



**KTH Land and Water
Resources Engineering**

HYDROGEOLOGICAL AND GEOCHEMICAL ASSESSMENT OF AQUIFER SYSTEMS WITH GEOGENIC ARSENIC IN SOUTHEASTERN BANGLADESH

**Targeting low arsenic aquifers for safe drinking water
supplies in Matlab**

Mattias von Brömssen

January 2012

TRITA-LWR PHD 1063

ISSN 1650-8602

ISRN KTH/LWR/PHD 1063-SE

ISBN 978-91-7501-214-8

Cover illustration:

Dularampur, Daudkandi, Bangladesh

(Photograph: Mattias von Brömssen©, 2004)

© Mattias von Brömssen 2012

PhD thesis

KTH-International Groundwater Arsenic Research Group

Department of Land and Water Resources Engineering

Royal Institute of Technology (KTH)

SE-100 44 STOCKHOLM, Sweden

Reference to this publication should be written as: von Brömssen, M. (2012) Hydrogeological and geochemical assessment of aquifer systems with geogenic arsenic in southeastern Bangladesh – Targeting low arsenic aquifers for safe drinking water supplies in Matlab. PhD thesis, TRITA LWR PhD 1063, 46 p.

Dedicated to my father, inspiring explorer!

FOREWORD

This thesis covers a crucial period of the work on the arsenic problems in groundwater in Bangladesh. Especially it includes the discovery of the local drillers' strategy to find low iron groundwater by assessing the colour of the sediments. With the link between mobilisation of arsenic along with iron which was published by our team 1997 this gave an immediate hint on means of predicting arsenic low groundwater during well construction. The strategy was discovered by the author of the thesis when he was advising a M.Sc. thesis project. The "sediment colour strategy" leads to a number of questions that has to be answered, notably the risk of cross contamination of arsenic low sediment sequences. Essentially three crucial issues are dealt with in the thesis, the groundwater flow pattern, the adsorption characteristics and redox buffering of the low arsenic layers. The insight gained indicates that the strategy of finding low arsenic aquifers is sustainable. The methods used comprised of groundwater and sediment sampling, detailed chemical analysis of water, sediment extractions, mineralogical investigations and hydrogeochemical- and groundwater flow modelling. However, the groundwater extraction for irrigation is a threat in the way it is practised today and would be even more so if low arsenic deep wells are constructed for the purpose.

Prof. Em. Gunnar Jacks
Stockholm, KTH, January 2012

ACKNOWLEDGEMENTS

I would like to express my heartfelt appreciation for my supervisor Prof. Prosun Bhattacharya at the Department of Land and Water Resources Engineering. Without Prof. Bhattacharya's encouragement, positivism and openness for new ideas and collaborations this study would not have happened. I am grateful for his friendship, lengthy academic discussions, generous support and valuable guidance throughout the study.

I would also like to express my sincere gratitude to my co-supervisors Prof. Kazi Matin Ahmed at Dhaka University and Prof. Em. Gunnar Jacks at KTH. Prof. Ahmed was always in the centre of the field-work in Bangladesh providing all necessary support and encouragement irrespectively the time of the day. He always extended his support not only in academic discussion but also for talk between friends, something I came to appreciate being far away from home. I am equally grateful to Prof. Jacks for his continued support and friendship along the course of the study. Thanks to Prof. Jacks I got incomparable academic discussion on groundwater chemistry as well as laboratory- and field work. Prof. Jacks is also recognised for providing several of the home made sampling devises.

I am grateful to the faculty, staff and fellow Ph.D. students at the Dept. of Land and Water Resources Engineering (LWR), KTH and Dept. of Geology at the University of Dhaka, Bangladesh. I am particular indebted to Prof. Aziz Hasan for helping me to understand many of the mineralogical aspects and to Mohammed Hossain (Tipu) for helping me sorting out our databases and providing me with GIS support. We have had very fruitful academic discussions. I am thankful to Ann Fylkner and Monica Löwén for providing support at the laboratory at LWR. I always got assistance at the laboratory, even on very short notice. I value the help from Prof. Carl-Magnus Mörth at the Dept. of Geology and Geochemistry, Stockholm University for providing laboratory analysis.

I would also like to thank the people involved in lengthy academic and technical discussions making this study worthwhile; Dr. Arif Mohiuddin Sikder at the Center for Environmental Studies, VCU, U.S., Prof. Jochen Bundschuh, at the Universidad Nacional de Salta, Argentina, also affiliate Prof. at KTH, Prof. Ondra Sracek at the Palacký University, Czech Republic, Lars Markussen at Ramböll Denmark and Dr. Clifford Voss at the USGS. A special thank is given to Dr. Sven Jonasson at Geologic in Göteborg AB for late-night but very fruitful discussions on groundwater flow modelling.

I am thankful to all the people at Dhaka University, Daudkandi and Matlab for making each of my stays and work unforgettable moments. Thank you Sarmin & Mainul, Moklesh, Bishwajit, Rajib, Samrat, Jahid, Aminul, Robi, Ratnajit, Omar, Malek as well as all the other local drillers at Matlab. I am also grateful for all the help and friendship I got from the M.Sc. students at KTH, University of Uppsala and University of Dhaka; Lisa Lundell, Linda Jonsson, Sarmin Sultana, Md. Rajib Hassan Mozumder, Annelie Bivén, Sara Häller, Md. Mokleshur Rahman and Pavan Kumar Pasupuleti. Gisela Ivarsson at the NGO Svalorna is acknowledged for her great hospitality and friendship during my stays in Dhaka. Likewise, Anisur Rahman at ICCDR,B-Matlab is recognised for his smile and letting me stay at their guesthouse in Matlab. I would like to thank the people of Satani, Daudkandi, for having me as guest at their homes.

Finally I would like to express my thanks to the Swedish International Development Cooperation Agency (Sida) for providing grants for research on “Options for safe drinking water in regions with high arsenic groundwater in Bangladesh” (Sida-SAREC dnr. 2002-129). MISTRAs Idea Support Grant, “Targeting arsenic-safe aquifers in regions with high arsenic groundwater and its worldwide implications”, made some of the field work in Bangladesh possible. I am likewise grateful to The Ramböll Foundation for providing funds for an adjoining research project “Sustainability of community driven initiatives to target arsenic safe groundwater as a drinking water source in Bangladesh” (Ramböll pnr. 61150619881) that gave me the opportunity to carry out my research studies while being employed at Ramböll.

Mattias von Brömssen
Stockholm, January 2012

LIST OF APPENDED PAPERS

Paper I

von Brömssen, M., Jakariya, M., Bhattacharya, P., Ahmed, K.M., Hasan, M.A., Sracek, O., Jonsson, L., Lundell, L., Jacks, G., 2007. Targeting low-arsenic in Matlab Upazila, Southeastern Bangladesh. *Science of The Total Environment* 379 (2–3): 121–132

Paper II

von Brömssen, M., Larsson, S.H., Bhattacharya, P., Hasan, M.A., Ahmed, K.M., Jakariya, M., Sikder, A.M., Sracek, O., Bivén, A., Doušová, B., Patriarca, C., Thunvik, R., Jacks, G., 2008. Geochemical characterisation of shallow aquifer sediments of Matlab Upazila, Southeastern Bangladesh – implications for targeting low-As aquifers. *Journal of Contaminant Hydrology* 99(1-4): 137-149

Paper III

Hasan, M.A., **von Brömssen, M.**, Bhattacharya, P., Ahmed, K.M., Sikder, A.M., Jacks, G., Sracek, O., 2009. Geochemistry and mineralogy of shallow alluvial aquifers in Daudkandi upazila in the Meghna flood plain, Bangladesh. *Environmental Geology* 57: 499–511

Paper IV

Robinson, C., **von Brömssen, M.**, Bhattacharya, P., Häller, S., Bivén, A., Hossain, M., Jacks, G., Ahmed, K.M., Hasan, M.A., Thunvik, R., 2011. Dynamics of arsenic adsorption in the targeted arsenic-safe aquifers in Matlab, South-eastern Bangladesh: insight from experimental studies. *Applied Geochemistry* 26: 624–635

Paper V

von Brömssen, M., Markussen, L., Bhattacharya, P., Ahmed, K. M., Hossain, M., Jacks, G., Sracek, O., Thunvik, R., Hasan, M. A., Islam, M., Rahman, M. M., 2011. Hydrogeological investigations for assessment of the sustainability of low-As aquifers as a safe drinking water source in regions with high As-groundwater in Matlab, Southeastern Bangladesh, *Manuscript*

LIST OF PAPERS NOT INCLUDED IN THE THESIS***Paper VI***

Jakariya, M., **von Brömssen, M.**, Jacks, G., Chowdhury, A. M. R., Ahmed, K. M., Bhattacharya, P., 2007. Searching for sustainable arsenic mitigation strategy in Bangladesh: experiences from two upazilas. *International Journal of Environmental Pollution* Vol. 31(3/4): 415-430

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

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, AL., 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

Paper IX

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 X

Sracek, O., Bhattacharya, P., Jacks, G., Gustafsson, J.P., **von Brömssen, M.**, 2004a. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. *Applied Geochemistry* 19: 169-180

Paper XI

Sracek, O., Bhattacharya, P., **von Brömssen, M.**, Jacks, G., Ahmed, K. M., 2004b. Natural enrichment of arsenic in groundwaters of Brahmanbaria district, Bangladesh: geochemistry, speciation modelling and multivariate statistics. In: *Natural Arsenic in Groundwater: Occurrence, Remediation and Management*. Edited by J. Bundschuh, P. Bhattacharya and D. Chandrasekharam Balkema, London, 133-144

TABLE OF CONTENT

<i>Foreword</i>	v
<i>Acknowledgements</i>	vii
<i>List of Appended Papers</i>	ix
<i>List of Papers not Included in the Thesis</i>	x
<i>Table of Content</i>	xi
<i>Abstract</i>	1
1. Introduction	1
1.1. Recognition and magnitude of high arsenic groundwater in Bangladesh	2
1.2. Chronic arsenic poisoning	3
1.3. Drinking water practice in rural Bangladesh	3
1.4. Lessons learned from previous mitigation activities	3
2. Research Objectives	4
3. Hydrogeological and Geochemical Context	4
3.1. Geological setting	4
3.2. Climate and precipitation	6
3.3. Hydrogeological setting	6
3.4. Arsenic geochemistry	7
3.5. High arsenic groundwater in Bangladesh	8
4. Material and Methods	10
4.1. Delineating sediment colours	10
4.2. Groundwater sampling and analysis	10
4.3. Sediment sampling	11
4.4. Mineralogical investigations	11
4.5. Sequential extraction and column experiments	11
4.6. Arsenic adsorption experiments	12
4.7. Geochemical modelling	13
4.8. Hydrological field investigations	14
4.9. Groundwater flow modelling	14
5. Results	15
5.1. Local drillers perception of sediments	15
5.2. Groundwater chemical composition	15
5.3. Sequence of aquifer sediments	16
5.4. Mineralogical investigations	18
5.5. Geochemical investigations	19
5.5.1. Bulk geochemical analysis	19
5.5.2. Sequential extractions	19
5.5.3. Geochemical modelling	20
5.6. Arsenic adsorption dynamics	21
5.7. Hydrogeological field investigations	22
5.7.1. Aquifer delineation based on drilling logs	22
5.7.2. Estimation of groundwater abstraction in Matlab	23
5.7.3. Hydrographs	23

5.7.4.	Hydraulic test	23
5.7.5.	¹⁴ C dating of groundwater	23
5.8.	Groundwater modelling	23
6.	<i>Discussion</i>	27
6.1.	Drillers' perception of sedimentary characteristics	27
6.2.	Groundwater chemical characterisation	27
6.3.	Mineralogy of sedimentary aquifers and relationship with high As groundwater	28
6.4.	Relationship between As and other elements at the water-solid interface	29
6.5.	Adsorption dynamics of As on oxidised sediments	30
6.6.	Groundwater flow	31
6.6.1.	Hydrographs and groundwater flow modelling	31
6.6.2.	Groundwater abstraction	31
6.7.	Targeting safe aquifers	32
6.8.	Groundwater management	32
7.	<i>Conclusions</i>	33
7.1.	The local drillers' ability to target and delineate arsenic safe aquifers	33
7.2.	The correlation between aquifer sediment colours and groundwater chemical composition	34
7.3.	The relationship between aqueous and solid phase geochemistry with emphasis on mobilisation of As	34
7.4.	Mineralogical description of sediments with emphasis on mobilisation of As	35
7.5.	Adsorption dynamics of arsenic in oxidised sediments	35
7.6.	Risk for cross-contamination between aquifers	35
7.7.	Concluding remarks	36
	<i>References</i>	37
	<i>Afterword</i>	45

ABSTRACT

Naturally occurring arsenic (As) in Holocene aquifers in Bangladesh have undermined a long success of supplying the population with safe drinking water. Arsenic is mobilised in reducing environments through reductive dissolution of Fe(III)-oxyhydroxides. Several studies have shown that many of the tested mitigation options have not been well accepted by the people. Instead, local drillers target presumed safe groundwater on the basis of the colour of the sediments. The overall objective of the study has thus been focussed on assessing the potential for local drillers to target As safe groundwater. The specific objectives have been to validate the correlation between aquifer sediment colours and groundwater chemical composition, characterize aqueous and solid phase geochemistry and dynamics of As mobility and to assess the risk for cross-contamination of As between aquifers in Daudkandi and Matlab Upazilas in SE-Bangladesh. In Matlab, drillings to a depth of 60 m revealed two distinct hydrostratigraphic units, a strongly reducing aquifer unit with black to grey sediments overlies a patchy sequence of weathered and oxidised white, yellowish-grey to reddish-brown sediment. The aquifers are separated by an impervious clay unit. The reducing aquifer is characterized by high concentrations of dissolved As, DOC, Fe and PO_4^{3-} -tot. On the other hand, the off-white and red sediments contain relatively higher concentrations of Mn and SO_4^{2-} and low As. Groundwater chemistry correlates well with the colours of the aquifer sediments. Geochemical investigations indicate that secondary mineral phases control dissolved concentrations of Mn, Fe and PO_4^{3-} -tot. Dissolved As is influenced by the amount of *Hfo*, pH and PO_4^{3-} -tot as a competing ion. Laboratory studies suggest that oxidised sediments have a higher capacity to absorb As. Monitored hydraulic heads and groundwater modelling illustrate a complex aquifer system with three aquifers to a depth of 250 m. Groundwater modelling illustrate two groundwater flow-systems: i) a deeper regional predominantly horizontal flow system, and ii) a number of shallow local flow systems. It was confirmed that groundwater irrigation, locally, affects the hydraulic heads at deeper depths. The aquifer system is however fully recharged during the monsoon. Groundwater abstraction for drinking water purposes in rural areas poses little threat for cross-contamination. Installing irrigation- or high capacity drinking water supply wells at deeper depths is however strongly discouraged and assessing sustainability of targeted low-As aquifers remain a main concern. The knowledge gained here can be used for developing guidelines for installing safe wells at similar environments in other areas of Bangladesh.

Key words: Arsenic, Bangladesh, drinking water, groundwater, sustainability, geochemistry, hydrogeology, modelling

1. INTRODUCTION

Access to safe drinking water is essential to health, a basic human right and a component of effective policy for health protection (WHO 2004). Elevated arsenic (As) concentrations of natural origin in drinking water derived from groundwater sources have been observed in several parts of the world. Today tens of millions of

people, mainly in developing countries, are affected by high naturally occurring (geogenic) As concentrations in drinking water exceeding WHO's provisional guide line value of 10 µg/l. High As groundwater in SE Asia exists in Bangladesh, India, Nepal, Vietnam and Cambodia. The problem is most acute in the Bengal Delta Plain of Bangladesh and in the adjoining state of West Bengal in India where it has

emerged as one of the greatest environmental health disasters of this century (Chakraborti *et al.* 2002, Smedley and Kinniburgh 2002, Bhattacharya *et al.* 2007). The global occurrences now make it a top priority water quality issue, second in order only to microbiological contamination of water (Kapaj *et al.* 2006).

Groundwater environments governing mobilisation of geogenic As can broadly be classified in three groups (Smedley and Kinniburgh 2002): i) strongly reducing aquifers, ii) high alkaline- and pH, mostly oxidising aquifers, and iii) aquifers containing elevated amounts of arsenopyrite and other sulphides. From a human health perspective, high As aquifers related to strongly reducing conditions are the ones which pose most serious problems because of its widespread. These aquifers are found in e.g. Bangladesh, India, Vietnam, Cambodia, and Pakistan (Smedley and Kinniburgh 2002). Arsenic is also commonly encountered in oxidising aquifers with high alkalinity and pH in e.g. the Chaco-Pampean region of Argentina where at least 1.2 million people (about 3 % of total population) are exposed to elevated As concentrations mobilised primarily from volcanic ash, interbedded or dispersed within sediments (Bhattacharya *et al.* 2006). In areas with sulphide ore bodies containing pyrite and arsenopyrite, in e.g. Sweden and Finland, As may be mobilised due to the oxidation of the sulphides (Welch *et al.* 2003).

In Bangladesh groundwater has been the main element for two recent achievements in the fields of i) access to safe drinking water and ii) food security through excessive use of groundwater in irrigation. Due to extensive use of groundwater, facilitated by easy availability of prolific aquifers, 97 % of the total population came under the coverage of safe water supply. The exponential increase in groundwater exploitation has been prompted by low cost technologies. The number of domestic water supply wells increased many folds over the last three decades (Ahmed *et al.* 2004). Though irrigation started in Bangladesh by

using surface water, the source has shifted from surface to groundwater and today about 70 % of the irrigation water is abstracted from the aquifers, which account for 85 % of the total abstracted groundwater (BGS and DPHE 2001). Because high As concentrations are commonly found in Bangladesh both in irrigation and drinking wells the success of achieving access to safe drinking water and food security is now at risk.

1.1. Recognition and magnitude of high arsenic groundwater in Bangladesh

High As groundwater was officially recognised in Bangladesh in 1993. Since then, the success in providing people with drinking and irrigation water in Bangladesh has been posed with threats due to As occurrences in groundwater. As nearly 30 % of the wells exceed the Bangladesh Drinking Water Standard (BDWS) of 50 µg/l, 30 to 70 million people previously considered to have access to safe water is now known to be exposed to high As through drinking water (Smith *et al.* 2000, BGS and DPHE 2001, Smedley and Kinniburgh 2002).

The As concentrations in groundwater are much above the WHO drinking water guideline (10 µg/l) and according to Smith *et al.* (2000) it is reasonable to think that more than 200 000 people will be affected by arsenicosis unless the exposure is reduced on an immediate basis. The effect on human health through exposure of geogenic As in groundwater is due to exposure through three pathways: i) intake of As through drinking groundwater, ii) intake of As through cooking processes, and iii) intake of crops irrigated with high As groundwater. It has previously been reported that drinking high As groundwater is the primary pathway for exposure of humans (Smith *et al.* 2000, Kapaj *et al.* 2006). Studies (Vahter *et al.* 2006) have shown that exposure through the food chain may contribute equally to the exposure of As. Arsenic transfer through food chain due to irrigation with high As water is becoming a matter of concern as many studies have reported As build-up in soil and

crops (Abedin *et al.* 2002, Al Rmali *et al.* 2005, Williams *et al.* 2005, Corell *et al.* 2006, Huq *et al.* 2006, Naidu *et al.* 2006, Williams *et al.* 2006). Thus, the presence of As in groundwater has become a major issue of management of both drinking- and irrigation water in the country.

1.2. Chronic arsenic poisoning

Drinking groundwater, eating food-crops irrigated with groundwater and using groundwater with elevated concentrations of As are the main exposure pathways in Bangladesh (Polya *et al.* 2009). Chronic As poisoning results from ingestion of elevated levels of As over a long period of time (UN 2001). The consequences of chronic As exposure are dependent on the susceptibility, the dose and the time course of exposure. The effects include different forms of skin disorders related to skin pigmentation such as leucomelanosis, melanosis, keratosis, skin cancer, lung cancer, cancer of the kidney and bladder, and can lead to gangrene. Estimation of annual excess deaths is in the order of thousands and disability-adjusted life years (DALY) of the order of hundreds of thousands (Polya *et al.* 2009) in Bangladesh. The sensitivity to As poisoning is clearly related to economic situation of the individuals which is related to nutrition status or better ability to get access to safe water (Milton *et al.* 2004, Sikder *et al.* 2005). The As poisoning case is structured in several ways by class and gender. Only rich people can afford the higher cost involvement in installing deeper wells, that are As safe, leaving behind the poor communities more vulnerable. The worse nutritional status of poor households, and particularly the women of those households, may mean that As contamination has more severe physiological consequences for them. The poorer sections of the society are likely to consume more water as they work harder. In addition they are also likely to consume more of arum tuber (*Arum phiphyllum*), which is found to contain higher contents of As (Roychowdhury *et al.* 2002).

1.3. Drinking water practice in rural Bangladesh

The water handling in rural Bangladesh is generally the task of women (Singh *et al.* 2005). The installation of hand tube wells (HTW) in the close proximity of the households has relieved the women of a lot of work in e.g. Bangladesh in terms of physical handling. Next to piped water supply the HTW are found to be the most acceptable to the people in an investigation in Bangladesh (Hoque *et al.* 2004). Hand tube wells together with improved personal hygiene have reduced the frequency of diarrhoeal diseases (Alam *et al.* 1989). However, it seems that the frequency of diarrhoea in children is more associated to the personal hygiene of the women than to the source of water (Alam and Wai 1991). Women are more aware than men about the As problem but nevertheless switching to safe wells was found to be marginal (Caldwell *et al.* 2005). Switching to safe wells may imply longer distances to the water source and more work, possibly exceeding the acceptability and capacity for work. Poverty consigns women to long periods of work in activities that bring little reward (Kendie 1996). The gendered impacts of As contamination of water are also becoming evident in other areas of women's lives: health and social status. Since elevated exposure to As causes skin ulcers and lesions, and many other symptoms, women and girls afflicted with As poisoning are suffering disproportionately both in terms of lack of medical attention and in being ostracized. Marriage of young women in As-affected areas is falling, and husbands are abandoning wives having visible symptoms of arsenicosis. All this lead to serious social consequences of groundwater poisoning for women in particular, even though arsenicosis can affect an entire family.

1.4. Lessons learned from previous mitigation activities

Different options and approaches have been implemented in rural settings including household and community filters, rainwater harvesting (RWH), pond sand filters (PSF)

and dug wells (DW). The implementation achievement of the different options has been assessed on several criteria, such as community acceptability, financial sustainability, and technical viability. It has been found that community acceptance of many of the options is low as people do not find them as convenient as the tubewells (Hoque *et al.* 2004, Jakariya *et al.* 2005, 2007, Johnston *et al.* 2010). The concept of drinking water from tubewells is well rooted in the daily life of the people in Bangladesh and women in the rural areas of Bangladesh are heavily burdened even with the provision of HTWs at short distance. Any additional task is thus likely to be difficult to handle in the long run, for instance the handling of filters on the household basis. This may be one reason for the failure of several of the options to As safe water that have been provided in Bangladesh.

