ARSENIC GEOCHEMISTRY IN THE ALLUVIAL AQUIFERS OF WEST BENGAL, INDIA

Implications for targeting safe aquifers for sustainable drinking water supply

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September 2013
**Cover illustration:**

*Top left:* Household hand pumped tubewell; *Top right:* Low-cost hand suction drilling technique used for household tubewell installation; *Bottom left:* Typical sediments recovered during drilling (*Photograph:* Ashis Biswas©, 2011); *Bottom right:* Piezometer nest at Chakudanga, Chakdaha (*Photograph:* Prosun Bhattacharya©, 2010)

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PhD Thesis

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Dedicated to my Family…
The presence of naturally occurring arsenic in groundwater has been designated as “The largest mass poisoning in human history”. While arsenic is an old poison familiar since ages to us, its presence in groundwater in concentrations causing chronic poisoning came as a surprise. In the Bengal basin the problem is especially serious as in the past decades the rural water supply has been more or less completely switched to groundwater with excessive arsenic. Remedial actions have been tested in the form of filters, water harvesting etc but have not been accepted due to cost or social reasons. This thesis is focused on the fact that excess arsenic is not ubiquitous in the shallow groundwater, accessible with local, affordable drilling technology. In the late 1990s the mechanism for arsenic mobilization into the groundwater was explained by redox reactions resulting in reduction of ferric oxyhydroxides releasing the adsorbed arsenic. This thesis shows that while this may be a major process there are several contributing processes that are needed to produce the toxic groundwater. The thesis has elucidated new findings regarding the sedimentary history and water pathways important for the redox chemistry and the arsenic mobilization. The thesis has demonstrated that the processes are site specific. Thus, the thesis gives new insights into the processes mobilizing arsenic into the groundwater. Additionally it presents also a number of means to identify arsenic low groundwater within the depth of 50 m, easily accessible with the cheap local drilling technology. This identification covers a range from simple ones such as observing the color of the precipitates found on well platforms to deeper insights into the sedimentology and reactions regarding redox and surface chemistry of the sediments, all which can prioritize an urgently needed remedy of the current situation.

Prof. Em. Gunnar Jacks
Stockholm, KTH, September 2013
ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to my main supervisor Prof. Prosun Bhattacharya at the Division of Land and Water Resources Engineering (LWR) for hosting me as the doctoral student at KTH Royal Institute of Technology (KTH). Without his support, encouragement and guidance it was not possible to complete my doctoral study at KTH.

I have heart-full appreciation for my co-supervisor Prof. Debashis Chatterjee at the Department of Chemistry (DC), University of Kalyani (KU). I am grateful to him for motivating me to pursue doctoral study and ensuring all-time access to his laboratory, logistic supports during field campaigns and the time for academic discussions. I am also thankful for giving me the opportunity to work as a research fellow in the collaborative project between DC-KU and Institute of Mineralogy and Geochemistry (IMG), Karlsruhe Institute of Technology (KIT), dealing with the investigation of role of microbiogeochemical processes in arsenic mobilization in the aquifers of Bengal Basin, prior to my joining as a doctoral student at KTH. This project has substantial contribution in my PhD study at KTH.

I am grateful to Prof. Gunnar Jacks at LWR, KTH, who also ensured unlimited access to him for any scientific discussion and was always ready to help me in the laboratory work. I have also enjoyed those non-scientific discussions with him, which have enriched me as human beings. I feel really fortunate having him in my advisory committee. I am equally thankful to Dr. Zsolt Berner (IMG, KIT), Dr. Bibhash Nath (School of Geosciences, The University of Sydney), Dr. Abhijit Mukherjee (Department of Geology and Geophysics, Indian Institute of Technology-Kharagpur) and Prof. Jon Petter Gustafsson (LWR, KTH) for their guidance at different stages of my research. I am also thankful to Prof. Berit Balfors at LWR, KTH for her revision of my thesis and afterward very fruitful discussion.

I would like to warmly acknowledge the supports of all of my co-authors in the papers. I am very much thankful to my friend Dr. Harald Neidhardt at IMG, KIT, currently at EAWAG, who was always ready to extend his support throughout my research. We have so many great memories during field work at Chakdaha together with Dr. Dominik Freikowski (Institute of Biology for Engineers and Biotechnology of Waste Water Treatment, KIT). I am also thankful to all of my colleagues and friends both at KU and KTH for ensuring a nice and homely working environment and keeping me always mentally fresh. Especially, I would like to thank Amit K. Kundu at DC, KU for taking care of sampling, when I was at KTH.

I would like to acknowledge the analytical support from DC, KU; IMG, KIT; Department of Geological Sciences (IGV), Stockholm University (SU) and Department of Solid State Chemistry, Institute of Chemical Technology in Prague (Dr. Barbora Doušová). I am also thankful to Bertil Nilsson and Ann Fylkner at LWR, KTH. Without such analytical supports it was not possible to finish my study on time. I am especially grateful to Prof. Carl-Magnus Mörtth at IGV, SU for discussing about different aspect of possible analysis over there and ensuring such supports, which has substantially developed the outputs of my research. I would like to thank Heike Siegmund (IGV, SU), who has always analyzed my samples with top priority. I would also like to acknowledge the support of Luminescence Laboratory (Prof. Helena Alexanderson) and
Radiocarbon Dating Laboratory of the Department of Geology, Lund University for the dating of aquifer sediments from my study area. I am thankful to Dr. Saugata Datta at Kansas State University for giving me the opportunity to work at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) with his research group and it is a lifetime experience for me.

I am thankful to P. K. Das (Bapi), N. Bhabani (Probhu), R. Das (Bapi) and S. Karmakar (Bablu) and his drilling team, who were always ready to work at the field even at very short notice. I would also like to acknowledge local villagers in my study area, especially Mr. Atul Chandra Mandal and Mr. Sadhan Ghosh for ensuring the unlimited access to their courtyards for piezometers installation and sampling campaign. I will remember the hospitality of Mashima (wife of Mr. Atul Chandra Mandal) throughout my life; I have access to their house like my home.

I would like to acknowledge the supports of Aira Saarelainen, Britt Chow and Jerzy Buczak to me as a PhD student at LWR, KTH. I am also grateful to my parents, parents-in-law and Mr. Mihir Khan for their love and mental support throughout my study. Lastly, it is the time to acknowledge some special one, who is at the same time friend, colleague and my wife, Dipti Halder. Without her supports and cooperation both academically and in the daily life, it was not possible to accomplish this research. Being with her, I can very easily switch off myself from the daily life concerns and concentrate into my own research. Does it seem I am selfish, indeed I am!!

The list cannot be completed without acknowledging the funding authorities. At first, I would like to acknowledge the Erasmus Mundus External Cooperation Window (EMECW-Action II) for providing me the doctoral fellowship through EURINDIA Program, which enabled me to pursue PhD study at KTH. I would also like to acknowledge the German Research Foundation (DFG) and the German Federal Ministry for Economic Cooperation and Development (BMZ) (Stu 169/37-1) for providing the funding for collaborative project between DC, KU and IMG, KIT. I am also thankful to the financial support to KTH-International Groundwater Arsenic Research Group (KTH-GARG) by Swedish International Development Cooperation Agency (Sida) and Swedish Research Council (VR) through the Swedish Research Link grant (VR-Sida, dnr: 348-2006-6005) and the Strategic Environmental Research Foundation (MISTRA) (Idea Support Grant, dnr: 2005-035-137). Without these fundings the research presented in the thesis could not be accomplished.

Finally, I want mention that doing PhD is a memorable journey in my life and I am extremely happy being at the end of this journey. I have learned so many things during this journey, which have enriched me in the professional field and also as human beings. The experiences that I have gained certainly would help me to complete the rest journey in my life successfully. Thank you all again!!

Ashis Biswas
Stockholm, September 2013
LIST OF APPENDED PAPERS AND MY CONTRIBUTIONS

This thesis is based on the following five papers, which are referred as corresponding Roman numerals throughout the text and are attached in the Appendix.

**Paper I**

I participated in designing of the project, executed the field work and laboratory analysis and performed lithological modeling, data analysis and main part of writing.

**Paper II**

I participated in designing of the project, executed the field work and major part of laboratory analysis and performed laboratory analysis and main part of writing.

**Paper III**

I participated in sediment sampling and piezometer installation, executed bi-weekly groundwater sampling and part of laboratory analysis and performed data analysis and main part of writing.

**Paper IV**

I performed all the modeling, data analysis and main part of writing.

**Paper V**

I participated in designing of the project, executed the field work and laboratory analysis and performed data analysis and main part of writing.

LIST OF PAPERS NOT APPENDED IN THE THESIS

**Paper VI**
Biswas, A., Majumder, S., Neidhardt, H., Halder, D., Bhowmick, S., Mukherjee – Goswami, A., Kundu, A.K., Saha, D., Berner, Z., Chatterjee, D.,

**Paper VII**


**Paper VIII**


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ABSTRACT

The natural occurrences of high (>10 µg/L) dissolved arsenic (As) in groundwater of Bengal Basin has put millions of people under the threat of chronic As exposure through drinking water. Present study has examined the processes that regulate As mobilization and its distribution in shallow aquifers and the potentiality of finding safe aquifers within shallow depth (<50 m) for drinking water supply. The results indicate that in terms of aquifer sediment colors and water quality two types of aquifer namely brown sand aquifer (BSA) and grey sand aquifer (GSA) can be distinguished within the depth, accessible by low-cost drilling. The redox condition in the BSA is delineated to be Mn oxyhydroxides reducing, not sufficiently lowered for As mobilization resulting in high Mn and low Fe and As in groundwater. While in GSA, currently the reductive dissolution of Fe oxyhydroxides is the prevailing redox process causing As mobilization into groundwater of this aquifer type. It is revealed that the vertical distribution of As and other aqueous redox parameters is related to the redox zonation within aquifer. The decoupling of As and Fe release into groundwater is evident in the shallowest part of aquifer because of Fe enrichment by weathering of silicate minerals especially of biotite, the precipitation of secondary mineral phases like siderite and vivianite and incomplete reduction of Fe oxyhydroxides. It is characterized that the seasonal variations of As and other aqueous solutes are limited within the upper portion of aquifer only (<30 m bgl) and can be related to seasonal cycling of redox status, aggregation and dispersion of As scavenging colloids, local groundwater abstraction and monsoonal recharge. The results of surface complexation modeling indicate that PO$_4^{3-}$ is the major competitor of As(III) and As(V) adsorption onto Fe oxyhydroxides. This study concludes that the reductive dissolution of Fe oxyhydroxides followed by competitive sorption reactions with the aquifer sediment is the process conducive for As enrichment in groundwater of Bengal Basin. Present study advocates that despite low concentration of As in groundwater, a rigorous assessment of attendant health risk for Mn is necessary prior to considering mass scale exploitation of the BSA for sustainable drinking water supply. This study also validates that TW platform colors can be used as a rapid screening tool for As and Mn in drinking water wells to prioritize As mitigation management.

