



**KTH Architecture and
the Built Environment**

**ARSENIC IN ALLUVIAL AQUIFERS IN THE
MEGHNA BASIN, SOUTHEASTERN
BANGLADESH: HYDROGEOLOGICAL AND
GEOCHEMICAL CHARACTERISATION**

Md. Aziz Hasan

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Cover Illustration:

Top left: Hand pumped tube well (HTW) used in the rural areas of Bangladesh; *Top right:* Nest of piezometers installed in the study area (*Photographs:* Mattias von Brömssen© 2003); *Bottom left:* Reduced grey aquifer sand; *Bottom right:* Oxidised sand lens in clays (*Photographs:* Md. Aziz Hasan© 2006)

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Doctoral Thesis
KTH-International Groundwater Arsenic Research Group
Department of Land and Water Resources Engineering
Royal Institute of Technology (KTH)
SE-100 44 STOCKHOLM, Sweden
E-mail: hasanma@kth.se

Department of Geology
University of Dhaka
Dhaka-1000, Bangladesh
E-mail: mahasan@univdhaka.edu

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Dedicated to my parents ...

ABSTRACT

Elevated levels of arsenic (As) in Bangladesh groundwater has emerged as a massive calamity exposing a large population to the risk of As toxicity from drinking water sources and agricultural products. Holocene alluvial aquifers in the delta- and flood-plains of the Ganges-Brahmaputra-Meghna (GBM) river systems are severely affected by high levels of As in groundwater. Groundwaters abstracted from Holocene alluvial aquifers of shallow depth (<150 m) contain As at concentrations mostly above WHO provisional drinking water guideline value of 10 µg/l whereas groundwater from the Holocene deeper aquifers (usually >150 m) and the Plio-Pleistocene aquifers contain low-As (<10 µg/l) water.

The study reveals that the local and regional scale variations in groundwater composition, levels of As concentrations and the redox conditions are governed by the geological attributes of the aquifers. Groundwater in the grey to dark grey argillaceous sediments where organic matter and micas are abundant contain high concentration of dissolved As. Concentrations of As is generally low in the groundwater abstracted from the light grey to yellowish brown arenaceous sediments. A major proportion of As in the dark grey sediments is bound to poorly crystalline and amorphous metal-oxyhydroxides, particularly Fe-oxyhydroxides, that are readily mobile. On the other hand, As concentrations in the light grey to yellowish brown sediments are low and predominantly bound to less mobile stable crystalline phases. Redox reactions linked to the degradation of organic matter are the potential mechanism of As mobilisation through reductive dissolution of Fe-oxyhydroxides in grey to dark grey sediments in the Holocene shallow aquifers. This is reflected in groundwater composition that is characterised by high concentrations of As, HCO₃⁻, Fe and dissolved organic carbon (DOC). However, concentration of dissolved Fe is probably controlled by the precipitation of secondary Fe-minerals like siderite (FeCO₃), vivianite [Fe₃(PO₄)₂·8H₂O] and pyrite (FeS₂). Weathering of biotite [K (Fe, Mg)₃ AlSi₃O₁₀ (F, OH)₂] is one of the major sources of Fe-oxyhydroxides in the sediment and thus plays a significant role in the processes of As mobilisation in groundwater.

High concentrations of As and salinity are the major constraints for groundwater development in the Holocene alluvial aquifers of the Meghna basin. The Holocene shallow aquifers (<150 m) are high in dissolved As and salinity, while the Holocene deeper aquifers (>150 m) are low in As but contains pockets of saline groundwater. Molar ratios of Cl⁻/HCO₃⁻ and Na⁺/Cl⁻ indicate mixing of relict seawater with the freshly recharged water in these aquifers. Groundwater abstracted from the Pliocene Dupi Tila aquifer located at relatively higher elevations along the eastern part of the Meghna basin is not affected by As and salinity. Stable hydrogen (δ²H) and oxygen (δ¹⁸O) isotopes indicate relatively fast groundwater recharge rate with insignificant evaporation effect in the Meghna basin. The groundwater samples from shallow aquifers show relatively wider variations in isotopic composition than the deeper ones indicating multiple recharge regimes.

Abstraction of groundwater from the Holocene deeper low-As aquifers for drinking purposes should thus be properly guided to minimise the risk of cross-contamination and installation of high-capacity irrigation wells in the deeper aquifers must be avoided for sustainable drinking water supplies.

Key words: Alluvial aquifer, groundwater, arsenic mobilisation, geology, Meghna basin, Bangladesh

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Md. Aziz Hasan

Stockholm, November 2008

LIST OF PAPERS

Papers included in the thesis

Paper I

Ahmed, K.M., Bhattacharya, P., **Hasan, M.A.**, Akhter, S.H., Alam, M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A., Sracek, O. (2004). Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Applied Geochemistry* 19(2): 181–200.

Paper II

Hasan, M.A., Ahmed, K.M., Sracek, O., Bhattacharya, P., von Brömssen, M., Broms, S. Fogelström, J., Mazumder, M.L., Jacks, G. (2007) Arsenic in shallow groundwater of Bangladesh: investigations from three different physiographic settings. *Hydrogeology Journal* 15: 1507–1522.

Paper III

Hasan, M.A., von Brömssen, M., Bhattacharya, P., Ahmed, K.M., Sikder, A.M., Jacks, G., Sracek, O. (2008). Geochemistry and mineralogy of shallow alluvial aquifers in Daudkandi upazila in the Meghna flood plain, Bangladesh. *Environmental Geology* (In press) doi:10.1007/s00254-008-1319-8.

Paper IV

Hasan, M.A., Bhattacharya, P., Sracek, O., Ahmed, K.M., von Brömssen, M., Jacks, G. (2008). Hydrogeochemical evaluation of groundwater along an E-W transect in the Meghna Basin, Bangladesh (Manuscript).

Papers not included in the thesis

Paper V

Bhattacharya, P., Ahmed, K.M., **Hasan, M.A.**, Broms, S., Fogelström, J., Jacks, G., Sracek, O., von Brömssen, M. & Routh, J. (2006) Mobility of arsenic in groundwater in a part of Brahmanbaria district, NE Bangladesh In: Naidu, R., Smith, E., Owens, G., Bhattacharya, P. & Nadebaum, P. (Eds.) *Managing Arsenic in the Environment: From soil to human health*. CSIRO Publishing, Melbourne, Australia, pp. 95-115. (ISBN: 0643068686).

Paper VI

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Paper VII

Mukherjee, A., von Brömssen, M., Scanlon, B.R., Bhattacharya, P., Fryar, A.E., **Hasan, M.A.**, Ahmed, K.M., Chatterjee, D., Jacks, G., Sracek, O. (2008) Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the Western (Bhagirathi sub-basin, India) and Eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin. *Journal of Contaminant Hydrology* 99(1-4): 31-48. (doi:10.1016/j.jconhyd.2007.10.005).

Paper VIII

Bhattacharya, P., von Brömssen, M., **Hasan, M.A.**, Ahmed, K M., Jacks, G., Sracek, O., Huq, S.M.I., Naidu, R., Smith, E., Owens, G. (2008). Arsenic mobilisation in the Holocene flood plains in Southcentral Bangladesh: Evidences from the hydrogeochemical trends and modeling results. In: Bhattacharya, P., Ramanathan, A.L., Mukherjee A.B., Bundschuh, J., Chandrasekharam, D. & Keshari, A.K. (eds.) *Groundwater for Sustainable Development: Problems, Perspectives and Challenges*. Taylor and Francis/A. A. Balkema, The Netherlands: 283-299.

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INTRODUCTION

Background

Bangladesh is one of the most densely populated countries of the world with over 140 million people living in an area of 147,570 km² (BBS, 2007). Geographically it is located at the tip of the Bay of Bengal (Fig. 1) and constitutes major part of the Bengal Basin, the largest sedimentary basin of the world. The Bengal Basin receives about one billion tons of sediment loads per year (Goodbred *et al.*, 2003) carried by the mighty Ganges-Brahmaputra-Mehgna (GBM) river system from the Himalayan and Indo-Burman range (Uddin & Lundberg, 1998). The Basin accommodates one of the largest delta complexes of about 16 km thick sedimentary sequence covering an area of more than 200,000 km² (Uddin & Lundberg, 1999).

Bangladesh is broadly divided into three major physiographic terrains, *viz.* the Tertiary Hills in the east, southeast and north-northeast; the Pleistocene Barind and Madhupur Terraces in the central north and Holocene plains in the remaining areas (Fig. 2a). The Holocene alluvial and fan deposits and Pliocene Dupi Tila sands are the major aquifers in the country. The aquifers are highly transmissive and generally multi-layered. About 97% of the population relies on groundwater for drinking purposes and more than 75% of total irrigation coverage is provided by the same source. An estimated 8-10 million hand pumped tube wells (HTWs) serves the drinking and household water supply and about 730,000 irrigation wells (IW) are operating in the rural areas of Bangladesh (BADC, 2002).

High concentrations of dissolved arsenic (As) in tube well water were first reported in West Bengal province of India back in 1978 (Goriar *et al.*, 1984; Guha *et al.*, 1988; Acharyya *et al.*, 1999). Later in 1993, Department of Public Health Engineering (DPHE) reported the presence of high As in groundwater of Bangladesh. Since then As has been detected in groundwaters in 60 of total 64 districts of

Bangladesh above WHO provisional guide line value of 10 µg/l (WHO, 2004) by the national surveys (BGS/DPHE, 2001; BAMWSP, 2002). The spatial distribution map of As in groundwater prepared by the British Geological Survey (BGS) and DPHE (BGS/DPHE, 2001) depicts that occurrence high As is mostly restricted to geologically young alluvial aquifers in the flood plains and delta plains of GBM river system (Fig. 2b).

Recent estimations suggest that nearly 85 million people are exposed to As toxicity through drinking groundwater in the Bengal Basin regions of Bangladesh and India (Michael & Voss, 2008). Long-term exposure to As in drinking water above permissible limit results in skin ailments termed arsenicosis that include melanosis, keratosis, and progressively leads to cancers of the skin and other organs, and may ultimately cause death (UN, 2001; Kapaj *et al.*, 2006). Despite the fatal health consequences, people in the rural areas are compelled to drink As contaminated groundwater as the surface water has greater risk of pollution with pathogens and other inorganic pollutants. The cost of treatment involved for purification of surface water is not affordable by the poor rural people. This has created a massive public health problem in this region and there are reports of over 100,000 arsenicosis patient in Bangladesh (Smith *et al.*, 2000; Charlet & Polya, 2006). Apart from health problem through drinking high As groundwater, irrigation with groundwater is also under threat as there are reports of significant intake As through food chain from rice and other vegetables (Farid *et al.*, 2003; Meharg & Rahman, 2003; Correll *et al.*, 2006; Huq *et al.*, 2006).