The options have their own strengths and limitations but none is as easy as fetching water directly from tubewells. Deep, pre-Holocene, aquifers (>150 m) are generally known to have low dissolved concentrations of As (BGS and DPHE 2001) and offer a possible alternative source of As-safe drinking water. However, drilling to depths more than 150 m is costly as it involves mechanised technique as compared to the locally available hand-percussion technique and may therefore not always be readily available. Though most options were not accepted many villagers realized the urgency for drinking safe water and thus two practices emerged based on the community's own initiative (van Geen *et al.* 2003, Jakariya *et al.* 2005): i) the preferred use of As safe hand tubewells that were painted green after examination by field personal, and ii) reinstalling tubewells to a presumed safe depth based on local drillers knowledge of the colour of the sediments and As occurrence.

2. RESEARCH OBJECTIVES

Keeping in mind the number of exposed people and the low rate of outcomes of the mitigation programmes driven by government and donor organisation for As

mitigation, it is obvious that there is an urgent need for the people themselves to find practical mitigation options. Thus the overall objective of the present research has been to assess the potential for rural people of Bangladesh themselves to target As safe groundwater for drinking purposes. The specific objectives of this study were to:

- i) Assess the potential for local drillers to target As safe aquifers at shallow depths (<100 m) on the basis of sediment colour and validate the possible correlation between aquifer sediment colours, groundwater chemical characteristics and dissolved concentrations of As (Paper I);
- ii) Characterize the aqueous and solid phase geochemistry together with the lithofacies and mineralogy of the shallow aquifers in the Meghna flood plain with emphasis on the geological controls of dissolved As (Paper II, Paper III);
- iii) To investigate the adsorption dynamics of As of oxidised and weathered alluvial sediments (Paper IV); and
- iv) To assess the risk for cross-contamination between aquifers containing high dissolved As and low As aquifers to be targeted for potable water (Paper V).

3. HYDROGEOLOGICAL AND GEOCHEMICAL CONTEXT

The investigations were done in Matlab and Daudkandi, south-east and east of Dhaka on the eastern side of the great river Meghna. Both areas are among the worst affected areas in Bangladesh. Matlab and Daudkandi are situated within the low-lying Meghna floodplain (Figure 1).

3.1. Geological setting

The Bengal basin accommodates one of the largest delta systems (a so-called "mega delta") of the world. Three mighty rivers, viz., the Ganges, Brahmaputra and Meghna carry enormous volume of sediments into the basin and have generated, with active subsidence, a colossal thickness of Tertiary and Quaternary sequence (Hasan *et al.* 2007). Since Miocene, deltaic sediments have prograded from the north, accumulating up to > 10 km of sediments towards the Bengal

Bay in the southeastern Bangladesh. The rivers are estimated to discharge an annual amount of 10^9 tons of sediments within the Bengal basin (Goodbred and Kuehl 2003).

Physiographically, Bangladesh covers the major part of the Bengal basin. This part of the basin is classified into three distinctive terrains (Figure 1). The Tertiary hill ranges occur in the east, southeast and north-northeast and consists of sandstones, shales and limestones (BGS and DPHE 2001). The hills have been formed due to collision of the Indian shield at the Indo-Burman boundary forming the Indo-Burman fold belt. The Pleistocene Barind and Madhupur Terraces in the central north and Holocene Terraces in the central north and Holocene plains are found as a thin sediment veneer in large part of the basin. The terraces are uplifted fluvial and alluvial deposits and include clay, silt, sand and pebbles from Pleistocene age that have been exposed to oxidation during the latest ice-ages. Groundwater within the terraces has been found to be low in dissolved As and the sediments are red, brown and yellowish in character. The Holocene sequence includes: piedmont deposits that occur mostly in the north; floodplain and other interchannel/overbank deposits of the Ganges-Brahmaputra-Tista-Meghna river system; delta plains of the Ganges-Brahmaputra-Meghna system; coastal plains and active sub-basins including large inland lakes or “haors and bil”. At Comilla, neotectonic uplift is occurring on the Comilla terrace (Goodbred and Keuhl 2003). The offshore sediments consist of a subaquatic delta prograding on the shelf.

The Quaternary sedimentation is believed to have been controlled dominantly by the global climate change coupled with the rise of the Himalayan orogen. A thick sequence of Quaternary sediment accumulated in the basin, especially in two distinctive environments and associated sub-environments in the north and south of the Ganges and lower Meghna Rivers. Coarser sandy strata have developed as channel facies under the fluvial regime in the north whereas finer clastic facies have

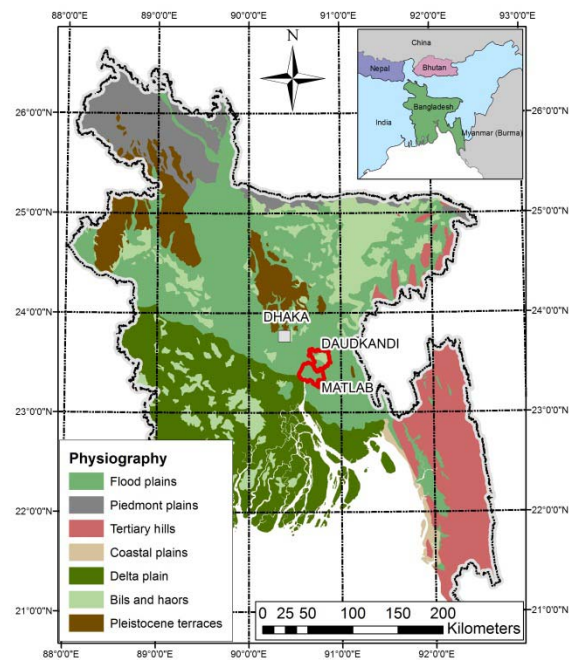


Figure 1. Physiography of Bangladesh and location of the study areas.

formed under the deltaic regime in the south. During the late Holocene time, as marine transgressions were waning, marshy or swampy lowlands developed in several parts of the basin giving rise to carbonaceous deposits such as peat and sediments rich in organic matter.

The flood plain is characterized by meander rivers, natural levees and back swamps. The upper part of the Holocene sequence includes the flood plains, fine-grained and/or muddy deposits, down to approximately 10 to 20 m (Umitsu 1987, 1993, Goodbred and Keuhl 2003). Below the floodplains are channel deposits including coarser sediments such as sand and gravel. The Holocene sequence reaches down to the depth of approximately 100 m, the deepest Holocene deposits being at the Meghna River. Goodbred and Kuehl (2003) identified oxidised surfaces at the depth of 80 m halfway between Comilla and Meghna and at shallow depth (<20 m). The floodplain composes non-calcareous grey to dark grey flood plain soil (Brammer 1996). A thick sequence of Quaternary sediment constitutes the substratum of the study area. The Holocene topmost sequence is composed of alluvial sand, silt and clay with

marsh clay. The location of the river channel of Meghna has been more or less the same during the last 18 kyr (Umitsu 1993). It can be assumed that the present location of Meghna also was the location of Paleo-Meghna river channel dating back to 120 kyr BP (BGS and DPHE 2001). Thus it can be assumed that the sediments near the present river channel are relatively coarser with high permeability. This can be seen in borelogs collected by DPHE/DFID/JICA (2006).

3.2. Climate and precipitation

As major parts of Bangladesh, the study areas, Matlab and Daudkandi, have three major climatic seasons, a moderately warm winter (November-February) followed by a hot summer (March-May) and the monsoon and rainy season (June-October). Temperature varies from approximately 10 to 36 °C. The rainfall in the area is 2,500 mm/yr where of 95 % is received during the monsoon period. Evapotranspiration in the region (data for Dhaka) is 1,602 mm/yr and varies from 89 to 188 mm/month peaking in April and May (BGS and DPHE 2001 and references therein; Figure 2).

3.3. Hydrogeological setting

The aquifer system of the Bengal basin is one of the most productive in the world. The alluvial Holocene aquifers of the delta plain are prolific and found within very shallow depths.

Groundwater levels in the Holocene aquifers lies very close to the surface and fluctuates with the annual rainfall pattern. Locally, groundwater level fluctuations are affected by heavy pumping and groundwater abstraction even though in most places the system is fully recharged during the monsoon season. Natural groundwater level amplitudes are in the order of 2-5 m over the year. As Bangladesh experiences a tropical monsoon climate with heavy rainfall during June to October, the groundwater levels start to increase during May/June and decreases in September/October. The groundwater levels are lowest during the end

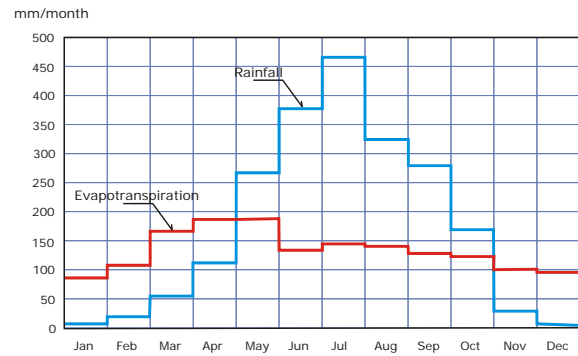


Figure 2. Long term monthly rainfall and potential evapotranspiration (average) for Dhaka City, 1953 -1977 (BGS and DPHE 2001).

of April to early May (BGS and DPHE 2000, Hasan *et al.* 2007).

Several attempts have been made to describe the aquifer distribution (UNDP 1982, EPC/MMP 1991, BGS and DPHE 2001, DPHE/DFID/JICA 2006, Mukherjee *et al.* 2007, 2008). Most aquifer models are based only on lithological units. A four-layer model was developed by EPC/MMP (1991) that could take vertical head differences into account and assess water balance adequately. The alluvial aquifers of Bangladesh are commonly semi-confined to confined. Transmissivity, hydraulic conductivity and storage coefficients have been determined from a large number of pumping tests (BGS and DPHE 2000). Most aquifer tests have been analysed by classical methods based on tests with partial penetration of the aquifers. Ravenscroft (2001) described three groundwater flow systems in Bangladesh: i) a local system down to 10 m, this system is a product of local topography such as levees, local hills, terraces, haors and bils and rivers, ii) an intermediate flow system with flow pathways down to a couple of 100 m driven by the larger terraces, major rivers etc. and iii) a basin-scale flow system, down to a depth of several 1,000 m. This system would include the entire Bengal basin with its borders in the Tertiary Hills in the east, the Indian shield in west, the Shillong plateau in north and the Bay of Bengal in the south.

Groundwater flow patterns have been affected because of heavy abstraction of groundwater for irrigation and drinking water purposes (Michael and Voss 2009a, b).

Domestic drinking water wells in rural areas of Bangladesh are generally small diameter hand-pump wells. These hand-pump wells can easily be installed to a depth up to 100 m depending on local geological conditions. Based on population and per capita use, groundwater abstraction for domestic usage can be calculated. Approximately 50 l/day/person is used for domestic purposes in Bangladesh, in some areas of rural Bangladesh as much as 30 mm/yr can be abstracted for domestic purposes (Michael and Voss 2008). However groundwater abstraction for irrigation purposes is about an order of magnitude more in rural areas and in some areas more than 600 mm/yr is used.

Today, the abstraction of groundwater for irrigation and drinking purposes, construction of water channels and embankments and road construction etc. have substantially changed the natural surface water and groundwater flow pattern. Humans have cultivated the area by constructing channels to lead the water to the rice fields, thus interfering the natural water system (Figure 3). The soil from the channels has been used to make dikes for roads and levees for the houses which have

resulted in ponds close to the houses. In the dry season, water pumped from the channels or abstracted groundwater is distributed to the rice fields via irrigation trenches.

3.4. Arsenic geochemistry

Arsenic is wide spread in the earth's crust, the average concentration is 1-2 mg/kg (Bhattacharya *et al.* 2002b, Sarkar 2002, Smedley and Kinniburgh 2002) and occurs as trace element in all rocks, soils and sediments. Weathering of minerals is the main source of As in sediments and soils. Oxidation of arsenopyrite (FeAsS) and other primary sulfide minerals are usually the primary source of As in soils and sediments (Bhattacharya *et al.* 2002a, Smedley and Kinniburgh 2002). In oxidised sedimentary systems As is sorbed onto the reactive surfaces of secondary oxyhydroxides of iron, aluminium and manganese (Dzombak and Morel 1990, Bhattacharya *et al.* 1997, Smedley and Kinniburgh 2002). Arsenic can be incorporated in diagenetic pyrite, formed in highly reduced sediment deposits. Due to this process the reduced conditions enhance the assimilation of As in some peat soils, bogs and the similar (Minkinen and Ylirokanen 1978).

Arsenic is an oxyanion-forming element and

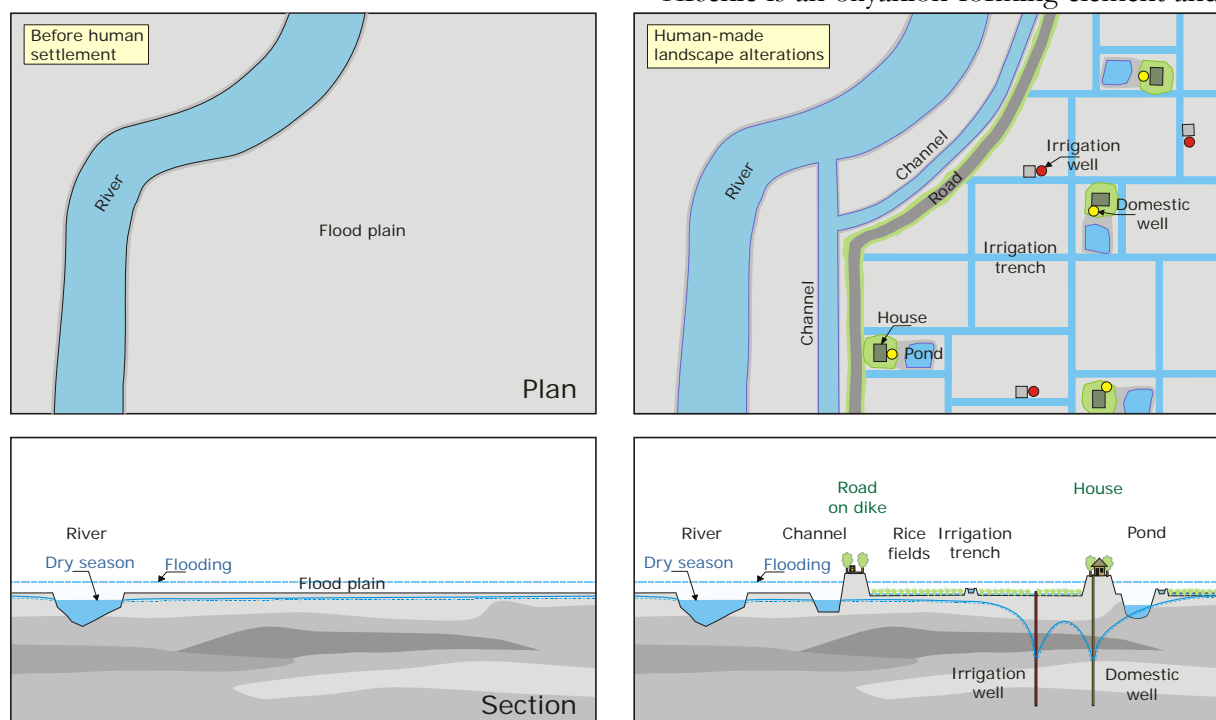


Figure 3. Illustration of the human interference on the natural water flow system.

occurs in several oxidation states. In natural sediment and water systems As mainly occurs in inorganic oxyanionic forms, arsenite (As^{III}) or arsenate (As^{V}). Arsenite has been considered the more toxic species, however recent studies has shown that most ingested arsenate is reduced to arsenite (Welch and Stollenwerk 2003). Therefore, the ingestion and exposure of both species may result in similar toxicological effect. In reducing environments and below pH 9, arsenous acid dominates in the form of $\text{H}_3\text{As}^{\text{III}}\text{O}_3^0$. At higher pH arsenous acid is deprotonated and form $\text{H}_2\text{As}^{\text{III}}\text{O}_3^-$ (Bhattacharya *et al.* 1997, Mandal and Suzuki 2002, Smedley and Kinniburgh 2002, Stüben *et al.* 2003, Welch and Stollenwerk 2003).

Redox conditions and pH are the main factors controlling the mobility of As in natural sediment-water systems since these factors control the behaviour of sulfide minerals and Fe(III)oxyhydroxides in the sediment-, water system. Further, the redox sensitive characteristics of As makes it vulnerable to mobilisation at typical groundwater pH, *i.e.* pH 6.5-8.5 under different redox conditions (Bhattacharya *et al.* 1997, Bhattacharya *et al.* 2002b, Smedley and Kinniburgh 2002, Sracek *et al.* 2000, 2004a).

The behavior of As can be conceptualized in three distinct redox-zones (Sracek *et al.* 2004a):

- 1) Shallow, oxidising zone with dissolved O_2 , in which Fe(III)-hydroxyoxides are stable and As is immobilised through adsorption;
- 2) Intermediate, moderately reducing zone without O_2 , in which Fe(III)-hydroxyoxides undergo reductive dissolution and As is released. In this zone, dissolved concentrations of Fe^{2+} can be controlled by precipitation of minerals like siderite and vivianite;
- 3) Deep reducing zone, where SO_4^{2-} is reduced with resulting formation of H_2S . In this zone, As can co-precipitate in secondary sulfides like As-rich pyrite. However, if concentration of dissolved SO_4^{2-} , and thus, generated H_2S is low, there is no

precipitation of secondary sulfides and As is mobile.

Ion competition play an important role in mobilising As adsorbed onto reactive surfaces. The dissolved ions compete either through direct competition for specific adsorption sites or indirectly through their influence on the electrostatic charge of the reactive surfaces. For mobilising adsorbed As into groundwater, the most important ions are $\text{PO}_4^{3-\text{tot}}$, SO_4^{2-} , HCO_3^- , and H_4SiO_4 of which $\text{PO}_4^{3-\text{tot}}$ is often the main competing ion (Welch and Stollenwerk 2003).

3.5. High arsenic groundwater in Bangladesh

High As groundwater in Bangladesh is derived from geogenic sources and is encountered in the Holocene alluvial aquifers of the Bengal Delta Plain (BDP), Bangladesh (BGS and DPHE 2001, Smedley and Kinniburgh 2002, Ahmed *et al.* 2004; Figure 4). It has been found that groundwater with elevated As concentrations are associated with anaerobic conditions and that As is mobilised through the reductive dissolution of iron oxyhydroxides (Fe(III)-oxyhydroxides) present as coatings on the sediments in reaction with organic matter. This mechanism was first described by Bhattacharya *et al.* (1997) and Nickson *et al.* (1998, 2000).

Through detailed studies of prevailing aquifer conditions, the main mechanisms of mobilisation and genesis of As in the aquifers have been delineated (Bhattacharya *et al.* 1997, Nickson *et al.* 1998, BGS and DPHE 2001, Smedley and Kinniburgh 2002, van Geen *et al.* 2003, Ahmed *et al.* 2004, Horneman *et al.* 2004, Hoque *et al.* 2004, McArthur *et al.* 2004, Sracek *et al.* 2004b, Bhattacharya *et al.* 2006, Bhattacharya *et al.* 2008, Uddin *et al.* 2011). However, in many of the regions the distribution of As is extremely heterogeneous, both laterally and vertically, and As safe and unsafe tubewells (installed in what is described as the same aquifer) are often found within <25 m from each other. On the basis of the described

geological settings, the prevailing aquifer conditions and the theories of mobilisation, many of the As safe tubewells should have high concentrations of As. Consequently, the “patchy distribution” has been explained in terms of “local variations in sedimentary characteristics, hydrogeological and hydrogeochemical conditions” (BGS and DPHE 2001, Bhattacharya *et al.* 2002a, 2002c, Smedley and Kinniburgh 2002, Bundschuh *et al.* 2004, McArthur *et al.* 2004, Ravenscroft *et al.* 2005, Bhattacharya *et al.* 2006) and hence no, or at the best a poor, explanation has been given for the As safe tubewells.

There are distinct spatial patterns in distribution of As in groundwater. It is evident that significantly large proportions of wells located in the southern sub-districts exceed the BDWS compared to the wells located in the north. A number of studies report that spatial distribution of As in groundwater is controlled by sub-surface geology, i.e. most wells located in the areas occupied by the young floodplains and deltaic sediments where As concentrations exceed BDWS (Figure 4). Water in wells installed in Holocene coarse fan deposits rarely exceeds the BDWS and wells developed in Pleistocene and older sediments never exceed the BDWS (BGS and DPHE 2001, Ahmed *et al.* 2004, Zheng *et al.* 2005).

There is a clear depth control in the occurrence of high As in groundwater in Bangladesh. The peak concentration occurs at around 20-50 m, whereas aquifers below have lower concentrations. BGS and DPHE (2001) reports that aquifers deeper than 150 m have consistently low concentrations of As. Other studies report occurrence of low As water at shallower (van Geen *et al.* 2004, von Brömssen *et al.* 2005) and at greater depths (Bhattacharya *et al.* 2002a, JICA 2002). However, BAMWSP data from 66 Upazila show that a larger proportion of wells from depth >150 m exceed the BDWS. These findings are contradictory to earlier studies and need further investigation. It has been established from different

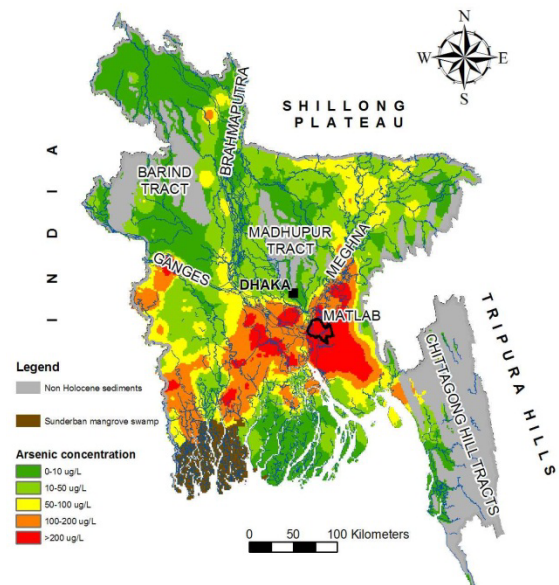


Figure 4. Map of Bangladesh showing the great rivers of Ganges, Brahmaputra and Meghna, the location of Matlab and the distribution of As in groundwater, after BGS and DPHE (2001).

studies that there is no specific depth for the occurrence of As safe water, rather it is controlled by the subsurface geology and hydrogeologic conditions (Ahmed 2005).

