Well | Latitude | Longitude | Depth | Sampling | Temp. | cond. | Eh | pH | Alkalinity | | DO | $As_{tot}$ | Mg | Ca | Mn | Cu | Rb | Sr | Mo | Ba | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | name | ID | (°N) | (°E) | (m) | Date | (°C) | (mS/m) | (mV) | | (meq/L) | | (μg/L) | (μg/L) | (meq/L) | (meq/L) | (μmole/L) | (μg/L) | (μg/L) | (μg/L) | (μg/L) | (μg/L) | (μg/L) |
| | | | | | | | | Orion meter and probe | | | Gran. Titration | | CHEMet | ICP-MS | | | | | ICP-MS | | | | |
| 1 | Dari Satyabandi | W4119 | 23.7871 | 90.6040 | 6 | 01/11/01 | 25.0 | 57 | -165 | 6.65 | 4.81 ± | 0.03 | >1000 | 280 | 0.8 | 0.8 | 22 | <0.1 | 1.5 | 223 | 1.5 | 130 | 0.0 |
| 2 | Dari Satyabandi | W4063 | 23.7857 | 90.6044 | 8 | 01/10/01 | 25.8 | 41 | -98 | 6.46 | 3.25 ± | 0.05 | 20 | 69 | 0.6 | 0.8 | 31 | <0.1 | 1.1 | 108 | 1.1 | 73 | 0.1 |
| 3 | Dari Satyabandi | W4068 | 23.7854 | 90.6035 | 8 | 01/09/01 | 25.9 | 49 | 58 | 6.47 | 3.38 ± | 0.08 | 600 | 9 | 0.8 | 0.9 | 25 | 1.2 | 0.9 | 141 | 1.6 | 87 | 2.5 |
| 4 | Dari Satyabandi | W4069 | 23.7859 | 90.6040 | 9 | 01/10/01 | 26.3 | 112 | -91 | 6.43 | 6.83 ± | 0.10 | 20 | 40 | 1.8 | 1.7 | 14 | 1.6 | 0.5 | 249 | 3.9 | 429 | 2.0 |
| 5 | Dari Satyabandi | W4067 | 23.7859 | 90.6036 | 9 | 01/13/01 | 26.0 | 101 | -32 | 6.31 | - | | 60 | 36 | 1.5 | 1.7 | 18 | 0.4 | 0.8 | 233 | 0.6 | 198 | 2.2 |
| 6 | Dari Satyabandi | W4108 | 23.7840 | 90.6025 | 12 | 01/07/01 | 26.0 | 99 | -150 | 6.38 | 6.08 ± | 0.06 | 40 | 417 | 1.5 | 2.0 | 91 | 7.3 | 0.7 | 360 | 1.9 | 149 | 0.8 |
| 7 | Dari Satyabandi | W4134 | 23.7857 | 90.6032 | 13 | 01/10/01 | 25.8 | 63 | -162 | 6.53 | 4.66 ± | 0.07 | <10 | 321 | 1.0 | 1.3 | 76 | 2.9 | 1.6 | 251 | 3.3 | 141 | 1.0 |
| 8 | Dari Satyabandi | W4146 | 23.7859 | 90.6045 | 13 | 01/10/01 | 25.8 | 71 | -161 | 6.79 | 6.49 ± | 0.09 | - | 346 | 1.0 | 1.4 | 51 | <0.1 | 1.9 | 222 | 5.3 | 165 | 0.2 |
| 9 | Dari Satyabandi | W4081 | 23.7863 | 90.6044 | 13 | 01/07/01 | 25.5 | 54 | -141 | 6.72 | 4.16 ± | 0.10 | <10 | 252 | 0.8 | 1.3 | 53 | <0.1 | 1.3 | 204 | 5.0 | 101 | 0.1 |