Key words: Bengal Basin; Groundwater; Arsenic; Redox processes; Competing ions; Sustainable drinking water Supply

1. INTRODUCTION

1.1. Definition of the problem

The presence of arsenic (As) in hydrologic systems is known for last one century since its occurrence in groundwater was first reported in Chaco-Pampean plain of Argentina in 1917 (Bundschuh et al., 2012). In the following decades, its presence in groundwater has been reported from almost the entire globe, including in the countries of Asia, Europe, Africa, North America, South America and Australia and designated as one of the largest environmental threats to the human population (Nordstrom, 2002; Nriagu et al., 2007). Nevertheless, the problem is most severe in the countries of South and Southeast Asia, specifically in Bangladesh and adjoining part of West Bengal (currently Paschim Banga), state of Eastern India (Polya and Charlet, 2009; Fendorf et al., 2010).
A physiographic area of ~200,000 km\(^2\), covering major part of Bangladesh and West Bengal (collectively known as Bengal Basin), constitutes one of the most densely populated areas in this globe containing more than 2\% of the total world population (Mukherjee et al., 2007a). Three major rivers, namely River Ganges, Brahmaputra and Meghna and their various tributaries and distributaries jointly drain the whole Bengal Basin and forms world’s 4\(^{th}\) largest riverine drainage to the ocean through the basin (Milliman and Meade, 1983; Goodbred and Kuehl, 2000; Mukherjee et al., 2009a). Thus, Bengal Basin is also known as Ganges-Brahmaputra-Meghna (GBM) basin (Mukherjee et al., 2007a). The unregulated disposal of sewage and industrial waste in these rivers and streams by the inhabitants of this region has made surface water unhealthy for drinking (Mukherjee et al., 2007a). Consequently, starting from early 1970s, millions of hand-pumped tubewells (TWs) have been installed as an initiative of both local households and governments to shift drinking water source from surface water to groundwater to avoid water borne diseases such as diarrhea, cholera, caused by the microbial pathogens (Fendorf et al., 2010). The easy accessibility of groundwater in the prolific aquifers of this region has also made it a preferred drinking water source. Currently, more than 95\% of the population rely on groundwater for domestic purposes (PHED 1993; BGS and DPHE 2001). The use of groundwater has even been intensified after the introduction of groundwater based irrigation following the period of “Green Revolution”, which has eventually ensured the food safety in India and Bangladesh (Harvey et al., 2005; Norra et al., 2005; Fendorf et al., 2010). Presently, 70\% of the irrigation is groundwater based, which constitutes almost 85\% of the total groundwater abstraction (BGS and DPHE 2001). However during these installations, the presence of As, an inorganic carcinogen, in groundwater of this region was not known. The presence of elevated As (>50 \(\mu\)g/L) in groundwater was first reported from West Bengal in 1978, when a survey of drinking water wells for As was conducted following the reporting of identifiable health outcomes from rural Bengal (Saha, 1984, Guha Mazumder et al., 1988). In the subsequent years, such enrichment was also accounted from the aquifers of Bangladesh (Dhar et al., 1997; Roy Chowdhury et al., 1999). It is reported that most of the TWs and pumps were installed in the shallow aquifers with depth ranging between 10 – 50 m, where the concentrations of dissolved As also usually peaks (UNICEF, 2003). Consequently, it is estimated that more than 60 millions of people, living in this region are at the risk of chronic As toxicity due to the consumption of As contaminated groundwater and dietary components (Chakrabarti et al., 2008; Chatterjee et al., 2010; Halder et al., 2012, 2013). The extent of human exposure has been designated as the largest mass poisoning in human history (Smith et al., 2000). The health outcomes of the prolonged exposure to As ranges from the development of different skin lesions like keratosis, hyperkeratosis, melanosis, leuko-melanosis and skin cancer to the cancer of lung, bladder and kidney, reproductive disorder, cardio vascular diseases, diabetes and may also affect children’s intellectual function (Kapaj et al., 2006; Vahter et al., 2006; Tseng, 2009; Wasserman et al., 2011). Considering the potentiality of these severe health burdens due to As exposure, World Health Organization (WHO) re-reviewed the provisional drinking water guideline value for As and decreased it to 10 \(\mu\)g/L (WHO, 1993).

1.2. Recent advancement in As research

1.2.1. Source of As in the aquifers of Bengal Basin

After first reporting of As in groundwater of Bengal Basin, considerable extent of researches have been undertaken, particularly from the part of Bangladesh, to characterize the sources and processes that lead to the enrichment of As in groundwater. It is quite well established that the source of As in groundwater is non-point and geogenic in nature. Since, the basin is
developed by the supply of enormous volume of sediment load carried by River Ganges and Brahmaputra, which enters into basin from the northwest and northeast respectively (Milliman and Meade, 1983; Goodbred and Kuehl, 2000; Mukherjee et al. 2009a), it is hypothesized that the source of As in the sediments of Bengal Basin lies in the Himalaya, perhaps the sulphidic minerals, the weathering product of crystalline metamorphic rocks (McArthur et al., 2004, Polizzotto et al., 2006). The Gondwana coal seems in the Rajmahal Basin, located in the upstream of River Ganges, sometimes has also been accounted as the source of As in the aquifer sediment (Acharya et al., 1999). McArthur et al. (2004) has proposed that probably during weathering of the source rocks, As containing sulphide minerals were oxidized to Fe oxyhydroxides, which were then deposited in the basin, while Polizzotto et al. (2006) indicated the oxidation of sulphide minerals after deposition. Beside Fe oxyhydroxides, other metal oxyhydroxides like Mn and Al, clay minerals and phyllosilicates like biotite also play key role in the As transport and cycling (Foster et al., 2000; Kent and Fox, 2004; Charlet et al., 2005; Chakraborty et al., 2007; Charlet et al., 2007; Seddique et al., 2008). However, the high As concentration in the groundwater of Bengal Basin does not coincide with high As concentration in the aquifer sediments (McArthur et al., 2004; Swartz et al., 2004; Nath et al., 2005, 2008a), which has led researchers to conclude that rather than source, the enrichment of As in groundwater is an artifact of groundwater evolution, governed by the interplay of various biogeochemical interactions (Harvey et al., 2006; Bhattacharya et al., 2007).

### 1.2.2. Redox processes controlling As mobilization in the aquifers of Bengal Basin

Starting from beginning, different As release mechanisms have been put forward to explain As enrichments in groundwater. Initially, the oxidation of As rich sulphide minerals by induced oxygen in the aquifer due to lowering of the water table as a consequence of heavy groundwater withdrawal was thought to be the processes of As release in the aquifers (Mallick and Rajgopal, 1995). However, practically, the absence of dissolved oxygen and low redox potential in the aquifers together with prevalence of dissolved Fe(II) and As(III) over Fe(III) and As(V) respectively have discarded this hypothesis. Meanwhile, the reducing condition in the aquifers has led researchers to introduce another hypothesis that As is released into groundwater due to the reductive dissolution of Fe oxyhydroxides onto which As was adsorbed or co-precipitated during sediment deposition, coupled to the mineralization of organic matter (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001; Bhattacharya et al., 2002; Harvey et al., 2002; Stüben et al., 2003; McArthur et al., 2004; Zheng et al., 2004; Charlet and Polya, 2006; Mukherjee and Fryar, 2008; Nath et al., 2008b). It is further established that under anaerobic condition, by gaining energy through degradation of organic matter certain metal reducing bacteria catalyze the processes of Fe oxyhydroxides reduction (Akai et al., 2004; Islam et al., 2004). Currently, this model of Fe oxyhydroxides reduction coupled with microbially mediated oxidation of organic matter is the most widely accepted mechanism of As release in groundwater of the reduced sedimentary aquifers (Fendorf et al., 2010), though the source of organic matter in the aquifers is still controversial (Harvey et al., 2002, 2006; Rowland et al., 2006; Sengupta et al., 2008; Farooq et al., 2010; Neumann et al., 2010; Datta et al., 2011; McArthur et al., 2012a; Lawson et al., 2013; Mailloux et al., 2013). It is also revealed that in the reduced aquifer sediments, often the co-existence of As with acid volatile and authigenic sulphide minerals is due to the sequestering of As from groundwater during precipitation of these minerals, when the redox status in the aquifers reaches to the stage of SO$_4^{2-}$ reduction (Lowers et al., 2007). Thus, it is considered that sulphides are not the source of As, but a sink of As in the reducing aquifers (McArthur et al., 2001; Bhattacharya et al., 2002; Nath et al., 2008b).
The location of As release due to the reductive dissolution of Fe oxyhydroxides within the aquifer sediment is also of lively debate. Considering, the very low concentration of As in the reduced aquifer sediments, of which a significant portion is also readily mobilizable, it is speculated that the dissolved As concentration in groundwater would have been flushed out, particularly after the onset of heavy groundwater withdrawal, in absence of potential source of As in the upper location of the depth, where As concentration in groundwater usually peaks (Harvey et al., 2005; Polizzotto et al., 2005; Harvey et al., 2006; Polizzotto et al., 2008). It is reported that the solid phase As concentration is relatively higher in the near-surface oxidized sediment (Swartz et al., 2004), which also gets continuous supply of As co-precipitated with sulphide minerals due to the sediment deposition in each year (Polizzotto et al., 2008). This higher enrichment of As in the near-surface sediment has motivated Polizzotto et al. (2005, 2008) to suggest that As is cycled at the oxic-anoxic redox front in the near-surface sediment as a response to the water table fluctuation. During summer season, when water table falls down, sulphide minerals are oxidized and As gets re-adsorbed into the resulting secondary Fe oxyhydroxides minerals. When, the water table again rises following the recharge anoxia develops in the aquifers and the secondary Fe oxyhydroxides are reduced releasing As into pore water. After release, As is preferentially transported laterally, which is pushed downward by the recharge from above and reaches the aquifer giving “bell-shaped” vertical profile of As distribution in the aquifer (Harvey et al., 2005; Polizzotto et al., 2005, 2008).