The depth-wise As distribution in Bangladesh is shown in Figure 5 (BGS and DPHE 2001). The mechanism of mobilisation of As, triggered by reductive dissolution of Fe(III)-oxyhydroxides in the Holocene aquifers, is a plausible explanation for the set of groundwater samples in zone marked A, while within zone B the geological model with older and oxidised Pleistocene aquifers with low inherent As concentrations seems applicable. These deeper safe tubewells have been coupled to the deeper oxidised and flushed Pleistocene aquifers (BGS and DPHE 2001, Ravenscroft 2001, Harvey *et al.* 2002, Stüben *et al.* 2003, van Geen *et al.* 2003, 2004, McArthur *et al.* 2004, Chatterjee *et al.* 2005). However, for the As safe tubewells within zone C ($n_c \approx 50\%$), a reappraisal of the geological and hydrogeological model and/or mobilisation theory needs to be addressed. In a few studies in Bangladesh (Harvey *et al.* 2002, van Geen *et al.* 2004) detailed aquifer and groundwater characteristics have been defined in such way that they have produced

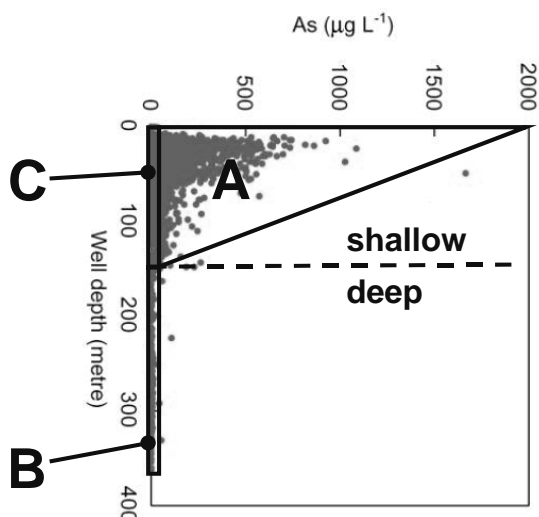


Figure 5. Depthwise distribution of As in hand tubewells for Bangladesh (BGS and DPHE 2001). Within area A and B the prevailing mobilisation theory is valid. However, for the tubewells at shallow depth with low As (C) which includes 54% of the samples the explanation of the low As concentrations are poorly described.

feasible hypotheses for explaining the great spatial distribution. In these studies the groundwater chemical composition has been correlated to specific aquifer sand characteristics. Previous studies have, in general, explored the reasons of As mobilisation in the groundwater and high-risk factors, but have not assessed the immobilisation processes and/or aquifer conditions favourable for low concentrations of mobilised As.

4. MATERIAL AND METHODS

Combinations of approaches were used to assess the hydrogeological prerequisites for delineation of low As groundwater in the aquifer system for further development by local and rural people in southeastern-Bangladesh. All work done have been aimed at enhancing the understanding of the aquifer system with emphasis on processes resulting in high concentrations of As in groundwater. Understanding the heterogenic distribution of As has been considered a key-factor. The methods used comprised of groundwater and sediment sampling, detailed chemical analysis of water, sediment

extractions, mineralogical investigations and hydrogeochemical- and groundwater modelling.

4.1. Delineating sediment colours

In the Matlab study area, a test of the drillers' perception of the sediment colour and the lithology of the aquifer sediments was done by having them to describe the local settings prior to three (A, B, C) drillings (Jonsson and Lundell 2004, Paper I). The boreholes were drilled with the hand-percussion technique and washed sediments were collected every 1.5 m or at any change of lithology. Texture and colour characteristics were described for each sediment sample by the drillers' and later compared with the Munsell standard soil colour chart for colour classification.

4.2. Groundwater sampling and analysis

Groundwater samplings were done in Matlab and Daudkandi following the procedure described by Bhattacharya *et al.* (2002b) and Paper I. Field parameters were measured and samples collected included filtered aliquot and aliquot filtered and acidified with suprapure HNO_3 (14 M) (Bhattacharya *et al.* 2002b). Arsenic speciation was performed in field with Disposable Cartridges® in the field (Meng *et al.* 2001). Major anions and cations, trace metals and As, as well as dissolved organic carbon (DOC) were analysed by standard analytical methods as described in Paper I and II.

In Matlab, the first round of groundwater sampling was carried out together with one of the experienced local drillers from 40 tubewells within an area of $2 \times 2 \text{ km}^2$ in two villages, Dighaldi and Mubarakdi, 3 km east of the Meghna river. These 40 tubewells were sampled during May 2004 at depths varying between 17-82 m. Depth and colour of the sediments, as described by the driller responsible for the installation, was recorded as well. Subsequently each groundwater sample was linked to the colour characteristics of the screen sediments. Four colours were used to describe washed

sediments characteristics in the area: black, white, off-white (buff), and red (orange/brown) (Paper I). Another set of groundwater samples were collected in January-February 2005 from the same set of 40 tubewells (Paper II). In 2006, 2008 and 2009, 20 out of the 40 tubewells were resampled. The later sampling rounds were done in order to monitor temporal water quality variations (Paper IV).

In Daudkandi, groundwater samplings were done in February-March 2004, in the village Dularampur. Groundwater samples were derived from hand tubewells and installed piezometers in the upper shallow aquifer to a maximum depth of 25 m (Paper III).

4.3. Sediment sampling

Sediments were collected both at Matlab and Daudkandi. In Matlab, washed and disturbed sediment samples were collected every 1.5 m to a total depth of 60 m from drillings conducted at three sites called A, B and C (Paper I). For proper characterisation of sediment geochemistry on undisturbed sediments, core drillings were done at location C (Paper I, II). The sites were chosen in order to get as diversified, with respect to texture and colour characteristics, sediments as possible. The core drilling in Matlab reached a depth of 63 m (200 ft) and was performed with a combination of a hammer technique and a donkey pump. Samples were taken every 1.5 m (5 ft) down to the depth of 30 m and between 30 and 60 m at an interval of 0.6 m (2 ft). The reason for short sampling interval below 30 m was to target and collect as much oxidised sediments (whitish to reddish in colour) as possible as the blackish reducing sediments have been studied more thoroughly by others as well as within this study (Paper III). Later the core-samples were split for lithological and mineralogical studies as well as sequential extraction. At that time, a coal-like vegetation remains were collected and sent for dating through ^{14}C analysis. The ^{14}C analysis was performed at the Radiocarbon Dating Laboratory in Lund using Single Stage Accelerator Mass Spectrometry

(SSAMS). Ten samples representing the depth of the drilling and whole colour spectra as described (Paper I) was selected for solid phase geochemical and mineralogical studies (Figure 6).

In Daudkandi, sediment samples were collected in March 2004 at the village Dularampur. Undisturbed core-samples were collected through core drilling performed with the same technique as described above. Samples were taken every 1.5 m (5 ft). The core-samples were split for lithological and mineralogical studies as well as sequential extraction. Approximately 20 g of sediment was air-dried; six samples from varying depth were used for later mineralogical and geochemical solid phase studies (Paper III).

4.4. Mineralogical investigations

The mineralogical studies included i) X-ray fluorescence (XRF) for analysis of the bulk composition of sediments, ii) X-ray diffraction (XRD) for targeting oxide, hydroxide, sulphide, sulfate and carbonate minerals and iii) scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDS) for qualitative characterisation of grain coatings and authigenic mineral phases. Analysis of the total organic content (TOC) for the solid phase was done as well. Detailed analytical methodology is given in Paper II and III.

4.5. Sequential extraction and column experiments

Operationally defined sequential extractions were performed on sediment core-samples from both Matlab and Daudkandi, although the procedures were slightly different (Paper II, Paper III).

On sediment samples from Matlab, six-step sequences of extraction were carried out: i) deionized water (DIW) for quantification of the water soluble fraction of As and other trace elements; ii) 0.01 M NaHCO_3 for the release of elements under high pH conditions; iii) 1 M Na acetate ($\text{C}_2\text{H}_3\text{NaO}_2$, NaAc) for elements bound to carbonate and phosphates phases (Dodd *et al.* 2000, Ahmed *et al.* 2004); iv) 0.2 M ammonium oxalate

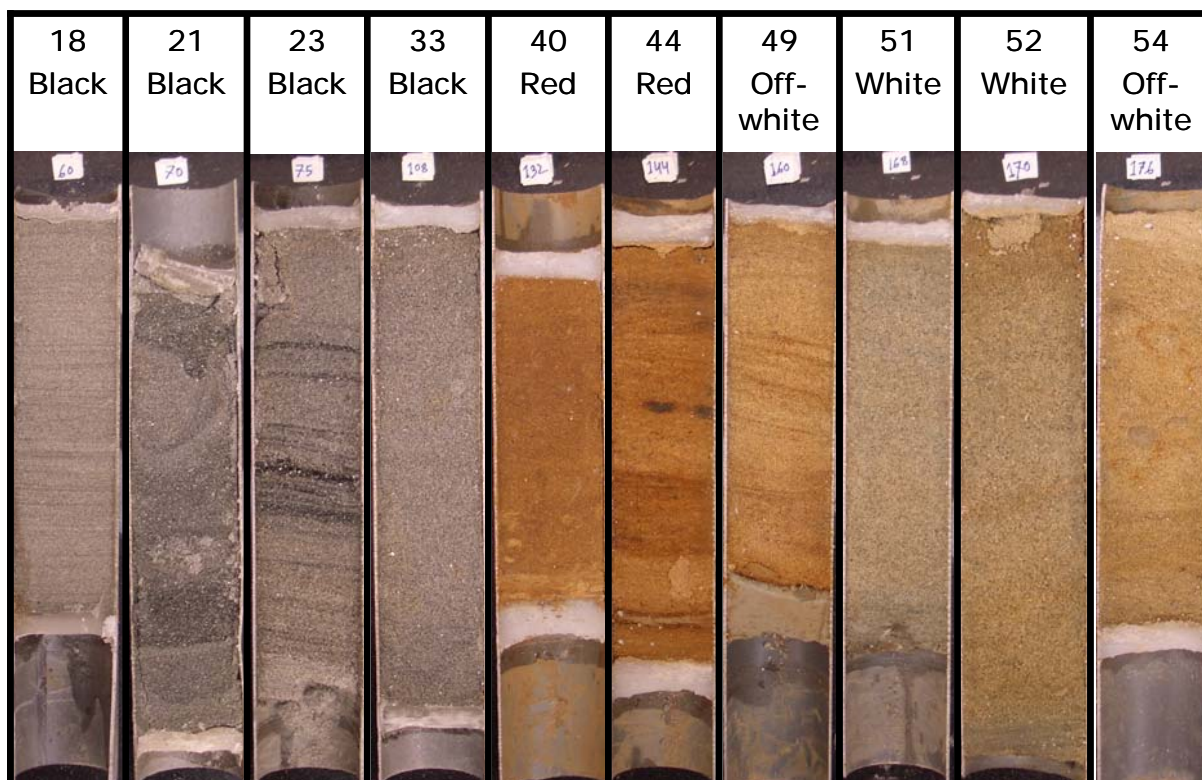


Figure 6. Photographs of the 10 sediment core samples that were used for extraction tests and mineralogical studies, the numbers on top of the cores represent the depth (in meter). The colour descriptions correspond to the colours described in Paper I.

($\text{NH}_4\text{C}_2\text{O}_4$) for quantification of Fe, Al, and Mn bound to amorphous oxides and hydroxides in the sediments; v) 0.2 M ammonium oxalate ($\text{NH}_4\text{C}_2\text{O}_4$) + 0.1 M ascorbic acid (Oxalate+AA) for residual amount of Fe, Al and Mn bound to oxides and hydroxides including crystalline phases; and vi) 7 M HNO_3 for determining As and other elements associated with the non-silicate minerals. The scheme followed the methods described by Wenzel *et al.* (2001) and Bhattacharya *et al.* (2006).

On sediment from Daudkandi, a four-step extraction was carried out. Two grams of air dried sediments were extracted with: i) 1 M sodium acetate (CH_3COONa , NaOAc) to estimate the elements bound to carbonates (Tessier *et al.* 1979, Filgueiras *et al.* 2002), ii) 0.2 M ammonium oxalate solution ($\text{NH}_4\text{C}_2\text{O}_4$) to quantify the elements in reducible phase i.e. poorly crystalline and amorphous oxyhydroxides (Bhattacharya *et al.* 2001, Wenzel *et al.* 2001), iii) 33 % hydrogen peroxide (H_2O_2) to estimate the oxidisable phase i.e. elements bound to organic matter and sulphides (Quevauviller

et al. 1993, Filgueiras *et al.* 2002), and iv) 7 M HNO_3 to estimate the residual phase that is not easily mobile (Claesson and Fagerberg 2003, Ahmed *et al.* 2004, Bhattacharya *et al.* 2006). The extracts were collected in vials and analysed by ICP-OES.

4.6. Arsenic adsorption experiments

Adsorption dynamics of the oxidised sediments from Matlab were investigated by extractions, batch isotherm experiments, and column experiments. Three oxidised (Paper I) sediments were selected for laboratory experiments, samples no. 1 and 3 were from borehole A (48.8 m and 53.3 m) and sample no. 2 was from borehole B (51.8 m).

For quantification of elements associated with amorphous oxides and hydroxides 0.2 M oxalate ($\text{NH}_4\text{C}_2\text{O}_4$) extractions were done. Total concentrations of the elements in the sediments were determined using 7 M HNO_3 extractions. Duplicates were performed on each sample (Paper IV). For batch adsorption isotherm tests, 2 g of drained sediments (sample no. 1-3) were mixed with 30 ml 0.01 M NaNO_3 and

sodium hydroxide (NaOH) and HNO₃ were added to adjust pH to 7. Subsequently distilled water with As(V) (as K₂HAsO₄) concentrations ranging from 0.2 to 100 mg/l were added. As(V) was used for the batch tests as it was considered to be the predominant sediment-bound As species in the oxidised aquifers (Stollenwerk 2007).

Later, column experiments were conducted to investigate influence of DOC on adsorption capacity of the sediment samples. Distilled water prepared with NaCl, NaHCO₃ and NaAs(III)O₂ corresponding to mean concentrations of As, Na, Cl in groundwater from tube wells installed in reducing sediments were used for the experiments. As(III) were used as this is the most abundant redox specie (Paper I). In a replicate column, 0.2 wt. % lactose was added. This was done in order to investigate the potential for DOC to stimulated reductive dissolution of Fe(III) and Mn(IV) oxyhydroxides.

4.7. Geochemical modelling

The geochemical modelling tools PHREEQC version 2.14.2 (Parkhurst and Appelo 1999) and Visual MINTEQ version 2.53 (Dzombak and Morel 1990, Allison *et al.* 1991) were used for:

- i) Calculation of saturation indices with the objective to identify possible mineral phases controlling the aqueous chemical composition and (Paper II);
- ii) Simulation of adsorbed and dissolved As for prevailing conditions with the objective to enhance the pattern of As adsorption and mobilisation, in aquifers of the study area (Paper II);
- iii) Simulation of the adsorption of As on oxidised sediments, as surface complexation reactions on generic hydrous ferric oxides, in order to investigate the adsorption dynamics of the oxidised sediments (Paper IV).

The thermodynamic relationships between species in solution and aquifer solid phases were established through the degree of saturation with respect to minerals (Paper II). Saturation index (SI) is defined as:

$$SI = \log \left(\frac{IAP}{K_{sp}} \right)$$

where IAP is the ion activity product and K_{sp} is the solubility product for a given temperature. When SI=0 (IAP=K_{sp}) the solution is at thermodynamic equilibrium with respect to a specific mineral and when SI>0 the water is supersaturated with respect to a mineral and vice versa. Calculation of SI was done to identify possible sinks and sources of dissolved elements and for further interpretation of possible reactions controlling the aqueous chemistry (Sracek *et al.* 2004a).

Simulation of As adsorption for prevailing aquifer conditions were done as surface complexation reactions on hydrous ferric oxides (Hfo) with the Diffuse Layer Model (DLM) (Dzombak and Morel 1990, Allison *et al.* 1991). The simulations comprised of a batch system of Hfo, adsorbed and dissolved As(III)-tot and dissolved PO₄³⁻-tot as described by Figure 7 and Paper II. It was assumed that As adsorption was controlled by pH, Hfo content, species of As and presence of PO₄³⁻-tot as competing ion (Smedley and Kinniburgh 2002, Sracek *et al.* 2004a, Gustafsson and Bhattacharya 2007). Input data came from Paper I and III and is specified in Paper II. Available amount of Hfo and As was derived from oxalate extraction and dissolved amounts (Paper II). A constant concentration of dissolved PO₄³⁻-tot was used as boundary condition simulating phosphate mineral phases in equilibrium with the groundwater described below. This assumption was based on the findings from speciation modelling showing phosphate mineral phases in equilibrium with the groundwater (see results below).

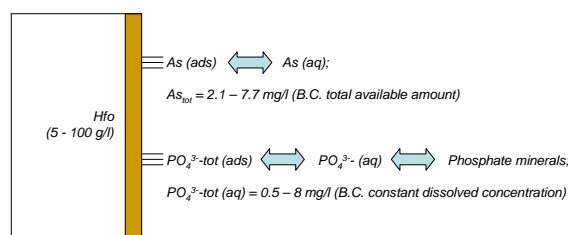


Figure 7. Conceptual model of the adsorption simulation.

Thus, the simulations calculated the amount of adsorbed and dissolved As and adsorbed amount of phosphate as a competing ion for As on available adsorption sites (Paper II).

For studying the As dynamics on oxidised sediments surface complexation reactions of As on generic hydrous ferric oxides ($Hf\phi$) were simulated using the Diffuse Layer Model of Dzombak and Morel (1990) using PHREEQC (Parkhurst and Appelo 1999) and Minteq.v4 database (Allison *et al.* 1990). The specific surface area of $600 \text{ m}^2/\text{g}$ and site densities of $0.2 \text{ mol weak sites/mol } Hf\phi$ and $0.005 \text{ mol strong sites/mol } Hf\phi$ were used. The amount of $Hf\phi$ was calculated based on the oxalate extraction (Fe_{ox}) and simulations results on surface composition were validated by comparing with analytical results from oxalate extractions. Saturation indices and adsorption isotherms were simulated using the PHREEQC programme (Paper IV).

4.8. Hydrological field investigations

Ten piezometer nests (Figure 8) were installed and hydraulic heads were monitored on weekly basis between May 2009 and October 2010 to prepare hydrographs at varying depth of the aquifer system and to investigate the vertical gradients within the aquifer system.

The hydrostratigraphy was later delineated through analysing drilling logs from the piezometer installations and ^{14}C analysis (incl. ^{13}C) was used for estimation of

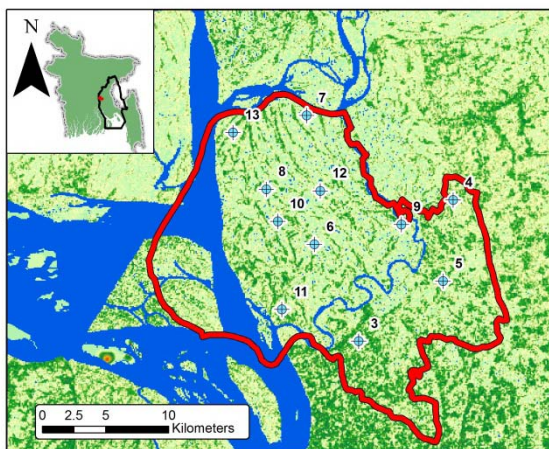


Figure 8. Map showing the location of piezometer nests, the red line shows the border of Matlab.

groundwater ages in the study area. Estimates of groundwater ages could give a clue of how the turnover time of groundwater in the aquifer system and thus substantial input for our understanding of the hydrogeological system. During 2006 and 2007 groundwater samples from the study area were analysed for carbon-14 (^{14}C). For the ^{14}C analysis, groundwater samples were collected from the tubewells, NaOH was added, and the bottles were transported to Dhaka University where inorganic carbon was precipitated as BaCO_3 . The substrate was later analysed at Radiocarbon Dating Laboratory at Lund University (<http://www.geol.lu.se/c14/en/>) for ^{14}C and ^{13}C for dating of groundwater.

For a better understanding of the human interferences on the hydrogeological system an irrigation well survey was performed in Matlab. The survey was done in order to estimate the total abstraction rate in the area. A total number of 601 irrigation tubewells from Matlab was identified and abstraction rate, operation time/season, depth and coordinates were obtained. All irrigation wells were later introduced into the groundwater models as individual wellpoints.

A conventional hydraulic test was done in January 2008 in order to determine hydraulic properties of the shallow aquifers including the vertical and horizontal hydraulic conductivity. The pumping test was carried out during January 2008 in the middle of the dry season. The drilling work, using hand-percussion technique, consisted of installation of 9 piezometres as described in Paper V (Figure 9). The pumping test was run with the yield of approximately $65 \text{ m}^3/\text{hr}$. The results from the test were analysed by standard analytical calculations as well as with a local groundwater model (Paper V).

4.9. Groundwater flow modelling

The computer code MODFLOW (Visual Moflow v. 4.1) was used to generate a three-dimensional finite difference groundwater model to study the groundwater flow of the aquifer system. A regional steady state- and

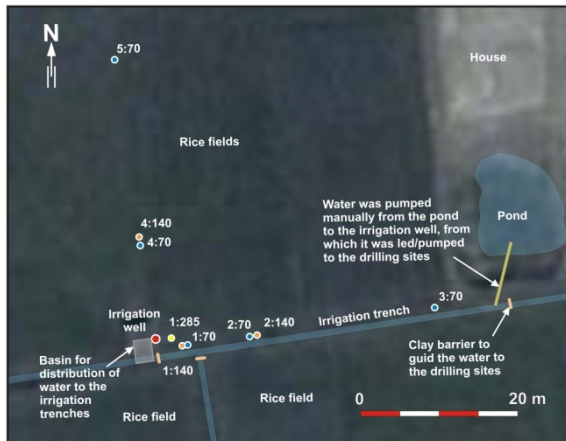


Figure 9. Set-up of the pumping test.

transient flow model was constructed. The model area covered eastern part of Bangladesh from the hilly region in the east to Meghna River in west. The models were run for both undisturbed and disturbed conditions including abstraction of groundwater for irrigation purposes. The steady state model was calibrated to match ^{14}C dating (Michael and Voss 2008) while the transient models were calibrated to match measured hydraulic heads in the piezometer nests. Surface water levels of Meghna were idealized for the use in the model (Paper V).

It can be assumed that at least one thick shallow aquitard exists (Paper V). DPHE/DFID/JICA (2006) describes a multi-layered system of aquifers and aquitards that have been used for further development of the regional models. Two major modelling approaches were used: i) a homogeneous anisotropic model with vertical hydraulic conductivity (K_v) \ll horizontal hydraulic conductivity (K_h) (Michael and Voss 2008), and ii) an anisotropic model where generic aquitards identified through exploratory drillings and aquifer delineation (DPHE/DFID/JICA 2006) were introduced. Hydraulic conductivity and storage properties were varied along with the presence of aquitards for the second (ii) modelling approach in order to meet calibration criteria (Paper V). Using both steady state and transient approach proved useful as the hydraulic properties better could be estimated.

5. RESULTS

5.1. Local drillers perception of sediments

The boreholes ($n=3$) that were drilled in Matlab confirmed the driller's perception of two separate lithological units as well as texture and colour of the sediments. As described by the drillers, a layer of black to grey sediments overlies a unit with yellowish-grey to reddish-brown sediment with a clayey layer in between at the depth of approximately 30-40 m. A comparison between the drillers description of washed sediments and the Munsel colour code resulted in the four major colour groups; black, white, off-white and red as shown in Figure 10. Beside these four colours, the local drillers mention yellow, blue and green sediment, although the two later were uncommon according to them. Many drillers are not only aware of the As problem but they also target certain sediment for avoiding high Fe, which can be identified in field, and As based on the sediment colour. In an interview of 10 drillers Jonsson and Lundell (2004) found a consensus among the drillers that the black sediments were unsafe with respect to As while the other sediment colours were safe.