| 10 | Dari Satyabandi | W4133 | 23.7853 | 90.6038 | 13 | 01/08/01 | 25.7 | 69 | -157 | 6.5 | 5.76 ± | 0.06 | - | 647 | 1.0 | 1.5 | 90 | 0.6 | 0.7 | 306 | 5.2 | 147 | 3.0 |
| 11 | Dari Satyabandi | W4132 | 23.7849 | 90.6033 | 13 | 01/08/01 | 25.8 | 77 | -91 | 6.56 | 5.11 ± | 0.08 | 40 | 97 | 1.1 | 1.5 | 44 | 0.6 | 0.6 | 252 | 2.9 | 322 | 0.9 |
| 12 | Dari Satyabandi | W4136 | 23.7852 | 90.6035 | 13 | 01/11/01 | 25.8 | 41 | -71 | 6.48 | 3.66 ± | 0.06 | 10 | 204 | 0.6 | 0.9 | 53 | <0.1 | 1.0 | 178 | 2.1 | 111 | 0.5 |
| 13 | Baylarkandi | W935 | 23.7795 | 90.6387 | 13 | 01/08/01 | 25.9 | 72 | -166 | 6.43 | - | | - | 402 | 0.9 | 2.1 | 6 | <0.1 | 4.2 | 422 | 2.9 | 102 | 0.0 |
| 14 | Baylarkandi | W938 | 23.7799 | 90.6386 | 14 | 01/12/01 | 25.5 | 68 | -165 | 6.63 | - | | - | 104 | 1.0 | 1.8 | 21 | <0.1 | 3.2 | 257 | 1.3 | 171 | 0.0 |
| 15 | Baylarkandi | W932 | 23.7802 | 90.6388 | 15 | 01/11/01 | 25.5 | 82 | -155 | 6.69 | - | | - | 231 | 1.0 | 2.0 | 20 | <0.1 | 2.8 | 355 | 1.7 | 183 | 0.0 |
| 16 | Dari Satyabandi | W4059 | 23.7855 | 90.6032 | 34 | 01/09/01 | 25.7 | 40 | 75 | 6.29 | 2.53 ± | 0.08 | - | 5.8 | 0.3 | 0.3 | 3 | <0.1 | 0.1 | 87 | 1.0 | 15 | 0.8 |
| 17 | Dari Satyabandi | W4135 | 23.7849 | 90.6036 | 34 | 01/23/01 | 26.1 | 39 | 25 | 6.29 | 2.74 ± | 0.03 | - | 4.6 | 0.2 | 0.3 | 2 | 0.5 | 0.2 | 87 | 1.0 | 15 | 2.0 |
| 18 | Dari Satyabandi | W4016 | 23.7865 | 90.6018 | 34 | 01/21/01 | 25.9 | 33 | 29 | 6.39 | 2.87 ± | 0.07 | - | 4.3 | 0.2 | 0.3 | 0.3 | <0.1 | 0.2 | 105 | 0.2 | 20 | 0.1 |
| 19 | Dari Satyabandi | W4120 | 23.7874 | 90.6035 | 36 | 01/19/01 | 26.1 | 34 | 26 | 6.19 | 4.81 ± | 0.03 | - | 4.5 | 0.2 | 0.3 | 5 | <0.1 | 0.3 | 83 | 0.4 | 12 | 0.5 |
| 20 | Dari Satyabandi | W4060 | 23.7865 | 90.6048 | 38 | 01/23/01 | 25.8 | 35 | 24 | 6.29 | 2.52 ± | 0.07 | - | 3.9 | 0.3 | 0.3 | 2 | 0.2 | 0.3 | 97 | 0.9 | 14 | 0.8 |
| 21 | Dari Satyabandi | DTW* | 90.4659 | 23.6926 | 107 | 01/23/01 | 26.7 | 5 | 52 | 6.57 | - | | - | 0.3 | 0.3 | 0.5 | 0 | <0.1 | 0.2 | 122 | 0.2 | 18 | 0.1 |
| 22 | Satyabandi | CW* | 90.6061 | 23.7868 | surface wate | 01/23/01 | - | - | - | - | - | | - | 8.4 | 0.7 | 1.1 | 10 | <0.1 | 2.4 | 190 | 1.8 | 51 | 1.7 |