1.2.3. Decoupling of As and Fe release in groundwater and the role of competing ions on the As mobilization processes

Meanwhile, decoupling of As and Fe release in the aqueous phase has been reported by many researchers based on both laboratory and field studies, which has provoked to play down the role of Fe oxyhydroxides reduction for the mobilization of As in groundwater (Horneman et al., 2004; van Geen et al., 2004, 2006; Burnol et al., 2007, Burnol and Charlet, 2010). Based on the observations of contrasting concentrations of As at similar levels of dissolved Fe in groundwaters, van Geen et al. (2008a) has inferred that the reduction of Fe oxyhydroxides is possibly a necessary condition, but not always sufficient to mobilize As in groundwater. Few studies have also discussed the possibility that after release of As into groundwater, its mobility is primarily determined by the extent of re-sorption onto the residual Fe oxyhydroxides present in the aquifer materials, until adsorption sites become saturated or solid sorbents are completely dissolved (Welch et al., 2000; Pedersen et al., 2006; von Brömssen et al., 2008). In this context, competing ions such as phosphate (PO$_4^{3-}$), bi-carbonate (HCO$_3^-$) and silicic acid (H$_4$SiO$_4$) might play a significant role in the enrichment of As by competing for similar adsorption sites of Fe oxyhydroxides (Smedley and Kinniburgh, 2002; Stollenwerk, 2003; Sracek et al., 2004; von Brömssen et al., 2008), though the competitive anion adsorption as an individual processes of As mobilization has been discarded by the researchers (McArthur et al., 2001). Nevertheless, the relative roles of these competing ions in the As mobilization processes is controversial. For example, many authors have reported that PO$_4^{3-}$ has a very strong affinity for adsorption sites of Fe oxyhydroxides and is a potential competitor for As adsorption in the natural environment (Manning and Goldberg, 1996; Acharyya et al., 1999; Jain and Loeppert, 2000; Gao and Mucci, 2001; Dixit and Hering, 2003). Throughout the aquifers of Bangladesh, van Genn et al. (2008a) have also found strong positive correlation between level of PO$_4^{3-}$ exchangeable As in the solid phase and dissolved As concentration in the groundwater and accounted the role of adsorptive equilibrium in the As mobilization. While, the studies conducted by Kim et al. (2000), Appelo et al. (2002), and Anawar et al. (2004) have emphasized on the role of HCO$_3^-$ for the mobilization of As in Bengal.
Basin aquifers, which is not again experimentally supported by other authors (Meng et al., 2000; Radu et al., 2005; Stachowicz et al., 2007). Some authors have also accounted for H$_4$SiO$_4$ adsorption as a competitor for As adsorption onto Fe oxyhydroxides (Swedlund and Webster, 1999; Meng et al., 2000; Christl et al., 2012). Based on the batch experiments involving multi-sorbate ions, Meng et al. (2002) again showed that although PO$_4^{3-}$, HCO$_3^-$ and H$_4$SiO$_4$ can compete with As(III) adsorption onto Fe oxyhydroxides, their effect on As(V) adsorption is very small even at high concentration and suggested that high mobility of As in Bengal Basin aquifers is due to their combined effect. Recently, by similar experiment and subsequent modeling, Stollenwerk et al. (2007) and Stachowicz et al. (2008) again have concluded that PO$_4^{3-}$ is the major competitor for As adsorption and in presence of significant concentration of PO$_4^{3-}$, the competition of HCO$_3^-$ becomes negligible.

1.2.4. Addressing the vertical, spatial and temporal variation of As distribution in the aquifers of Bengal Basin

The studies so far conducted have indicated that sub-surface geology broadly controls the vertical distribution of As in the aquifers of Bengal Basin. The occurrence of high dissolved As in groundwater is mostly confined to the shallow aquifers (depth <60 m) of Holocene sediments, while deep (depth >150 m) Pleistocene aquifers are primarily safe (<10 µg/L) (BGS and DPHE, 2001; Horneman et al., 2004; Ravenscroft et al., 2005; Michael and Voss, 2008; Burgess et al., 2010), with occasional exception especially in West Bengal (Mukherjee et al., 2011). Indeed, there is also distinct vertical trend of As distribution within shallow aquifers (Harvey et al., 2005).

Another important aspect of As enrichment within shallow aquifers is its spatial distribution. It is reported that the concentration of As in groundwater may vary laterally from unsafe to safe within a scale of 10 – 100 m, which often constrains the identification of safe regions and exact As mobilization mechanism (van Geen et al., 2003). Attempts have been made at various hydrological aspects to constrain the underlying reason(s) of such heterogeneity, while outcomes are often contradictory. The studies by Harvey et al. (2005, 2006) have pointed out that because of very flat basinal topography, the 3D groundwater flow system is mostly dominated by the local scale flow, influenced by massive groundwater withdrawal, with recharge and discharge areas often within the scale of tens of meters. This local scale flow system and the resulting transport of As determine the spatial and vertical heterogeneity of As distribution within the shallow aquifers. It is also proposed that the high rate of groundwater withdrawal can accelerate As mobilization by enhancing the transport of degradable organic matter with recharge water from the surface and thus preserving reducing condition in the shallow aquifers (Harvey et al., 2002; 2005; Lawson et al., 2013). While, van Geen et al. (2008a) have emphasized on the role of differential flushing histories of aquifers determined by sub-surface geology, as the regulator for regional and local scale spatial distribution of As in groundwater. It is reported that the aquifers beneath the thick aquitard are more reducing because of limited recharge and thus enriched with elevated level of As. While the aquifers, which are overlain by permeable sandy soils, are regularly supplied with oxygen and other oxidants with the recharge water that limit the mobilization of As in the aquifers (Aziz et al., 2008; Weinman et al., 2008). By conducting electromagnetic conductivity survey at the same area of present study, Métral et al. (2008) and Nath et al. (2010) have also reported the presence of sandy lenses within surface clay aquitard and described their role as a passage of focused recharge of oxidant rich water causing spatially variable redox conditions in the underlying aquifer. Stute et al. (2007) further proposed that the effect of enhanced drawdown of labile carbon from surface because of massive groundwater extraction on the As mobilization processes in shallow aquifers might also be offset by the increased rate of groundwater flushing.
By monitoring As concentration in shallow groundwater over 10 years from West Bengal, McArthur et al. (2010) have reported all possible scenarios such as decrease, increase and no change in As concentration over the time. Mukherjee et al. (2008) however, have considered the extent of overlapping redox zonation as playing the key role for spatial and vertical distribution of As in groundwater of Bengal Basin.

The seasonal variation of As concentration in the aquifers of Bengal Basin have also been monitored. The findings again often differ regarding the time period and extent of change in As concentration, depth of the aquifer that experiences maximum variation and the processes that regulate the seasonal cycling of As in aquifer (for review see Chatterjee et al., 1995; BGS and DPHE, 2001; Cheng et al., 2005, 2006; Ravenscroft et al., 2006; Sengupta et al., 2006; van Geen et al., 2007; Dhar et al., 2008; Bhattacharya et al., 2011; Farooq et al., 2011 and Planer-Friedrich et al., 2012). The seasonal variation in groundwater As concentration can have severe consequence on exposure scenario of the people, who are drinking presumably safe water and thus important to understand properly (Cheng et al., 2005).

1.3. Current status of different mitigation activities and future scope

Based on the understandings so far gained from the previous studies, the governments of West Bengal, India and Bangladesh have taken various mitigation strategies together with different international aid agencies to ensure safe drinking water supply among the affected population. The undertaken strategies include treatment of surface water (pond as well as river water), rain water harvesting, installation of dug wells, TW switching (changing of drinking water source from high As TWs to nearest low As TWs), installation of deep TWs (depth >150 m) and distribution of households and community filters (Ahmed et al., 2006; Jakariya et al., 2007a). Nevertheless, the community acceptance of most of these strategies is not very promising, because of technical, economical and social constraints (Ahmed et al., 2006; Jakariya et al., 2007a; Nath et al., 2008c; Johnston et al., 2010). People living in the rural villages do not prefer alternative drinking water sources other than TW water located within their premises. Ironically, the use of TW water for domestic purpose is deeply embedded into the daily life of the rural villagers (Johnston et al., 2010). Thus, TW switching and deep TW installation only gained popularity and effectively reduced the number of exposed population (Ahmed et al., 2006). However, the installation of deep TWs requires advanced drilling technology, which increases the installation cost (500 - 1200 USD) several times as compared to the shallow TWs installation (depth <60 m, cost 50-120 USD) (Hug et al., 2011). Rural villagers cannot afford this cost to install household deep TWs, instead they need to depend on the community TWs, which are also few in number or on the deep TWs, installed by wealthier people in the community. It is worth to note that in the rural villages, water for domestic purposes is mostly collected by the women (Singh et al., 2005). The collection of water from deep TWs, which are often at long distance from the household, tremendously increases the workload of the women, who are already engaged in the domestic works for extended period in the daily life (von Brömssen, 2012). Additionally, villagers are also reluctant to collect drinking water from TW, owned by someone else, a powerful social burden to access safe drinking water by means of TW switching and deep TW installation (Johnston et al., 2010). Consequently, 57% of the exposed populations in Bangladesh are compelled to drink As contaminated water (Ahmed et al., 2006). Thus, to prioritize sustainable As mitigation management and achieve the United Nations (UN) Millennium Development Goals (MDGs) of halving the proportion of population having no access to sustainable safe drinking water worldwide by 2015 (Target 7C), it becomes extremely imperative to delineate safe aquifers within shallow depth, which can be targeted by the locally available cheap drilling technology.
1.4. Rationale of the thesis

The above presented review of the findings made by recent studies indicates that despite considerable progress towards the consensus of As mobilization, findings are sometimes contradictory. Further refinement of the understandings regarding various biogeochemical processes that regulate the As mobilization in the subsurface shallow aquifers is urgently needed. These improved understandings can help regional and global policy makers as well as National and International funding agencies immensely to mitigate the problem by sustainable water resources management.

Few recent studies have investigated the ongoing indigenous drilling practice by local drillers in the rural Bengal and attempted to correlate aquifer sediment color with the occurrence of As in groundwater (van Geen et al., 2003; von Brömssen et al., 2007; Pal and Mukherjee, 2008; McArthur et al., 2008; Pal and Mukherjee, 2009; Bundschuh et al., 2010; McArthur et al., 2011). It is reported that grey sand aquifers (GSA) are mostly contaminated with dissolved As (>10 µg/L), whereas brown sand aquifers (BSA) may be safe (<10 µg/L) (e.g. von Brömssen et al., 2007; McArthur et al., 2008, 2011). Consequently this BSA has been proposed as an alternative drinking water source, which can be targeted by locally available cheap drilling technology (von Brömssen et al., 2007; McArthur et al., 2011). However, before advocating for targeting this aquifer for safe drinking water supply it is necessary to investigate its regional distribution and subsurface geologic architecture at different geographic locations of the basin. Furthermore, it is also necessary to undertake a detailed hydrogeochemical investigation to constrain the underlying reason for the occurrence of low dissolved As in groundwater of BSA that can highlight its long term sustainability for safe drinking water supply.