Arsenic in the environment

Arsenic, a toxic metalloid, occurs naturally in the earth's crust in elemental state or as compounds. Concentration of As is typically low (1-5 mg/kg) in igneous and metamorphic rocks but slightly high (5-10 mg/kg) in soils and sedimentary rocks (Bhattacharya *et al.*, 2002a; Smedley and Kinniburgh, 2002). More than 200 As bearing minerals are found

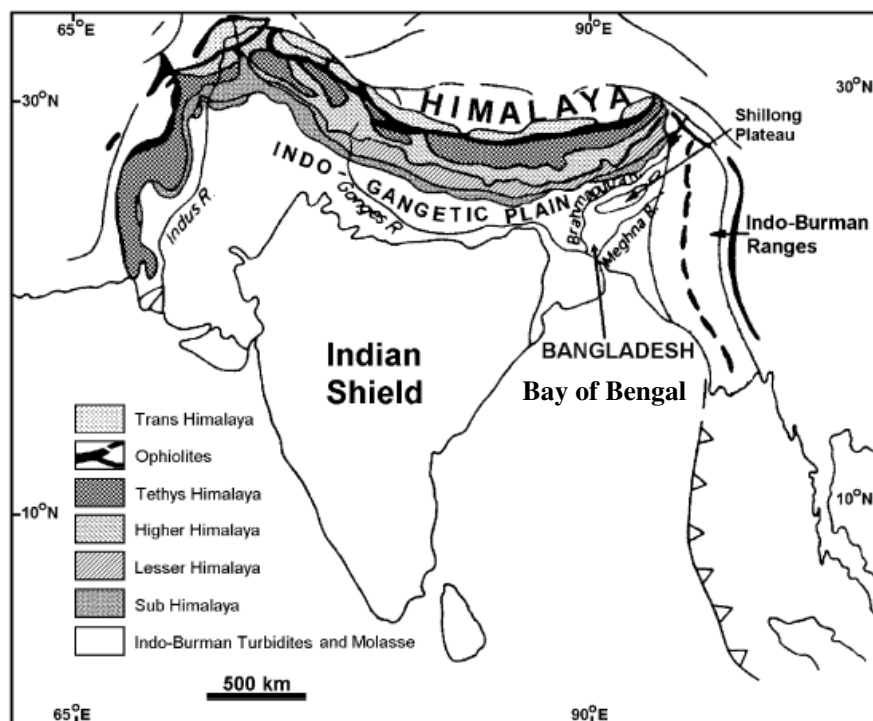


Figure 1. Regional geological setting of the Bengal Basin (after Uddin & Lundberg, 1998).

in the crustal rocks in different form such as sulphides, oxides, arsenates, arsenites etc. and of which the sulphides, specially arsenopyrite (FeAsS) and As bearing pyrite (FeS_2) are most common. Arsenic is released in the environment e.g. in air, water and soil either from natural sources through volcanic activity and weathering of As-bearing minerals or by human activities such as mining, smelting, burning coals, use of pesticides, herbicides, wood preservatives and discharge from other chemical industries. Weathering of minerals in the crustal rocks, in particular oxidation of primary sulfide minerals is the main source of As in sediments and soils (Bhattacharya *et al.*, 2002a; Smedley & Kinniburgh, 2002).

Naturally occurring As is generally leached into the groundwater system by the interaction of water with rocks, minerals and soils in different geological, hydrogeological and geochemical environment. Concentration of As in groundwater varies over a wide range from less than a microgram to several hundred microgram per litre with a typical concentration of less than 10 microgram per litre. High concentrations of As ($>10 \mu\text{g/l}$) in

groundwater from natural geological source is reported from many parts of the world such as Bangladesh, India, Nepal, Pakistan, China, Myanmar, Cambodia, Vietnam, Taiwan, Iran, Mongolia, Hungary, Romania, Ghana, Nigeria, Nicaragua, Argentina, Chile, Bolivia, Peru, Mexico, Australia, Canada and United States of America (Bhattacharya *et al.*, 1997, 2002a, 2006b; Welch *et al.*, 2000; BGS/DPHE 2001; Mandal & Suzuki, 2002; Nickson *et al.*, 2005; Bundschuh *et al.*, 2006; Berg *et al.*, 2007; O'Shea *et al.*, 2007; Mukherjee *et al.*, 2008a).

Geochemistry and mobility of arsenic

Arsenic occurs in both inorganic and organic forms in natural geochemical environments. Organic forms of As contain carbon and hydrogen while inorganic As usually occurs in combination with other element like oxygen, sulphur etc. Unlike other toxic metals such as lead (Pb), copper (Cu), cobalt (Co) that occurs as cations (positively charged ions) in the aqueous environment, inorganic As occurs as oxyanions (negatively charged ions combined with oxygen) typically in the form of trivalent arsenite [As(III)] or

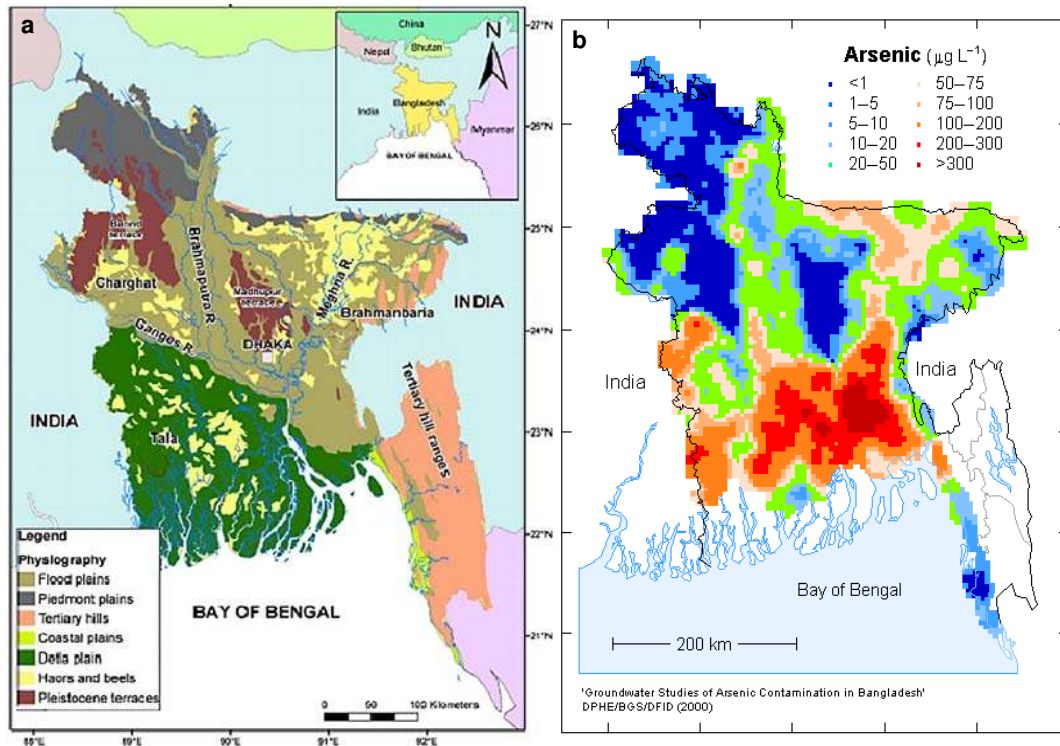


Figure 2. a) Major physiographic divisions of Bangladesh and b) spatial distribution of arsenic in groundwater (BGS/DPHE, 2001).

pentavalent arsenate [As(V)] species. Arsenite is generally more mobile and toxic as compared to As(V) (Korte & Fernando, 1991). However, some of the recent studies have indicated that As(V) is reduced into As(III) in the human body (Meliker & Nriagu, 2007). Thus, exposure to both inorganic species of As are equally toxic for humans. Further, As may exist in two more oxidation states (-3 and 0) in the environment.

The distribution of different As species in the aqueous system is presented in the Eh-pH diagram (Fig. 3). In natural groundwater, arsenic acid ($\text{H}_3\text{As}^{\text{V}}\text{O}_4$) and its protonated forms dominate under oxidizing environments, while arsenious acid ($\text{H}_3\text{As}^{\text{III}}\text{O}_3$) dominates in reducing environments (Fergusson & Gavis, 1972; Schnoor, 1996; Mukherjee & Bhattacharya, 2001; Mandal & Suzuki, 2002; Smedley & Kinniburgh, 2002). Organic forms of As are not common in the environment and thus of less concern from public health point of view (Meliker & Nriagu, 2007).

Occurrence of natural As in groundwater is not only dependent on the As concentrations in soils and sediment but also controlled by the adsorption/desorption processes and redox reactions (Bhattacharya *et al.*, 2002a; Sracek *et al.*, 2004; Polizzotto *et al.*, 2006). Metal (Fe, Mn and Al)-oxyhydroxides, in particular Fe(III)-oxyhydroxides are the most common adsorbents for anions including As in the soils and sediments (Sullivan & Aller, 1996; van Geen *et al.*, 2004; Meharg *et al.*, 2006; Mitsunobu *et al.*, 2008). Inorganic As-oxyanions are usually adsorbed onto the reactive surface of metal-oxyhydroxides by inner-sphere complexation (Fendorf *et al.*, 1997; Manning *et al.*, 1998; Goldberg & Johnston, 2001; Gustafsson & Bhattacharya, 2007).

Reduction of these metal-oxyhydroxides is crucial for mobilisation of As into the groundwater system. Presence of organic matter in the sediment plays a vital role for redox reactions in a sediment-water system (McArthur *et al.*, 2004; Meharg *et al.*, 2006). Degradation of organic matter by micro-organisms releases electrons which reduces

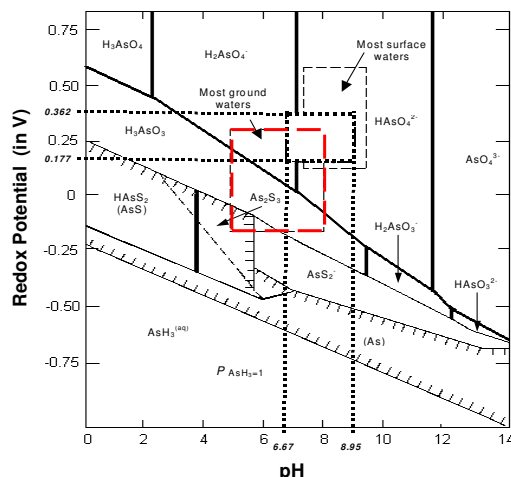


Figure 3. Eh-pH diagram for As at 25°C and 1 bar with total As 10.5 M and total S 10⁻⁵ M. (Adapted from Fergusson and Gavis, 1972; Schnoor, 1996).

Fe(III)-oxyhydroxides to soluble Fe²⁺ and thereby releases the adsorbed As (Drever, 1997; Rowland *et al.*, 2007; Postma *et al.*, 2007).

Mobilisation of As into the groundwater of shallow alluvial aquifers in the Bengal Basin by reductive dissolution of Fe(III)-oxyhydroxides in presence of organic matter is well documented and widely accepted as the principal mechanism (Bhattacharya *et al.*, 1997, 2001, 2002a,b, 2006a; Nickson *et al.*, 1998, 2000; BGS/DPHE, 2001; McArthur *et al.*, 2001; Smedley & Kinniburgh, 2002; Dowling *et al.*, 2002). However, apart from Fe(III)-oxyhydroxides, other metal oxyhydroxides such as manganese (Mn), aluminum (Al) and phyllosilicates like biotite and clay minerals may also play an important role in As cycling and mobilisation (Foster *et al.*, 2000; Breit *et al.*, 2001; Kent & Fox, 2004; Saunders *et al.*, 2005; Chakraborty *et al.*, 2007; Seddique *et al.*, 2008). Mobilisation of As due to oxidation of pyrite (Chowdhury *et al.*, 1999) and widespread application of phosphate fertilizer (Acharyya *et al.*, 2000) are not consistent with the geological and geochemical evidences revealed by several studies (Bhattacharya *et al.*, 1997, 2001; Nickson *et al.*, 2000; BGS/DPHE, 2001; Harvey *et al.*, 2002; Zheng *et al.*, 2004; Swartz *et al.*, 2004; Ahmed *et al.*, 2004; Hasan *et al.*, 2007; Mukherjee *et al.*, 2008b).