*** DTW: Deep tube well and CW: canal water**

These waters were not analyzed for the whole suite of elements, but conductivity, $HCO_3^-$, $Ca^{2+}$, $Mg^{2+}$, Mn in shallow aquifer were 70 ± 21 mS/m, 5 ± 1.3 meq/L, 1.46 ± 0.44 meq/L, 1.02 ± 0.3 meq/L, 41 ± 28 µmole/L, respectively. Concentrations were 3-10 fold lower in deep aquifers. Conductivity, $HCO_3^-$, $Ca^{2+}$, $Mg^{2+}$, Mn in deep aquifer (>30 m) were 31 ± 13 mS/m, 3.1 ± 1 meq/L, 0.25 ± 0.05 meq/L, 0.33 ± 0.08 meq/L, 2 ± 1.9 µmole/L, respectively (Table 5.4).

Surface water collected in the stream next to Site A contained clearly detectable amount of As at 8 µg/L. This water also has Ca, Mg, Rb, Sr, and Ba concentrations more similarly to the shallow aquifer groundwater than to the deep aquifer water. Whether this As is a result of shallow groundwater discharging to the stream remains to be explored.

### 5.5.5. Saturation Index by PHREEQC

Not surprisingly, ground waters were found to be undersaturated with respect to minerals with high solubility such as halite (NaCl) and gypsum ($CaSO_4$, $2H_2O$) (Table 5.5). Ground waters were also found to be undersaturated with respect to several carbonate minerals, including calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and in most cases, rhodochrosite ($MnCO_3$). Most ground waters were found to be supersaturated with respect to kaolinite ($Al_2SiO_5(OH)_4$), a secondary clay mineral.