Another important task regarding groundwater based supply of safe drinking water is the demarcation of safe aquifers regionally. Considering the large extent of vertical and spatial heterogeneity in As distribution, demarcation of safe aquifers needs testing of water samples from thousands of TWs. From public health perspective, it is also not acceptable to assess emerging health risk regionally, by sporadic testing of TWs for As. Further, because of temporal variation of As (McArthur et al., 2010; Bhattacharyya et al., 2011), and the future risk of cross-contamination of the current safe aquifers due to large scale groundwater abstraction (Michael and Voss, 2008; Burgess et al., 2010; Mukherjee et al., 2011), it is important to monitor As concentration in the drinking water sources on long term basis in the post-mitigation period. Recently, elevated manganese (Mn) in drinking water has also been identified as an underlying threat to the human population worldwide (Wasserman et al., 2006; Buschmann et al., 2007; Ljung and Vather, 2007; Bouchard et al., 2011). Prolonged consumption of drinking water containing high Mn may cause neurotoxic effects, like diminished intellectual function in children (Wasserman et al., 2006; Bouchard et al., 2011). Therefore, it is necessary to monitor both As and Mn in all the drinking water sources of a region on a regular basis as a part of the sustainable drinking water management (WHO, 2004).

Measuring As and Mn in groundwater to identify safe aquifers and monitoring them in the post-mitigation period is a challenging task from the point of view of technology, manpower, time, social acceptance, and economy for the countries like India and Bangladesh, which are most affected. It is almost impossible to test all the TWs using standard analytical methods. Hence, van Geen et al. (2005) and Jakariya et al. (2007b) advocated for the use of field test kit for mass screening of As in TW water. A number of commercially available field test kits, e.g. Merck, Hach EZ, Quick arsenic, Wagtech Digital Arsenator (WFTK) and Chem-In Corp field test kit (CFTK) have been deployed at a mass scale (van Geen et al., 2005; Steinmaus et al., 2006; Jakariya et al., 2007b; Sankaramakrishnan et al., 2008). However, use of these test kits also needs trained personnel. Moreover, most of these field test kits are based on the principle of generating arsine gas, which is very harmful.
even at trace level (Hussam et al., 1999). The minimum time required for As measurement in a single sample by these kits is 20 minutes, which is also time consuming (Sankara-ramakrishnan et al., 2008), and most importantly, these kits are not available to the rural villagers to check contamination level in their own well. For Mn, Hach field test kit (model MN-5) is available in the market, but its reliability has not been properly examined yet.

Recently, McArthur et al. (2011) has proposed that the color of stain developed on the TW platform, where available, may guide to screen for As in TW installed in shallow aquifers. In southern part of West Bengal, they have been observed that TWs with platform of black stains, arising due to possible precipitation of manganese oxides, produce As free water (<10 µg/L). Whereas, TWs having platform of red stains, arising due to possible precipitation of iron oxides, produce As enriched water (>10 µg/L). Therefore, it is expected that groundwater enriched with high As, possibly would be low in Mn and vice versa. Thus, looking into the TW platform color can be an alternative mass screening option for As and Mn in the well water. However, before recommendation, its potentiality as a screening tool needs to be assessed further.

2. RESEARCH OBJECTIVES

The objectives of the research, presented in the thesis can be broadly grouped into two parts: (a) refinement of the current understandings of the processes that regulate As mobilization in the sub-surface shallow aquifers and (b) assessing the potentiality of targeting safe aquifers within shallow depth for drinking water supply in As affected regions and the development of a screening tool for As and Mn in drinking water wells. The specific objectives are:

i) Delineation of shallow hydro-stratigraphic framework by subsurface lithologic investigations and assessment of hydrogeochemical contrasts at different aquifers to constrain the sedimentological controls on the spatial distribution of As, Fe and Mn in groundwater of shallow aquifers (Paper I & II).

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Fig. 1. Study area maps showing a. physiographic settings of Bengal Basin and location of Chakdaha Block of Nadia District, West Bengal, India in Bengal Basin (modified from Neidhardt et al., 2013a) b. location of 29 boreholes and 6 west – east traverses along which lithologic cross-sections have been prepared (showing in Fig. 2), groundwater sampling points for detailed hydrogeochemistry and location of piezometer installation sites over the study area. The satellite images were acquired from Google Earth 6.0.2.
ii) Assessment of the geochemical processes that regulate vertical and temporal variation of As in shallow aquifer by combining detailed geochemical characterization of the aquifer sediments and piezometric hydrogeochemical monitoring study at two sites with high and relatively low dissolved As concentration in groundwater (Paper III).

iii) Understanding the role of competing ions on the As mobilization processes by surface complexation modeling of temporal variability of As in shallow aquifer (Paper IV).

iv) Assessing the potentiality of targeting safe aquifers for drinking water supply within shallow depth in As affected regions (Paper I & II).

v) Validation of the TW platform colors as a rapid screening tool for As and Mn in drinking water wells (Paper V).

3. MATERIALS AND METHODS

3.1. Study area (Paper I, II, III, IV & V)

The study area is located at Chakdaha Block of Nadia District, West Bengal, 60 km north of Kolkata city and approximately 170 km inland, from the present coastline of Bay of Bengal (Fig. 1). Geographically the study area represents the stable shelf part of central western Bengal Basin (Fig. 1) (Mukherjee et al., 2009a). The River Hooghly (distributaries of River Ganges) and Ichamati bound the study area in the west and east respectively. The area is very flat; elevation varies within almost 0 – 20 m above mean sea level (Neidhardt et al., 2013a). Throughout the area the prominent geomorphological features are abandoned channel, meandering scars, oxbow lakes and ponds (Fig. 1), which highlight the frequent changes in channel courses in recent past (Nath et al., 2005; Neidhardt et al., 2013a). The current land use pattern is mostly dominated by agricultural lands, where cultivation of seasonal crops (rice, jute and vegetables) is intensive throughout the year. The irrigation for the agricultural activities is entirely groundwater based and the absorption rate peaks usually in the months of December – April for the Boro Rice cultivation.

Three climatic seasons: i) winter (November – February), ii) tropical summer (March - June) and iii) monsoon (July – October) can be distinguished over the year with temperature approximately ranging between 10 °C – 40 °C with total yearly precipitation of around 2000 mm. Generally, >90% of the total yearly precipitation occurs in the monsoon season, inundating a significant part of the study area. The last severe flooding occurred in the year of 2000, when major part of the study area was inundated. Currently, flooding is the only form of active sedimentation processes in this area. Hydrogeologically, the aquifers of the study area represent part of the “Sonar Bangla Aquifer” (Mukherjee et al., 2007a).

3.2. Drilling of exploratory boreholes and lithologic modeling for delineation of shallow hydrostratigraphic framework (Paper I)

In order to investigate the distribution of different aquifers and aquitards within shallow depth, 29 boreholes with almost equal spacing (Fig. 1) were drilled over 100 km² area during the period of March to May 2011, by locally available hand suction drilling technology (Ali, 2003), which usually can reach up to 50 m below ground level (bgl). The washed sediment samples were collected from each 1.5 m (5 feet) interval; while, sampling frequency was higher when visible change in the lithology and color was noticed during drilling. The colors (black, grey, olive to pale blue and brown) of the sediments were determined just after recovery, prior to atmospheric oxidation. Sediments were classified into the three major litho types of clay, sandy clay and sand. The sediment of the litho type clay and sand represents aquitard and aquifer respectively, while sandy clay represents aquitard with higher permeability. Based on these litho types and colors, lithologs for the boreholes were prepared (Appendix Fig. A.1 of Paper I).
Using the 29 lithologs, a 3D lithologic model for the area was developed by the visualizing software RockWorks ver. 15 (RockWare, Golden, CO, USA). The lithological data of each borehole were interpolated three dimensionally by the algorithm of “litho-blending”. The model was optimized by changing the node spacing and the final model was selected that showed least sensitivity towards change in the grid size (Mukherjee et al., 2007a). The final model has the resolution of 100 m (X) x 100 m (Y) x 0.5 m (Z), which results in node spacing of 99 (X) x 95 (Y) x 99 (Z), with total number of 931,095 solid grids, each having the volume of 5000 m$^3$. Finally, using this 3D lithologic model, 6 west – east 2D lithologic cross-sections and a number of plan-view map that represents the distribution of aquifers and aquitards over the study area at a specific depth were developed (Mukherjee et al., 2007a). For further details reader is referred to Paper I.

3.3. Dating of aquifer sediments (Paper I)

A total of 4 (borehole: BH-13 depth: 15.2 m and 25.8 m bgl; borehole: BH-2 depth: 10.6 m bgl and borehole: BH-6 depth: 34.8 m bgl) organic rich peaty sediments were collected during drilling for $^{14}$C age dating. The samples were analyzed at the Lund University Radiocarbon Dating Laboratory by Single Stage Accelerator Mass Spectrometer (SSAMS) (National Electrostatic Corp. (NEC), Wisconsin, USA). The precision of the analysis was ±50 $^{14}$C years. The $^{14}$C ages were calibrated with reference to atmospheric data from Reimer et al. (2009) by the software OxCal v3.10 (Blaauw and Heegaard, 2012).

A new drilling was conducted in April 2013, at just 1 m apart from the old drilled hole of BH-13 for the coring of OSL dating. Two samples were collected at the depths of 37.3 m bgl (BH-13_OSL_1) and 43.6 m bgl (BH-13_OSL_2). After recovery, the core tubes were wrapped with multiple layers of aluminum foil and black colored insulating tape and preserved at complete darkness. The samples were analyzed within two months of sample collection at the Lund Luminescence Laboratory, Lund University. Only the central part of each core tube was sampled for the analysis. Large single aliquots of 180 – 250 μm quartz grains in cups were analyzed in a Risø TL/OSL reader model DA-20. For further details of the dating of aquifer sediments reader is referred to Paper I.

3.4. Screening of TWs to determine spatial distribution of As, Fe and Mn in shallow aquifers (Paper I, III, IV & V)

A total of two surveys were conducted over the study area. First survey was conducted in November – December 2007 over the entire Chakdaha Block (~400 km$^2$) by sampling groundwater from 181 existing tubewells for the hydrochemical characterization of different aquifers in the area. Based on the spatial distribution of dissolved As, Fe and Mn only. The details of the analysis of As, Fe and Mn in these samples have been reported in Paper V (Paper I & V).

The second survey was conducted in March - May 2011 with higher sampling resolution, when a total of 423 existing TWs installed in shallow aquifers were sampled over an area of 100 km$^2$ (density 4.23 TWs/km$^2$), extending from River Hooghly in the west to the margin of site 1 in the east (23.02-23.14°N; 88.49-88.62°E). This time groundwater samples were collected for the determination of As, Fe and Mn only. The details of the analysis of As, Fe and Mn in these samples have been reported in Paper V (Paper I & V).