5.2. Groundwater chemical composition

The groundwater chemical data is presented in detail in Paper I, II and III. Groundwater samples from Daudkandi ($n=8$; sampled yr 2004) were collected from hand-tubewells and piezometers within a depth of 25 m installed in grayish to blackish sediments while samples from Matlab ($n=40$; sampled yr 2004 and 2005) were collected from hand-tubewells to a maximum depth of 82 m installed in sediments representing a wide range of colours as described above.

The groundwater is circum neutral with a pH value ranging from 6 to 7 and predominantly of Ca-Mg- HCO_3 or Na-Cl- HCO_3 type. Groundwater from Daudkandi and black sediments from Matlab were typically of Ca-Mg- HCO_3 . Chloride concentrations varied between 10 and

893 mg/l with the highest concentrations in red samples from Matlab.

High dissolved organic content (DOC) and NH_4^+ found in the samples from Daudkandi and black samples from Matlab (average = 1.6 and 1.1 mg/l respectively). In general the groundwater had low concentrations of SO_4^{2-} and NO_3^- (average = 1.3 and 1.5 mg/l respectively) and high concentrations of HCO_3^- , Fe and Mn (average = 499, 4.2, 1.6 mg/l respectively). High PO_4^{3-} -tot and As concentrations were found in samples from Daudkandi and black samples from Matlab (maximum = 8.0 mg/l and 422 $\mu\text{g/l}$ respectively) while both PO_4^{3-} -tot and As were generally low in white and red samples. Speciation of As(III) and As(V) showed that on an average 98 % of the samples from Matlab were As(III).

The samples from Matlab, classified into the four colour groups, reflect distinct groundwater composition. Groundwater abstracted from black sediment had relatively higher concentrations of NH_4^+ , DOC, Fe, PO_4^{3-} -tot, As and relatively low Mn and SO_4^{2-} concentrations indicating strongly reducing conditions (Figure 11). Samples from Daudkandi showed similar pattern as samples abstracted from black sediments in Matlab. In contrast,

groundwater collected from the oxidised sediments in Matlab (white, off-white and red samples, see below) showed relatively high concentrations of Mn and low Fe concentrations.

Water chemistry of the 20 tubewells that were sampled over the years of 2004-2009 was relatively stable with few exceptions (Paper IV). This result has later been validated in a more extensive study, in Matlab, by Bhattacharya *et al.* (2011).

5.3. Sequence of aquifer sediments

In both study areas a partly oxidised topsoil consisting of clayey and silty sediments to a depth of 2-7 m that are light-grey to yellowish-grey in colour followed by blackish to greyish sequences of fining upward cycles that represents fluvial sediments of Holocene age (Goodbred *et al.* 2003, Paper I, II, III).

In Matlab, where the drillings reached a depth of 60 m, two separate lithological units were identified (Paper I and III). A layer of black to grey sediments overlies a unit with white, yellowish-grey to reddish-brown sediment. The two units are separate by 5-10 m thick hard clayey shale, shifting from light grey to brownish red in its colour. The upper sequence (unit 1) reaches a depth

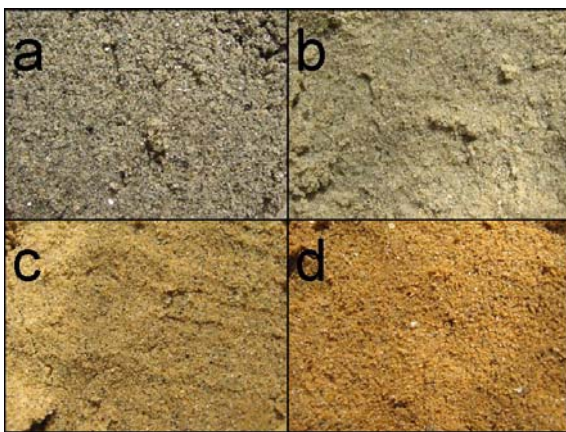


Figure 10. Colour description of the sequence of sediments according to the drillers and their Munsell classification (below) and representative photographs (left) of moist sediment from each group as described by the local drillers from the three boreholes: a) black; b) white; c) off-white and d) red.

Drillers description and colour class	Black	White	Off-white	Red/Yellow
Munsell description	Olive black ⇔ Dark greyish yellow	Grey ⇔ Yellowish grey	Dark greyish yellow ⇔ Olive yellow	Yellowish brown ⇔ Reddish brown
Munsell code	5Y 3/1 ⇔ 2.5 5/2	5Y 4/1 ⇔ 2.5Y 5/3	2.5Y 4/2 ⇔ 5Y 6/3	2.5Y 5/4 ⇔ 5YR 3/4

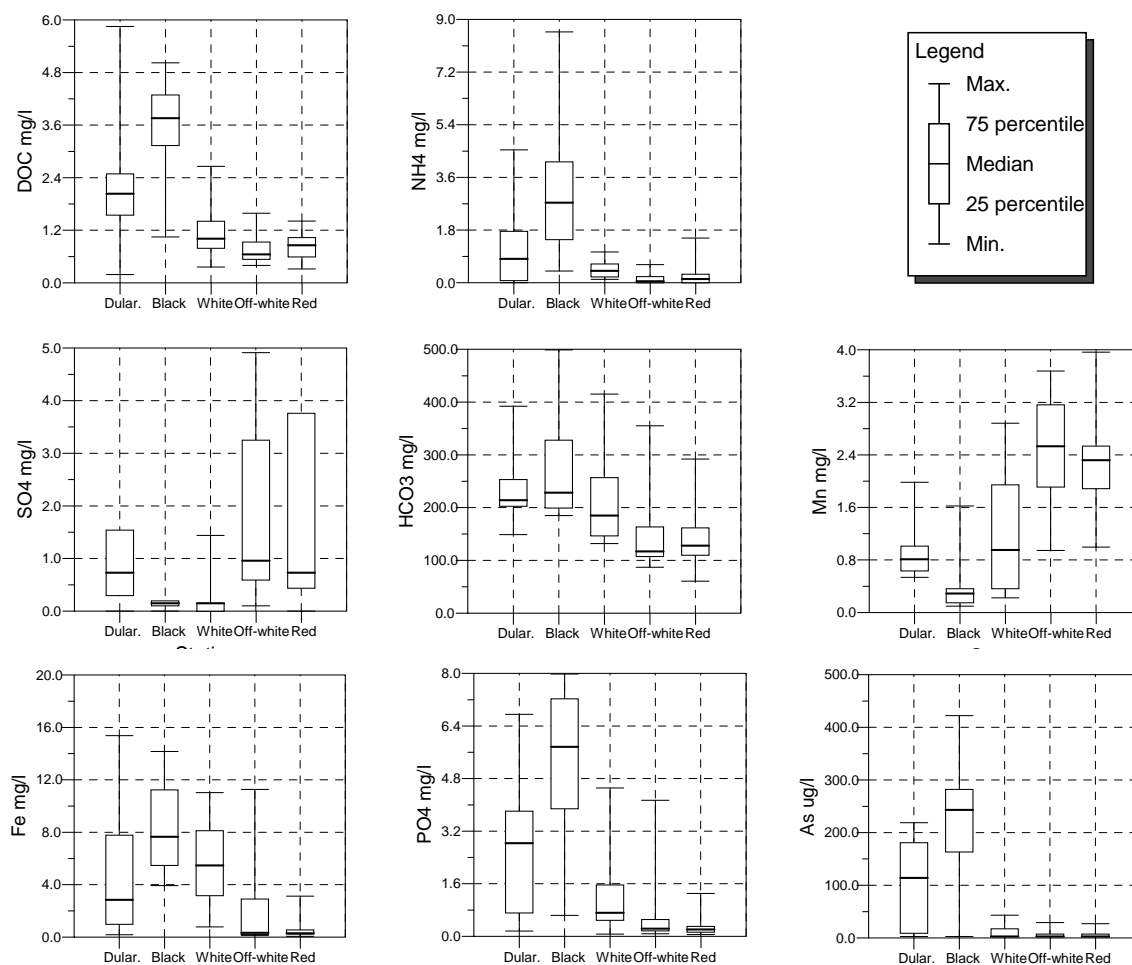


Figure 11. Box and whisker plots of dissolved organic content (DOC); NH_4^+ ; SO_4^{2-} , HCO_3^- , Mn_{tot} , Fe_{tot} , PO_4^{3--tot} and As_{tot} for sample locations ($n=8$) at Dularampur (Dular.) and Matlab ($n=40$; sampled during yr. 2004 and 2005); samples from Matlab are classified according to colour of sediment at depth of installation of screen.

of approximately 35-55 m and below the topsoil follows a fining upward cycle of sand, silt and clay (Paper I). This upper sequence, as well as the sediments studied in Daudkandi, are of Holocene age and have not been exposed to any extensive weathering.

Ocular and stereomicroscope examination of sediment show that the sands are fine to medium grained with quartz and potassium feldspars and plagioclase, accompanied with substantial content of micas and ferromagnesian minerals such as hornblende. These minerals dominate the sediments of the upper sequence in Matlab and Daudkandi. Dark coloured ferromagnesian, biotite and opaque minerals are responsible for the dark colour. In both

areas these minerals jointly with organic matter (OM) forms black bands at varying depth (Figure 12).

In Matlab, bioturbated hard shale was found at a depth of 35- 40 m (Unit 2A, Figure 12) from core-drilling (Paper III). This shale separated the two major units identified at the Matlab sampling site. The colour of the shale is grey in colour and indicate shallow marine depositional environment. Based on the ^{14}C analysis of the vegetation matter found incorporated in the shale it has been estimated that these sediments had an age of approximately 8,000 yr. This indicates that a marine transgression took place at that time. This is consistent with other studies by Goodbred *et al.* (2003) showing that at around 7,000–9,800 yr BP bioturbated

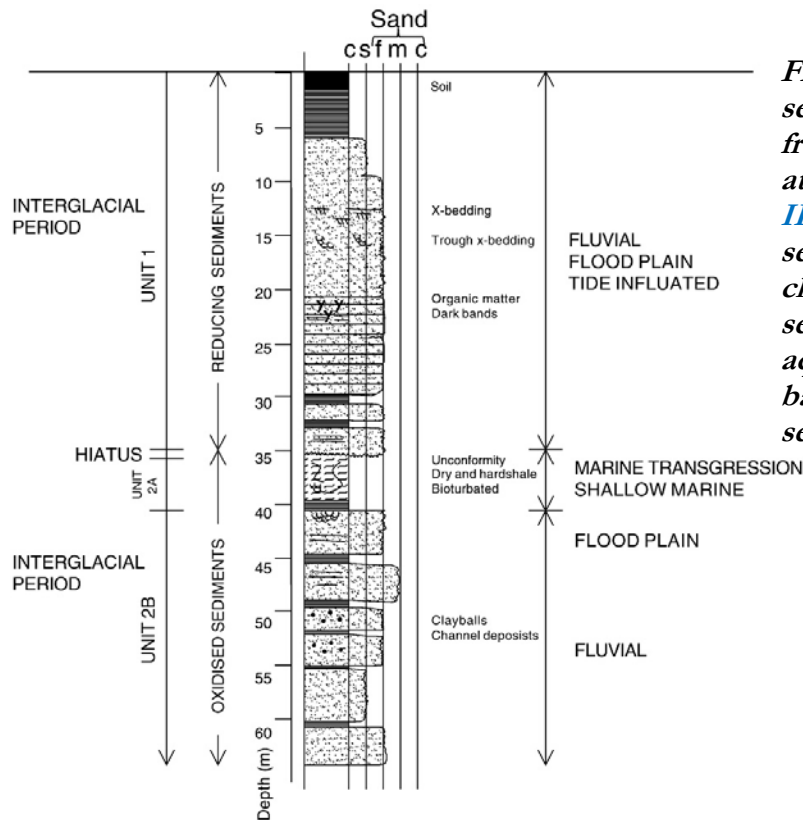


Figure 12. *Idealised sequence of sediments from Matlab (core-drilling at site C, Paper I, Paper II) with the diagnostic sedimentological characteristics of the sequence of sedimentary aquifers of the study area, based on the recovered sediment cores.*

sediments were deposited in the Bengal basin. The identification of an unconformity between the shale and the upper Holocene unit confirms that the lower unit has been exposed to weathering and oxidation and that the two units correspond to two interglacial periods.

Ocular inspection of the core samples from the weathered unit (Unit 2B) show lower abundance of biotite. Coatings of Fe(III)-oxyhydroxides on quartz, feldspars and other light and whitish minerals results in the yellowish to reddish colours of the sediments.

Investigations of the core samples derived from the lower oxidised unit (Unit 2B, Fig. 4) show that these sediments were also exposed to weathering and oxidation while the sea level in the BDP was significantly lower (Umitsu 1987, 1993, van Geen *et al.* 2004, McArthur *et al.* 2004). These sediments have lower abundance of biotite. Fe(III)-oxyhydroxides coatings on quartz, feldspars and other mineral grains are responsible for the reddish colour of the sediments.

5.4. Mineralogical investigations

X-ray diffraction (XRD) of reducing sediments from Daudkandi revealed that quartz, feldspar, mica, amphibolite and kaolinite constitute the bulk minerals. Carbonate minerals occurs throughout the profile while more of them in the yellowish topsoil in the form of siderite (FeCO_3) and ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$). Iron oxides occurs as hematite (Fe_2O_3) throughout while magnetite was identified only in the yellowish topsoil at the depth of 2.44 m. Although expected, Goethite (FeOOH) was not identified, probably due to the analytical sensitivity.

XRD analysis of the sediments from Matlab showed that the sands were dominated by quartz, potassium-feldspar (orthoclase) and plagioclase (anorthite and albite). The uppermost reducing unit was rich in biotite and ferro-hornblende while the lower weathered unit had lower amount of these minerals.

Through the scanning electron microscopy together with EDS spectra iron oxides, likely goethite (FeOOH), were identified within the yellowish grey sediment at 2.44 m depth

in Daudkandi. Likewise, amorphous iron oxide with traces of As on a biotite grain from the micaceous layer at 16.46 m depth was identified. Octahedral and framboidal pyrite on the same biotite grain was recognized (Figure 13).

5.5. Geochemical investigations

5.5.1. Bulk geochemical analysis

Major elements, As and TOC bulk chemical analysis of Daudkandi samples showed that the vertical distribution of TOC, iron (Fe_2O_3), aluminium (Al_2O_3), magnesium (MgO) and potassium (K_2O) followed the trend of As (As_{tot}) peaking in the dark bands in the sediment rich in mica. Although the amount of Mn (MnO) and phosphorous (P_2O_5) are low they follow the same trend as As while sodium (Na_2O) and calcium (CaO) show the opposite. The amount of organic matter, TOC, in the sediments ranged from 0.66 to 2.94 wt. %, this is consistent with other findings (McArthur *et al.* 2001, Anawar *et al.* 2003, McArthur *et al.* 2004). There was a strong correlation between As and iron ($r^2=0.79$) and between As and TOC ($r^2=0.89$). The source of iron and magnesium is minerals like biotite and hornblende while the potassium and aluminium source is muscovite and potassium feldspars. Clay mica, illite is the other major source, especially in the fine sediments.

The semi-quantitative XRF analysis on the Matlab sediments showed that Fe was approximately 65 times higher than Mn for both reducing and weathered aquifer sediments. Higher FeO and MnO coincided with the micaceous dark bands in the reducing unit and the very reddish sediment sample from 40 and 44 m b.g.l. CaO, MgO and P_2O_5 were lower in the oxidised sequence while SiO_2 was generally higher.

Based on the bulk chemical composition of the Daudkandi samples' normative mineral calculations were done using SEDNORM (Cohen and Ward 1991). The analysis indicated that silicate minerals were dominating, e.g. quartz, feldspar, mica and kaolinite. The amount of quartz was lower in

the dark micaceous- and biotite rich layers depending on textural variation within the aquifer sediments (Paper I). Lower abundance of quartz was compensated by higher amount of kaolinite, mica, hematite, and siderite. Hematite (iron oxide) clearly peaked at the dark coloured micaceous bands. Small amounts of apatite were found while pyrite was only found in one sample at the depth of 16.46 m.

5.5.2. Sequential extractions

The total As (As_{tot}) concentrations in Matlab sediments were low, maximum total content was 3.5 mg/kg and found in the reducing sequence (Figure 14). As_{DIW} and $\text{As}_{\text{NaHCO}_3}$ contents were all below detection limit (b.d.l. 130 $\mu\text{g}/\text{kg}$) and Fe and Mn_{DIW} and NaHCO_3 phases were insignificantly low as compared to the other phases. The highest As_{NaAc} as well as As_{Ox} values coincide with reducing sample from 23 m depth, but except that sample As_{NaAc} and As_{Ox} contents were of the same magnitude in both sequences. The As ammonium oxalate and acetic acid fraction (As_{OxAA}) holds most of the As in half of the samples indicating As is bound to crystalline Fe(III)-oxyhydroxide phases.

The concentrations of extractable Fe and Mn for all fractions were relatively higher in the reducing sequence as compared to the

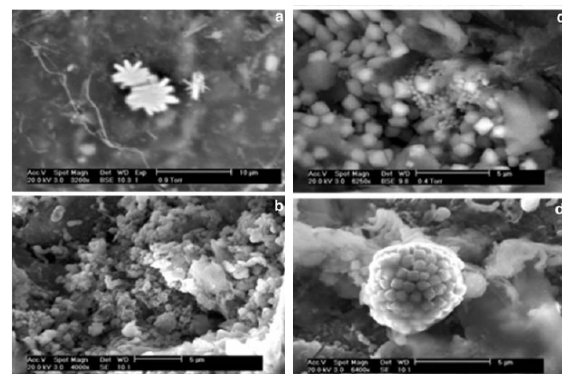


Figure 13. SEM images showing: a) iron oxide (goethite, FeOOH) on biotite grain in the yellowish grey topsoil at the depth of 2.44 m; b) amorphous iron oxide with traces of As on a biotite grain in the dark grey micaceous sediment at 16.46 m depth; c) octahedral authigenic pyrite; and d) framboidal pyrite on the same mica grain.

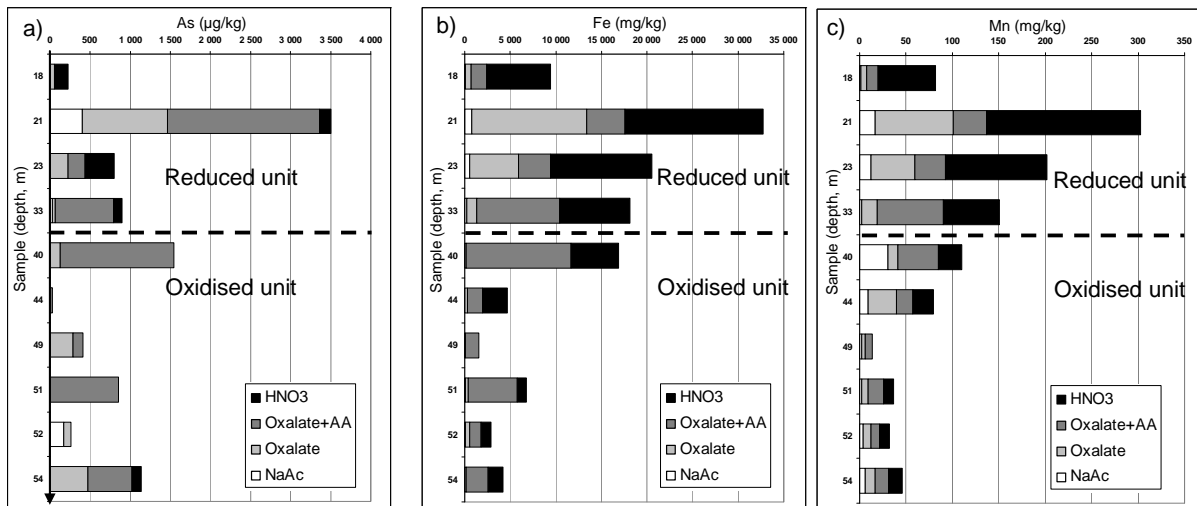


Figure 14. Depth wise distribution of extractable phases of As, Fe and Mn. DIW and NaHCO_3 from Matlab sediment samples fractions are not shown as those concentrations were insignificantly low as compared to the other fractions.

oxidised sequence for white and off-white samples while the very red sample (from 40 m depth) were also relatively high. Fe_{total} and Mn_{total} as well as Fe_{Ox} and Mn_{Ox} correlate well and $\text{Fe}_{\text{total}}/\text{Mn}_{\text{total}}$ are almost constant (average 112, std. 35) for all samples although $\text{Fe}_{\text{Ox}}/\text{Mn}_{\text{Ox}}$ is distinctively different between reducing (average 107, std. 24) and oxidised sediments (average 35, std. 19). As_{Ox} and Fe_{Ox} correlates very well for the samples from the reducing sequence although the number of samples ($n=4$) is low. The $\text{Fe}_{\text{OxAA}}/\text{Fe}_{\text{Ox}}$ ratio for the reducing unit is lower than for the oxidised unit and Fe_{Ox} is much lower here than in the reducing unit. While performing the sequential extraction it was noted that the colour of the red sediments changed during the OxAA extraction step from red to whitish. The results are consistent with other findings (BGS and DPHE 2001, Anawar *et al.* 2003, Swartz *et al.* 2004, Zheng *et al.* 2005, Meharg *et al.* 2006, Breit *et al.* 2006, 2007).

Sequential extraction on samples from Daudkandi showed that ammonium oxalate extractable As (As_{Ox}) dominated in the dark grey sediments with relatively higher TOC, biotite and other micas with a maximum concentration of 3.05 mg $\text{As}_{\text{Ox}}/\text{kg}$. As_{Ox} is very low (b.d.l.) in the upper light grey to yellowish grey oxidised unit. Here the residual fraction of As, As_{HNO_3} , constituted the bulk of As of 0.62 mg/kg. Hydrogen

peroxide extractable As ($\text{As}_{\text{H}_2\text{O}_2}$), i.e. bound to organic matter and sulphides, also peaked in the dark grey sediments rich in organic matter. Sodium acetate extractable As (As_{NaAc}) that determines the carbonate associated As is only detected in one sample (16.46 m). Poorly crystalline and amorphous Fe, Mn and Al (Fe_{Ox} , Mn_{Ox} , Al_{Ox}) reach its maximum at the same dark grey, high mica, biotite and TOC, samples as As_{Ox} though aluminium is found mainly in the residual phase (Al_{HNO_3}). Total extractable As (all phases added) varies between 1.03 and 5.24 mg/kg with a minimum in the upper light grey to yellowish grey weathered horizon and a maximum in the organic matter rich dark grey horizon.

5.5.3. Geochemical modelling

Calculations of Saturation Indexes (SI) indicates that groundwater from both the reducing and oxidised sequence of Matlab is near saturation with respect to Fe(III)-oxyhydroxides.