Research objectives

The overall objectives of the research were to enhance the current knowledge base on the occurrence, source and mobilisation of As into the groundwater of Bangladesh, with special emphasis on the Meghna basin in southeastern Bangladesh. The specific objectives of the study were to:

- i) evaluate the local and regional scale variability in groundwater composition and As concentration in Bangladesh;
- ii) compare the groundwater chemistry and factors controlling mobilisation of As in the aquifers at different physiographic settings of Bangladesh;
- iii) identify lithofacies sequences, and geochemical and mineralogical characterisation of the sediments to determine the mode of As occurrences and its mobilisation into groundwater;
- iv) assess the changes in groundwater chemistry along a basinal transect to understand the control of geology and hydrogeology on the hydrogeochemical processes in relation to As and salinity in the groundwater; and
- v) integrate the hydrogeological and geochemical characteristics of the sedimentary aquifers as a tool for management of groundwater resources for drinking water supply.

The study area

Location and climate

The study area that covers the middle Meghna basin, lies east of the river Meghna with an aerial extent of about 1500 sq. km (Fig. 4). The area is characterised by low-lying delta plains and flood plains with meander channels, meander scrolls, natural levee and back swamps formed by the river Meghna and its tributaries with elevations ranging between 1-4 m above sea level. The alluvial aquifers in the delta and flood plains of the Meghna basin is one of the most severely affected areas of Bangladesh where 60-90% of HTWs are pumping water with As above Bangladesh drinking water standard (BDWS) of 50 µg/l (BGS/DPHE, 2001; BAMWSP, 2002).

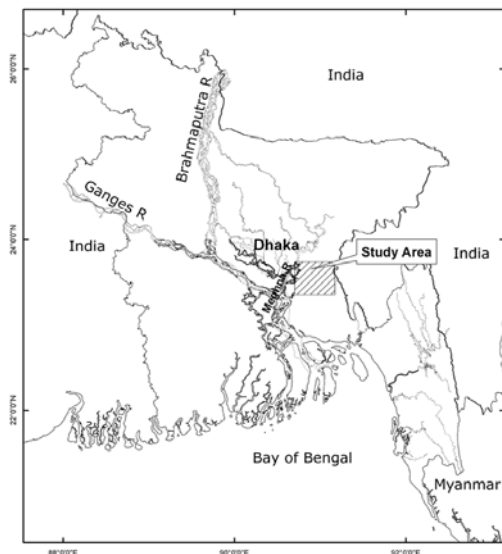


Figure 4. Location map of the study area.

The study area experiences three major climatic seasons viz. a hot summer (March–May), followed by monsoon or rainy season (June–October) and a moderate winter season (November–February) like other parts of Bangladesh. The temperature gradually rises from 10°–12°C in winter to a maximum of about 36°C in summer. The average annual rainfall in and around the study area is over 2,500 mm (according to Bangladesh Meteorology Department) and about 95% of its total rainfall is received during May to October (wet period) and rest 5% of rainfall is received during November to April (dry period).

Geology and hydrogeology

The Quaternary sediments, composed of sand, silt and clay, constitute the surface geology of the study area. The sediments are heterogeneous in both texture and mineral composition. The unconsolidated alluvial sands of Holocene age form the aquifer system in the delta plains and flood plains in the western part of the area while older Pliocene Dupi Tila sands that occurs at shallow depth in the elevated eastern part serves as the main aquifer. The aquifers are unconfined to leaky confined in nature. Groundwater occurs mostly within 5 m below ground level (bgl) and water level fluctuates between 2 and 6 m with annual

recharge–discharge conditions maintaining the hydrodynamic equilibrium. However, the extent of fluctuation varies widely depending on the intensity of irrigation withdrawal of groundwater.

MATERIALS AND METHODS

The papers discussed in the thesis are based on the literature survey, review of existing data, collection and laboratory analyses of groundwater and sediment samples. The groundwater analyses include measurements of on-site parameters, major ions (cations and anions), trace elements, speciation of As and stable isotopic compositions. The investigations on the aquifer sediment include sedimentological, mineralogical and geochemical analyses of undisturbed samples (core samples) collected from As affected areas at different depths.

Arsenic in the alluvial aquifers of Bangladesh (Paper I)

A state of the art overview of the status of As in groundwater of Bangladesh is presented in *Paper I* and essentially describes the previous works carried out by various organisations, scientists and research projects of the KTH-International Groundwater Arsenic Research Group between 1999-2004. The paper discusses occurrences of As in major geomorphic and stratigraphic units of Bangladesh. Groundwater and sediment samples were collected from 14 selected As affected aquifers across the country. Sediment investigations include lithofacies and provenance analyses, bulk mineralogy under petrographic microscope and selective extraction of As, Fe, Mn, Al, P and S in the sediment samples. Groundwater samples were analysed for major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- and HCO_3^-), minor ions (PO_4^{3-} , NH_4^+), dissolved organic carbon (DOC), trace elements (As, Fe and Mn) and determination of As(III) and As(V). Hydrochemical modelling for calculations of saturation index of selected minerals in the groundwater was also carried out.

Investigations from three physiographic units (*Paper II*)

Paper II addresses variability in groundwater composition and As from shallow aquifers in different physiographic settings. Detailed hydrochemical analyses was carried out on 94 groundwater samples collected from three upazilas (subdistricts) located at three physiographic units viz. Ganges flood plain (GFP) Meghna flood plain (MFP) and Ganges delta plain (GDP) at Charchat, Rajshahi district, Brahmanbaria Sadar in the Brahmanbaria district, and Tala, Satkhira district respectively. The overall objective of this study was to establish the basic hydrogeochemical attributes and to relate the groundwater chemistry and As mobilisation in the shallow aquifers with varying nature of sedimentation and depositional environment. Groundwater analyses include major ions, minor ions, DOC, trace elements and speciation of As mentioned in the previous section. Groundwater chemistry data was used to identify hydrochemical facies and the correlation between various redox sensitive parameters. Speciation modelling was carried out using PHREEQC (Parkhurst & Appelo, 1999) to evaluate the solubility control of dissolved Fe and Mn species. Thermodynamic data for As were taken from the data base of the program MINTEQA2 (Allison *et al.*, 1991).

Geochemistry and mineralogy of shallow aquifers in the Meghna flood plain (*Paper III*)

Paper III deals with geochemical analyses of sediments (core samples) and groundwater of the shallow alluvial aquifers along a depth profile in Daudkandi upazila in the Meghna flood plain. The aim was to investigate the relationship between aqueous and solid phase geochemistry, in order to highlight the geological controls of As mobilisation in the shallow aquifers. An operationally defined 4-step sequential extraction was carried out on the sediment samples to quantify As, Fe, Mn and Al bound to carbonates (sodium acetate extractable); poorly crystalline and amorphous metal (Fe, Mn, Al)-oxyhydroxides (ammonium oxalate extractable); sulphides

plus organic matter (hydrogen peroxide extractable) and residual (nitric acid extractable) phases. The analyses of sediment also include determination of total organic carbon (TOC), quantification of major elements by x-ray fluorescence (XRF) spectroscopy and identification of primary and secondary mineral phases by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

Hydrogeochemistry along an E-W transect in the Meghna basin (*Paper IV*)

This paper adopts a comprehensive approach to delineate the aquifer geometry, hydrogeological condition, overall groundwater quality and hydrogeochemical processes active in the shallow and deep aquifer systems in the Meghna basin. A total of 160 groundwater samples of different depth ranges (12-303 m) from 6 upazilas of Comilla district were analysed. Emphasis has been given to depict the changes in groundwater chemistry with subsurface geology i.e. change in lithofacies along a transect from east to west in the study area stretching about 50 km (Fig. 5). An E-W geological cross-section was prepared from existing lithologs to see the change in lithofacies. Groundwater chemistry data was interpreted to show the variations in hydrochemical facies, hydrogeochemical processes, salinity and As concentrations with

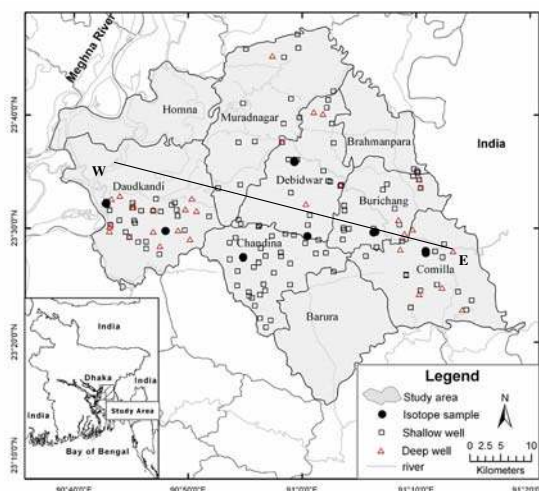


Figure 5. Map of the middle Meghna basin, showing the groundwater sampling locations, geological section line (E-W).

the change in geology both vertically and laterally along the transect.

Stable oxygen and hydrogen isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were also determined to understand the groundwater recharge process between the shallow and deep aquifers along the transect.

RESULTS

Arsenic in groundwater of Bangladesh and its relation to geology

Concentrations of As in the groundwater of Bangladesh vary over the major physiographic and stratigraphic units with different sedimentation history and depositional environment. Geologically younger Holocene alluvial aquifers in the plain lands are found most affected by groundwater As contamination in comparison to the aquifers in the older Pleistocene uplands and Tertiary Hills which are least affected. Shallow alluvial aquifers in delta plains and flood plains of the GBM river system are severely contaminated where 60-80% HTWs are affected. The aquifers in the coastal plains are also highly

contaminated with As. However, the Holocene alluvial fan deposits (Piedmont plains) are characteristically low in groundwater As where less than 20% HTWs are contaminated (*Paper I*). Maximum As concentrations occur at depths between 20 and 50 m whereas samples shallower than 10 m and deeper than 150 m are very low in As. (BGS/DPHE, 2001, Ahmed *et al.*, 2004). However, reports of low level As at shallow depths (<150m) (van Geen *et al.*, 2002; von Brömssen *et al.*, 2007) suggest that the distribution of groundwater As is not controlled only by the depth factor but by the subsurface geology and redox conditions of the aquifers.