3.5. Piezometer installation for hydrogeochemical monitoring and collection of aquifer sediment cores (Paper III & IV)

Based on the spatial distribution of dissolved As in shallow aquifers as determined by first screening of TWs, two representative sites at
the village of Sahispur (Site 1: 23°04'15.5"N, 88°36'33.5"E) and Chakudanga (Site 2: 23°04'58"N, 88°38'13"E), with high and relatively low dissolved As concentration in groundwater respectively were selected for piezometers installation and aquifer sediment coring. Two sites are located about 10 km and 13 km east of the River Hooghly respectively (Fig. 1). At each of the two sites, 5 piezometers, namely well A, B, C, D and E, were installed over an area of 25 m² using the procedure described in Biswas et al. (2011). The screen of the piezometers were placed at different depth within the top shallow aquifer (Site 1 – A: 12-21 m, B: 22-25 m, C: 26-29 m, D: 30-33 m and E: 34-37 m; Site – 2: A: 12-21 m, B: 24-27 m, C: 30-33 m, D: 36-39 m and E: 42-45 m) to collect multi depth groundwater samples. The closest irrigation well to the piezometers installation site at site 1 & 2 is installed at a distance of 300 m and 75 m respectively at the depth of 24 m. The irrigation well at site 2 operates almost throughout the year with maximum intensity in dry period, while the well at site 1 mainly operates in dry period only. At site 1, there is a pond just at the vicinity (within 1 m) of the well installation site, while at site 2 the closest pond is at the distance of 75 m (Paper III).

Continuous sediment cores were collected during drilling of the deepest piezometer (well E) at each site, using a split-spoon core barrel lined with a PVC tube of 0.65 m length. After the core recovery, for detailed geochemical characterization a sub-set of sample (~50 g) was collected from the bottom of the barrel into HDPE bags and sealed twice under N₂ atmosphere. After sample collection, sediment core barrels were also preserved in the field by flushing with N₂, followed by rubber capping and sealing with insulating tape at both ends of the barrel. After being returned to the

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**Fig. 2.** Six west – east lithologic cross-sections along the traverses shown in Fig. 1. Aquifer-1, 2 and 3 represents Aquifer-1, 2 and 3 respectively.
laboratory samples were preserved at -19 °C until analysis to prevent oxidation and microbial activity (Paper III).

3.6. Geochemical characterization of aquifer sediment (Paper III)

The sediment samples collected from the two piezometer installation sites were analyzed for grain size, differentiating as fine gravel (>2 mm), coarse sand (<2 – >0.63 mm), medium sand (<0.63 – >0.2 mm), fine sand (<0.2 – >0.063 mm) and silt and clay (<0.063 mm). The major and trace elements were quantified by Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF: Epsilon5, PAN-analytical) in dried and homogenized samples. Total organic carbon (TOC) content was determined with a carbon-sulfur-analyzer (CSA: CS 2000 MultiLine F/SET-3 Eltra) after decarbonation with HCl. Mineralogical identification in the sediment samples was conducted by powder X-ray diffraction (XRD: D500 Kristalloflex, Siemens). Furthermore, a total of 17 representative samples were selected from the soil horizon (n = 4) and screen position of the piezometers (n = 13) at two sites to identify the potential As host phases in the aquifer sediment by a 7 steps sequential extraction procedure as modified by Eiche et al. (2008) from the method of Keon et al. (2001), Wenzel et al. (2001) and van Herreweghe et al. (2003). For further details of analytical procedures and quality assurance reader is referred to Paper III.

3.7. Groundwater sampling and analysis for detailed hydrogeochemistry (Paper II, III & IV)

As a part of the intensive hydrogeochemical monitoring program to characterize the different processes that regulate As mobilization in the sub-surface shallow aquifers, the piezometers at the two sites were sampled in 15 days interval over a period of 20 months (December 2008 – July 2010). The regular sampling interval at both sites was interrupted once, in the month December 2009, when pumping and in-situ bio-stimulation experiment was conducted at site 1 and 2 respectively (results have been presented in Neidhardt et al. 2013b and Neidhardt, 2012 respectively). The sampling was resumed again from January 2010. Groundwater samples were collected for the analysis of major cations and trace elements, anions, Fe speciation, As speciation, dissolved organic carbon (DOC) and stable isotopic composition of δ²H and δ¹⁸O with field measurement of piezometric head, alkalinity (in the form of HCO₃⁻), pH, redox potential (Eh), electrical conductivity (EC) and temperature (T). The detailed groundwater sampling protocol has been reported in Paper III. Additionally, pond water samples from four major ponds of the two sites and the small one just at the vicinity of site 1 were sampled once in 2012 for the determination of δ²H and δ¹⁸O. Monthly cumulative rain water samples were also collected during monsoon in 2012 at the rooftop of Department of Chemistry, University of Kalyani for the determination of δ²H and δ¹⁸O. The daily rainfall data over the monitoring period was collected from the nearest (25 km from the study sites) available weather monitoring site at Directorate of Research, Bidhan Chandra Krishi Viswavidyalaya (BCKV), Kalyani, West Bengal, India. The samples for anions and Fe speciation were analyzed overnight of sampling to minimize redox alteration. While, the samples for major and trace elements, δ²H and δ¹⁸O, As speciation and DOC analysis were stored at 4 °C until analysis. The detailed analytical procedures and quality assurance have been reported in Paper III & IV.

To characterize salient hydrogeochemical contrasts at different aquifers within shallow depth over an area of 100 km², in April 2011, 57 groundwater samples were collected from the existing TWs installed close to the 29 drilled borehole locations (Fig.1). From each TW, four sets of groundwater samples were collected for the analysis of Fe speciation and DOC, anions, major cations and trace elements and As speciation. The details of sampling, analytical procedure and quality assurance have been reported in Paper II.
3.8. Multivariate statistical analysis (Paper II)

Multivariate statistical analysis was performed to assess the hydrogeochemical contrast at different shallow aquifers over the study area. In order to characterize the decisive hydrogeochemical parameters responsible for redox zonation in different shallow aquifers as well as to classify groundwater samples \( (n = 57) \) according to different redox zones discriminant analysis was performed \( (\text{Lee et al., 2008; Hus et al., 2010}) \). A two group (less and strong reducing zone) model was adopted for this analysis. Groundwater samples were initially grouped according to sediment color of the screening depth of TWs in the aquifers. In order to explain the evolution of groundwater chemistry, specifically the occurrence of dissolved As and Mn in terms of association of the hydrogeochemical parameters factor analysis was performed. Principal component analysis (PCA) was adopted to transform the data set into factors. The criterion was set to extract factors with eigenvalue only greater than 1 \( (\text{Kaiser, 1958; Davis, 1987; Reyment and Joreskog, 1993; Liu et al., 2003}) \). The software package IBM SPSS Statistics 19 was used to perform multivariate statistical analysis. For further details of multivariate statistical analysis reader is referred to Paper II.

3.9. Geochemical modeling (Paper II, III & IV)

Two types of geochemical modeling, namely equilibrium speciation modeling and surface complexation modeling were performed. The objectives of the equilibrium speciation modeling were to calculate the value of \( P_{\text{CO}_2} \) and saturation indices \( (\text{SI} = \log [\text{IAP} \times \text{KT}^{-1}]) \), where IAP and KT are ion activity product and equilibrium solubility constant at ambient temperature respectively) of major mineral phases that may regulate the groundwater chemistry in the aquifers \( (\text{Paper II & III}) \). The equilibrium speciation modeling was performed by using the geochemical software package of Visual MINTEQ ver. 3.0 with default database \( (\text{Gustafsson, 2011}) \) \( (\text{Paper III}) \) and PHREEQC ver. 2.8 with \textit{water4f} database \( (\text{Parkhurst and Appelo, 1999}) \) \( (\text{Paper II}) \). Furthermore, the values of pe \( \text{(where } pe = 16.9 \times \text{Eh at 25}^\circ \text{C) corresponding to } \text{Fe(III)/Fe(II)} \text{ and As(V)/As(III)} \text{ redox couples were also calculated from the measured concentration of Fe(III), Fe(II) and As(V), As(III) respectively by PHREEQC to identify the key redox process that regulates redox potential in the aquifers (Paper II).}

To assess the role of different surface complexation reactions onto aquifer materials on the mobilization of As in groundwater, it was attempted to model the temporal variability of As in groundwater of two sets of piezometers by simulating surface complexation model (SCM) \( (\text{Paper IV}) \). Two different SCMs, viz. 2-pK diffuse layer SCM for ferrihydrite, as proposed by Dzombak and Morel \( (\text{1990}) \) \( \text{(here after referred as D&M SCM)} \) and 3-plane CD-MUSIC SCM for goethite, developed by Hiemstra and Van Riemsdijk \( (\text{1996}) \) have been simulated by the geochemical code Visual MINTEQ ver. 3.0 \( (\text{Gustafsson, 2011}) \). The reason for the selection of two SCMs has been discussed in Paper IV. For D&M SCM of ferrihydrite, the parameters were set to default values as in Visual MINTEQ, while the CD-MUSIC SCM for goethite was parameterized according to Jessen et al. \( (\text{2012}) \). For further details of the model setup and databases used for the simulation of two SCMs reader is referred to Paper IV.

The sorbent contents in the two SCMs were normalized for individual well by equilibrating the first monitoring sample of the specific well. The sorbent content was varied until the modeled dissolved As(III) and As(V) agreed with their measured concentrations \( (\text{Appendix Table A.1 of Paper IV}) \). It was hypothesized that the amount of sorbent content in the sediment and total As content in the system \( (\text{As}_{\text{adsorbed}} + \text{As}_{\text{dissolved}}) \) for a particular well remained the same over the monitoring period; only the variation in pH and concentrations of competing ions deter-
mined the extent of partitioning of As between sorbent and aqueous phase and thus the temporal variation of As in the groundwater. Consequently, the sorbent content in the specific SCM and total As content in the system for a particular well were kept constant during the equilibration of all groundwater samples, collected from the same well. The total As content in the system for a particular well was calculated by adding the readily mobilizable and specifically adsorbed As content in the sediment of screen position [converted to g/L assuming the porosity and grain density of aquifer sediment as 0.3 and 2.65 g/cm³ respectively (Jessen et al., 2012)] to the average dissolved As content in groundwater of the respective well. The readily mobilizable and specifically adsorbed pools of As in the sediment samples was extracted in the first two steps of sequential extraction.
with 0.05 M \((\text{NH}_4)_2\text{SO}_4\) and 0.5 M \(\text{NaH}_2\text{PO}_4\) respectively (Eiche et al., 2008).