## Table 5.5. Phreeqc calculation for saturation indices (SI) of monitoring wells

| **MW* ID** | **Anhydrite** $CaSO_4$ | **Calcite** $CaCO_3$ | **Dolomite** $CaMg(CO_3)_2$ | **Gypsum** $CaSO_4{:}2H_2O$ | **Halite** $NaCl$ | **Hydroxyapatite** $Ca_5(PO_4)_3OH$ | **Kaolinite** $Al_2Si_2O_5(OH)_4$ | **$MnHPO_4$(C)** $MnHPO_4$ | **Rhodochrosite** $MnCO_3$ | **Siderite** $FeCO_3$ | **Vivianite** $Fe_3(PO_4)_2{:}8H_2O$ | **Ionic Strength** **($e^{-03}$)** | **ΣMC-ΣMA** **(meq/L)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A-1** | -2.3 | -0.8 | -1.9 | -2.1 | -7.7 | -0.1 | **8.2** | **2.7** | -0.3 | **0.9** | **1.9** | 9.7 | 0 |
| **A-2** | -2.3 | -0.8 | -1.9 | -2.1 | -7.9 | **1.1** | **7.6** | **2.8** | -0.3 | **0.3** | **0.9** | 6.5 | 0 |
| **A-3** | -4.0 | -0.3 | -0.8 | -3.8 | -7.9 | **3.6** | **8.7** | **3.3** | 0.3 | **1.1** | **3.3** | 8.9 | 0 |
| **A-4** | -4.0 | -0.1 | -0.2 | -3.8 | -7.3 | **3.7** | **9.3** | **2.5** | -0.2 | **1.4** | **3.5** | 10.7 | 0 |
| **A-5** | -4.1 | -1.5 | -2.9 | -3.9 | -7.2 | -2.8 | **9.0** | **1.5** | -1.4 | -0.1 | -0.5 | 4.8 | 1 |
| **A-6** | -4.4 | -1.5 | -3.2 | -4.2 | -7.5 | -3.2 | **10.1** | **1.1** | -1.9 | -0.3 | -1.3 | 4.4 | 0 |
| **A-7** | -3.9 | -1.4 | -3.1 | -3.7 | -7.6 | -2.0 | **9.6** | **1.7** | -1.3 | -0.3 | -1.0 | 4.0 | 1 |
| **A-8** | -3.5 | -1.3 | -3.0 | -3.3 | -7.3 | -1.3 | **8.5** | **1.2** | -1.9 | -1.8 | -5.3 | 4.6 | 1 |
| **B-1** | -2.2 | -0.6 | -0.9 | -2.0 | -6.7 | **1.1** | **10.0** | **2.7** | -0.5 | **1.0** | **2.8** | 13.8 | -4 |
| **B-2** | -2.9 | -0.7 | -1.2 | -2.7 | -6.9 | **1.5** | **9.4** | **3.2** | -0.1 | **1.1** | **3.2** | 10.1 | -4 |
| **B-3** | -2.6 | -0.1 | -0.5 | -2.4 | -6.9 | **4.3** | **8.6** | **2.9** | -0.2 | **1.3** | **3.7** | 12.8 | -2 |
| **B-4** | -4.9 | -1.0 | -1.5 | -4.7 | -7.5 | -0.3 | **9.6** | **3.1** | 0.0 | **1.5** | **4.2** | 8.0 | -5 |
| **B-6** | -5.3 | -1.4 | -1.6 | -5.1 | -8.1 | -1.8 | **7.9** | **2.1** | -1.1 | **1.0** | **3.2** | 6.9 | -2 |
| **B-7** | -5.6 | -1.6 | -2.1 | -5.4 | -7.9 | -3.3 | **7.6** | **2.1** | -0.7 | **0.9** | **2.4** | 5.1 | -1 |
| **B-8** | -5.6 | -1.8 | -2.6 | -5.4 | -8.4 | -5.5 | **8.0** | **1.2** | -1.1 | 0.0 | -1.2 | 4.0 | -1 |
| **C-1** | -3.8 | -1.7 | -3.6 | -3.6 | -8.6 | -2.5 | **7.4** | **2.6** | -1.0 | **0.6** | **2.7** | 4.1 | 0 |