Lithofacies and provenance analyses

The vertical lithofacies sequence prepared from the lithological logs of shallow depth collected from exploratory boreholes done by Bangladesh water development board (BWDB) in various As affected areas show that the sediments are composed of sand, silty sand, silty clay and clay which can broadly be grouped into two distinct lithofacies association - a sandy channel-fill

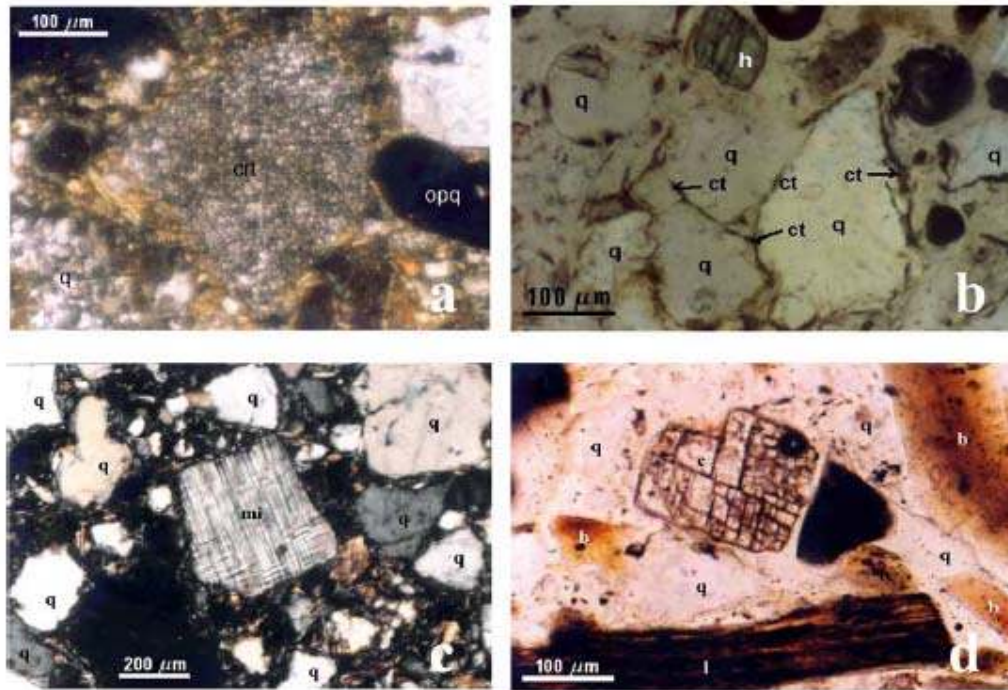


Figure 6. Photomicrographs of aquifer sands in thin sections (a) abundance of matrix; (b) thick and discontinuous coating on quartz; (c) thin and partial coating on silicate grains; (d) abundance of altered biotite and few non-opaque heavy minerals. (Abbreviations: ct: coating; q: quartz; mtx: matrix; c: calcite; b: biotite; g: garnet; t: tourmaline; h: hornblende).

association and a silty-clayey over bank association indicating fluvial environment of deposition (*Paper I*). The aquifer sands are mostly fine grained with variable matrix content (4–14%). Sands are typically composed of quartz (47–70%), lithic grains (4–17%), mica (muscovite and biotite, 2–15%), feldspar (1–8%) and chlorite (trace–8%) where biotite flakes show evidence of alteration. Quartz is mostly monocrystalline with minor polycrystalline type. The lithic grains are mainly of sedimentary and metasedimentary origin. Silicates, particularly quartz, show thick to thin ferruginous coatings (Fig. 6). Provenance analysis from quantitative detrital modes of quartz, feldspar and lithic grains suggests aquifer sands are derived from quartzite recycled orogen source (*Paper I*).

Salient geochemical trends

Groundwater chemistry

The pH of groundwater in the Bengal Basin is near neutral to slightly alkaline with low

dissolved oxygen (DO). The Eh values suggest a mildly oxidizing (positive value) to moderately strong reducing (negative value) character of the aquifers (*Paper I*). The groundwater is Ca–Mg–HCO₃ to Ca–Na–HCO₃ type. However, presence of Na–Cl type water has been reported in the coastal areas and in several other parts of the country (Ahmed, 1994; Bhattacharya *et al.*, 2002b, 2006a; Hasan *et al.*, 1997, Hoque *et al.*, 2003; Hasan *et al.*, 2007). Anion composition is generally dominated by HCO₃⁻ with very low amount of SO₄²⁻ and NO₃⁻. Chloride (Cl) concentrations are variable depending on location and depth of the aquifer. Phosphate (PO₄³⁻) concentrations on the other hand, are slightly high (up to 8.75 mg/l). Some variations are observed in the distribution of major cations (Ca²⁺, Mg²⁺ and Na⁺) with depth as well as region. Considerable variability is also noted in the levels of total As (2.5–846 µg/l), total Fe (0.4–15.7 mg/l) and Mn (0.02–1.86 mg/l) in the groundwater samples both as a function of depth and location. Arsenite, As(III), is the dominant

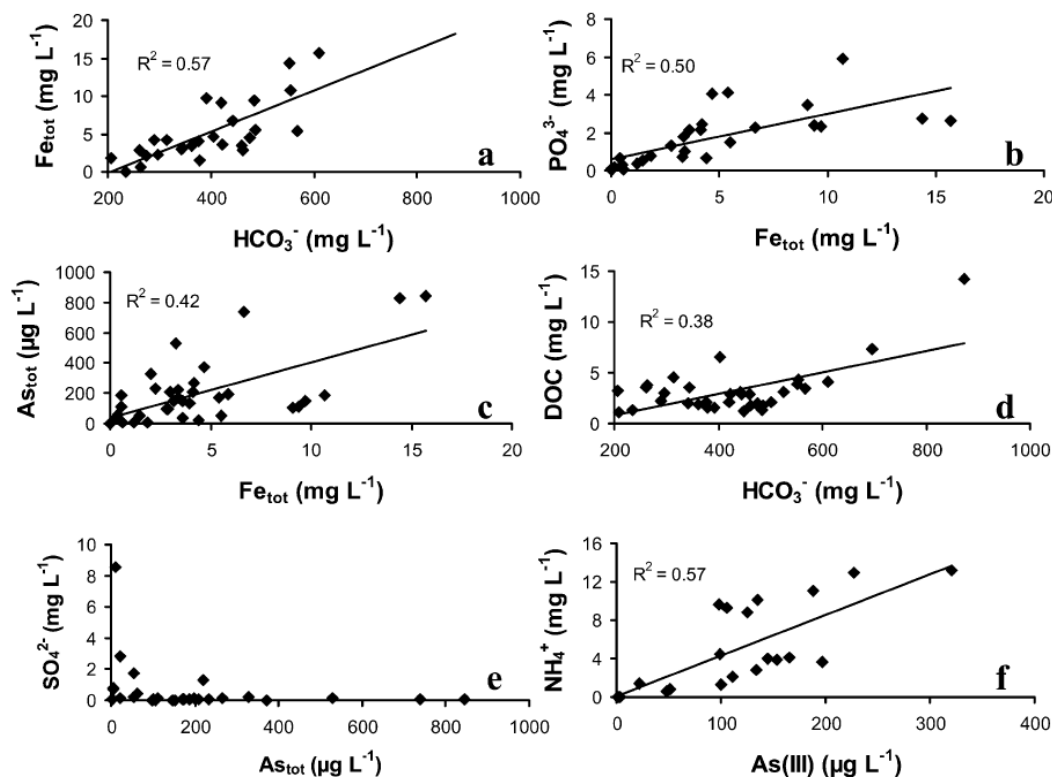


Figure 7. Trends for variations of the salient chemical parameters in the groundwaters of Holocene aquifers in Bangladesh and their relationship (a) HCO₃⁻ vs Fe_{tot}; (b) Fe_{tot} vs PO₄³⁻; (c) Fe_{tot} vs As_{tot}; (d) HCO₃⁻ vs DOC; (e) As_{tot} vs SO₄²⁻; and (f) As(III) vs NH₄⁺.

species in these groundwaters (67-99%). Iron shows moderately strong positive correlation with HCO_3^- and PO_4^{3-} but exhibits weak positive correlation ($r^2 = 0.42$) with As (Fig. 7a-c). Weak correlation between Fe and As may be due to precipitation secondary iron minerals like siderite (FeCO_3) and vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] (Nickson *et al.*, 2000; Sracek *et al.*, 2001; Ahmed *et al.*, 2004; Bhattacharya *et al.*, 2008; Itai *et al.*, 2008) that is indicated by saturation indices (SI) for siderite and vivianite in these groundwater (**Paper I**). Concentration of dissolved organic carbon (DOC) in the Holocene aquifers is relatively high (1.15-14.2 mg/l) and shows moderate correlation with HCO_3^- (Fig. 7d). Total As (As_{tot}) does not show any correlation with SO_4^{2-} (Fig. 7e) but a good correlation is observed between As(III) and NH_4^+ (Fig. 7f) in the groundwater samples.

Sediment chemistry

Selective extraction results of 16 sediment samples at different depths (3-132 m) from two boreholes in northern (Chapai Nawabganj) and one in southern (Tala) Bangladesh are presented in **Paper I**. Nitric acid (HNO_3) extractable As (As_{HNO_3}), Fe (Fe_{HNO_3}), Mn (Mn_{HNO_3}), Al (Al_{HNO_3}) and P (P_{HNO_3}) varied considerably with depth and lithology in the range of 0.5-17.7 mg/kg, 5.8 -26.5 g/kg, 0.05 - 0.5 g/kg, 3.8-19.1 g/kg and 0.16–0.51 g/kg respectively. The values are comparable with the total concentration of these elements determined by XRF analyses (BGS/DPHE, 2001). Concentrations of sulphur (S_{HNO_3}) vary 7.5 to 1306 mg/kg and peaks in the finer sediments with high organic matter. Ammonium oxalate extraction, on the other hand gives a quantitative estimation of the elements bound to poorly crystalline oxides and hydroxides (Bhattacharya *et al.*, 2001). Oxalate extractable fractions of these elements i.e. As_{ox} , Fe_{ox} , Mn_{ox} , Al_{ox} and P_{ox} ranged between 0.1 – 8.6 mg/kg, 0.4-5.9 g/kg, 0.005-0.45 g/kg, 0.1 - 1.32 g/kg and 0.005-0.144 g/kg respectively and also shows considerable variability with depth and lithology. Strong positive correlation of As_{ox} with Fe_{ox} , Mn_{ox} and Al_{ox} indicates mobilisation

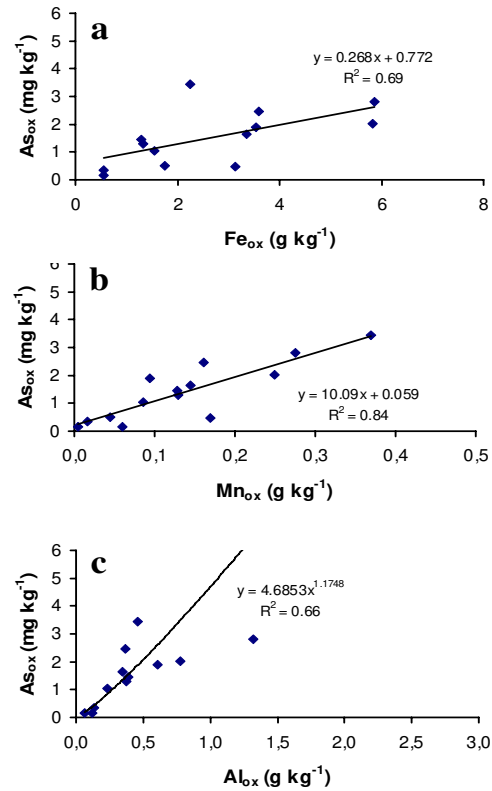


Figure 8. Variation in oxalate extractable arsenic (As_{ox}) with a) Fe_{ox} ; b) Mn_{ox} ; and c) Al_{ox} in the aquifer sediments.

of As through dissolution of metal-oxhydroxides (Fig. 8a-c).