3.10. Testing TW platform colors as a screening tool for As and Mn in well water (Paper V)

To evaluate the potentiality of TW platform colors as a screening tool for As and Mn in well water, during second screening of 423 TWs the major coloration on each TW platform, where available, was also examined carefully in the field. The picture of TW platform was also captured by a digital camera (Kodak C183, 14 MP, 3X optical zoom). The platform color was re-examined in the laboratory by another person observing these pictures to avoid any biasness. The mutual agreement on color classification was more than 87%. All disagreements (n = 54) were for the separation of mixed colored platforms from red (n = 46) and black (n = 8) colored platforms; whereas none of the red colored platforms were classified as black and vice versa during re-examination. Four indices, namely sensitivity, specificity, efficiency and predictive values were calculated, with respect to WHO drinking water guideline as well as national drinking water standard for As and with respect to national drinking water standard for Mn, to validate TW platform color tool at different specific drinking water standards. For further details reader is referred to Paper V.

4. Results

4.1. Accuracy of the lithologic model (Paper I)

Out of the total number of TWs sampled in two blanket surveys (in 2007 and 2011) (n = 181 + 423), 325 TWs were installed in the area enclosed by the borehole locations and had screen position within the maximum drilling depth (50 m) and thus lithologic information around screen position was known. In order to assure the true representativeness of a TW to a specific hydrostratigraphic unit, only these 325 TWs have been used for subsequent statistical analysis in order to investigate the accuracy of 3D lithologic model.

The accuracy of the lithologic model was tested by assuming that the screen of all 325 TWs was placed in the sand and the depth of TWs reported by the TW owner during sampling was correct. For the purpose of accuracy test, the depth of the TWs up to midpoint of the screen was considered. Our field experience indicates that the screen length of the TWs with depth <30 m is usually 1.8 m, while for the TWs of depth >30 m, the screen length is 3.6 m in the study area. Consequently, in order to determine the depth of the TWs up to midpoint of screen, 1 m and 2 m was subtracted from the total well depth of <30 m and >30 m respectively. In the next step, the TWs at each specific depths were grouped together and placed on the lithologic plan-view map of the corresponding depth to test whether the screen position of the TWs were located at the sand units. The accuracy analysis reveals that according to the proposed lithologic model 277, 11 and 37 TWs are placed in sand, sandy clay and clay respectively, which indicates 85% accuracy of the model.

4.2. Shallow hydrostratigraphic framework in the study area (Paper I)

Six 2D west-east lithologic cross-sections over the study area have been shown in Fig. 2. Additionally, few plan-view maps representing the distribution of aquifer and aquitard at different specific depths over the study area have been presented in Appendix Fig. A.2 of Paper I. These cross sections and plan view maps represent the distribution of a very complex aquifer-aquitard framework within the drilling depth. The surface sandy clay layer is extended over the entire study area and the thickness varies spatially between 2 – 9 m, becoming thin along the east margin of the study area (BH-4, BH-7, BH-16) (Fig. 2). In the upper portion of the surface sandy clay layer the presence of plant debris was common and the sediment was mostly light brown in color (Fig. 3). The mottles of brown to black colored Fe and Mn oxyhydroxides were visible in the water table fluctuation zone (2 – 5 m bgl) (Fig. 3). According to the type of formation, three types of aquifer can be distinguished within
the drilling depth. Aquifer-1 is unconfined, extending continuously just underneath the surface sandy clay layer to the depth of 50 m bgl, where drilling was stopped. Aerially the aquifer-1 is distributed along the northwest and east margin of the study area, parallel to the River Hooghly and Ichamati respectively (Fig. 2, Appendix Fig. A.2 of Paper I). Very fine to medium sized sand of dark grey color with a very little portion of silt are prevailing in the aquifer-1 (Fig. 3), representing the palaeo channel (PC) sequence (McArthur et al., 2008), deposited by River Hooghly and Ichamati. Occasionally, very thin films of organic carbon rich clay layers are interbedded within the aquifer-1, particularly along the east margin of the study area (BH-6, BH-7, BH-16) (Fig. 2).

The overbank deposition of dark grey to black colored soft sandy clay to clay layer of thickness 15 – 30 m is extensive along the central floodplain (north – south transect) that widens towards southwestern part of the study area (Fig. 2). Within these overbank deposits, two sub-layers of black peaty sediment (Fig. 3) are observed within the depth ranges of 5 – 15 m bgl and 14 – 32 m bgl (Fig. 2). The thickness of the peaty sediment layer in the lower part varies between 0.5 – 9 m (average: 3.42 m) and is more extensively distributed over the study area, compared to that observed in the upper depth interval (thickness: 1.5 – 3.0 m, average: 1.78 m) (Fig. 2). Sometimes the aquifer is formed locally within these overbank deposits; however, its vertical extension is very much limited within 25 m bgl and has been classified as aquifer-2 (Fig. 2). Throughout the area, the aquifer-2 is laterally connected to the aquifer-1, except at the borehole BH-8 along the cross section E-E’ (Fig. 2). Fine to medium size sand of dark grey color is prevailing in this aquifer also (Fig. 3). However, visibly, the silt content in this aquifer sediment is higher, compared to that in aquifer-1. As discussed below, the chemical composition of groundwater at these two aquifers is also similar. Thus, because of similar color of the aquifer materials, hereafter the aquifer-1 and 2 are collectively designated as grey sand aquifers (GSA) and constitute 40% (1.84 × 10³ m³) of the total drilled volume (4.65 × 10³ m³).

Aquifer-3 is distributed along the central (north - south transect) and southwestern part of the study area, underneath the overbank deposits, representing the palaeo interfluve (PI) aquifer (McArthur et al., 2008) of the study area and is vertically extended up to the depth, where drilling was stopped (Fig. 2). Since, in all the locations drilling was stopped before reaching the next clay aquitard, currently we do not have exact information of the thickness of this aquifer. However, according to the driller's opinion, this aquifer generally extends up to a depth of around 60 m bgl. Aquifer-3 represents 10% (4.8 × 10³ m³) of the total drilled volume and is mainly composed of brown colored medium to coarse sand. Occasionally, the presence of fine to medium sized gravel was also observed during drilling (Fig. 3). The grain size and intensity of brown color of the aquifer sediment were noticed to decrease with increasing depth of the aquifer (Fig. 3), as also noticed by Hoque et al. (2012) at Barasat, North 24-Parganas, West Bengal (45 km south of the present study area).

Because of color of the aquifer materials, hereafter this aquifer is designated as brown sand aquifer (BSA). Though, throughout the area, this aquifer is laterally connected to the aquifer-1, in all the boreholes it is markedly separated from the overlying overbank deposits by the successive sequences of olive to pale blue and brown colored hard clay layers (Fig. 2 and Fig. 3). The thickness of the olive to pale blue clay layer spatially varies between 0.9 – 6.1 m (average: 3.3 m) within the depth range of 23 – 35 m bgl. While, the thickness of brown clay layer varies between 1.5 – 7.5 m (average: 3.89 m) in the depth interval of 24 – 36 m bgl, except in two boreholes (BH-11 and 12) in the southwestern part of the study area. In these two boreholes the brown clay layer continued from 21 m bgl to the depth of 50 m bgl, where drilling was stopped (Fig. 2). However, the driller confirmed the presence of BSA at the base of brown clay layer around the depth of 70 – 80 m bgl.
Arsenic geochemistry in the alluvial aquifers of West Bengal, India

The brown to black patches of Fe and Mn oxyhydroxides were also common in the brown colored clay layers (Fig. 3). Goodbred and Kuehl (2000) have designated this clay as palaeosol of lateritic uplands and McArthur et al. (2008) have further classified it as Last Glacial Maximum Palaeosol (LGMP). Similar shallow hydrostratigraphic framework have also been reported as close as at Barasat (McArthur et al., 2008, 2011; Hoque et al., 2012) and from other parts of Bengal Basin (van Geen et al., 2002, 2003; von Brömssen et al., 2007; Pal and Mukherjee, 2008; von Brömssen et al., 2008; Pal and Mukherjee, 2009).

4.3. Ages of the aquifer sediment and assessment of the Holocene sedimentation rate (Paper I)

The results of OSL dating of the two sand samples and \( ^{14} \)C ages of the four peaty sediments, collected from the different drilling depths of the study area have been given in Table 1. The results indicate that the sand samples, collected from the aquifer-3 at the depth of 37.3 m bgl and 43.6 m bgl of BH-13 corresponds to the age of 72 ± 7 ka and 66 ± 7 ka respectively. Since the luminescence characteristics of sample BH-13_OSL_2 were not as good as the first sample, the age of this sample (66 ± 7 ka) should be considered as minimum age of the sample. However, the close agreements of ages of the two samples confirm that these sediments were deposited around 70 ka. Out of the four samples dated for \( ^{14} \)C, three represent the overbank deposits and fourth one was retrieved from the inter-bedded clay layer in channel fill sands. For the overbank deposits, the oldest age of 9.51 ± 0.02 ka is observed for the sediment at the depth of 25.8 m bgl in BH-13 (Table 1). The other peaty sediments retrieved from the depth of 15.2 m bgl in the same borehole and 10.6 m bgl in BH-2 correspond to the age of 7.21 ± 0.03 ka and 2.99 ± 0.04 ka respectively (Table 1). For channel fill deposit, the \( ^{14} \)C dating of peaty sediment collected from the depth of 34.8 m bgl in BH-6 has yielded the age of 5.63 ± 0.02 ka. It is interesting to note that despite the higher depth (9 m) of sample collection for the channel deposits, the age is ~ 4 ka younger compared to the deepest sediment collected from the overbank deposits (Table 1).