| **C-2** | -4.1 | -1.7 | -3.6 | -3.9 | -8.8 | -2.5 | **7.3** | **2.7** | -0.6 | **1.0** | **3.5** | 4.5 | 0 |
| **C-3** | -4.6 | -1.7 | -3.5 | -4.4 | -8.9 | -1.9 | **6.9** | **2.6** | -0.9 | **0.9** | **3.5** | 3.6 | 0 |
| **C-4** | -4.2 | -1.0 | -2.1 | -4.0 | -8.6 | **1.3** | **7.5** | **2.9** | -0.5 | **1.0** | **3.6** | 5.1 | 0 |
| **C-5** | -3.6 | -2.0 | -4.1 | -3.4 | -7.8 | -3.9 | **11.0** | **1.6** | -1.6 | -0.4 | -0.5 | 3.6 | 2 |
| **E-1** | -3.3 | -0.6 | -1.2 | -3.1 | -8.8 | **0.9** | **7.3** | **2.3** | -0.5 | **0.2** | **-0.2** | 7.4 | 1 |
| **E-2** | -3.4 | -0.7 | -1.5 | -3.2 | -9.0 | **1.9** | **7.0** | **2.9** | -0.3 | **1.0** | **3.3** | 6.0 | 0 |
| **E-3** | -4.1 | -0.3 | -0.7 | -3.9 | -9.0 | **3.5** | **7.8** | **3.0** | **0.0** | **1.3** | **3.9** | 7.7 | 0 |
| **E-4** | -4.1 | -0.4 | -1.0 | -3.9 | -7.7 | **3.0** | **11.6** | **2.7** | -0.4 | **1.4** | **4.3** | 9.3 | 0 |
| **E-5** | -4.2 | -0.6 | -1.3 | -4.0 | -7.1 | -0.2 | **8.3** | **1.5** | -1.0 | -0.3 | -0.8 | 9.7 | 0 |
| **F-1** | -3.1 | -1.7 | -3.5 | -2.9 | -8.2 | -7.5 | **5.4** | -1.6 | -3.4 | -3.3 | -12.3 | 3.2 | 0 |
| **F-2** | -3.5 | -2.2 | -4.3 | -3.3 | -9.2 | -8.4 | **5.2** | **0.5** | -1.5 | -3.1 | -11.2 | 2.1 | 0 |
| **F-3** | -5.1 | -2.4 | -3.5 | -4.9 | -9.6 | -7.4 | **7.2** | **2.2** | -0.5 | -0.7 | -2.5 | 2.2 | -1 |
| **F-4** | -4.6 | -1.9 | -2.7 | -4.4 | -9.0 | -4.4 | **9.3** | **3.1** | **0.1** | -0.1 | -0.4 | 3.5 | -3 |
| **F-5** | -7.8 | -0.4 | -0.8 | -7.6 | -8.8 | 3.3 | **10.2** | **3.2** | **0.1** | **1.3** | **3.8** | 6.7 | -2 |
| **F-6** | -5.3 | -1.9 | -2.7 | -5.1 | -5.6 | -6.7 | **7.5** | **1.8** | -0.5 | **0.2** | -1.0 | 15.4 | -1 |
| **G-1** | -3.9 | -0.3 | -0.8 | -3.7 | -9.1 | **3.9** | **7.0** | **3.0** | -0.2 | **1.3** | **4.2** | 9.5 | 0 |
| **G-2** | -3.7 | -0.3 | -0.9 | -3.5 | -9.2 | **4.6** | **9.6** | **2.8** | -0.8 | **1.1** | **4.2** | 9.8 | 0 |
| **G-3** | -4.1 | 0.0 | -0.4 | -3.9 | -8.6 | **4.8** | **5.7** | **3.1** | **0.2** | **1.3** | **3.8** | 7.9 | -1 |
| **G-4** | -5.8 | -0.1 | -0.1 | -5.6 | -8.2 | **5.9** | **8.1** | **3.3** | **0.3** | **1.3** | **4.2** | 8.3 | -1 |
| **G-5** | -3.8 | -0.9 | -1.9 | -3.6 | -5.6 | -1.5 | **8.5** | **2.1** | -0.5 | -0.3 | -2.2 | 16.2 | -1 |