Extraction with sodium acetate was performed to estimate the amount of Fe, Mn and P in the carbonate minerals like siderite, rhodochrosite and unstable phosphate mineral such as vivianite. Plots of As_{ox} against Fe_{acet} and $\text{Fe}_{\text{ox}} - \text{Fe}_{\text{acet}}$ as independent variables (**Paper I**) reveal clear association of As_{ox} with the Fe-oxhydroxide phase ($\text{Fe}_{\text{ox}} - \text{Fe}_{\text{acet}}$). Samples with relatively high Fe_{acet} fraction suggest presence of siderite and vivianite in the sediment.

Comparison of groundwater chemistry and arsenic concentration in three physiographic settings

Investigation from three physiographic settings viz. Ganges flood plain (GFP) in the north of the river Ganges, Meghna flood plain (MFP) in the east of the river Meghna and Ganges delta plain (GDP) in the south of the river Ganges shows considerable variations in groundwater chemistry and As

Table 1. Summary of the results of chemical composition of groundwater samples from the three physiographic domains GFP (Charghat), MFP (Brahmanbaria) and GDP (Tala)

Parameters	Charghat, Rajshahi District (n=36)			Brahmanbaria Sadar, Brahmanbaria District (n=29)			Tala, Satkhira District (n=29)		
	Min	Max	Median	Min	Max	Median	Min	Max	Median
Well depth (m)	15.2	79.2	36.3	18.3	75.6	29.0	24.4	62.5	48.7
Temp (°C)	26.2	27.5	27.5	25.7	27.1	26.3	26.4	28.9	27.8
pH	6.2	7.8	7.0	6.4	7.6	6.9	6.4	7.5	6.9
Eh (mV)	41	288	194.5	184	259	184	-40	210	-8
EC (µS/cm)	290	498	408	128	2,080	620	523	1300	719
HCO ₃ (mg/L)	191	339	267	74	663	412	328	567	422
Cl (mg/L)	1.5	34.7	3.1	4.0	519	15.4	9.0	148.2	39.5
NO ₃ (mg/L)	BDL	8.6	1.0	BDL	4.9	0.2	0.01	3.4	0.06
SO ₄ (mg/L)	BDL	12.4	1.6	BDL	34.4	0.5	BDL	3.6	BDL
PO ₄ (mg/L)	0.1	2.0	0.2	0.1	16.3	2.9	3.0	6.8	4.5
Na (mg/L)	6.9	48.5	17.9	4.6	574	39.2	10.9	45.9	20.0
K (mg/L)	0.7	6.5	1.65	0.8	26.3	6.8	2.2	20.7	4.7
Mg (mg/L)	7.1	47.8	20.6	4.3	73.3	27.3	17.3	41.2	24.6
Ca (mg/L)	8.1	74.6	42	11.5	93.3	41.8	70.6	130.9	86.1
NH ₄ (mg/L)	BDL	2.4	0.35	0.03	16.1	4.1	2.9	12.5	7.5
DOC(mg/L)	0.5	2.5	1.3	0.8	21.8	4.7	1.5	4.3	2.4
Fe (mg/L)	0.04	7.6	0.17	0.07	10.3	1.3	2.6	10.7	4.2
Mn (µg/L)	316	1648	875	3.3	1,218	41	57.3	214	83.2
As (µg/L)	1.2	600	3.7	2.0	439	115.5	68.6	186.6	128.1
As ³⁺ (µg/L)	BDL	341	2.6	BDL	302	53	44.2	138.2	94.6

BDL below detection limit

concentrations (*Paper II*). The Eh values (corrected with respect to standard hydrogen electrode) indicate low to moderate reducing conditions at GFP (+0.04 to +0.29 V) and MFP (+0.18 to + 0.26 V) sites but moderate to strong reducing condition at GDP (-0.4 to +0.21 V) site. Electrical conductivity (EC) varies considerably between the three sites; it is low (290–498 µS/cm) at GFP but relatively high (523–1,300 µS/cm) at GDP, which is probably due to tidal influence in the delta region. A wider variability in EC (128–2080 µS/cm) at the MFP site indicates presence of relict seawater (BADC, 1992; Hoque *et al.*, 2003). The groundwaters of GFP and GDP sites are dominantly Ca–Mg–HCO₃ type while that of MFP site are of mixed type with some wells with Na–HCO₃ type water.

A summary of the groundwater composition presented in Table 1 show significant variations among three sites. Concentrations of total iron (Fe), manganese (Mn) and other redox sensitive parameters such as DOC, HCO₃⁻, SO₄²⁻, NO₃⁻ and NH₄⁺ show distinct relationship with the total dissolved As in the groundwater (*Paper II*). Relatively high median concentrations of NO₃⁻ (1.0 mg/l), SO₄²⁻ (1.6 mg/l) and low NH₄⁺ (0.35 mg/l) at GFP site indicate a relatively elevated redox status of the aquifer system which is consistent with the low As (median value 3.7

µg/l), low Fe (median value 0.17 mg/l) and high Mn (median value 875 µg/l) in the groundwater. On the contrary, high median concentrations of NH₄⁺ (7.5 mg/l) and low NO₃⁻ and SO₄²⁻ together with high concentrations of As (median value 128 µg/l), Fe (median value 4.2 mg/l) and low Mn (median value 83.2 µg/l) suggest a strong reducing condition at the GDP site. Groundwater with low As and high Mn relative to Fe (Fig. 9) indicates preferential Mn(IV) reduction in the system that buffers redox condition (Drever, 1997; von Brömssen *et al.*, 2007; Hasan *et al.*, 2007). The samples from MFP site show wider variability in As concentrations as well as in other redox

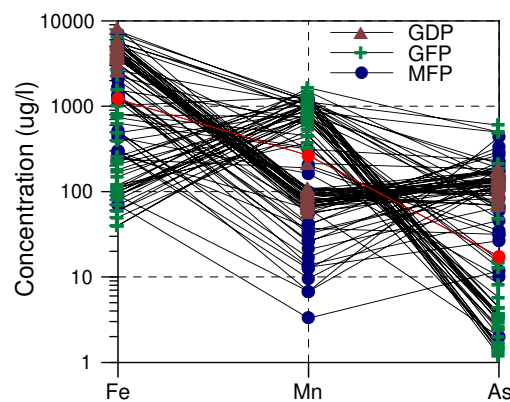


Figure 9. Relationship between the Fe, Mn and As in the groundwater.

sensitive parameters. Elevated levels of NH_4^+ in the reduced aquifers are most probably the result of dissimilatory reduction of NO_3^- (Appelo & Postma, 1999; Bhattacharya *et al.*, 2006a). Relatively higher concentrations of HCO_3^- and DOC at GDP and MFP sites (Table 1) further demonstrate the redox status of the aquifers. Degradation of organic matter in the Holocene alluvial aquifers of the Bengal Basin is linked to redox reactions and elevated level of HCO_3^- and DOC in the aquifers (Routh *et al.*, 2000; McArthur *et al.*, 2004; Bhattacharya *et al.*, 2002a,b, 2006a; von Brömssen *et al.*, 2007; Mukherjee & Fryar 2008).

Calculations of saturation indices (SI) show that the groundwater at GFP site is generally undersaturated with respect to siderite but at near equilibrium to supersaturated with respect to rhodochrosite. The SI value of rhodochrosite is negative but that of siderite is positive for all the samples at GDP site. Most samples are at equilibrium or supersaturated with respect to siderite but undersaturated with respect to rhodochrosite at MFP site. Many of the samples at GDP site and some at MFP site are also supersaturated with respect to vivianite (*Paper II*).

Vertical geochemical profile and mobility of As

Vertical geochemical profile of groundwater and sediment samples from a shallow alluvial aquifer of Daudkandi upazila in the Meghna flood plain depicts that the subsurface geology i.e. texture, mineral composition and organic matter content in the sediment controls concentration and mobilisation of As in the groundwater (*Paper III*). The undisturbed sediment samples (core samples) show variations in colour, texture and organic matter content (Fig. 10). The uppermost aquifer (<6.5 m depth) is yellowish grey in colour while the aquifer below is grey to dark grey in colour with layers rich in organic matter and mica.

Vertical profiles of groundwater chemistry show (Fig. 11) that the upper part of the aquifer, which is yellowish grey in colour, has intermediate redox potential as indicated by

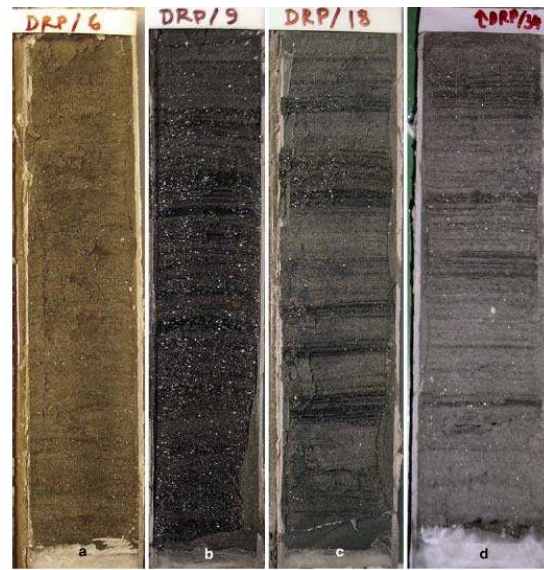


Figure 10. Photograph of core samples showing a) upper yellowish grey sand; b) lower dark grey micaceous sand rich in OM; c and d) grey sand with layers of OM.

low concentrations of As, Fe and HCO_3^- but relatively high Mn, SO_4^{2-} and NO_3^- . The lower part of the aquifer that is grey to dark grey in colour and contains organic matter and mica is high in As (>10 $\mu\text{g/l}$) coupled with high Fe and HCO_3^- . It shows low Mn concentration compared to Fe and very low SO_4^{2-} and NO_3^- . Microbially mediated degradation of organic matter in the lower grey to dark grey sediments has most probably initiated the redox reactions and subsequent dissolution of Fe(III)-oxyhydroxides as evidenced from elevated

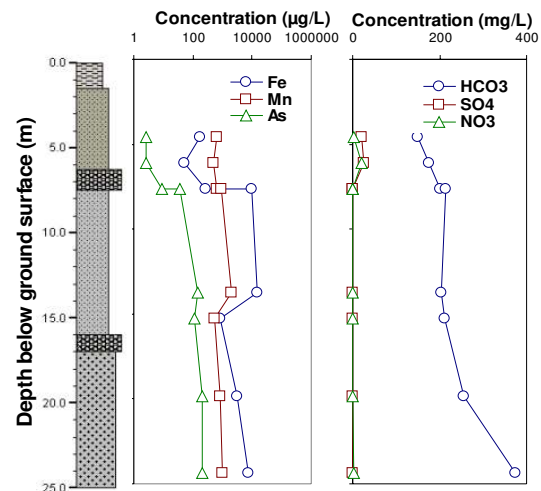


Figure 11. Vertical profile of the concentrations of As and other redox sensitive parameters in groundwater.