Three \( ^{14} \)C dates, available for the sediment of overbank deposits have been used to assess the Holocene sedimentation rate. The linear interpolation of the age-depth relation indicates that within the period of early Holocene to mid Holocene (9.50 – 7.00 ka) the rate of sedimentation was 4.61 m/ka, which was decreased to 1.09 m/ka in the mid Holocene to late Holocene period (7.00 – 3.00 ka). It is worthwhile to mention that Sarkar et al. (2009) by compiling their \( ^{14} \)C dates from Barasat to the published \( ^{14} \)C dates from southern West Bengal, have estimated the sedimentation rates as 4.4 m/ka and 0.5 – 1.2 m/ka for the periods of early Holocene to mid Holocene and mid Holocene to late Holocene respectively. The close agreements of our estimations to that of Sarkar et al. (2009) indicate that probably these Holocene sedimentation rates are regionally valid at least for the whole western Bengal Basin.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lab. ID</th>
<th>Borehole</th>
<th>Depth (m bgl)</th>
<th>Age (ka)</th>
<th>Calibrated age (ka)</th>
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<td>B2_35</td>
<td>LuS 10074</td>
<td>BH-2</td>
<td>10.6</td>
<td>2.86 ± 0.05</td>
<td>2.99 ± 0.04</td>
</tr>
<tr>
<td>B6_115</td>
<td>LuS 10075</td>
<td>BH-6</td>
<td>34.8</td>
<td>4.90 ± 0.05</td>
<td>5.63 ± 0.02</td>
</tr>
<tr>
<td>B13_50</td>
<td>LuS 10076</td>
<td>BH-13</td>
<td>15.2</td>
<td>6.25 ± 0.06</td>
<td>7.21 ± 0.03</td>
</tr>
<tr>
<td>B13_85</td>
<td>LuS10077</td>
<td>BH-13</td>
<td>25.8</td>
<td>8.51 ± 0.06</td>
<td>9.51 ± 0.02</td>
</tr>
<tr>
<td>OSL Dating</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>BH-13_OSL_1</td>
<td>Lund 13011</td>
<td>BH-13</td>
<td>37.3</td>
<td>72 ± 7</td>
<td></td>
</tr>
<tr>
<td>BH-13_OSL_2</td>
<td>Lund 13012</td>
<td>BH-13</td>
<td>43.6</td>
<td>66 ± 7</td>
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</tbody>
</table>
4.4. Distribution of As, Fe and Mn in groundwater of different aquifers (Paper I)

The aquifer type-wise classification indicates that out of the 277 TWs, for which screen is placed within sand units according to the proposed lithologic model, 128, 35 and 114 TWs are installed in the aquifer-1, aquifer-2 and aquifer-3 respectively. The results of the determination of As, Fe and Mn in groundwater collected from these TWs have been provided in Appendix Table A.1 of Paper I and their aquifer type-wise distributions have been presented in Fig. 4. The results indicate that the concentrations of dissolved As and Fe are relatively high in aquifer-1 and 2, compared to aquifer-3. In 88% (n = 113) and 83% (n = 29) of the TWs, installed in aquifer-1 and 2 respectively the concentration of As exceeds WHO provisional drinking water guideline of 10 µg/L. In contrast, in 75% (n = 85) of the TWs of aquifer-3 the concentration of As is <10 µg/L and more specifically the concentration is <2 µg/L in 55% (n = 63) of the wells. If the national drinking water standard for As in India and Bangladesh (50 µg/L) is considered, 41% (n = 52) and 43% (n = 15) of the TWs of aquifer-1 and 2 respectively are unsafe and for aquifer-3, 91% (n = 104) TWs are safe. Similarly, in aquifer-1 and 2 the concentration of Fe is <1 mg/L in only 6 (5%) and 2 (6%) TWs respectively and the concentration is >5 mg/L in 66 (52%) and 11 (31%) of the TWs respectively. However, in aquifer-3 the concentration of Fe in 82 TWs (72%) is <1 mg/L and only in 9 (8%) TWs the concentration exceeds 5 mg/L (Fig. 4).

The distribution of dissolved Mn in aquifers shows opposite trend to that of As and Fe, the concentration being high in aquifer-3 and low in aquifer-1 and 2 (Fig. 4). In 80% of the TWs of aquifer-1 (n = 102) and aquifer-2 (n = 28) the concentration of Mn is below the value of previous WHO
drinking water guideline (400 µg/L), while the concentration exceeds this cut-off value for 85% (n = 97) of the TWs installed in aquifer-3. If the national drinking water standard of India for Mn (300 µg/L) is considered as the cut-off value, the extent of contamination in the TWs of aquifer-3 becomes 89%. More specifically, in 16% (n = 18) of these TWs the concentration of Mn is >1500 µg/L with a maximum concentration of 3396 µg/L. The results indicate that the aquifer-1 and 2 are very much similar in terms of water quality and thus collectively considered as GSA because of grey color of the aquifer sand as mentioned before. Hereafter, the aquifer-wise hydrogeochemical comparison is limited in terms of color of the aquifer sand such as BSA and GSA only. The spatial distributions of As, Fe and Mn in BSA and GSA have been shown in Fig. 5, which indicates that the TWs in BSA with exceptionally high concentration of As, Fe and Mn are mostly located along the margin, which supports the findings of McArthur et al. (2011, 2012b) at Barasat, West Bengal. However, no such pattern in the spatial distributions is observed for the TWs installed in GSA (Fig. 5). Similar aquifer type-wise distribution patterns of As, Fe and Mn in groundwater have also been reported from different parts of Bengal Basin (van Geen et al., 2003; McArthur et al., 2004; Jakariya et al., 2007a; Stollenwerk et al., 2007; von Brömssen et al., 2007; Pal and Mukherjee, 2008, 2009; Bundschuh et al., 2010; McArthur et al., 2011; Robinson et al., 2011; Hoque et al., 2012; McArthur et al., 2012b).

**Fig. 5. Spatial distribution of As, Fe and Mn at grey sand aquifer (GSA) and brown sand aquifer (BSA). The lithologic plan view map at the depth of 21 m and 39 m below ground level has been used as the base map for GSA and BSA respectively.**
4.5. Hydrogeochemical contrast between BSA and GSA (Paper II)

4.5.1. Major ion chemistry

The physical properties and ionic compositions of groundwater samples collected from BSA and GSA have been summarized in Supplementary Data (SD) of Paper II. The results indicate that in both aquifers groundwater has circum-neutral pH (6.87 – 7.48) with similar temperature range (26.3 – 28.2 °C). The ranges of electrical conductivity (BSA: 501 – 935 µS/cm, median: 663 µS/cm; GSA: 356 – 1177 µS/cm, median: 715 µS/cm) suggest roughly similar extents of water-sediment interactions in both aquifers. The groundwater in both aquifers is predominantly of Ca-Mg-HCO₃ type. However, other hydrochemical facies, particularly of mixed ion type such as Ca-Mg-HCO₃-Cl, Ca-Mg-Na-HCO₃, and Ca-Na-Mg-HCO₃ are also sometimes present due to the local enrichment of particular ions. There is no significant difference between major ion concentrations in groundwater of the two aquifers, except for comparatively enrichment of K⁺ (median: GSA – 4.42, BSA – 2.32 mg/L) and Cl⁻ (median: GSA - 18.4, BSA - 6.49 mg/L) in groundwater of

![Image of redox zonation in the aquifer](image-url)
The enrichment of Cl in groundwater of GSA is also consistent with relatively higher EC in this aquifer. The ranges of calculated $P_{\text{CO}_2}$ indicate that for both BSA (range: $10^{-3.42} - 10^{-2.91}$ atm, median: $10^{-3.01}$ atm) and GSA (range: $10^{-3.63} - 10^{-2.61}$ atm, median: $10^{-3.05}$ atm) groundwater samples (except one sample from GSA) have higher $P_{\text{CO}_2}$ than the atmospheric $P_{\text{CO}_2}$ ($10^{-3.5}$ atm). The calculation of SI further reveals that groundwater samples in both aquifers are nearly at equilibrium with calcite and dolomite (Paper II).

4.5.2. Distribution of redox sensitive species

In all groundwater samples collected from BSA and GSA the concentration of DO and NO$_3^{-}$ is below detection limit (BDL). The comparison of observed pe values (calculated from measured Eh) with that correspond to Fe(III)/Fe(II) and As(V)/As(III) redox couples reveals that the observed pe values for the samples of BSA and GSA fall respectively along the upper and lower end of calculated pe range of the Fe(III)/Fe(II) redox couple (Fig. 6). This comparison suggests that though the redox condition in both aquifers is controlled by the Fe(III)/Fe(II) redox equilibrium, the groundwater in GSA is more reducing than groundwater in BSA. The groundwater in GSA is more enriched with species such as PO$_4^{3-}$, NH$_4^+$ and SO$_4^{2-}$ compared to groundwater in BSA (Fig. 7). Despite enrichment of SO$_4^{2-}$ in GSA, the concentration is not very high (range: BDL – 26.2 mg/L, median: 0.30 mg/L). Strong pungent odor of hydrogen sulphide (H$_2$S) was noted in few wells from GSA during sampling. However this odor does not necessarily correspond with low SO$_4^{2-}$ concentration in groundwater. Moreover, the odor of H$_2$S was absent in groundwater of BSA. This indicates that SO$_4^{2-}$ reduction

**Fig. 7. Distribution of redox species in groundwater of BSA and GSA. The legend of the box whisker plot is same as Fig. 4.**
is not entirely responsible for low \( \text{SO}_4^{2-} \) concentration in groundwater of the study area. The scarcity of sulphidic minerals in the aquifer sediment might also limit the initial concentration of \( \text{SO}_4^{2-} \) in groundwater (Mukherjee and Fryar, 2008). Though in Bangladesh, von Brömssen et al. (2007) have reported the enrichments of DOC and \( \text{HCO}_3^- \) in groundwater of GSA; in present study the concentrations are similar in both aquifers (Fig. 7). The distribution of As, Fe and Mn in the sampled TWs further supports the findings of blanket survey as mentioned in section 4.4 (Fig. 7). In GSA, As is predominantly present as As(III) [% of As(III) range: 75 – 100, median: 95.6], whereas for samples collected from BSA, when As concentration exceeds instrumental detection limit is mostly present as As(V) [% of As(V) range: 5.41 – 100, median: 100, excluding BDL values]. Though, in both aquifers Fe is predominantly present as Fe(II), the extent of predominance is significantly higher in GSA (range: 84.1 – 100%, median: 94.5%), compared to BSA (range: 36.6 – 97.2%, median: 71.2%) (Paper II).

The distribution of SI for the major mineral phases, which may regulate the concentration of Fe(II) and Mn(II) in groundwater reveals that groundwater in BSA are mostly at equilibrium with respect to rhodochrosite (\( \text{MnCO}_3 \)), whereas equilibriums with respect to siderite (\( \text{FeCO}_3 \)) and vivianite [\( \text{Fe}_6(\text{PO}_4)_3;8\text{H}_2\text{O} \)] are prevailing in groundwater of GSA (Paper II). Saturation Indices values further indicate that MnHPO\(_4\) and Fe(III) mineral phases such as ferric hydroxide [\( \text{Fe(OH)}_3 \)], goethite (\( \text{FeOOH} \)), hematite (\( \text{Fe}_2\text{O}_3 \)) and magnetite (\( \text{Fe}_3\text{O}_4 \)) are stable in both aquifers of the study area (Paper II).

### 4.5.3. Discrimination of groundwater samples (Paper II)

The canonical discriminant function coefficients for each hydrogeochemical parameters have been summarized in SD of Paper II. The canonical correlation value of 0.91 indicates that two groups model explain 83% variation among the hydrogeochemical parameters. The corresponding discriminant loadings of each hydrogeochemical parameter suggest that the concentrations of \( \text{PO}_4^{3-} \), Fe and \( \text{NH}_4^+ \) together with the value of Eh are the main discriminators to predict membership of groundwater samples to the less or strong reducing group (Paper II). The ‘hit ratio’ (overall predictive accuracy of the discriminant function) value of 96.5% (Table 2) strongly supports the successful classification of groundwater samples as less or strong reducing, based on sediment color of the screening depth of respective TW. All the groundwater samples of BSA are reclassified as less reducing (100% accuracy), whereas only 2 groundwater samples (#HG14 and #HG22) of GSA, which were initially grouped as strong reducing are classified as less reducing (94.3% accuracy) by discriminant analysis (Table 2).