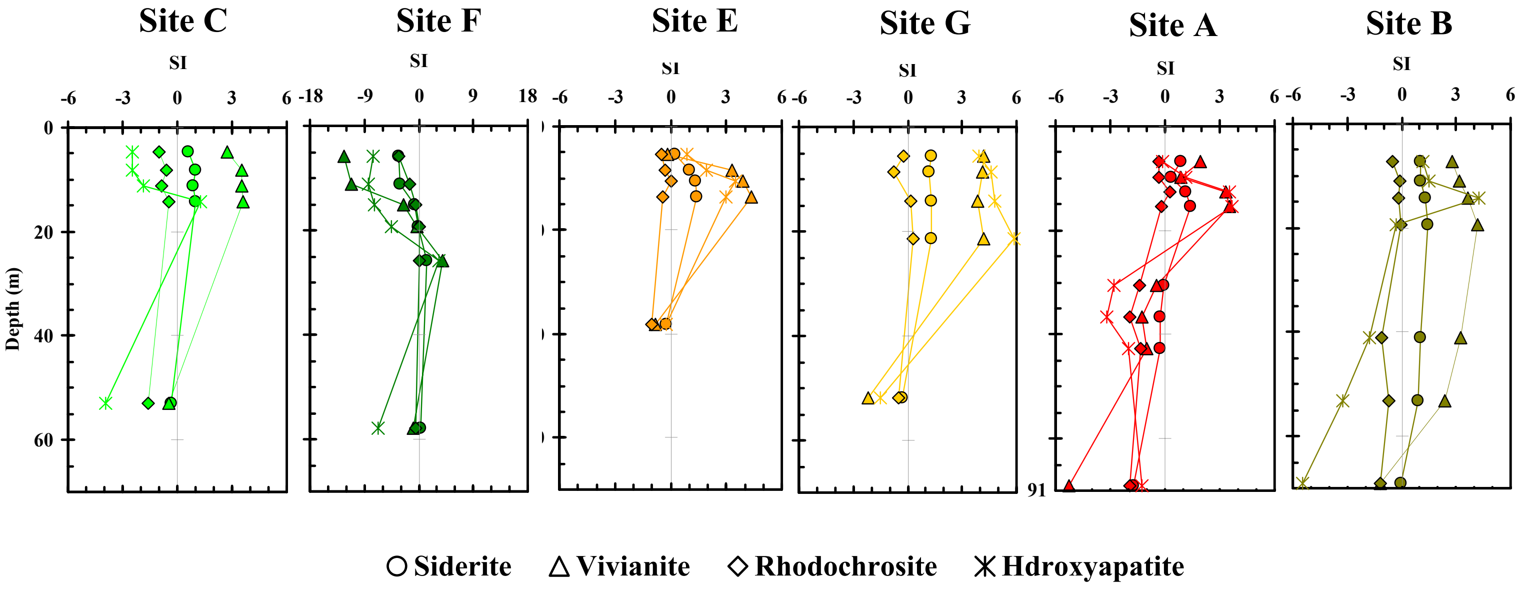

**Figure-5.4.** Depth profiles of SI value for Fe and P mineral phases in shallow and deep aquifers of all sites. Sites are arranged similar to Fig. 5.3. Different symbols are used to indicate different mineral phases as listed in the legend; solid circle (siderite; $FeCO_3$), solid triangle (vivianite; $Fe_3(PO_4)_2$, $8H_2O$), solid diamond (rhodochrosite; $MnCO_3$), star (hydroxyapatite; $Ca_5(PO_4)_3OH$) with respective colors for different sites as shown color bar for Sites C, F, E, G, A and B similar to Fig. 3. Note that in Sites A and B, the depth just immediate below the 60 m represents the much larger depth; 91 m, as shown along the Y-axis for these two sites.

Pleistocene deep aquifer waters from Sites A, C, E and G but not Site F were found to be undersaturated with respect to siderite ($FeCO_3$), another carbonate mineral. Holocene deep aquifer waters at Site B was supersaturated with respect to siderite except the deepest well at 91 m (Fig. 5.4). Shallow groundwater from Sites A, B, C, E, G were all supersaturated with respect to siderite ($FeCO_3$). Only the 4 shallow wells (6 – 19 m) at Site F were undersaturated with respect to siderite ($FeCO_3$). F-26 m was the only shallow well at Site F that is super saturated with respect to siderite ($FeCO_3$), and is separated by a silty formation from the other shallower wells at the site, with significantly older water (Table 5.2) and different chemistry (Table 5.3).

One unique feature of the Bangladesh shallow groundwater is its high P concentrations. As a result, groundwaters were found to be supersaturated with respect to several phosphate minerals. Again, other than the 4 shallow wells at Site F, shallow ground waters from Sites A, B, C, E and G were supersaturated with respect to vivianite ($Fe_3(PO_4)_2,8H_2O$). Shallow groundwaters from all Sites A, B, C, E, F and G were supersaturated with respect to $MnHPO_4$ but not the shallowest well from Site F. Finally, shallow ground waters from Sites A, B, E and G were supersaturated with respect to hydroxyapatite ($Ca_5(PO_4)_3OH$) but not waters from C (except C-14 m) and F (Table 5.5).

## *5.6. Discussion*

### 5.6.1. Redox conditions and As concentrations

Elevated As concentrations were found when waters displayed negative ORP values between about -50 mV and -200 mV (Table 5.3), consistent with As mobilization under reducing conditions observed throughout Bangladesh (Zheng et al., 2004). In the shallow aquifer, only two wells out of 41wells sampled displayed positive ORP values. The concentration of As was 0.5 μg/L at F-6 m with an ORP value of +112 mV (Table 5.3). The concentration of As was 9 μg/L for W4068 with an ORP value of +58 mV (Table 5.4).

A reducing condition, however, is not the only parameter that contributes to As mobilization. This is because for waters with OPR values between -100 mV and -200 mV, groundwaters from Sites C, F and E had ~ 3 times lower As than those from Sites A and B. An extreme comparison is C-14 m and A-13 m. Both wells displayed similar ORP value of about -160 mV. However, the concentration of As is only 73 mg/L for C-14 m but is 517 mg/L for A-13 m. This suggests that other properties unique to each site also contribute to As mobilization. At least one such property is known to be different between the two sites: the phosphate-extractable sediment As concentration. The P-extractable sediment As was ~0.3 mg/kg at Site C but was 1.7 mg/kg at Site A (van Geen et al., 2006; Zheng et al., 2005).