The modelling indicated that the groundwater in the reducing unit was slightly supersaturated with respect to siderite (FeCO_3) and vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$) ($\text{SI}_{\text{max}} \sim 1$ and 3, respectively) while undersaturated in the oxidised unit with respect to the same mineral phases. SI values for siderite and vivianite correlated well with concentration of dissolved Fe. All samples

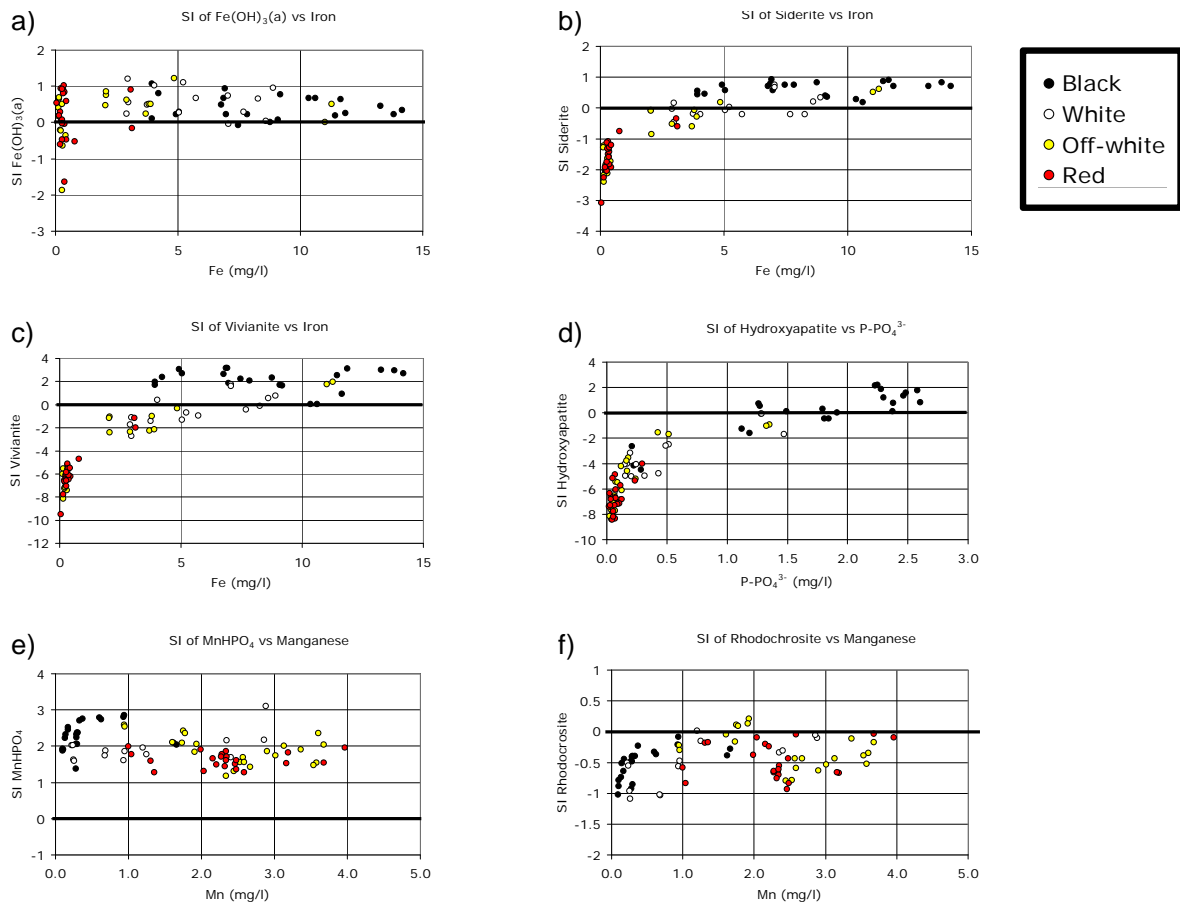


Figure 15. Bivariate plots showing the dependency of the modelled SI values for: a) $Fe(OH)_3(a)$ vs. Fe ; b) siderite vs. Fe ; c) vivianite vs. Fe ; d) hydroxyapatite vs. PO_4^{3-} ; e) $MnHPO_4$ vs. Mn ; and f) rhodochrosite vs. Mn .

were in near saturation with respect to rhodochrosite ($MnCO_3$) and supersaturated with respect to $MnHPO_4$. Groundwater from the reducing sequence was in near saturation with respect to hydroxyapatite ($(Ca_5(PO_4)_3(OH))$), but was undersaturated with respect to the same mineral phase in the oxidised unit (Figure 15).

Modelling surface complexation of $As(III)$ onto Hfo in the high As - and reducing aquifer unit suggested that $As(III)$ adsorption was mainly controlled by the amount of Hfo in solid phase. The pH-value is of less importance as pH-values were stable and did not vary within the study area, like in the many other parts of Bangladesh.

Further, it was shown that a competing ion was needed to obtain reasonable results, i.e. simulated conditions with high dissolved As concentrations. If no competing ion was added all As was adsorbed, thus dissolved

concentrations of PO_4^{3-} -tot is of importance for the high dissolved concentrations of As , as seen in Figure 16 that shows the simulated dissolved concentrations of $As(III)$ vs. dissolved PO_4^{3-} -tot, used as competing ion in the simulations. Site specific groundwater samples are also shown in the diagram. There is a distinct correlation between both simulated and measured concentrations of dissolved As and PO_4^{3-} -tot.

5.6. Arsenic adsorption dynamics

The extractions performed on three oxidised sediment samples in Paper IV showed that As concentrations were relatively low. Both oxalate and HNO_3 extractions were in accordance with previous extractions (Paper II) with As content between <1.3 mg/kg – 2.4 mg/kg and Fe_{Ox} between 94 and 134 mg/kg. The simulation of surface composition of the oxidised sediments gave

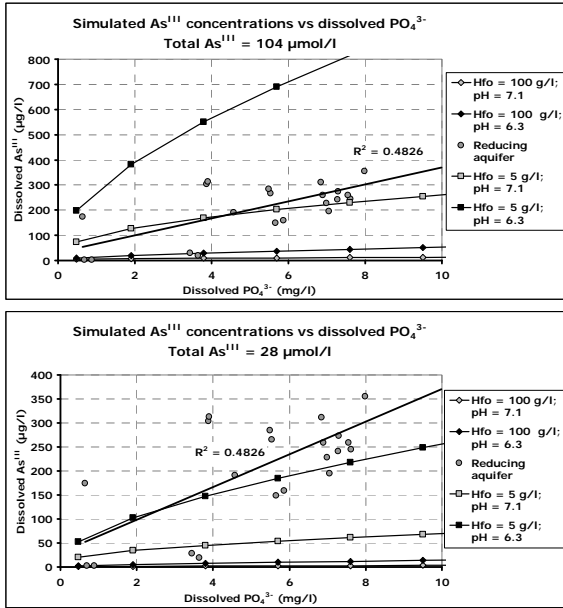


Figure 16. Simulation of adsorbed and dissolved As(III) for the system with hydrous ferric oxides (Hfo), As(III) and PO_4^{3-} using the Diffuse Layer Model. Figure a) shows results with maximum amount of As found in the sediments and b) with the minimum amount.

a good match between the predicted concentration of adsorbed species and those extracted from the amorphous minerals (Figure 17). Simulated adsorbed As is predicted to be approximately 1 mg/kg as As(V).

The batch experiments showed that the oxidised sediments had good capability to adsorb As(V) (>400-500 mg/kg). The sediments adsorbed As(V) for the highest concentrations indicating all adsorption sites were not yet saturated. However, simulation of adsorption isotherm gave poor matching

with observed data and the model under predicted the adsorption potential of As(V) (Paper IV). Also the column experiments showed that the adsorption capacity was high, over the experiment period 90-99 % of the influent As ($[As]=1,900 \mu\text{g/l}$) was adsorbed. The effluent concentration varied between 20-200 $\mu\text{g/l}$. Further, the results showed that adsorption sites were not saturated with respect to As although addition of lactose in the replicate column decreased the adsorption capacity. In the replicate column, high dissolved Fe and Mn in the effluent indicated that lactose worked as electron donor in the experimental column system with subsequent drop in pH-value down to 5 (possibly due to H^+ production as lactose is oxidised; c.f. near-neutral for column without lactose) and concurrently reductive dissolution of Fe(III) and Mn(IV) oxyhydroxides (Paper IV). Also Ca and Si concentrations in effluent from lactose column were comparably higher.

5.7. Hydrogeological field investigations

5.7.1. Aquifer delineation based on drilling logs

Shallow, intermediate and deep aquifers could be delineated based on generalized description of sediments (Mozumder 2011) and the subsurface sequence to a depth of 250 m b.g.l. has been divided into six hydrostratigraphic units. The aquitard between shallow and intermediate aquifer is significant from hydraulic viewpoint while the aquitard between intermediate and deep

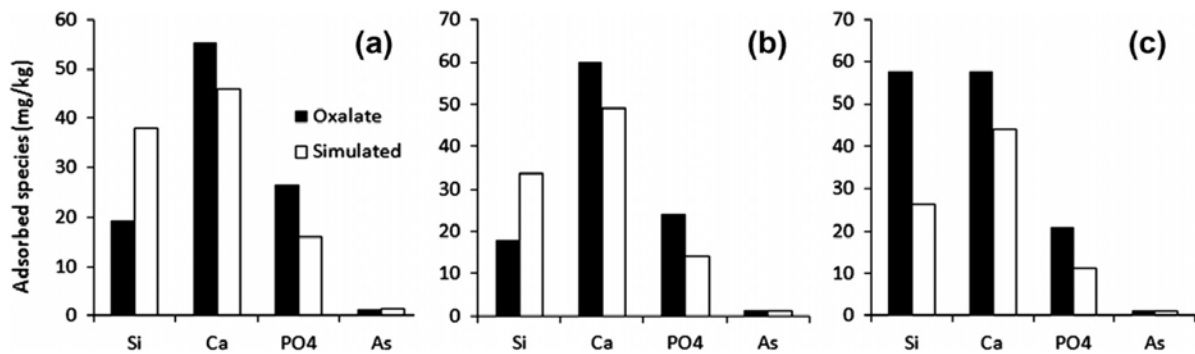


Figure 17. Distribution of adsorbed species measured from oxalate extraction and simulated using PHREEQC surface complexation model. Results are shown for sample no. 1, 2 and 3.

aquifer is less significant (Paper V).

5.7.2. Estimation of groundwater abstraction in Matlab

The abstraction of groundwater for irrigation purposes for Matlab (both North and South) was estimated to be 176 mm/yr of which 81 % was abstracted from depths above 50 m b.g.l. and 95 % above 75 m b.g.l. The irrigation season is between November to June with the heaviest irrigation from January to April. Further, the irrigation wells are not evenly distributed in the area but are rather distributed in clusters. The vertical flow and risk for cross-contamination will be correlated to the abstraction rate.

5.7.3. Hydrographs

The hydrographs (Figure 18) showed that:

- i) A vertical downward gradient was evident in all nests with an annual average, between shallowest and deepest piezometer, of 0.006 (maximum is 0,029; nest 7). In four of the nests a reverse gradient can be seen during the winter period of November to January.
- ii) Groundwater level amplitudes varied between 1.0 and 5.1 m. Highest amplitudes concur with clusters of irrigation wells, in the deepest piezometers. The system was fully recharged during the monsoon season.
- iii) The hydrographs from piezometer nests indicate the presence of two to three separate aquifer units, i.e. shallow- (0-50 m b.g.l.), intermediate- (50-100 m b.g.l.) and deep aquifer (100-250 m b.g.l. or deeper). The aquitard between deep and intermediate aquifer is not that obvious as the one between the shallow and intermediate.

In three nests (no. 4, 5 and 9) hydraulic head of deep and intermediately deep piezometers were below the mean sea level during the end of the heavy irrigation period.

5.7.4. Hydraulic test

Piezometers 2:70, 3:70, 4:70, 5:70 and the private wells represented a relatively homogenous hydrostratigraphic unit with transmissivity (I) and leakage coefficient

(P'/m') of 3.8×10^{-3} m²/s and 1.3×10^{-7} 1/s respectively. The reservoir was estimated to be approximately 20 m separated from the reservoir at 42 m b.g.l. by a 10 m layer of lower vertical permeability. Based on this assumption, the average horizontal permeability (K_h) was calculated to be 2×10^{-4} m/s and the vertical permeability (K_v) 1.3×10^{-6} m/s. The simulation of the pumping test, by a homogeneous and anisotropic model using MODFLOW and the parameter estimation module (PEST) resulted in corresponding values of vertical and horizontal hydraulic conductivities (Paper V).

5.7.5. ¹⁴C dating of groundwater

Groundwater is older than 1,000 yr at the depth below approximately 25 m. Corrected groundwater ages (Paper V) and depth is linearly correlating with ages ranging to 11,960 yr indicating very restricted groundwater flow across the aquifers. Estimated groundwater ages concur with previous studies by Aggrey et al. (2000), Hoque (2010) and Saha *et al.* (2011). If analysed ¹⁴C ages are extrapolated, young groundwater would be expected at a depth of approximately 25 m b.g.l. The estimated groundwater ages coincide with an assumed vertical groundwater flow with a vertical gradient of 0.01 and vertical hydraulic conductivity (K_v) of 1.5×10^{-8} m/s, which is reasonable values for both gradient and hydraulic conductivities (Figure 19).

5.8. Groundwater modelling

An anisotropic homogeneous modelling approach (calibrated with MODPATH and estimated ¹⁴C dating of groundwater) was difficult to calibrate with good accuracy (Paper V). The models that best fit the measured groundwater ages resulted in too young groundwater at shallow and intermediate depth and too old at deeper depth. The groundwater ages at depth were unrealistic old and not in accordance with previous findings by Hoque (2010) nor by Aggarwal (2000). Based on the aquifer delineation a four layer model was also developed that improved the calibration of

estimated groundwater ages. The differences in regional groundwater flow pattern between the homogeneous anisotropic model and the 4 aquifer/aquitard model are

illustrated in Figure 20.

There was no attempt to calibrate the transient model with specific measured hydraulic heads from all piezometer

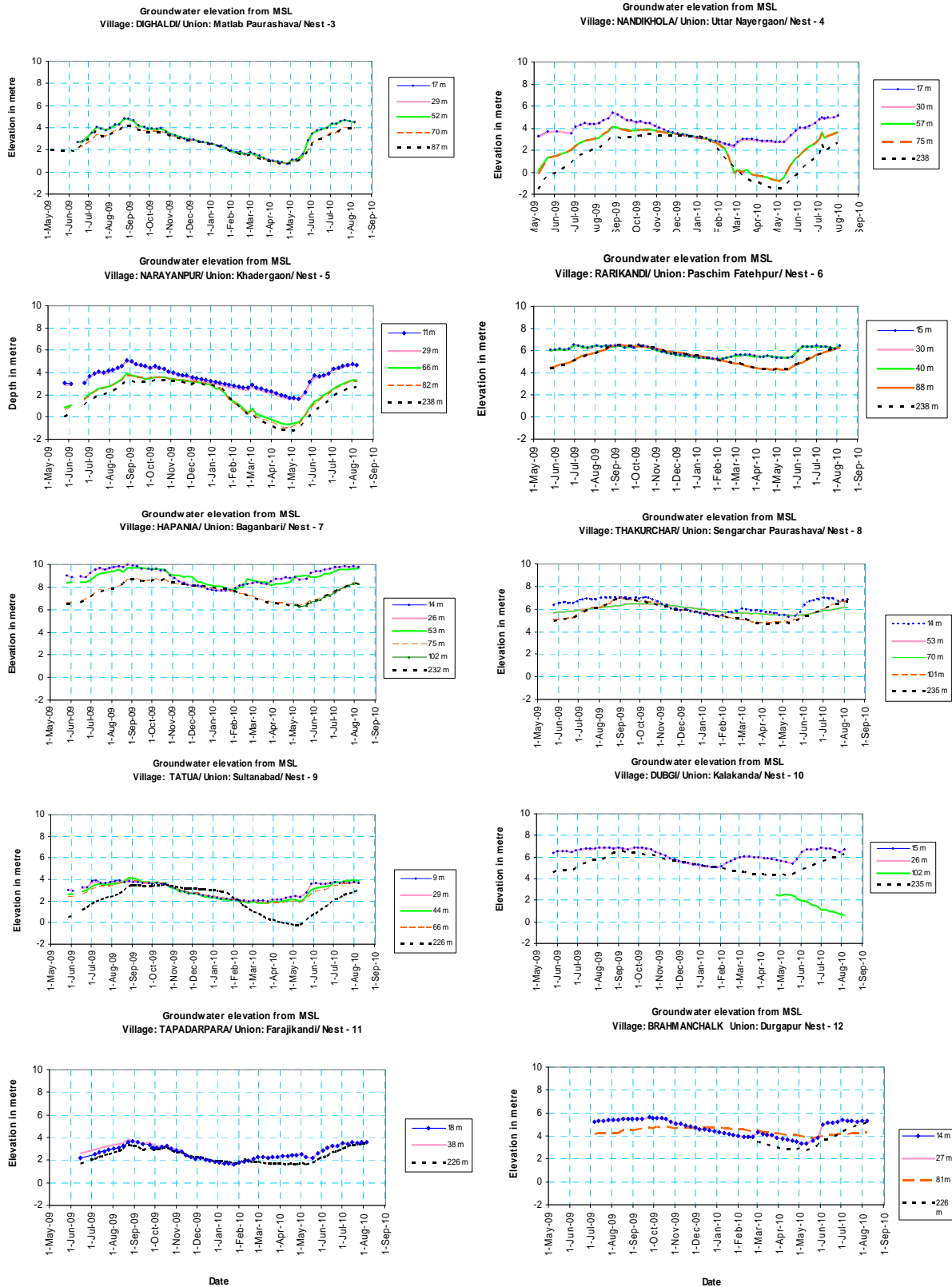


Figure 18. Hydrographs of the 12 piezometer nests.

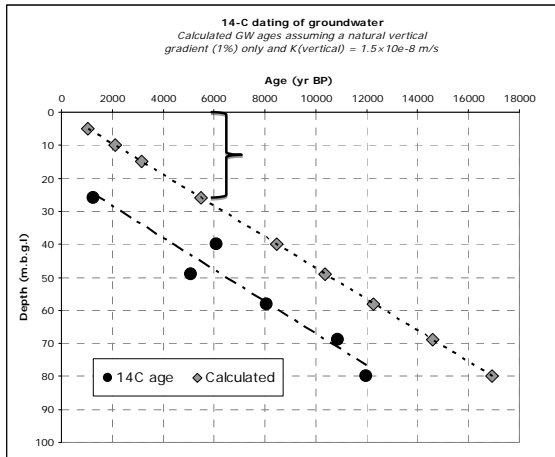


Figure 19. Analyzed ^{14}C -ages of groundwater samples and calculated ages based on downward vertical flow.

installations because of the lack of specific hydrostratigraphic geometry. However, the model was updated continuously based on the steady state flow models and output from transient model. Four approaches were used:

- i) Homogeneous anisotropic model (same as for steady state flow model);
- ii) 4 aquifers/aquitard model (same as for steady state flow model);
- iii) 3 aquifers/aquitard model, merging aquifer 3 and 4 to increase the stress on the deeper aquifers as observed in piezometers;
- iv) 2 layer model (aquifers 1 was merged with aquifer 2 and 3 with 4 in order to increase the stress on the deeper aquifers, i.e. piezometers at >200m depth, that have been observed in field but that was difficult to model).

Evaluation of the modelling results, as well

as input data are given in Paper V. Altogether approximately 50 variations were run to meet the evaluation criteria set up based on established hydrographs (see above): i) amplitude and seasonal fluctuation of hydraulic heads; ii) vertical downward gradient; iii) observed pumping effect; and iv) aquifer delineation with different pattern in hydrographs from the same piezometer nest.

Simulating pumping effect could be done rather well, at depth this was more difficult as observations in the deepest installed piezometers (>200 m b.g.l.) showed relatively large influence while no or very few identified irrigation wells were installed at those depths.

Hydrographs for piezometers installed at depth between 50 or 100 m b.g.l. to a depth of 200 m b.g.l. coincided and in order to simulate this, a 3 aquifer model was developed that met evaluation criteria better than the 4 aquifer model. Simulating higher amplitude at deep depth than at intermediate depth, observed in a couple of piezometer nests, could not be done satisfactory as well as lowering the hydraulic head below the mean sea level. In any case, the nests with the major pumping influence coincide with identified clusters of irrigation wells (Figure 21).

Using a homogeneous anisotropic model was not very successful for meeting the evaluation criteria as this modelling approach did not reproduce the vertically

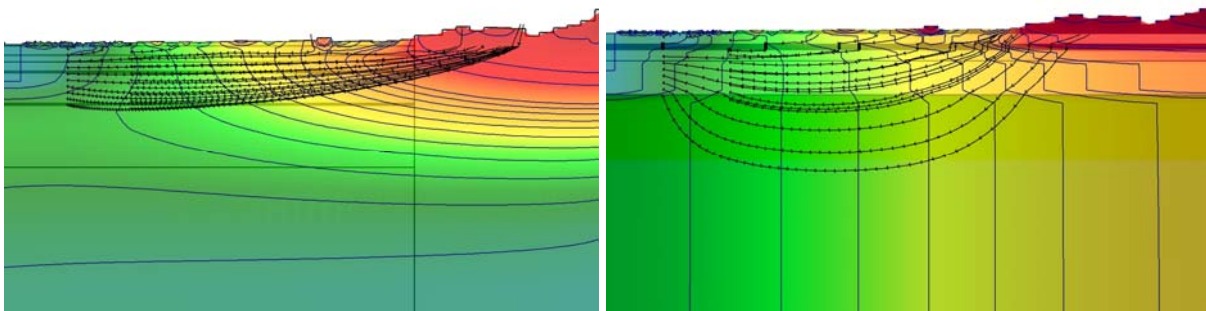


Figure 20. Left) Cross-section of model homogeneous anisotropic model; Right) Cross-section of the 4 aquifer/aquitard model. Cross-sections are from west to east across the study area. Time marks of the backward particle tracking are set to 1,000 yr. Blue lines are piezometric heads.