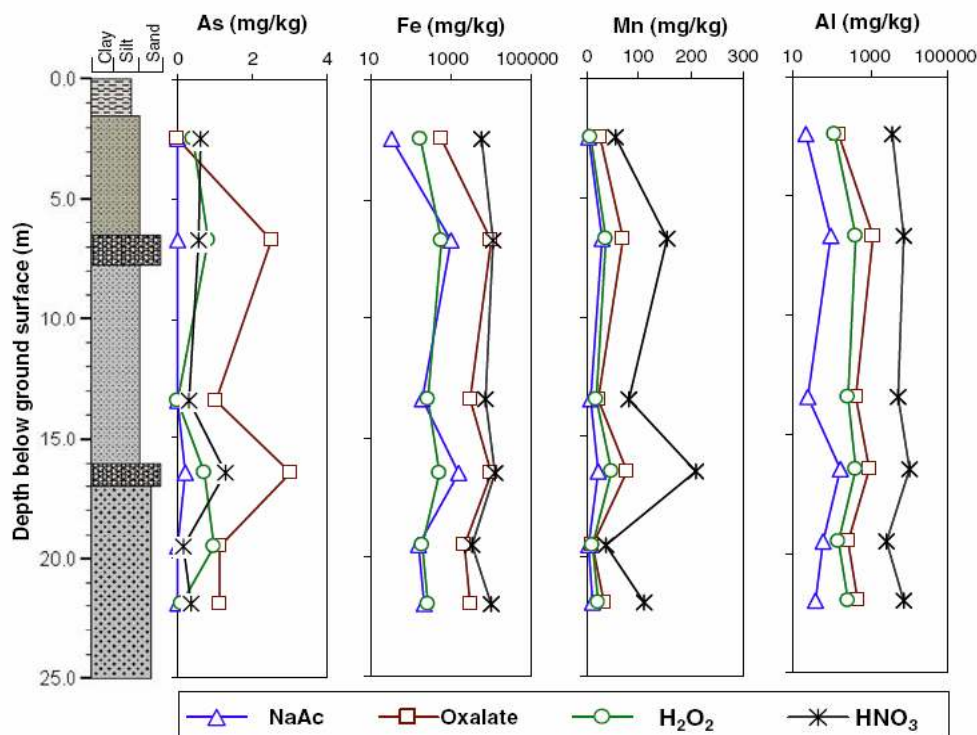


Figure 12. Depth profiles of extractable phases of As, Fe, Mn and Al in the sediments.

levels of dissolved Fe, As and HCO_3^- .

Depth profiles of sequential extraction data (Fig. 12) reveals that As bound to poorly crystalline and amorphous metal (Fe, Al, Mn)-oxyhydroxides i.e. oxalate extractable As (As_{ox}) are dominant in the grey to dark grey sediment. Maximum concentration of As_{ox} (3.05 mg/kg) is observed in the mica and organic matter rich dark grey sediment. On the contrary, As_{ox} is very low in the upper most yellowish grey sediment where the residual phase, which is not easily mobilised, constitutes the bulk of As (0.62 mg/kg) concentrations. Arsenic bound to sulphide and organic matter ($\text{As}_{\text{H}_2\text{O}_2}$) also peaks in the dark grey sediment rich in organic matter. However, As association with carbonate phase (As_{NaAc}) is not detected in any of the samples except in the dark grey sediment (0.21 mg/kg) at 16.46 m depth. Correlation of As_{ox} with Fe_{ox} , Mn_{ox} and Al_{ox} suggest very strong association of As with the Fe-oxyhydroxide phase ($R^2 = 0.9335$, $p < 0.001$) rather than Mn-oxyhydroxide phase ($R^2 = 0.5709$, $p < 0.02$). However, a strong positive correlation between As_{ox} and Al_{ox} ($R^2 = 0.8646$, $p < 0.01$) suggest contribution of clay

minerals on As mobilisation. Concentration of total organic carbon (TOC) and total As (As_{total}) peak in the dark grey sediment rich in organic matter. Very strong positive correlation between TOC and As_{total} ($R^2 = 0.8902$, $p < 0.004$) further demonstrates the association of As with organic matter of in the sediments.

Siderite (FeCO_3) and hematite (Fe_2O_3) have been identified throughout in the sequence but magnetite is observed only in the upper yellowish grey sediment by x-ray diffraction (XRD). Scanning electron microscopy reveals presence of crystalline goethite in the upper yellowish grey sediment and amorphous Fe-oxyhydroxides with traces of As in the grey to dark grey sediment mostly as grain coatings. Authigenic pyrite has also been identified in the dark grey sediment (Fig. 13) indicating active sulphate reduction and prevalence of strong reducing condition (Hasan *et al.*, 2008).

Change in lithofacies along the E-W transect in the Meghna basin

An E-W geological cross section (Fig. 14) stretching about 50 km through the middle

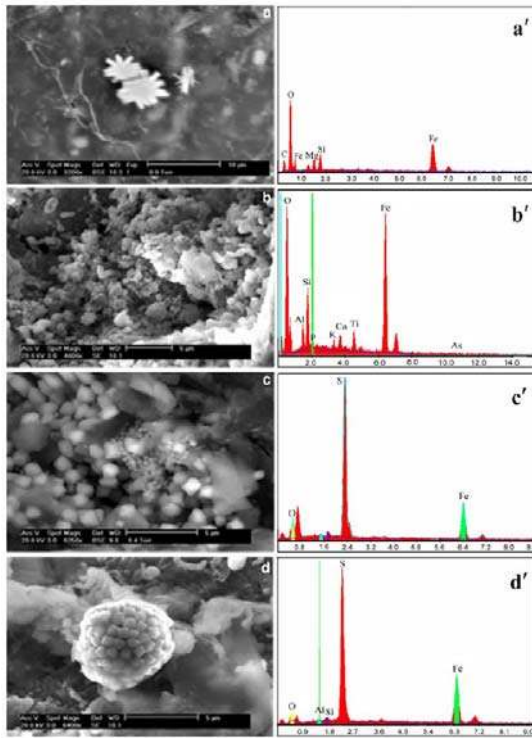


Figure 13. SEM images and respective EDS spectra showing (a, a') acicular iron oxide (goethite) on a biotite grain in the upper yellowish grey oxidised sediment at 2.44 m depth; (b, b') amorphous iron oxide with traces of As on a biotite grain in the dark grey micaceous sediment at 16.46 m depth; (c, c') octahedral authigenic pyrite and (d, d') framboidal pyrite on the mica grain.

Meghna basin constructed from lithological logs show a sharp change in lithofacies between the east and west (**Paper IV**). The eastern part is characterised by arenaceous (sandy) facies while the western part represents dominantly argillaceous (sand, silt and clay) facies. The abrupt change in lithofacies between the eastern and western part of the transect, probably indicates a fault along the Lalmai Hills (Morgan & McIntire, 1959). The sandy sequence in the eastern part is most likely the Pliocene Dupi Tila Formation that occurs at shallow depth in the eastern part of the Lalmai Hills called Lalmai terrace (Bakr, 1977) and the western part is representing the Holocene alluvial deposits. The Holocene alluvial deposits are heterogeneous in nature where shallow aquifers (<150 m) are relatively more argillaceous than the deeper (>150 m) ones.

Groundwater chemistry and geochemical processes along the transect

Electrical conductivity varies over a wide range between 146-4990 $\mu\text{S}/\text{cm}$ in the aquifers of the study area. Occurrence of high EC (>1000 $\mu\text{S}/\text{cm}$) in groundwater is found both in shallow and deeper aquifer but restricted only in the western part (Fig. 15 a,b). The spatial distribution pattern of EC

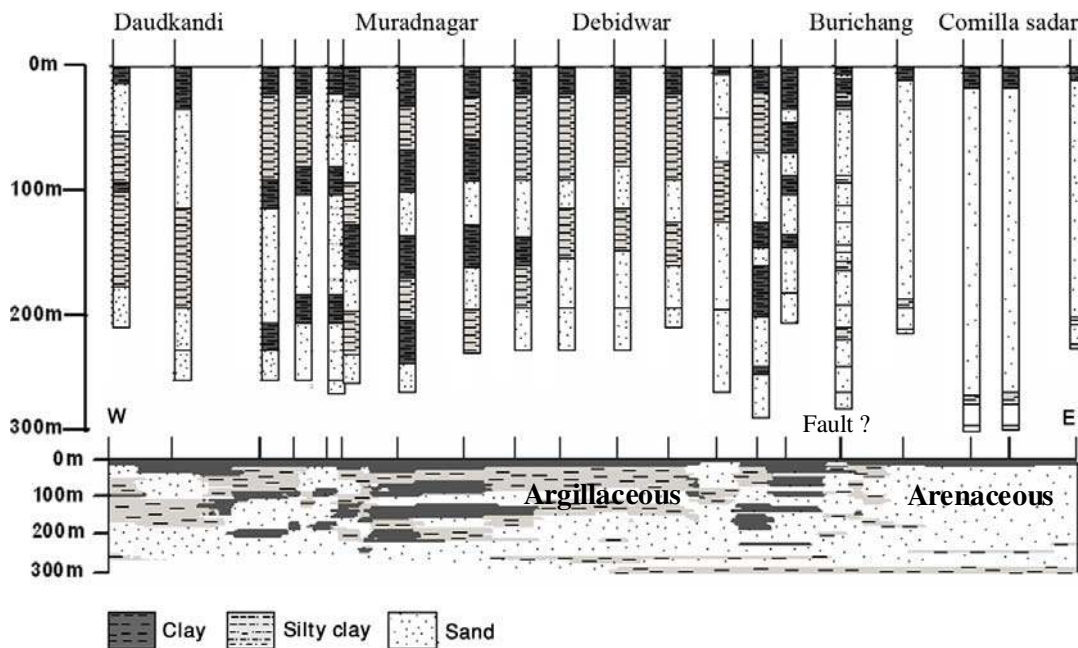


Figure 14. Change in lithofacies along an E-W transect in the Meghna basin (horizontal distance is about 50 km).