### 5.6.2. Contrast in nutrient content between shallow and deep aquifers

Several nutrients important for microbial activities are systematically higher in the shallow aquifer waters than the deep aquifer waters (Fig. 5.3). This difference, however, is especially great for ammonia-N (Fig. 5.3) and, not surprisingly, total nitrogen at 5 sites except for Site E (Table 3.3). But it is difficult at this point to determine which nutrient might be limiting microbial activity in the deep aquifer. It is worth pointing out that most nutrients, TOC, ammonia and P increases with depth at Sites C, F and E. Tritium-helium dating of groundwater at these three sites also show a depth gradient, with increasing age with depth. On the first order, the increase of ammonia concentrations with depth appear to result from remineralization of organic matter. The increase of P, however, could be complicated because both remineralization of organic matter as well as any processes that release As from sediment will also likely release P. The increase of TOC concentrations may also be related to microbial remineralization of organic matter, except it is not known how labile these TOCs are.

Regardless of how and why many of the nutrients become elevated in the shallow aquifer water, our data demonstrate that understanding of whether microbial activity is the key to As mobilization is nutrient limited or not in the deep aquifer is crucial. This is because if infiltration or leakage of shallow aquifer water to the deep aquifer occurs, it will significantly modify the biogeochemical reactions in the deep aquifer by introducing more As, more nutrients, perhaps more labile carbon and a different microbial community.

### 5.6.3. Decoupling between As, P and Fe

Although reductive dissolution of Fe-oxides has been widely accepted as the first order control on As mobilization in the Bangladesh aquifer, the lack of correlation between groundwater As and Fe has remained a puzzling feature. Several explanations have been proposed. Iron reduction without dissolution was proposed a potential mechanism to decouple As and Fe release (van Geen et al., 2004). Reductive dissolution of As-bearing Fe oxides near the surface and then transport to depths was proposed as an alternative mechanism to explain the significantly decoupled redox state and groundwater As distribution (Polizzotto et al., 2005). The mineral precipitation calculations show that groundwater Fe concentrations are regulated by precipitation reactions of siderite and vivianite in the shallow aquifer (Figure 5.4). Siderite has been identified by XRD studies of Holocene aquifer sediment in our study area (Gavreli, unpublished data) and at other sites in Bangladesh (Ahmed et al., 2004; Nickson et al., 2000; Sracek et al., 2001). The groundwater Fe were supersaturated to siderite and vivianite at 5 sites in Araihazar suggest that processes releasing Fe is recent and probably ongoing because solutions can not remain at supersaturated state forever.

While As and P release were coupled in shallow groundwater > 5 yrs old (Chapter 3), phosphate was found to be supersaturated with respect three minerals. The results suggest that processes releasing P to the groundwater are recent and probably ongoing. Processes releasing P to groundwater include remineralization of organic matter and reductive dissolution or reduction of Fe oxides. This implies that process that release As could also be recent and ongoing.

## *5.7. Conclusions*

This study confirms that reducing conditions are key to the mobilization of As in Bangladesh shallow aquifer, where most of the As species exist as arsenite. However, As concentrations are significantly decoupled from Fe and P, in part because Fe and P concentrations are regulated by several mineral precipitation reactions. The supersaturation of Fe and P with respect to these minerals, however, indicates that processes release them are recent or even ongoing. And this implies that mobilization of As is also an ongoing process in the subsurface.

The Holocene shallow and deep aquifers are of Ca-Mg-$HCO_3$ type while the Pleistocene deep aquifer is of Na-K-$HCO_3$ type. Sulfate is a very minor component of all groundwater. In addition, there is a remarkable difference in several nutrients, especially between the Holocene shallow aquifer and the Pleistocene deep aquifer. Future studies of the implication of the nutrient contrast on As mobility in both aquifers and viability of deep aquifer as a drinking water source are much needed.

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## 5.9. References

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