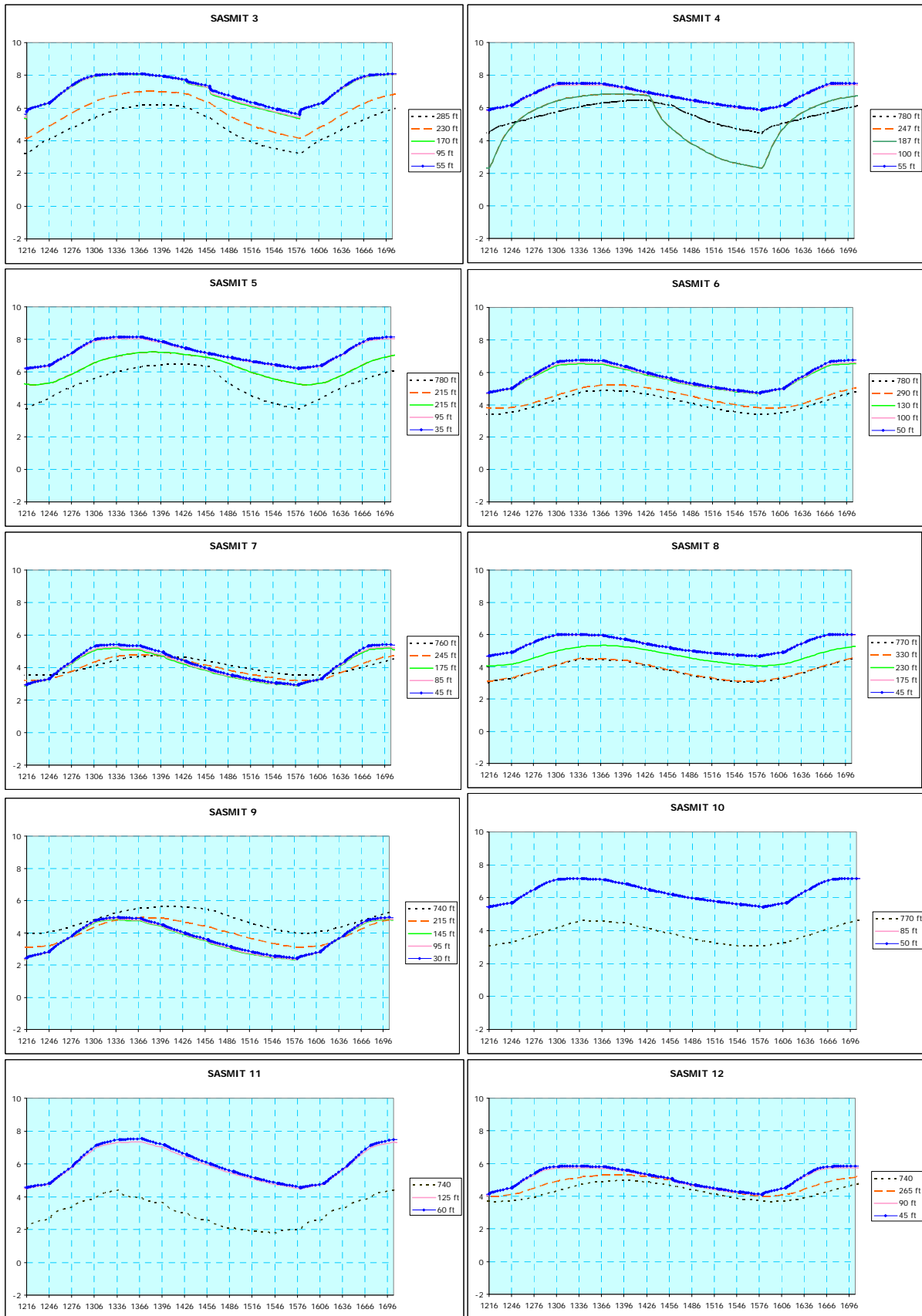


Figure 21. Simulated hydraulic heads of a three aquifer/aquitard model meeting the evaluation criteria well (simulation *T_20m*, see Paper V supplementary information), this model met the evaluating criteria for nest 3, 5, 8 and 12 well, for nest 4, 6, 7 fairly well and not too good for nest 9, 10 and 11.

Table 1. Suggested aquifer properties based on results from the transient flow model.

	Depth m b.g.l.	K_h m/s	K_v m/s	S_s 1/m
Aquifer 1	0-50	10^{-5} - 10^{-4}	10^{-6} - 10^{-4}	5×10^{-4} - 5×10^{-3}
Aquifer 2	75-100	10^{-6} - 10^{-5}	10^{-6} - 10^{-5}	10^{-5} - 10^{-4}
Aquifer 3	>100	10^{-6} - 10^{-5}	10^{-6} - 10^{-5}	10^{-6} - 5×10^{-6}

downward gradient identified in the hydrographs if not $K_h/K_v \leq 100$ which was unrealistic according to the steady state model for the aquifer system to the depth of 250 m b.g.l. Further, this approach did not meet the evaluation criteria for pumping effects well either (Paper V).

Instead, models with 3 or 4 aquifers with separating aquitards in between met the evaluation criteria better and combining the models that best fit the evaluation criteria results in a high yield 3 aquifer/aquitard model separated by two or three aquitards with decreasing S_s and K towards depth (Table 1, Figure 21). The suggested model properties fit well the steady state model.

Further, the groundwater models noticeably visualised local flow-systems driven by local topography down to the depth of approximately 30 m b.g.l. as well as a deeper regional flow system (Figure 22).

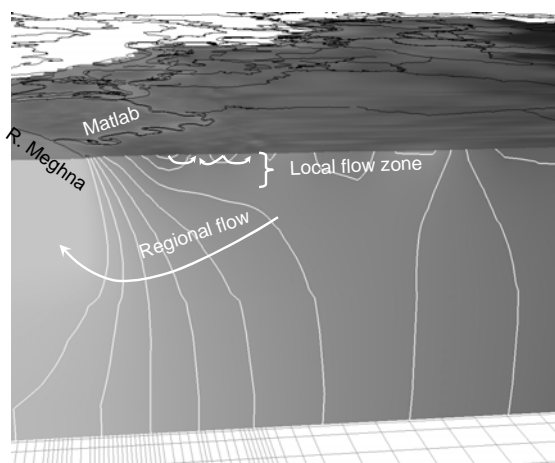


Figure 22. Simulation illustrating the two flow systems.

6. DISCUSSION

6.1. Drillers' perception of sedimentary characteristics

The drillers' awareness of high As groundwater has changed the installation practise of hand tubewells in Matlab. Today, local drillers target sediments at deeper depth, preferably to red sediments in order to avoid high As (Paper I). The new practise is conveyed to local villagers when agreeing on terms of conditions for the installations and if possible local drillers wait for villagers to save money for a deeper well (unpublished data from Matlab). The test done (Paper I) and later experiences (Paper II, III, IV, V) clearly showed the possibility for the local drillers to target certain sediments and aquifer units based on their knowledge of local geological conditions. The change in installation practise also indicates the possibility to even further change the installation practise to target As low aquifer, if they can be delineated.

6.2. Groundwater chemical characterisation

The groundwater chemical composition is in accordance with the earlier studies in different part of Bengal basin (Bhattacharya *et al.* 1997, Nickson *et al.* 1998, BGS and DPHE 2001, Smedley and Kinniburgh 2002, van Geen *et al.* 2003, Ahmed *et al.* 2004, Sracek *et al.* 2004b, McArthur *et al.* 2004, Bhattacharya *et al.* 2006, Kar *et al.* 2010), thus the characteristics of the study area with respect to distribution of As and its relationship with local variations in sedimentary and hydrogeochemical conditions seems universal for the Bengal basin. At the same time, the distribution of As in groundwater is extremely

heterogeneous, both horizontally and vertically. The patchy distribution of As in these aquifers indicates that local variations in sedimentary characteristics and hydrogeochemical conditions play a crucial role for mobilisation and immobilisation of As (BGS and DPHE 2001, Bhattacharya *et al.* 2004, von Brömssen *et al.* 2005, Stollenwerk 2005, Stollenwerk *et al.* 2007, Paper I, Paper II). Based on groundwater chemical composition (Paper I, II, III, IV) it appears that microbial-mediated oxidative degradation of organic matter is responsible for driving redox reactions with following reductive dissolution of Fe(III)-oxyhydroxides and subsequent release of adsorbed As. Oxidation of organic matter is reflected by elevated concentration of HCO_3^- and depletion of NO_3^- and SO_4^{2-} (Appelo and Postma 1999, Akai *et al.* 2004).

The groundwater chemical study in Matlab suggests that groundwater at intermediate depth is mixed between fresh groundwater and relict marine saltwater; this indicates a slow flushing rate and turn-over time of the groundwater system although salt groundwater may be trapped in clayey layers and gradually diffusing into the aquifers. Unfortunately, no study on pore-water composition on aquitards in the high As groundwater regions has been found which could have elucidated how clay formations contribute to the groundwater chemical composition. Further, low DOC concentrations in the oxidised unit indicate that sedimentary organic matter has been oxidised during the sub-aerial period. The trend of relatively higher HCO_3^- in groundwater samples from reducing units and black sediments indicates its generation in redox reactions (Nickson *et al.* 2005). Generally the groundwater is anoxic with elevated concentrations of dissolved As, Fe and Mn. However redox characterisation of the groundwater samples abstracted from sediments of different colours reflect distinct groundwater composition indicating reductive dissolution of Fe(III)-oxyhydroxides (Paper I, II and III) with subsequent release of As in black sediments while redox status in the oxidised unit is not

sufficient for reduction of Fe(III) minerals, while the redox status is sufficiently low for reduction of Mn(IV) solid phases (Paper I).

The poor correlation between Fe and As indicate solid phase reactions controlling dissolved Fe in the groundwater. Further, either high dissolved As or high Mn is found in the groundwater samples also indicating secondary phases controlling Mn in the system. The positive and negative correlations are in accordance with previous and recent findings in the Bengal basin (BGS and DPHE 2001, Hug *et al.* 2011). High Mn concentrations in the groundwater may pose a problem for the development of the oxidised unit due to possible health consequences (Wasserman *et al.* 2011).

There is no evident trend of increasing concentrations of As in the tube well water tested in this study (Paper IV), nor in the more extensive study by Bhattacharya *et al.* (2011) from Matlab. However, in a study by van Geen *et al.* (2007) in Araihasar, 25 km east of Dhaka, As did increase in 4 out of 51 community wells over a five yr period. Human induced arsenic mobilisation, due to heavy extraction of groundwater with subsequent withdrawal of surface water, rich in highly reactive organic compounds, into underlying aquifers do seem reasonable (Polya and Charlet 2009), though Datta *et al.* (2011) state that perennial ponds are not an important source of DOC to groundwaters with high As concentrations. Geological settings and abstraction rate will undoubtedly control the risk of human induced arsenic mobilisation.

6.3. Mineralogy of sedimentary aquifers and relationship with high As groundwater

Generally, the delta- and flood plains are rich in mica (5–30 %) out of which biotite comprises about 65–75 % of the total mica (Brammer 1996). The weathering of biotite and other micas adds to the formation of Fe(III)-oxyhydroxides in the sediment. Relatively higher amount of Fe_{NaAc} in the grey to dark grey sediment indicates presence of carbonate phase like siderite in the aquifer sediments which would be in

accordance with geochemical simulation results from the Matlab study area (Paper II).

The correlation between As_{Ox} and Al_{Ox} , Mn_{Ox} and Fe_{Ox} ($R^2=0.86$; 0.57 ; 0.93 respectively; $n=6$) suggests that, besides Fe(III)-oxyhydroxides and Mn(IV)-oxides, Al-oxides (HAO)/amorphous $Al(OH_3)$, clay minerals and other phyllosilicates may also act as potential sinks for As (Manning and Goldberg 1997, Yan *et al.* 2000, Breit *et al.* 2001, Stollenwerk 2003, Reza *et al.* 2010). This has however not been further investigated. The very strong correlation between As_{total} and TOC ($R^2 = 0.89$) have been recognised in studies by Reza *et al.* (2011) indicating that As is also derived from terrestrial region or the Himalayas.

Scanning electron microscopy could identify octahedral and framboidal authigenic pyrite (FeS_2) on the same biotite grain indicating active sulphate reduction and prevalence of strong reducing condition although no As was detected in the pyrite phase. However As incorporation into authigenic pyrite depends on availability of sulphur supplied by bacterial sulphate reduction (Lowers *et al.* 2007).

The presence of amorphous Fe(III)-oxyhydroxide and pyrite on a single biotite grain indicate overlapping redox condition and supports partial redox equilibrium model (Mukherjee *et al.* 2008). There is probably redox heterogeneity at micro scale with strong redox gradients. Also, secondary ferrous minerals like siderite may precipitate as coatings over Fe(III)-oxyhydroxides preventing further dissolution (Uddin *et al.* 2011). Occurrence of Fe(III)-oxyhydroxide with siderite and pyrite has been observed in other settings (Tuccillo *et al.* 1999, Vencelides *et al.* 2007). Redox disequilibrium is frequently observed (Postma and Jakobsen 1996).

6.4. Relationship between As and other elements at the water-solid interface

The lithofacies and genesis of reducing Holocene sediments as well as weathered

oxidised reddish (sometimes described as brown) sediments previously reported (Umitsu 1993, Goodbred and Kuehl 2000, van Geen *et al.* 2004, Stollenwerk *et al.* 2007) from other parts the Bengal basin correlate well with the findings from Matlab and Daudkandi (Paper I, II, III). The presence of authigenic goethite in brown sediment (Lowers *et al.* 2007) and pyrite in the grey sediment of Bangladesh was documented by several authors (Nickson *et al.* 2000, Akai *et al.* 2004).

Elevated concentrations of dissolved Fe and Mn is prone to be generated through reductive dissolution of solid oxide- and hydroxide phases of Fe(III) and Mn(IV) (Mukherjee *et al.* 2008). Highest dissolved concentrations of both these elements would be expected in groundwater from the reducing aquifer unit as redox-conditions are sufficiently low and distinctively higher contents of amorphous Fe and Mn (Fe_{Ox} and Mn_{Ox}) are found in the reduced unit. However, relatively higher dissolved Mn concentrations are found in the oxidised aquifer unit. This implies that secondary mineral phases may control the aqueous concentrations of Mn in the reduced aquifer unit. Calculating saturation indices based on the groundwater analytical results showed that rhodochrosite and $MnHPO_4$ are near saturation and/or slightly supersaturated in both reducing and oxidised unit. Thus these minerals may act as sinks for dissolved Mn generated by reductive dissolution processes. Siderite, vivianite and possibly Fe(III)-oxyhydroxides may, in addition to redox processes and according to SI calculations, control dissolved Fe concentrations in the reducing unit.

As amorphous phases of Fe(III)-oxyhydroxides as well as Mn(IV) oxides were much higher in the reducing unit dissolved As concentrations would be expected to be lower in these sediments assuming Fe(III)-oxyhydroxides being the main sorbent (Paper II). This is however in contrast to analytical results with much higher dissolved As concentrations in the reducing unit (Paper I, II). Modelling As(III)

adsorption onto *Hfo* using fixed concentrations of PO_4^{3-} -tot assuming PO_4^{3-} -tot being in equilibrium with mineral phases controlling dissolved PO_4^{3-} -tot, as competing ion, resulted in realistic concentrations of dissolved and adsorbed As. Simulating the system without PO_4^{3-} -tot resulted in all As being adsorbed. The modelling exercise clearly showed the importance of considering PO_4^{3-} -tot as competing ion for understanding the genesis of high As groundwater. Validation of the results by mineralogical studies could not be done within the scope of this study but is suggested for further studied.

Through calculation of SI possible secondary minerals controlling dissolved concentrations of Fe, Mn and PO_4^{3-} -tot could be identified. Based on that complexation modelling of As could be set up giving further output on the genesis of high As groundwater, its heterogeneous distribution and interaction with other groundwater elements such as Fe, Mn and PO_4^{3-} -tot at the solid-aqueous interface.

6.5. Adsorption dynamics of As on oxidised sediments

Simulation of surface composition of the oxidised sediment samples with PHREEQC using November 2006 mean water chemistry for tube-wells ($n=20$; [Paper IV](#)) and Fe_{Ox} extraction analytical data for derivation of *Hfo* gave a good match between simulated amounts of As, as well as other ions that compete for adsorption sites, and extracted from amorphous minerals. Discrepancies between simulated and analytical results may be because of varying water composition and sediment characteristics and/or influence of other sorbents not considered. Nevertheless, simulation of surface composition was possible validating the significance for Fe(III)-oxyhydroxides acting as a sorbent and sink for As if cross-contamination through oxidised sedimentary layers occur.

Simulation of adsorption isotherms resulted in a poor match between calculated concentrations and analysed. The model underpredicted the adsorbed As. However,

the batch tests were done with too high concentrations (up to 100 mg/l) of As as compared to what is found in the groundwater. The poor match may indicate that other mineral play an important role as sorbents for As. Further reasons for mismatch was not investigated as the concentrations of As used for the batch experiments were much too high. Instead it is recommended that new experiments on adsorption isotherms are done.

The column experiment illustrated that the oxidised sediment had a high capacity for adsorbing As. Throughout the experiment saturation was not reached although up to 8 mg As/kg sediment was adsorbed. However, even though a high amount of As was continuously adsorbed relatively high concentrations of As was found in the effluent (20-200 $\mu\text{g/l}$). This may be the result of short circuit in the column or kinetic restrictions for As to adsorb. Adding lactose distinctly affected the adsorption capacity as well as the concentration of As in the effluent resulting in concentrations up to 1,700 $\mu\text{g/l}$ at the end of the experiment. Concentrations of Fe and Mn in the effluent increased over time in the replicate column to more than three orders of magnitude compared to the columns without lactose. The increase of Fe and Mn correlated with the subsequent increase of As in the effluent. Lactose clearly triggered the reductive dissolution in the sediments. From redox sequence, reductive dissolution of Mn(IV) oxides should occur before iron and even though this did occur in one column it occurred simultaneously in the two others. This is because the processes are microbially mediated.

As dissolved organic carbon from surface and/or groundwater from reducing aquifer units may infiltrate As-low oxidised units and deeper As-safe aquifers, increased DOC may increase the reductive dissolution of oxyhydroxy-minerals decreasing adsorption capacity and/or triggering As release. Lactose is however different from the natural complex organic matter abundant in the aquifer that is strongly controlled by kinetics ([Mc Arthur et al. 2004](#)).

6.6. Groundwater flow

6.6.1. Hydrographs and groundwater flow modelling

The hydrographs proved to give useful data on which some very important conclusions could be made. The vertical hydraulic gradient identified over the top 250 m of the aquifer system was unexpected but could be simulated rather easily with the groundwater model. This validates that these conditions would occur also during undisturbed groundwater flow conditions. It also identifies Matlab as a recharge area although adjacent to river Meghna. The hydrographs could further be used for identification and delineation of the different aquifer suggesting a three aquifer system to the depth of approximately 250 m b.g.l. This gives useful and necessary input for further groundwater modelling and monitoring hydraulic heads in piezometer nests is considered a necessity for further groundwater flow studies. The hydrographs did also identify areas with high groundwater abstraction rate. Though abstraction rate is high locally, the system is fully recovered during the monsoon period, this can give useful data for further estimation on mass-transport of dissolved elements vis-à-vis cross-contamination scenario and sustainability of As-low aquifers. The groundwater flow model could be calibrated for evaluation criteria reasonable well and validated the results from the hydrographs. The model further demonstrated that groundwater abstraction induces a distinct vertical groundwater flow. Using both a steady state and a transient model showed useful for calibration and delineation of the aquifers and combining the models that best fit the evaluation criteria results in a high yield 3 aquifer/aquitard model with decreasing Ss and K towards depth. The groundwater model visualized shallow local flow-systems and a regional deeper one.

In three nests, close to irrigation pump clusters, the hydraulic head of the deep and intermediately deep piezometers were found to be below the mean sea water level during the end of the heavy irrigation period

(March to May). This was very difficult to model but can be a result of pumping only. However identified irrigation wells were relatively shallow in these areas as compared to piezometer installations and this behavior should be further investigated in order to explain it thoroughly. Flooding of the lowlands was not included in the models. This would possibly result in a more regional flow-pattern. If surface water levels would have been taken into account it would result in less distinct local flow-patterns. The homogeneous anisotropic model approach was less successful than the 3 aquifer/aquitard approach. Further groundwater modelling should thus take into account the heterogeneity of the aquifer system.

6.6.2. Groundwater abstraction

The estimation of groundwater abstraction for irrigation purposes in Matlab showed that almost 180 mm/yr is used which is in accordance with what has previously been presented and approximately six times of what is used for domestic purposes in Matlab (Michael and Voss 2008). Assuming pumping induces local vertical groundwater flow, the groundwater velocity would be 0.8 m/yr. As irrigation- and hand tubewells are very much placed in clusters it may well be that induced vertical groundwater flow is several meters per year locally. This will stimulate cross-contamination of As. However, as long as irrigation wells are placed at shallower depth than drinking water tubewells irrigation may not induce cross-contamination. At the same time, adsorption processes needs to be taken into account that could slow the process (Stollenwerk *et al.* 2007, Radloff *et al.* 2011, Paper II, IV). Additionally, Stute *et al.* (2007) presented a linear correlation between young (<40 yr) groundwater ages and As concentration in shallow (<20 m) wells in Araihasar (25 km east of Dhaka), proposing that either the kinetics of As mobilisation or removal of As due to flushing is the mechanism for low As groundwater in very young groundwater. Nevertheless, irrigation by groundwater needs to be managed in a

sustainable way and its impact on today safe groundwater sources needs to be further investigated and taken into account when further developing delineated As-low aquifers. It is evident that the hydrological control on dissolved As in the aquifer systems needs to be further investigated.

6.7. Targeting safe aquifers

Nickson *et al.* (2000) argued that identification of the mechanism of As release to groundwater help to provide a framework to guide the placement of As safe wells. In spite of this, BGS and DPHE (2001) argued that the extreme heterogeneous distribution of As would make detailed mapping and investigation of As concentrations in tubewells, as an option for As safe and shallow (<150 m) tubewells, too difficult. However, it has through this study been shown (Paper I) that local drillers can, and prefer to, install tubewells in oxidised aquifer units, primarily because of low concentrations of dissolved Fe (that can be observed in field by the drillers). Correlating colour characteristics of the sediments and the relative risk for high As now provides new insights on how to delineate As low aquifer (Paper I, Hoque *et al.* 2011). Though Mn may pose a problem, Hug *et al.* (2011) have shown that it is possible to avoid both As, Mn and high Cl by targeting safe depths for installation of tubewells. This information can be used by local drillers to target As low aquifers. At the same time, in Matlab, numerous of As mitigation interventions by ICDDR,B, BRAC, NGO Forum, Sida, Columbia University undisputable have increased the awareness level thus creating a good platform for the local drillers to further develop the groundwater resource.

The local drillers' initiative is cost effective considering the problems and costs that need to be incurred to maintain the existing alternative safe water option available in Bangladesh. It has been observed that relatively well-off families are installing tubewells independently while 4-5 poor households are getting united to raise the required amount of money to have this

option in a common place jointly selected by them. This mitigation approach comes from peoples' own initiative in contrast to other options and is one of the major advantages of this mitigation approach.

6.8. Groundwater management

In spite of a large dependence on groundwater and its growing demand, there has been little impetus on the management of groundwater resources (Ahmed 2005). There is a pressing need to improve the groundwater management in the country for safe and sustainable use. The issue of As management is very wide and includes management of water resources, sources of water supplies, provision of alternative sources, health aspects, social aspects, agricultural issues etc. For management of As in groundwater, a pragmatic mitigation policy is needed with a holistic approach. Legal and institutional reforms are necessary to address the issue. Concepts of safe drinking water and integrated water resources management should be adopted in order to manage the problem. Proper assessment has to be performed to avoid substitution of new risks while implementing alternative sources. The Arsenic Policy Support Unit (APSU) and WHO have developed several models for assessing risks (and risk-substitution) for provided safe drinking water options as well as models for Water Safety Plans (WSP) (APSU 2005, WHO 2004) that can be used for implementation of options for safe drinking water. Community participation has to be ensured in the management by raising the level of awareness about the quality and quantity of the vital resource. Sustainable mitigation options cannot be achieved without involving the local community in the planning and development processes. Awareness raising and community mobilisation are two top priorities for implementing a sustainable safe water project in the village areas. There is still a large proportion of the As-affected population who are not aware or educated on the health risks associated with long-term ingestion of As contaminated groundwater. The WHO guideline (WHO 2004) for safe

drinking water gives a “framework for safe drinking water” that comprises five key components (Figure 23):

- i) health-based targets based on an evaluation of health concerns;
- ii) system assessment of the drinking water supply from source to consumer;
- iii) operational monitoring of the control measures;
- iv) management plans documenting the system assessment and monitoring plans and describing actions to be taken in normal operation and incident conditions;
- v) a system of independent surveillance that verifies that the above are operating properly.