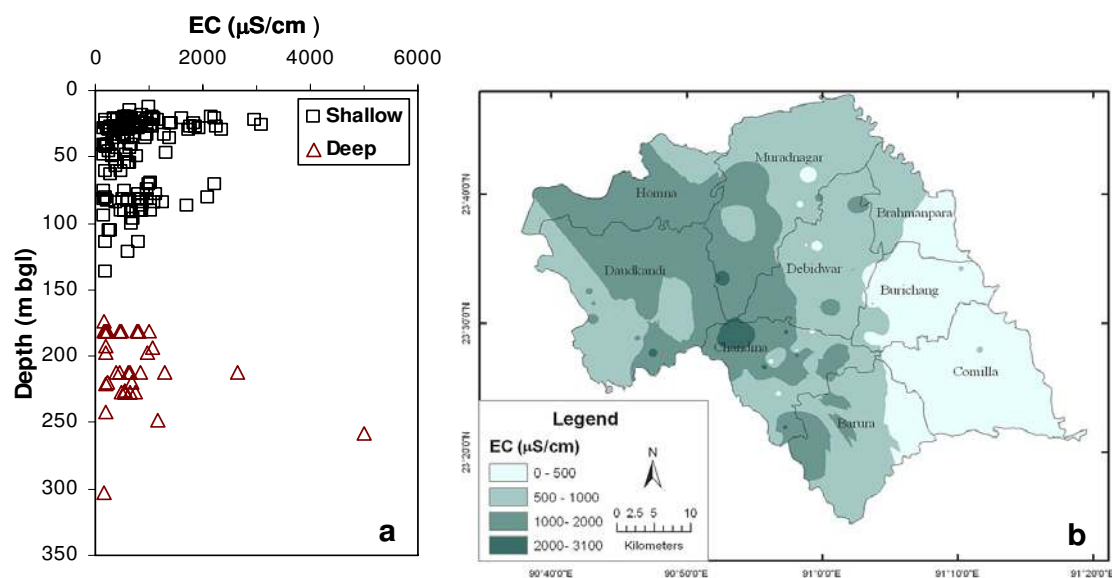


Figure 15. a) Vertical and b) spatial distribution pattern of groundwater EC in the Meghna basin.

for shallow aquifer (Fig. 15b) indicates presence of pockets of saline groundwater in the western part. It has been hypothesised that origin of such groundwater is the result of mixing of fresh water with the ancient seawater trapped within the formation during Holocene sea level transgression (BADC, 1992). The Holocene sea level rise between 7000-5000 years before present (BP) has a great influence on the nature of sedimentation and groundwater quality in the Bengal Basin (BADC, 1992; Goodbred & Kuehl, 2000). A significant number of samples in the western part along the transect have molar ratio of $\text{Cl}^-/\text{HCO}_3^- > 1$ indicating seawater mixing but all the samples in the eastern part of the area have $\text{Cl}^-/\text{HCO}_3^- < 1$ indicating fresh water which is consistent with EC map. Molar ratio of Na^+/Cl^- suggests silicate weathering is the source of Na^+ in the eastern part ($\text{Na}^+/\text{Cl}^- > 1$) while mixing of fresh water and seawater ($\text{Na}^+/\text{Cl}^- \sim 1$) is active in the western alluvial aquifer (*Paper IV*). Dominance of silicate weathering in the eastern Dupi Tila aquifer is also evidenced from $\text{HCO}_3^-/\text{SiO}_2$ molar ratio of less than 5 (Hunslow, 1995).

Concentrations of dissolved As ranges from below detection limit ($< 5.2 \mu\text{g/l}$) to as high as $678 \mu\text{g/l}$ along the transect (*Paper IV*). Depth profile of As in the groundwater (Fig. 16a) shows that occurrences of high concentrations (exceeding WHO guide line

value of $10 \mu\text{g/l}$) is maximum in the shallow aquifers ($< 150 \text{ m}$) and the deeper aquifers ($> 150 \text{ m}$) are mostly below WHO guide line value. Spatial distribution of groundwater As in the shallow aquifers (Fig. 16b) further depicts the typical patchy occurrences of high As in the alluvial aquifers of western part in the study area. However, concentration of As in the groundwater of eastern part of the study area representing Pliocene Dupi Tila aquifer is mostly less than $10 \mu\text{g/l}$. Concentrations of HCO_3^- and DOC is considerably high in the Holocene alluvial aquifer (west of 91.1° longitude) than the eastern part (Fig. 17a,b). Molar ratio of $\text{HCO}_3^-/\text{SiO}_2$ indicates silicate weathering is predominant in the eastern part (Fig. 17c). Plot of molar $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus HCO_3^- (Fig. 17d) shows all the samples, except a few, are placed well below the 1:1 line where HCO_3^- exceeds $\text{Ca}^{2+} + \text{Mg}^{2+}$ suggesting carbonate weathering is not a dominant process and the source of high HCO_3^- is other than carbonate weathering.

Quaternary sedimentation in the Bengal Basin took place in a fluvio-deltaic environment under shallow marine influence where abundant organic matter was co-deposited (Ravenscroft, 2001; Umitsu, 1993; Goodbred & Kuehl, 2000; Meharg *et al.*, 2006). The source of excess HCO_3^- as well as DOC in the Holocene alluvial aquifers in the Bengal Basin is most likely the result of

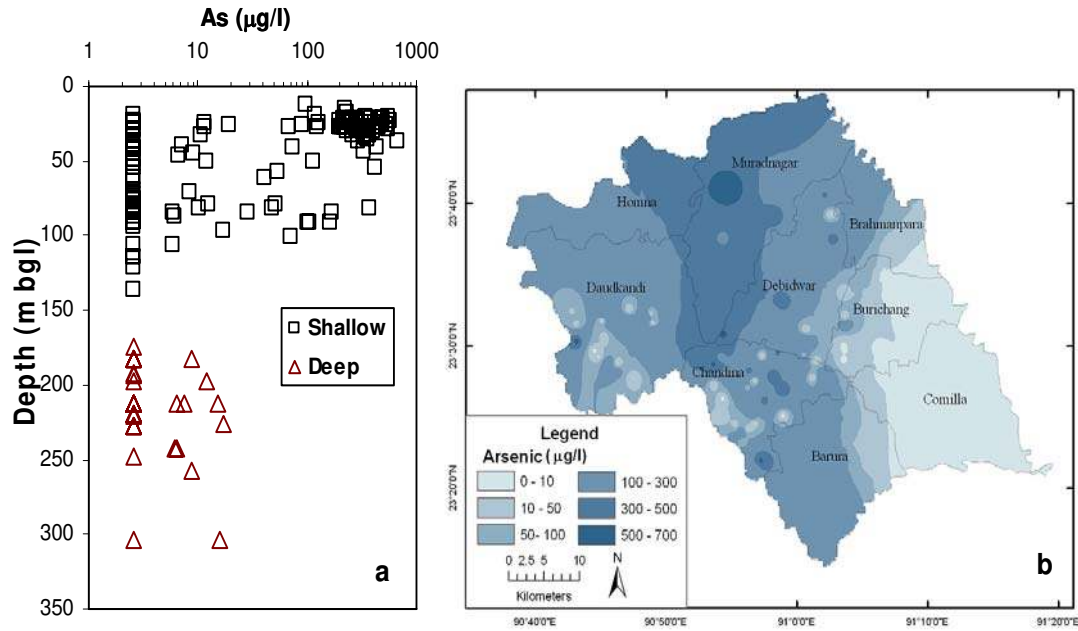


Figure 16. a) Vertical and b) spatial distribution pattern of groundwater As in the study area.

oxidative degradation of organic matter in the sediment (Bhattacharya *et al.*, 2001; Ravescroft *et al.*, 2005, Hasan *et al.*, 2007; Mukherjee *et al.*, 2008b).

The groundwater is supersaturated with respect to magnetite (Fe_3O_4), hematite (Fe_2O_3) goethite (FeOOH) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) throughout the transect both in shallow and deep aquifers but slightly

undersaturated to supersaturated with respect to ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) and siderite (FeCO_3) in the Holocene shallow aquifers (*Paper IV*). The composition of groundwater in the Pliocene aquifers is found to be near equilibrium to supersaturated with respect to ferrihydrite but mostly undersaturated with respect to siderite. On the contrary, the groundwater is

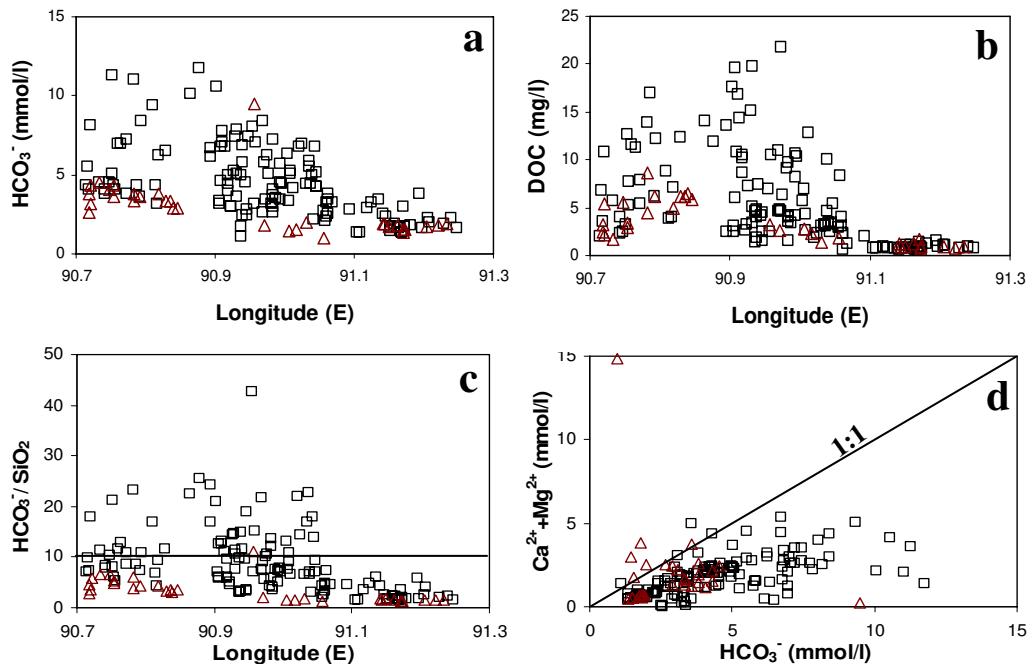


Figure 17. Variations in concentrations of: a) HCO_3^- ; b) DOC; c) $\text{HCO}_3^-/\text{SiO}_2$ in the groundwater samples along the transect, and d) correlation of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^-

undersaturated with respect to pyrolusite (MnO_2) and manganite (MnOOH) throughout the transect but undersaturated to near equilibrium with respect to rhodochrosite (MnCO_3) in the Holocene shallow aquifers indicating minor precipitation of dissolved Mn as rhodochrosite is possible in the Holocene shallow aquifers.

Plots of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ (Fig. 18) shows that the groundwater samples are clustered along the World Meteoric Water Line (WMWL) indicating the recharge is relatively fast and evaporation of infiltrating water is insignificant. The groundwater samples from shallow aquifers show a wider isotopic value both for $\delta^2\text{H}$ (-35.57 ‰ to -15.25 ‰) and $\delta^{18}\text{O}$ (-5.87 ‰ to -2.62 ‰) than the deeper aquifer samples (-25.77 ‰ to -15.94 ‰ and -4.05 ‰ to -3.5 ‰ respectively) indicating multiple recharge areas for shallow groundwater and relatively large degree of homogenisation of deep groundwater.

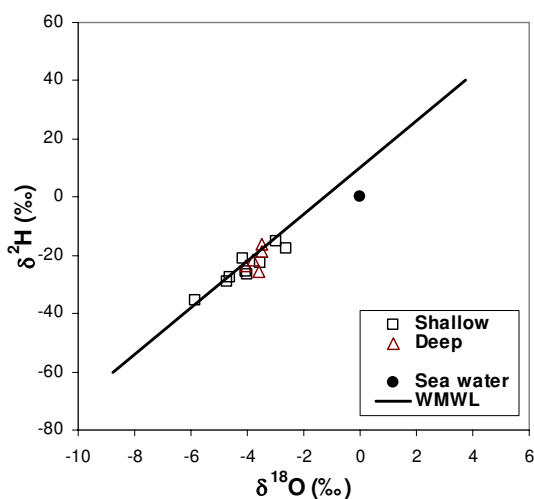


Figure 18. Stable isotopic ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) composition of shallow and deep aquifers.