The guidelines also provide additional supporting information concerning water quality hazards, etc. The framework gives a rational management scheme for providing safe drinking water. However, concerning elevated concentrations of geogenic As in groundwater in rural Bangladesh and many other regions (e.g. Argentina, China, Vietnam, India) it seems hard to implement the framework as most of the people collect drinking water from privately owned household tube wells and live in rural areas. Even though WSPs can be formulated for many of the regions, which would enable risk assessment of the various options, surveillance and monitoring of single point water sources is difficult and thus obstructing the most important aspects in implementing WSPs, which require feedback information from the field for continuous

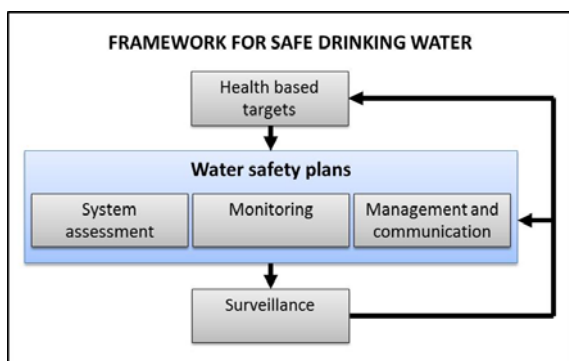


Figure 23. World Health Organisations “framework for safe drinking water” (WHO 2004).

assessment of sustainability and risks.

The adverse effects of As in groundwater used for irrigation water on crops and aquatic ecosystems is also of major concern. In addition to potential human health impacts caused by ingestion of food containing As, the potential for reduced crop yield due to As build-up in the soil is an active area of research. The fate of As in agricultural soils is often less well studied compared to groundwater, and in general has been studied in the context of As uptake by different plants (Al Rmali *et al.* 2005, Williams *et al.* 2005, Corell *et al.* 2006, Huq *et al.* 2006, Naidu *et al.* 2006, Williams *et al.* 2006). Effect of As on crop quality and yield is becoming a major worldwide concern, particularly for rice which forms the staple for many South-Asian countries where groundwater is widely used for irrigation. The presence of As in groundwater has become a major issue of management of both drinking and irrigation water in the country even though it has not been addressed properly in the same context. Clearly groundwater abstraction for irrigation purposes is in conflict with sustainable use of groundwater for drinking purposes (Michael and Voss 2008, Hoque 2010, Paper V).

7. CONCLUSIONS

7.1. The local drillers’ ability to target and delineate arsenic safe aquifers

The local driller’s awareness of frequent problems with elevated As concentrations in tubewell water have made them change their installation practice. Using straightforward descriptions of the sediments texture, colour characteristics and content of dissolved Fe they now install tubewells to deeper depth targeting off-white (buff) or red/brownish sediments. Through monitoring by As mitigation intervention programmes they have also acquired feed-back on their installations further developing their installation practices. The drillers’ perception and local knowledge of the lithological sequences in their respective working areas

are excellent (Paper I). The drillings carried out at the beginning of the study (Paper I) demonstrated the drillers' perception of actual the subsurface lithological conditions. There were minor discrepancies between the drillers' colour classification of the sediments and the Munsell descriptions. Later studies (Paper II, III, IV, V) verified the drillers skills for identifying different lithological units and aquifers.

If local drillers could target safe aquifers, it would be a very viable option for As mitigation as the practice of using tubewells is deep-rooted in the rural peoples mind. There is a good potential for educating local drillers to target safe aquifers. Undoubtedly groundwater will be further developed for drinking water purposes both in rural and urban areas of Bangladesh. Involving the nations many drillers in this process, enhancing their awareness and knowledge will help them targeting safe aquifers and decrease peoples exposure to As. However, further delineation of these safe aquifers on local scale (e.g. thana wise) as well as sustainable management of them is necessary.

7.2. The correlation between aquifer sediment colours and groundwater chemical composition

Groundwater abstracted from the blackish sediments of the shallow Holocene aquifer is characterised by high concentrations of As, PO_4^{3-} -tot, NH_4^+ , DOC, Fe and low SO_4^{2-} , whereas the oxidised low-As aquifers are characterised by high Mn, low NH_4^+ , DOC, Fe, and PO_4^{3-} -tot (Paper I, II, IV). Reductive dissolution of Fe (III)-oxyhydroxides under strongly reducing conditions of the black to grey sediments is the cause for mobilisation of As (Paper I, II, III, IV). However high PO_4^{3-} -tot concentrations seems to be competing for adsorption sites thus increasing As mobility (Paper II).

Groundwater chemical composition correlated well with the colour of the aquifer sediments. Generally the groundwater is anoxic but redox conditions in the shallow and intermediate aquifers (down to 100 m b.g.l.) follows a trend from very reducing

conditions for black (as described by the drillers) sediments with increasing redox potential in sequence through white, off-white to red sediments. Furthermore, the heterogenic distribution of elevated concentration of As can be explained by the sediment characteristics in the study area (Paper I).

7.3. The relationship between aqueous and solid phase geochemistry with emphasis on mobilisation of As

The oxalate extractions showed that the FeOx/MnOx -ratio for the reducing black-greyish sediments were distinctively higher than for the oxidised unit. This demonstrates that amorphous Fe(III)-oxyhydroxides are more inclined to weathering and oxidation than amorphous Mn oxides and hydroxides. Geochemical modelling revealed that Fe, Mn and PO_4^{3-} -tot are influenced by formation of secondary minerals in addition to redox processes (Paper II).

Elevated concentrations of dissolved Fe and Mn is prone to be generated through reductive dissolution of solid oxide- and hydroxide phases of Fe(III) and Mn(IV). High dissolved concentrations of both these elements would be expected in groundwater from the reducing aquifer unit as redox-conditions are sufficiently low and distinctively higher contents of amorphous Fe and Mn (FeOx and MnOx) are found in the reduced unit. However, dissolved Fe is higher in groundwater of the reduced unit while Mn concentration is relatively higher in the oxidised unit even though groundwater redox conditions and extractions of amorphous phases of Fe and Mn (FeOx , MnOx) suggests otherwise. Using geochemical models demonstrated that secondary phases e.g. rhodochrosite, siderite, vivianite, and possibly MnHPO_4 , hydroxyapatite and Fe(III)-oxyhydroxides control the concentrations of these elements as well as PO_4^{3-} -tot in the aquifers. A plausible extended explanation (as compared to what is presented in Paper I) on how Fe, Mn, As, PO_4^{3-} -tot, pH and HCO_3^- interacts

at the solid aqueous interface of the sediments could be shown because of geochemical modelling. Geochemical modelling based on experimental data demonstrated that the mobility of As is largely influenced by Hf_0 , pH and competing ions. In addition to reductive dissolution of Fe(III)-oxyhydroxides it is expected that relatively high PO_4^{3-} -tot concentrations compete for adsorption sites is stimulating As mobilisation (Paper II).

7.4. Mineralogical description of sediments with emphasis on mobilisation of As

Decomposition of organic matter induce reductive dissolution of Fe(III)-oxyhydroxides and mobilisation of As into the groundwater. Active reduction in the grey to dark grey aquifer is also indicated by the depletion of dissolved SO_4^{2-} and formation of authigenic pyrite. Studies by SEM and XRD could identify amorphous Fe(III)-oxyhydroxides in the mica rich dark grey reduced sediment, mostly as grain coatings. In the yellowish grey oxidised topsoil dominance of crystalline iron oxides and hydroxides like magnetite, hematite and goethite. Weathering of biotite seems to plays a crucial role for generation of Fe(III)-oxyhydroxide (Paper III).

The total extractable As in the uppermost (few meters below surface) yellowish grey oxidised sediments in Daudkandi were low and mostly in recalcitrant phase compared to grey and dark grey reduced sediment in the shallow Holocene aquifer. Extraction studies showed that As is dominantly bound to poorly crystalline and amorphous metal (Fe, Al, Mn) oxyhydroxide phases with very strong positive correlation with Fe(III)-oxyhydroxides. Nevertheless, As is also associated with organic matter and sulphide phase (Paper III).

7.5. Adsorption dynamics of arsenic in oxidised sediments

Laboratory investigations on As adsorption dynamics demonstrates that the oxidised sediments have a high capacity to absorb As. For batch isotherm experiments As(V) was

used because sampling of tube-wells indicate this is the dominant aqueous redox species in the oxidised sediments. It is suggested that the adsorption of As(III) is examined as well. Simulations of the experimental isotherms underpredict the adsorption capacity. This may indicate that that crystalline Fe(III) oxides, Mn(IV) oxides, Al(III) oxides and clay minerals may also contribute to the adsorption capacity of the sediment (Paper IV).

Column experiments on oxidised sediments with As(III) and lactose added to the influent water showed that the adsorption capacity may be decreased by high levels of DOC or other electron donors. The column experiments demonstrated that the decreased adsorption capacity was due to the reductive dissolution of Fe(III)-oxyhydroxides and Mn(IV)-oxides. However, in natural aquifers with present DOC the reactions are expected to be much slower as DOC is a much more complex molecule. The adsorption processes are however very complex and not yet fully understood. Further investigations on mineralogy, laboratory experiments as well as geochemical modelling are needed for prediction of the aquifers susceptibility influx of high As and DOC groundwater (Paper IV).

7.6. Risk for cross-contamination between aquifers

The groundwater models developed proved a useful tool for enhancing the understating of the groundwater flow system when combined with field observations of seasonal hydraulic head monitoring in piezometer nests and ^{14}C analysis with subsequent dating of groundwater (Paper V).

Hydrogeological field investigations and groundwater flow modelling demonstrated that Matlab acts essentially as a recharge area even though the area is adjacent to river Meghna. The groundwater simulations could identify at least two flow-systems; i) a deeper regional horizontal flow system with recharge areas at the Tripura Hills in the east and ii) small local flow systems driven by

local topography and with local groundwater recharge. The local flow systems reach a depth of approximately 30 m b.g.l. in Matlab for calibrated groundwater models and is consistent with analysed ^{14}C ages that indicate that young groundwater should be expected down to a depth of approximately 25 m b.g.l. while being older below ($>1,000$ yr). This demonstrates that the groundwater flow at depth (below local flow system) for natural and undisturbed system is very slow (Paper V).

Irrigation wells are accountable for more than 85 % of the groundwater abstraction. Pumps are placed in clusters which have implications on local flow dynamics and risk for cross-contamination. Pumping during irrigation season was evidently observed in piezometer nests although the aquifer system was fully recharged during and after the monsoon season. The downward vertical gradient observed in piezometer nests was consistent with modelling results. As very few deep irrigation wells are installed the vertical gradient appears to be a result of aquifer properties. However the model demonstrated that irrigation wells will substantially change the local flow patterns during the irrigation season, especially around pump clusters. Irrigation- and/or production wells will induce a vertical flow. The vertical flow and risk for cross-contamination will be concurrent to the abstraction rate. The cause of hydraulic head of certain deep piezometers being below the

mean sea water level during the end of the heavy irrigation period are still unanswered but can only be a result of groundwater abstraction. In Matlab, a high yield three aquifer model to a depth of 250 m b.g.l. best fit field-observations (Paper V).

7.7. Concluding remarks

Local driller target low-As aquifers as a viable option for providing people with safe drinking. If low As aquifers can be delineated by features local drillers can use for installation of safe drinking water tubewells, this option should be promoted on national as well as local scale. Even so, this study has highlighted that risk for cross-contamination may occur locally. Installing irrigation or production wells for heavy abstraction at depth without proper management on the aquifers sustainability is strongly discouraged (Paper V, Michael and Voss 2008, Burgess et al. 2010). Improved monitoring of tube wells is strongly encouraged (van Geen et al. 2007, Polya and Charlet 2009, Bhattacharya et al. 2011).

The results from this and similar studies can further contribute to develop a pragmatic management and mitigation policy with a holistic approach for the future use of the groundwater resources for drinking water supplies. Assessing sustainability of low As aquifers in regions with elevated concentrations remain a main concern.

REFERENCES

- Abedin, M. J., Cresser, M. S., Meharg, A. A., Feldmann, J., Cotter-Howells, J., 2002. Arsenic accumulation and metabolism in rice (*Oryza Sativa* L.). *Environmental Science and Technology* 36: 962-968.
- Aggarwal P.K., Basu A.R., Poreda R.J., Kulkarni K.M., Froehlich K., Tarafdar S.A., Ali M., Ahmed N., Hussain A., Rahman M., Ahmed S.R., 2000. Isotope hydrology of groundwater in Bangladesh: implications for characterization and mitigation of arsenic in groundwater. IAEA-TC Project: BGD/8/016, IAEA, Vienna.
- Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A., Sracek, O., 2004. Arsenic contamination in groundwater of alluvial aquifers in Bangladesh: An overview. *Applied Geochemistry* 19(2): 181-200.
- Ahmed, K.M., 2005. Management of the groundwater arsenic disaster in Bangladesh. In: Bhundschuh, Bhattacharya and Chandrashekharam (eds) *Natural Arsenic in Groundwater: Occurrence, Remediation and Management*. Taylor and Francis Group, London.
- Akai, J., Izumi, K., Fukuhara, H., Masuda, H., Nakano, S., Yoshimura, T., Ohfuji, H., Anwar, H.M., Akai, K., 2004. Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. *Applied Geochemistry* 19:215-230.
- Al Rmalli, S.W., Haris, P.I., Harrington, C.F. & Ayub, M., 2005. A survey of arsenic in foodstuffs on sale in the United Kingdom and imported from Bangladesh. *Science of The Total Environment* 337: 23-30.
- Alam, N. and Wai, L., 1991. Importance of age in evaluating effects of maternal and domestic hygiene practices on diarrhoeas in rural Bangladeshi children. *Journal of Diarrhoeal Diseases Research* 9(2): 104-110.
- Alam, N., Wojtyniak, B., Henry, F.J., Rahaman, M.M., 1989. Mother's personal and domestic hygiene and diarrhoea incidence in young children in rural Bangladesh. *International Journal of Epidemiology* 18(1): 242-247.
- Allison, J.D.D., Brown, S., Novo-Gradac, K.J., 1991. MINTEQA2, a Geochemical Assessment Data Base and Test Cases for Environmental Systems. EPA, Athens, GA, U.S.
- Anawar, H.M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., Kato, K., 2003. Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *Journal of Geochemical Exploration* 77:109-131.
- Appelo, C.A.J., Postma, D., 1999. *Geochemistry, groundwater and pollution*. AA Balkema Publishers, 536 pp.
- APSU, 2004. Arsenic Policy Support Unit Interim report. Risk Assessment of arsenic mitigation options, RAAMO II, Phase II Report, May 2005. International Training Network Centre, ITN, Bangladesh.
- BGS and DPHE, 2001. Arsenic contamination of groundwater, vol 2, Final Report, BGS Tech. Rep. WC/00/19, British Geological Survey, Keyworth.
- Bhattacharya, P., Chatterjee, D. and Jacks, G., 1997. Occurrence of Arsenic-contaminated Groundwater in Alluvial Aquifers from Delta Plains, Eastern India: Options for Safe Drinking Water Supply. *Water Resources Development* 13(1): 79-92.
- Bhattacharya, P., Jacks, G., Ahmed, K.M., Routh, J. and Khan, A.A., 2002a. Arsenic in Groundwater of the Bengal Delta Plain Aquifers in Bangladesh. *Bulletin of Environmental Contaminants and Toxicology* 69: 538-545.
- Bhattacharya, P., Frisbie, S.H., Smith, E., Naidu, R., Jacks, G., Sarkar B., 2002b. Arsenic in the Environment: A Global Perspective. In: B.Sarkar (Ed.) *Handbook of Heavy Metals in the Environment*, Marcell Dekker Inc., New York, pp. 147-215.

- Bhattacharya, P., Mukherjee, A.B., Jacks, G. and Nordqvist, S., 2002c. Metal contamination at a wood preservation site: characterisation and experimental studies on remediation. *The Science of The Total Environment* 290(1-3): 165-180.
- 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.
- 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, AL., 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.
- Bhattacharya, P., Hossain, M., Rahman, S.N., Robinson, C., Nath, B., Rahman, M., Islam, M., von Brömssen, M., Ahmed, K.M., Jacks, G., Chowdhury, D., Rahman, M., Jakariya, M., Persson, L-Å., Vahter, M., 2011. Temporal and seasonal variability of arsenic in drinking water wells in Matlab, southeastern Bangladesh: A preliminary evaluation on the basis of a 4 year study. *Journal of Environmental Science and Health, Part A* 46: 1177-1184.
- Brammer, H., 1996. *The Geography of the Soils of Bangladesh*. University Press Ltd.
- Breit, G.N., Yount, J.C., Uddin, M.N., Muneem, A.A., Lowers, H.A., Driscoll, R.L., Whitney, J.W., 2006. Compositional data for Bengal delta sediment collected from boreholes at Srirampur, Kachua. Bangladesh. US geological survey open-file report 2006, 1222, 58 pp.
- Breit, G.N., Yount, J.C., Uddin, M.N., Muneem, A.A., Lowers, H.A., Berry, C.J., Whitney, J.W., 2007. Compositional data for Bengal delta sediment collected from a borehole at Rajoir, Bangladesh. US geological survey open-file report 2007, 1022, 46 pp.
- von Brömssen, M., 1999. Genesis of high arsenic groundwater in the Bengal delta plains, West-Bengal and Bangladesh, Stockholm. M.Sc. thesis, LWR, KTH.
- von Brömssen, M., Bhattacharya, P., Ahmed, K.M., Jakariya, M., Jonsson, L., Lundell, L., Jacks, G., 2005. Targeting safe aquifers in regions with elevated arsenic in groundwater of Matlab Upazila, Bangladesh. In: Lombi, E., Tyrell, S., Nolan, A., McLaughlin, M., Pierzynski, G., Gerzabek, M., Lepp, N., Leyval, C., Selim, M., Zhao, F., Grant, C., Parker, D. (eds.) *ICOBTE 8-2005, Symposium 4, 8th International Conference on the Biogeochemistry of Trace Elements (April 3-7, 2005)*, Book of Abstracts, Adelaide, Australia: 190-191.
- von Brömssen, M., Jakariya, M., Bhattacharya, P., Ahmed, K.M., Hasan, M.A., Sracek, O., Jonsson, L., Lundell, L., Jacks, G., 2007. Targeting low-arsenic in Matlab Upazila, Southeastern Bangladesh. 2007. Targeting low-arsenic aquifers in Matlab Upazila, Southeastern Bangladesh. *Science of The Total Environment* 379(2-3): 121-132.
- von Brömssen, M., Larsson, S.H., Bhattacharya, P., Hasan, M.A., Ahmed, K.M., Jakariya, M., Sikder, A.M., Sracek, O., Bivén, A., Doušová, B., Patriarca, C., Thunvik, R., Jacks, G., 2008. Geochemical characterisation of shallow aquifer sediments of Matlab Upazila, Southeastern Bangladesh – implications for targeting low-As aquifers. *Journal of Contaminant Hydrology* 99(1-4): 137-149.
- Bundschuh, J., Farias, B., Martin, R., Storniolo, A., Bhattacharya, P., Cortes, J., Bonorino, G., Alboury, R., 2004. Grounwater arsenic in the Chaco-Pampean Plain, Argentina: Case study from Robles County, Santiago del Estero Province. *Applied Geochemistry* 19(2): 231-243.
- Burgess, W.G., Hoque, M.A., Michael, H.A., Voss, C.I., Breit, G.N., Ahmed, K.M., 2010. Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. *Nature Geoscience* 3: 83-87.

- Caldwell, B.K., Smith, W.T., Caldwell, J.C., Mitra, S.N., 2005, Trends in water usage and knowledge of arsenicosis in Bangladesh. *Poulation. Space and Place* 11(4): 211-223.
- Chakraborti, D., Rahman, M.M., Paul, K., Chowdhury, U.K., Sengupta, M.K., Lodh, D., Chanda, C.R., Saha, K.C., Mukherjee, S.C., 2002. Arsenic calamity in the Indian Subcontinent: What lessons have been learned? *Talanta* 58: 3-22.
- Chatterjee, D., Roy, R.K., Basu, B.B., 2005. Riddle of arsenic in groundwater of Bengal Delta Plain-role of non-inland source and redox traps. *Environmental Geology* 49: 188-206.
- Claesson, M. and Fagerberg, J., 2003. Arsenic in ground water of Santiago del Estero – Sources, mobility patterns and remediation with natural materials. Master Thesis, Dept. of Land and Wat. Res. Eng., KTH, Stockholm, Sweden, TRITA-LWR-EX-03-05, 59 pp.
- Cohen, D., Ward, C.R., 1991. Sednorm-a program to calculate a normative mineralogy for sedimentary rocks based on chemical analyses. *Computers and Geosciences* 17(9):1235-1253.
- Correll, R., Huq, S.M.I., Smith, E., Owens, G., Naidu, R., 2006. Dietary intake of arsenic from crops. 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. p. 251-268.
- Datta, S., Neal, A.W., Mohajerin, T.J., Ocheltree, T., Rosenheim, B.E., White, C.D., Johannesson, K.H., 2011. Perennial ponds are not an important source of water or dissolved organic matter to groundwaters with high arsenic concentrations in West Bengal, India. *Geophysical Research Letters* 38, L20404.
- DPHE/DFID/JICA, 2006. Development of Deep Aquifer Database and Preliminary Deep Aquifer Map. Department of Public Health Engineering (DPHE), Government of Bangladesh, and Arsenic Policy Support Unit (APSU), Japan International Cooperation Agency (JICA), Bangladesh, Dhaka.
- Dzombak, D.A. and Morel, F.M.M., 1990. *Surface Complexation Modelling-Hydrous Ferric Oxide*. John Wiley, New York, USA, 393 pp.
- EPC/MMP, 1991. Dhaka Region Groundwater and Subsidence Study, Final Report. Engineering and Planning Consultants, Dhaka and Sir M. Macdonalds and Partners, UL. Report for Dhaka Water Supply and sewerage. Authority under assignment to the World Bank.
- Filgueiras, A.V., Lavilla, I., Bendicho, C., 2002. Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring* 4: 823-857.
- van Geen, A., Zheng, Y., Versteeg, R., Stute, M., Horneman, A., Dhar, R., Steckler, M., Gelman, A., Small, C., Ahsan, H., Graziano, J.H., Hussain, I., Ahmed, K.M., 2003. Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh. *Water Resources Research* 39(5): 1140-55.
- van Geen, A., Rose, J., Thorai, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: evidence from sediment incubations. *Geochimica et Cosmochimica Acta* 68(17): 3475-86.
- van Geen, A., Cheng, Z., Jia, Q., Seddique, A.A., Rahman, M.W., Rahman, M.M., Ahmed, K.M., 2007. Monitoring 51 community wells in Arahazar, Bangladesh, for up to 5 years: Implications for arsenic mitigation. *Journal of Environmental Science and Health Part A* 42: 1729-1740.
- Goodbred S.L., Kuehl S.A., Steckler M.S., Sarker M.H., 2003. Controls on facies distribution and stratigraphic preservation in the Ganges–Brahmaputra delta sequence. *Sedimentary Geology* 155: 301–16.
- Gustafsson, J.P., Bhattacharya, P., 2007. Geochemical modelling of arsenic adsorption to oxide surfaces. In: Bhattacharya, P., Mukherjee, A.B., Bundschuh, J., Zevenhoven, R., Loeppert, R.H. (Eds.), *Arsenic in Soil and Groundwater Environment: Biogeochemical Interactions*,

- Health Effects and Remediation, Trace Metals and other Contaminants in the Environment, vol. 9. Elsevier B.V., Amsterdam, The Netherlands, pp. 153-200.
- Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science* (298): 1602-6.
- 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
- Hasan, M.A., von Brömssen, M., Bhattacharya, P., Ahmed, K.M., Sikder, A.M., Jacks, G., Sracek, O., 2009. Geochemistry and mineralogy of shallow alluvial aquifers in Daudkandi upazila in the Meghna flood plain, Bangladesh. *Environmental Geology* 57: 499–511.
- Hoque, B.A., Hoque, M.M., Ahmed, T., Islam, S., Azad, A.K., Ali, N., Hossaina, M., Hossain, M.S., 2004. Demand-based water options for arsenic mitigation: an experience from rural Bangladesh. *Public Health* 118(1):70-7.
- Hoque, M.A., 2010. Models for Managing Deep Aquifer in Bangladesh, Ph.D. Thesis. Univ. College London, UK.
- Hoque, M.A., Burgess, W.G., Shamsudduha, M., Ahmed, K.M., 2011. Delineating low-arsenic groundwater environments in the Bengal Aquifer. *Applied Geochemistry* 26: 614-623.
- Horneman, A., van Geen, A., Kent, D. V., Mathe, P. E., Zheng, Y., Dhar, R. K., O'Connell, S. O., Hoque, M. A., Aziz, Z., Shamsudduha, M., Seddique, A. A., Ahmed, K. M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles. *Geochimica et Cosmochimica Acta* 68(17): 3459-3473.
- Hug, S.J., Gaertner, D., Roberts, L.C., Schrimmer, M., Ruettimann, T., Rosenberg, T.M., Badruzzaman, A.B.M., Ali, M.A., 2011. Avoiding high concentrations of arsenic, manganese and salinity in deep tubewells in Munshiganj District, Bangladesh. *Applied Geochemistry* 26: 1077-1085.
- Huq, S.M.I., Correll, R. & Naidu, R., 2006. Arsenic accumulation in food sources in 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, pp. 279-290.
- Jakariya, M., Rahman, M., Chowdhury, A.M.R., Rahman, M., Yunus, M., Bhiuya, A., Wahed, M.A., Bhattacharya, P., Jacks, G., Vahter M., Persson, L.-Å., 2005. Sustainable safe water options in Bangladesh: experiences from the Arsenic Project at Matlab (AsMat). In: Bundschuh, J., Bhattacharya, P., Chandrashekharam, D. (Eds.) *Natural Arsenic in Groundwater: Occurrence, Remediation and Management*. A.A. Balkema, Taylor and Francis Group, London, pp. 319-330.
- Jakariya, M., von Brömssen, M., Jacks, G., Chowdhury, A.M.R., Ahmed, K.M., Bhattacharya, P., 2007. Searching for sustainable arsenic mitigation strategy in Bangladesh: experience from two upazilas. *International Journal of Environment and Pollution* 31(3/4): 415-430.
- JICA-Japanese International Development Agency, 2002. The study on the groundwater development of deep aquifers for safe drinking water supply to arsenic affected areas in western Bangladesh. Kokusai Kogyo Co. Ltd., and Mitsui Mineral Development Engineering Co. Ltd.
- Johnston, R. B., Hanchett, S., Khan, M.H., 2010. The socio-economics of arsenic removal. *Nature Geoscience* 3: 2-3.

- Jonsson, L., Lundell, L. 2004. Targeting safe aquifers in regions with arsenic-rich groundwater in Bangladesh. Case study in Matlab Upazila. Minor Field Studies No 277. Swedish University of Agricultural Sciences, SLU External Relations, Uppsala. ISSN 1402-3237.
- Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P., 2006. Human health effects from chronic arsenic poisoning - A Review. *Journal of Environmental Science and Health Part A* 41: 2399-2428.
- Kar, S., Maity, J.P., Jean, J-S., Liu, C-C., Nath, B., Yang, H-J., Bundschuh, J., 2010. Arsenic-enriched aquifers: Occurrences and mobilization of arsenic in groundwater of Ganges Delta Plain, Barasat, West-Bengal, India. *Applied Geochemistry* 25: 1805-1814.
- Kendie, S.B., 1996. Some factors influencing effective utilisation of drinking water facilities: women, income and health in north Ghana. *Environmental Management* 20(1): 1-10.
- Lowers, H.A., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Uddin, M.N., Muneem, A.A., 2007. Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. *Geochimica et Cosmochimica Acta* 71: 2699-2717.
- Mandal, B.k. and Suzuki, K.T., 2002. Arsenic round the world: a review. *Talanta* 58: 201-235.
- Manning, B.A., Goldberg, S., 1997. Adsorption and stability of arsenic(III) at the clay mineral–water interface. *Environmental Science Technology* 31: 2005-2011.
- McArthur, J.M., Ravencroft, P., Safiullah, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanism for sedimentary aquifers in Bangladesh. *Water Resources Research* 37: 109-117.
- McArthur, J.M. et al., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Applied Geochemistry* 19: 1255-1293.
- Meharg, A.A., Scrimgeour, C., Hossain, S.A., Fuller, K., Cruickshank, K., Williams, P.N., Kinniburgh, D.G., 2006. Codeposition of organic carbon and arsenic in Bengal Delta Aquifers. *Environmental Science Technology* 40: 4928-4935.
- Meng, X., Korfiatis, G.P., Christodoulatos, C., Bang S., 2001. Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system. *Water Research* 35(12): 2805-2810.
- Michael, H.A., Voss, C.I., 2008. Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. *Proceedings of the National Academy of Sciences of the United States of America* 105: 8531–8536.
- Michael, H., Voss, C., 2009a. Controls on groundwater flow in the Bengal Basin of India and Bangladesh: regional modeling analysis. *Hydrogeology Journal* 17: 1561–1577.
- Michael, H., Voss, C., 2009b. Estimation of regional-scale groundwater flow properties in the Bengal Basin of India and Bangladesh. *Hydrogeology Journal* 17: 1329–1346.
- Milton, A.H., Hasan, Z., Shahidullah, S.M., Sharmin, S., Jakariya, M.D., Rahman, M., Dear, K., Smith, W., 2004. Association between nutritional status and arsenicosis due to chronic arsenic exposure in Bangladesh. *International Journal of Environmental Health Research* 14(2): 99-108.
- Minkinen, P. and Yliruokanen, I., 1978. The arsenic distribution in Finnish bogs. *Kemia-Kemi*: 331-335.
- Mozumder, M. R.H., 2011. Aqueous Phase Geochemical Characterisation and Delineation of Low Arsenic Aquifers in Matlab Upazila, SE Bangladesh. M.Sc. Thesis, Royal Institute of Technology, LWR-EX-11-08, ISSN 1651-064X

- Mukherjee, A., Fryar, A.E., Howell, P., 2007. Regional hydrostratigraphy and groundwater flow modeling of the arsenic affected western Bengal basin, West Bengal, India. *Hydrogeology Journal* 15: 1397–1418.
- 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 between the Bhagirathi and Meghna sub-basins, Bengal basin, India and Bangladesh: effects of overlapped redox zones on dissolved arsenic. *Journal of Contaminant Hydrology* 99(1-4): 31-48.
- Naidu, R., Smith, E., Owens, G., Bhattacharya, P., Nadebaum, P., 2006. *Managing Arsenic in the Environment: From Soil to Human Health*. CSIRO Publishing, Melbourne, Australia, 656 pp.
- Nickson, R., McArthur, J., Burgess, W.G., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. *Nature* 1998: 395-338.
- Nickson, R., McArthur, J., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Applied Geochemistry* 15: 403-413
- Nickson, R.T., McArthur, J.M., Shrestha, B., Kyaw-Myint, T.O., Lowry, D., 2005. Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan. *Applied Geochemistry* 20(1):55-68.
- Parkhurst, D.L., Appelo, C.A.J., 1999. *Users's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-reaction, One-dimensional Transport and Inverse Geochemical Calculations*. U.S. GEOLOGICAL SURVEY, Denver, Colorado, USA. 99-4259.
- Polya, D., Charlet, L., 2009. Rising arsenic risk? *Nature Geoscience* 2: 383-384.
- Polya, D.A., Mondal, D. And Giri, A.K., 2009. Quantification of deaths and DALYs arising from chronic exposure to arsenic in groundwaters utilized for drinking, cooking and irrigation of food crops in Preedy and Watson (Eds) *Handbook of Disease Burdens and Quality of Life Measures*, Springer-Verlag, pp 702-728.
- Postma, D., Jakobsen, R., 1996. Redox zonation: equilibrium constraints on the Fe(III)/SO₄-reduction interface. *Geochimica et Cosmochimica Acta* 60(17): 3169-3175.
- Quevauviller, P., Rauret, G., Griepink, B., 1993. Single and sequential extraction in sediment and soils. *International Journal of Environmental Analytical Chemistry* 51:231-235.
- Radloff, K.A., Zheng, Y., Michael, H.M., Stute, M., Bostick, B.C., Milhajlov, I., Bounds, M., Huq, M.R., Chowdhury, I., Rahman, M.W., Schlosser, P., Ahmed, K.M., van Geen, A. 2011. Arsenic migration to deep groundwater in Bangladesh influenced by adsorption and water demand. *Nature Geoscience*, NGE0 12833.
- Ravenscroft, P., McArthur, J.M., Hoque, B.A., 2001. Geochemical and palaeohydrological controls on pollution of groundwater by arsenic. In: Chappell WR, Abernathy CO, Calderon RL (eds) *Arsenic exposure and health effect IV*. Elsevier, Oxford, pp. 53-57.
- Ravenscroft, P., Burgess, W., Ahmed, K., Burren, M. and Perrin, J., 2005. Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting. *Hydrogeology Journal* 13(5-6): 727-751.
- Reza, S.A.H.M., Jean, J-S., Lee, M-K., Yang, H-J., Liu, C-C., 2010. Arsenic enrichment and mobilization in the Holocene alluvial aquifers of the Chapai-Nawabganj district, Bangladesh: A geochemical and statistical study. *Applied Geochemistry* 25: 1280-1289.
- Reza, S.A.H.M., Jean, J-S., Lee, M-K., Luo, S-D., Bundschuh, J., Li, H-C., Yang, H-J., Liu, C-C., 2011. Interrelationship of TOC, As, Fe, Mn, Al and Si in shallow alluvial aquifers in Chapai-Nawabganj district, Bangladesh: implication for potential source of organic carbon. *Environmental Earth Science* 63: 955-967.

- Robinson, C., Hossain, M., von Brömssen, M., Bhattacharya, P., Häller, S., Bivén, A., Jacks, G., Ahmed, K.M., Hasan, M.A., Thunvik, R., 2011. Dynamics of arsenic adsorption in the targeted arsenic-safe aquifers in Matlab, South-eastern Bangladesh: insight from experimental studies. *Applied Geochemistry* 26: 624–635.
- Roychowdhury, T., Uchino, T., Tokunaga, H., Ando, M., 2002. Survey of arsenic in food composites from an arsenic-affected area of West Bengal, India. *Food and Chemical Toxicology* 40(11): 1611-21.
- Saha, D., Sinha, U.K., Dwivedi, S.N., 2011. Characterization of recharge processes in shallow and deeper aquifers using isotopic signatures and geochemical behaviour of groundwater in an arsenic-enriched part of the Ganga Plain. *Applied Geochemistry* 26: 432-443.
- Sarkar, B., 2002. *Heavy metals in the environment*. Marcel Dekker, Inc., New York, 725 pp.
- Sikder, M.S., Maidul, Z.M., Ali, M., Rahman, M.H., 2005. Socio-economic status of chronic arsenicosis patients in Bangladesh. *Mymensingh Medical Journal* 14(1): 50-53.
- Singh, N., Jacks, G., Bhattacharya, P., 2005. Women and community water supply programmes: An analysis from a socio-cultural perspective. *Natural Resources Forum* 29(3): 213-223.
- Smedley, P.L. and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17(5): 517-568.
- Smith, A.H., Lingas, E.O. and Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of the World Health Organization* 78(9): 1093-1103.
- Sracek, A., Bhattacharya, P., Jacks, G. and Gustafsson, J.P., 2000. Mobility of arsenic and geochemical modeling in groundwater environment. In: G. Jacks, P. Bhattacharya and A.A. Khan (Editors), *Groundwater Arsenic Contamination in the Bengal Delta Plains of Bangladesh: Proceedings of the KTH-Dhaka University Seminar*.
- Sracek, O., Bhattacharya, P., Jacks, G., Gustafsson, J.-P. and von Brömssen, M., 2004a. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. *Applied Geochemistry* 19(2): 169-180.
- Sracek, O., Bhattacharya, P., von Brömssen, M., Jacks, G., Ahmed, K. M., 2004b. Natural enrichment of arsenic in groundwaters of Brahmanbaria district, Bangladesh: geochemistry, speciation modelling and multivariate statistics. In: *Natural Arsenic in Groundwater: Occurrence, Remediation and Management*. Edited by J. Bundschuh, P. Bhattacharya and D. Chandrasekharam Balkema, London.
- Stollenwerk, K.G., 2005. *Arsenic Attenuation by Oxidized Aquifer Sediments, Bangladesh, Behavior of Arsenic in Aquifers, Soils and Plants: Implications for Management*. International Maize and Wheat Improvement center (CYMMYT), Cornell University, Texas A&M University, United States Geological Survey, Geological Survey of Bangladesh, Dhaka, Bangladesh.
- Stollenwerk, K.G., Breit, G.N., Welch, A.H., Yount, J.C., Whitney, J.W., Forster, A.L., Uddin, M.N., Majumder, R.K., Ahmed, N., 2007. Arsenic attenuation by oxidised sediments in Bangladesh. *Science of The Total Environment* 379: 133-150.
- Stüben, D., Berner, Z., Chandrasekharam, D. and Karmakar, J., 2003. Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing conditions. *Applied Geochemistry* 18(9): 1417-1434.
- Stute, M., Zheng, Y., Schlosser, P., Horneman, A., Dhar, R.K., Hoque, M.A., Seddique, A.A., Shamsudduha, M., Ahmed, K.M., van Geen, A., 2007. Hydrological control of As concentrations in Bangladesh groundwater. *Water Resources Research* 43, W09417.
- Swartz, C.H., Blute, N.K., Bodruzzaman, B., Ali, M.A., Brabander, D., Jay, J., Besabcon, J., Islam, S., Hemond, H.F., Harvey, C., 2004. Mobility of arsenic in a Bangladesh aquifer: inferences

- from geochemical profiles, leaching data, and mineralogical characterization. *Geochimica et Cosmochimica Acta* 68 (22): 4539-4557.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51:844-851.
- Tuccillo, M.E., Cozzarelli, I.M., Herman, J.S., 1999. Iron reduction in the sediments of a hydrocarbon-contaminated aquifer. *Applied Geochemistry* 14:655-667.
- Uddin, A., Shamsudduha, M., Saunders, J.A., Lee, M-K., Ahmed, K.M., Chowdhury, M.T., 2011. Mineralogical profiling of alluvial sediments from arsenic-affected Ganges-Brahmaputra floodplain in central Bangladesh. *Applied Geochemistry* 26: 470-483.
- Umitsu M., 1987. Late Quaternary sedimentary environment and landform evolution in the Bengal lowland. *Geographical Review of Japan* 60: 164-78.
- Umitsu M., 1993. Late Quaternary sedimentary environments and landforms in the Ganges Delta. *Sediment Geology* 83:177-86.
- UN, 2001. United Nations Synthesis Report on Arsenic in Drinking Water. Draft report.
- UNDP, 1982. Groundwater Survey: The Hydrogeological Conditions of Bangladesh. UNDP Technical Report DP/UN/BGD-74-009/1, 113 pp.
- Vahter, M.E., Li, L., Nermell, B., Rahman, A., Arifeen, A.E., Rahman, M., Persson, L-Å., Ekström, E-C., 2006. Arsenic Exposure in Pregnancy: A Population-based Study in Matlab, Bangladesh. *Journal of Health, Population and Nutrition* 24(2): 236-245.
- Wasserman, G.A., Liu, X., Parvez, F., Factor-Litvak, P., Ahsan, H., Levy, D., Kline, J., van Geen, A., Mey, J., Slavkovich, V., Siddique, A.B., Islam, T., Graziano, J.H., 2011. Arsenic and manganese exposure and children's intellectual function. *NeuroToxicology* 32: 450-457.
- Welch, A.L. and Stollenwerk, K.G., 2003. *Arsenic in Ground Water, Geochemistry and Occurrence*. Kluwer Academic Publishers, Boston, 475 pp.
- Vencelides, Z., Sracek, O., Prommer, H., 2007. Modelling of iron cycling and its impact on the electron balance at a petroleum hydrocarbon contaminated site in Hnevice, Czech Republic. *Journal of Contaminant Hydrology* 89: 270-294.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* 436: 309-323.
- WHO, 2004. *Guidelines Drinking Water Quality, Third edition, Volume 1, Recommendations*. Geneva 2004 515 pp.
- Williams, P. N., Price, A. H., Raab, A., Hossain, S. A., Feldmann, J., Meharg, A. A., 2005. Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. *Environmental Science and Technology* 39: 5531-5540.
- Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J., Meharg, A. A., 2006. Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. *Environmental Science and Technology* 40: 4903-4908.
- Yan, X-P., Kerrich, R., Hendry, M.J., 2000. Distribution of arsenic (3), arsenic (5) and total inorganic arsenic in porewaters from a thick till and clay rich aquitard sequence, Saskatchewan, Canada. *Geochimica et Cosmochimica Acta* 62: 2637-2648.
- Zheng, Y., van Geen, A., Stute, M., Dhar, R., Mo, Z., Cheng, Z., Horneman, A., Gavrieli, I., Simpson, H.J., Versteeg, R., Steckler, M., Grazioli-Venier, A., Goodbred, S., Shahnewaz, M., Shamsudduha, M., Hoque, M.A., Ahmed, K.M., 2005. Geochemical and hydrogeological contrast between shallow and deeper aquifers in two villages of Araihasar, Bangladesh: implication for deeper aquifers as drinking water sources. *Geochimica et Cosmochimica Acta* 69(22): 5203-5218.

AFTERWORD

By chance I ended up spending more than a year in West-Bengal, India and Bangladesh, traveling more than ten times back and forth for my studies on high arsenic groundwater in the Bengal basin and possible mitigation options.

In 1997 I was looking for an opportunity to do my M.Sc. thesis in a developing country. I had little success until I heard that Prof. (*Dr. at that time*) Prosun Bhattacharya was looking for a student to apply for a Minor Field Study Scholarship Programme funded by the Swedish International Development Cooperation Agency (Sida). The problem was that the submission was due next Monday and our first meeting was on Friday afternoon. Since I had three days to finish the application I made a lame excuse at the class I was attending and headed for the library looking for background material and a place to read and write (*at that time searching information on internet was not as easy as it is now*).

During 1998 I spent four months at Kalyani University 50 km north of Kolkata (*Calcutta at that time*) doing my field work. Staying at the research scholars' hostel at Kalyani working with Prof. (*Dr. at that time*) Debashis Chatterjee and his team is one of my most memorable moments. Until today we are still in contact and I enjoy meeting him every time. We have always had long and rich philosophical talks. In 1999 I finished my M.Sc. thesis and started at Ramböll (*my current employer and Scandiaconsult at that time*) working as environmental consultant investigating contaminated land and groundwater.

In 2001 I and Prosun applied for a Ph.D. grant from Sida (*Sida-SAREC at that time*) without any success but a year later we tried again, this time with a fresh new, and much more appealing, headline: “Options for safe drinking water in regions with high arsenic groundwater”. That made the trick and in 2003 I could start my Ph.D. studies at KTH.

At the beginning I was on a leave from Ramböll but eventually me, Prosun, Prof. Em. (*Prof. at that time*) Gunnar Jacks and Prof. Kazi Matin and Dr. (*Mr. at that time*) Md. Jakariya in Bangladesh managed to develop three major research- and action research projects funded by Sida (2008-2013), MISTRA (2006-2010) and The Ramböll Foundation (2006-2010). The Ramböll Foundation project gave me the opportunity to do my Ph.D. at Ramböll being fully financed. For the MISTRA project I and Prosun spend only six hours writing the prequalification application the same day it was due (*good ideas seems to appear late*). I still owe Estifanos (*Dr. by now*) a bottle of whiskey (*he is now in the USA*) for helping posting the application. He ran or biked (*I don't remember now*) as fast as he could to the post-office at Central station handing the application in, five minutes before closing time (*21:00*). If you ever visit Sweden again, you can collect that bottle from me. The Sida funded project, Sustainable Arsenic Mitigation (SASMIT), is still running and is to be finished by 2013. I have learned a lot from that project, and not only scientific stuff.

From 2003 until today I spent almost half of my working hours on this Ph.D. and the adjoining projects. At the same time I also had the fantastic opportunity to spend more than a year at home on parental leave with my daughter Maja and my son Elias, the children my wife Åsa gave birth to in 2007 and 2009. We were married in 2008. The studies and work has included tedious travels back and forth to Bangladesh for field work, travelling for conferences in USA, Taiwan, Sweden and Australia, meeting fantastic people, making new friends, staying in the most unlikely places and debating high arsenic groundwater and possible mitigation options with hundreds of people. I have carried more than a thousand groundwater samples and numerous of kilos of

sediment samples back to Sweden as well as high quality chemicals to Bangladesh without the custom ever stopping me (*although I have had to explain myself a couple of times*).

I will never forget the time I spent with friends in rural and remote villages in Bangladesh or the trip me and Åsa made to Sunderban looking for tigers, staying the night alone in the watching tower (*we did see foot-prints*) nor the chance we got to spend an unforgettable weekend as invited guests at a remote tea-estate in Sreemangal, Sylhet. I have despaired many times along the course when nothing worked, everything took too long time (*you know what I mean if you have experienced the Dhaka traffic*), no one wanted to help, results were neither as expected nor in favour of the hypothesis I had been working on for a year or more. During field work I have had stomach problems so many times I cannot count them. The time I went dehydrated during a field-trip I thought I would die; thank god I was staying at friends in Dhaka. But eventually, and with lots and lots of the help and encouragement from family and friends in Sweden, Bangladesh, India, Czech Republic, Argentina and USA I have now finally (Prosun!!!) been able to present this Ph.D. thesis.

Mattias von Brömssen

Stockholm, January 2012