DISCUSSIONS

Arsenic contamination in the groundwater of Bangladesh shows distinct and significant variability both in regional and local scale with the change in geological and hydrogeological conditions (*Papers I & II*). The studies reveal that the Holocene shallow alluvial aquifers in the delta plains, flood

plains and coastal plains are the regions that are severely affected by groundwater As contamination. On the other hand, Holocene deeper aquifers with light grey coarser sand and the older Plio-Pleistocene aquifers are very low in As. The Holocene sediments that were deposited in a fluvio-deltaic environment characterized by sand-silt-clay and abundant organic matter (Umitsu, 1993; Goodbred & Kuehl, 2000; Ravenscroft 2001; Meharg *et al.*, 2006) are found most vulnerable for groundwater As contamination.

Presence of biogenic methane (CH_4) in the Holocene aquifers supports the microbial fermentation of organic matter (Ahmed *et al.*, 1998) and formation of high HCO_3^- and DOC (Routh *et al.*, 2001; Aiken, 2002; Ahmed *et al.*, 2004). Low levels of SO_4^{2-} and NO_3^- with relatively high NH_4^+ , PO_4^{3-} and detectable amount of dissolved sulphide in some aquifers reflect reducing environment of these aquifers (*Paper I*). Conversion of NO_3^- to NH_4^+ and SO_4^{2-} to H_2S is common in a sequence of redox reactions. However, microbial degradation of organic matter may also produce NH_4^+ (Aiken, 2002). Elevated levels of PO_4^{3-} are likely the result of release of adsorbed PO_4^{3-} on to the Fe(III)-oxyhydroxides through reductive dissolution (McArthur *et al.*, 2001; Bhattacharya *et al.*, 2002b, Hasan *et al.*, 2007) or dissolution of secondary mineral phases like vivianite (Ahmed *et al.*, 2004, von Brömssen *et al.*, 2008). Microbial degradation of organic matter in the Holocene aquifers initiates favourable conditions for redox reactions facilitating reductive dissolution of Fe(III) and thereby mobilising adsorbed As into groundwater (Bhattacharya *et al.*, 1997; Nickson *et al.*, 1998; Routh *et al.*, 2000; McArthur *et al.*, 2004; Ahmed *et al.*, 2004; Postma *et al.*, 2007; Akai *et al.*, 2008). Moderate to strong positive correlation of As with HCO_3^- , DOC and Fe (*Papers I & II*) validates the release mechanism of As by reductive dissolution of Fe(III)-oxyhydroxides facilitated by microbial degradation of organic matter. However, variability in correlation between As and Fe are probably controlled by the precipitation

of Fe as secondary siderite, vivianite and pyrite (Nickson *et al.*, 2000; Sracek *et al.*, 2001; Ahmed *et al.*, 2004; Hasan *et al.*, 2007; Itai *et al.*, 2008). Considerable variability in groundwater chemistry, redox condition and As concentrations is observed in the Holocene aquifers at different geologic settings of the Bengal Basin (*Paper II*).

Geochemical characterisation of sediment samples show that total As in the sediment varies from <1 mg/kg to 17.7 mg/kg. Maximum concentrations of As is found in the finer sediment (silt and clay) rich in organic matter (usually dark grey in colour) while coarser sediment (sandy) with light grey colour and oxidised reddish sediment are low in As (*Papers I & III*). Selective and sequential extraction data reveals that maximum load of As is bound to metal (Fe, Mn, Al)-oxyhydroxides, particularly poorly crystalline and amorphous Fe-oxyhydroxides, in the grey sediments that are easily mobilised into the groundwater under reduced conditions (*Papers I & III*). On the contrary, majority of As load in the light grey and reddish sediments are in residual phase indicating their association with stable crystalline phases. The results are consistent with the findings from Matlab upazila in the Meghna basin (von Brömssen *et al.*, 2008). Association of As with carbonates and sulphides are insignificant in most of the sediments. However, strong positive correlation between TOC and total As in the organic matter rich sediment suggest association of As with organic matter (*Paper III*). A perfect match of Fe (Fe_2O_3) concentrations with the maxima and minima trends of As and TOC in the vertical profile further suggest strong association of Fe, As and TOC in the sediments. Co-deposition of Fe, organic carbon and As in the vegetated wetland sediments of the Bengal delta plains are described by Meharg *et al.*, 2006. Weathering of biotite is also playing a crucial role in the contribution of Fe-oxyhydroxides as evidenced from higher amount of oxalate extractable Fe (Fe_{ox}) in the micaceous sediment as well as presence of amorphous Fe-oxyhydroxides on biotite grains as grain coatings observed under SEM (*Paper III*).

The role of micas on adsorption of As are also documented from other areas in India and Bangladesh (Chakraborty *et al.*, 2007, Seddique *et al.*, 2008).

Hydrogeochemical profile along the E-W transect in the Meghna basin depicts variations in groundwater chemistry with the change in lithofacies (*Paper IV*). The argillaceous facies in the western part of the transect, representing the Holocene aquifer, were deposited in a deltaic regime under shallow marine condition while the arenaceous facies in the eastern part, representing the Pliocene aquifer, were deposited in a fluvial regime. Occurrences of saline groundwater pockets in the western part of the transect, suggest influence of relict seawater trapped in the sediment during deposition under shallow marine condition. Almost entire southern part of the GBM delta system, including the study area, was under marine influence (Ravenscroft, 2001; Shamsudduha & Uddin, 2007) during the last sea level rise between 7000-5000 years before present (Goodbred & Kuehl, 2000).

The groundwater chemistry in the western part is characterised by high concentrations of HCO_3^- , DOC and As indicating active degradation of organic matter and subsequent redox reactions in the aquifers. On the contrary, the groundwater in the eastern part is low in HCO_3^- , DOC and As but relatively high in silica suggest silicate weathering is the dominant geochemical process. Release of As from the aquifer sediments in response to groundwater level fluctuations due to extensive irrigation (Acharyya *et al.*, 2000, Harvey *et al.*, 2002) is not a valid mechanism in the Meghna basin. Long term groundwater level hydrographs (Fig. 19) show that the fluctuation of groundwater levels is almost in the similar range in the western (Daudkandi, Muradnagar, Debidwar, Chandina) and eastern (Burichang, Comilla) part with distinct variations in the groundwater As concentrations (*Paper IV*).

Though the Holocene deeper aquifers (>150 m depth) in the Meghna basin are low in As (mostly <10 $\mu\text{g/l}$), risk of cross-contamination from shallow aquifers

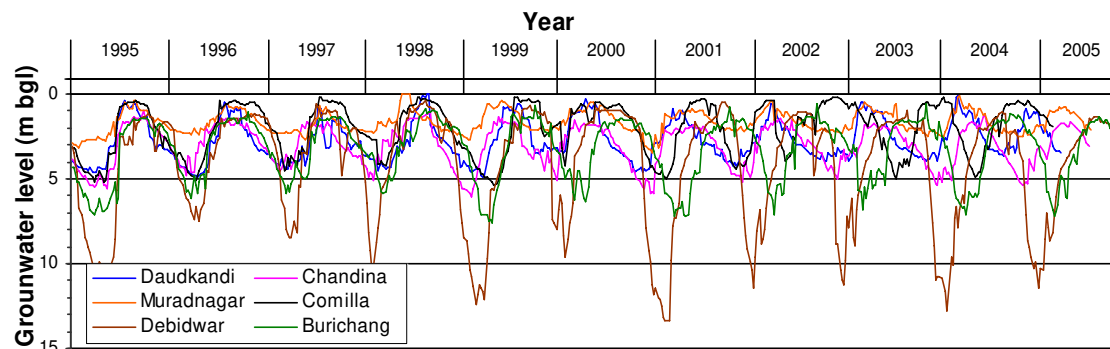


Figure 19. Long term groundwater level hydrographs of the Meghna basin.

(Burgess *et al.*, 2007) can not be ignored because the deeper aquifers are not separated from the shallow ones by continuous impermeable layers. Extensive abstraction of groundwater for irrigation from the deeper aquifers may increase the risk many fold. However, the processes such as retardation and sorption may reduce the vertical migration of As significantly (Stollenwerk *et al.*, 2007). Groundwater modeling studies by United States Geological Survey (USGS) suggested combination of deep pumping for drinking water and shallow pumping for irrigations as the ideal option for groundwater management in the As affected areas of Bangladesh (Michael & Voss, 2008). However, the question of As entering into the food chain through irrigation with high-As groundwater still remains.

CONCLUSIONS

Arsenic contamination in the shallow alluvial aquifers of the Bengal Basin is geogenic and very extensive in terms of geographic distribution and number of exposed population. Considerable variabilities in redox conditions, groundwater chemistry and As concentrations have been observed in the affected areas both in vertical and horizontal scale. Such variations in geochemical character of groundwater is linked with the local geology (*Paper I and II*).

Holocene shallow alluvial aquifers in the delta plains and flood plains of lower GBM river system that were deposited in fluvio-deltaic environment are severely affected by groundwater As contamination. Dark grey

sediments with abundant organic matter are most vulnerable for the release of high As in groundwater (*Paper III*). Maximum load of solid phase As in the dark grey sediment is found associated with poorly crystalline to amorphous Fe(III)-oxyhydroxides and organic matter (*Paper I and III*). Weathering of biotite, which is abundant in the alluvial sediment, is one of the major source of amorphous Fe(III)-oxyhydroxides in the sediment and thus plays significant role on adsorption of As (*Paper III*). Redox reactions linked to oxidative degradation of organic matters in the Holocene alluvial aquifers favours reductive dissolution of Fe and other metal (Mn, Al)-oxyhydroxides and thereby release of adsorbed As into the groundwater.

Change in lithofacies and geological age of the aquifer sediment show marked variations in groundwater quality in the Meghna basin (*Paper IV*). Groundwaters in geologically younger Holocene sediment of dominantly argillaceous facies are high in As (>10 µg/l), HCO_3^- and DOC. However, the concentrations of As (<10 µg/l), HCO_3^- and DOC are low in the wells placed in the deeper arenaceous and older Pliocene aquifers. Fluctuations in groundwater level due to annual recharge and discharge do not show any significant influence on the mobilisation of As into the groundwater.

Salinity and high levels of dissolved As in the Holocene shallow alluvial aquifers are the major constraints for drinking and irrigation water supply in the Meghna basin. Salinity is caused by the presence of relict seawater in

areas with sluggish groundwater movement and incomplete flushing (*Paper IV*). The Holocene deeper aquifers are low in As but contains pockets of saline groundwater. There are risks of cross-contamination of As from Holocene shallow aquifers because the deeper aquifers are not separated from the shallow ones by continuous impermeable layers. Groundwater from the Holocene deeper aquifer should be used only for drinking purposes and current practice of lowering the tube wells to the deeper low-As aquifers should be guided properly so that the risk of cross-contamination remains minimal. Installation of high-capacity irrigation wells in the deeper aquifer will certainly increase the risk of cross-contamination. Groundwater flow and contaminant transport modelling need to be undertaken for assessing sustainability of the deeper low-As aquifers.

The present study shows linkages of As concentrations in groundwater to i) geological settings, ii) hydrogeological environment, and iii) hydrogeochemical process in the aquifers. It is important to understand these linkages in order to develop a holistic approach for future management of groundwater resources.

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