### 4.5.4. Delineation of factors responsible for groundwater evolution (Paper II)

The mutual covariance of the hydrogeochemical parameters indicates that the major ions are strongly positively correlated to each other and also individually positively correlates to EC (Paper II). Arsenic shows strong positive correlation with \( \text{NH}_4^+ \), Fe and \( \text{PO}_4^{3-} \) and negative correlation with Eh, whereas the correlations of Mn to these parameters are opposite to that of As (Paper II). Dissolved organic carbon does not show any significant correlation to other hydrogeochemical parameters (Paper II). Based on

<table>
<thead>
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<th>Table 2. Classification results of discriminant analysis.</th>
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<td>Aquifer condition</td>
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<td>-------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Strong reducing</td>
</tr>
<tr>
<td>Less reducing</td>
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<tr>
<td>Total</td>
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</tbody>
</table>
among the four factors, factor 1 (26.8% variance) has strong positive loadings of major ions and EC (Fig. 8), which in turns is responsible for total dissolved solids in groundwater. Factor 2 (26.1% variance) has positive loadings of Fe, NH₄⁺, PO₄³⁻ and As and negative loading of Eh and Mn (Fig. 8). This factor can be termed as As mobilization as well as Mn immobilization factor. The spatial distribution of factor scores of this As mobilization and Mn immobilization factor for each well closely overlaps with the distribution of GSA in the study area (Fig. 9a), which indicates that this factor is mainly prevailing in GSA. Factor 3 possibly represents two chemical processes. The positive loadings of DOC and NH₄⁺ and negative loading of SO₄²⁻ (Fig. 8) characterize the SO₄²⁻ reduction process, whereas the positive loadings of Si⁴⁺, Na⁺ and HCO₃⁻ together with negative loadings of pH (Fig. 8) suggest the weathering of plagioclase minerals (NaAlSi₃O₈). However, the spatial distribution of factor 3 scores does not indicate any prevalence to a particular aquifer (Fig. 9b), which might signify that two chemical processes are occurring separately in two aquifers. Factor 4 has only positive loadings of Al and Cl (Fig. 8).

4.6. Detailed geochemical investigation in As rich aquifer at two study sites (Paper III, & IV)

4.6.1. Lithology, mineralogy and elemental composition of aquifer sediment (Paper III)

Drilling at both sites revealed a typical architecture of As rich aquifer, where channel fill aquifer sand is overlaid by silty clay layer of overbank deposit forming the surface aquitard (Fig. 10). The surface aquitard extended down to 3.35 m and 3.20 m below ground level (bgl) at site 1 and site 2 respectively. Underneath this aquitard, a continuous aquifer extended down to the drilling depth of 39.2 m at site 1 and 45.5 m at site 2. At site 1, a clay rich layer was encountered at the depth of 39.2 m and
drilling was terminated, while no such layer was found at site 2. Hydrostratigraphically, the aquifer at both sites represents PC sequence of the study area as identified in section 4.2. During drilling, groundwater was met at the depth of 3.35 m and 3.20 m bgl at site 1 and site 2 respectively. At both sites the groundwater table fluctuation zone (site 1: 2.05 – 4.65 m; site 2: 1.45 – 3.85 m) was reflected by the presence of reddish brown to black mottles of Fe and Mn oxy-hydroxides. The determination of grain size reflects that throughout the aquifer though, fine to medium sand with varying proportion of silt predominate, their relative distributions vary significantly within the profile (Fig.10). No peat layer was encountered within the drilling depths. At both the sites, the dark grey color (10YR 4/1) of the aquifer materials reflects strong reducing condition in the aquifer.

The bulk mineralogy at the two sites is highly similar. In the sandy part of the sediment profile detrital quartz predominates, which is successively followed by feldspars, carbonates (calcite and dolomite), mica (muscovite, phlogopite) and chlorite. The qualitative identification of Fe-rich accessory minerals in the magnetically pre-concentrated sample fractions further indicates the presence of traces of magnetite, hematite, garnet (almandine), biotite (phlogopite), chloritoid, actinolite and minerals presumably of epidote type. The identification of clay minerals in samples from silt and clay rich sediments has revealed the presence of smectite, kaolinite and very likely illite too. The identified minerals have also been reported as the most common mineral constituents in the sediments of Bengal Basin by previous studies (Pal et al., 2002; Nath et al., 2005, 2008a; Seddique et al., 2008; Mukherjee et al., 2009a).

The depth profiles of the As, Fe\(_2\)O\(_3\), MnO\(_2\) and total organic carbon (TOC) content
Fig. 10. Vertical profiles of grain size distribution, As, Fe₂O₃, MnO₂ and TOC content throughout the sediment column at site 1 and site 2.

Throughout the sediment column at the two sites are also very much similar (Fig. 10). The concentrations of these elements are usually high at the top silty clay layer of the sediment profile at both the sites, particularly where reddish brown to black colored Mn and Fe oxyhydroxides occur. Here high contents of As (up to 122 mg/kg at site 1) are also accompanied by comparatively high concentrations of other trace elements like Zn, Ni and Cu (Neidhardt et al., 2013a). In contrast, the As concentrations in the aquifer sand of site 1 (range: 2.27 – 7.30 mg/kg; median: 3.43 mg/kg; n = 55) and site 2 (range: 1.80 – 12.6 mg/kg; median: 2.92 mg/kg; n = 64) are mostly below the upper limit of baseline As concentration in the deltaic earth crust of 5 – 10 mg/kg (Fig. 10) (Smedley and Kinniburgh, 2002). Similarly, the concentration of TOC is also mostly very low throughout the aquifer sand at both sites, except the lower part of the sediment profile at site 1 (Fig. 10). Similar depth profiles of these elements in aquifer sediments have also been reported in other fluvo-deltaic system (for e.g. Berg et al., 2008). The enrichment of As in the sediment columns of both sites strongly and positively (r = >0.7) correlates with the enrichments of Fe, TOC and trace elements such as Ti, Ni, Cu and Zn, commonly associated with Fe oxyhydroxides, which possibly suggests that As is mainly bound to the Fe oxyhydroxides and organic matter in the aquifer sediments of both sites. Similar associations of As with Fe and organic matter have also been reported by the previous studies conducted in Bangladesh (Horneman et al., 2004; Swartz et al., 2004; Meharg et al., 2006). Though, the correlation of As with silt and clay contents in the sediment is not strong.
(r = 0.37) at site 1, the association is prominent (r = 0.83) at site 2.

4.6.2 Fractionation of As, Fe and Mn in aquifer sediment (Paper III)

The sequential extractions of the aquifer sediments indicate that except for sediments collected from the depth of 2.65 m and 23.5 m of site 1, a major fraction (median: site 1 - 49%, site 2 – 63%) of the solid phase As is extractable with 0.5 M PO$_4^-$ solution (F2) (Fig. 11), which represent specifically adsorbed pool of As. Similar findings have been reported also from other parts of the study area (Métral et al., 2008), Bangladesh (van Geen et al., 2008a, b), and Red River Delta in Vietnam (van Geen et al., 2008b; Berg et al., 2008). Nevertheless, there is a significant difference in the distribution of remaining pool of As in sediments at the two sites. At site 1, the remaining fraction of solid phase As is almost equally distributed among the NH$_4^+$-oxalate (F4, 14%), DCB (F5, 11%) and HNO$_3$/H$_2$O$_2$ (F7, 15%) extraction steps with only a small fraction extractable with HCl (F3, 7%). However, at site 2, the second largest pool of As is extractable with HCl (F3, 15%) with a minor fraction in steps F4 (7%) and F5 (4%) (Fig. 11). It is also of worth to note that for the sediments at both sites, the amount of As release in the extraction with (NH$_4$)$_2$SO$_4$ (F1) targeting the readily mobilizable pool of As is mostly BDL (Fig. 11). This observation does not support the findings from Meghna riverbank sediment, where 15% of solid phase As was reported to be mobilizable by deionized water (Polizzotto et al., 2006). Similarly, the absence of detectable amount of As in the extraction with HF/H$_2$BO$_3$ (F6) for the sediments at both sites (Fig. 11) does not support the incorporation of As into the crystal lattice of silicate minerals, as it was reported in previous studies (Foster et al., 2000; Charlet et al., 2005; Seddique et al., 2008).

In contrast to As, however, the major pool of Fe (site 1 - 50%, site 2 – 57%) is released in the extraction with HF/H$_2$BO$_3$ (F6) (Fig. 11), representing that the weathering of silicate minerals, which are abundant in the aquifer sediment, can be a potential source of dissolved Fe in groundwater. At both sites, the second largest pool of Fe in the sediment is extractable with HCl (site 1 - 13%, site 2 - 15%) (Fig. 11), which represents a significant presence of Fe in association with secondary phases of acid volatile sulphides and carbonates and/or very amorphous oxides. Further, a significant content of Fe in the sediment of both sites is also mobilizable with PO$_4^-$ (site 1 - 10%, site 2 - 9%), indicating the possible adsorption of Fe(II) on the mineral surface (Fig. 11). The remaining pool of Fe is amorphous to crystalline oxides and degree of crystallization is comparatively higher at site 2 (Fig. 11).

Fractionation of Mn in the aquifer sediment closely resembles the Fe fractionation. At both sites the extraction with HF/H$_2$BO$_3$ (F6) releases a large amount of Mn from the sediment (site 1 - 28%, site 2 - 31%). At both sites the amount of Mn, representing crystalline oxides is very low (site 1 - 4%, site 2 - 3%), indeed the amount of amorphous Mn oxides is comparatively much higher at site 2 (site 1 - 7%, site 2 - 33%) (Fig. 11). Similar to Fe, a significant amount of Mn is also incorporated to the phases of acid volatile sulfides and carbonates or presents as very amorphous oxides (site 1 - 13%, site 2 - 11%) and is potentially mobilizable with PO$_4^-$ (site 1 - 20%, site 2 - 13%) (Fig. 11).

Thus, by combining the associations of As with other elements in the sediment columns together with the sequential extraction results it can be summarized that As in the aquifer sediments is mainly associated with very amorphous to crystalline Fe oxides with a small portion in the Mn oxides as well. Major portion of this As is readily exchangeable with PO$_4^-$.

Additionally, at site 1, a portion of As is also bound to the organic matter. Association of Fe and Mn into the secondary phases of acid volatile sulfides and carbonates are also common in the aquifer of both sites.

4.6.3 Hydraulics of the aquifer at two monitoring sites (Paper III)

The cumulative precipitation between two successive sampling events and the corres-
**Fig. 11.** Fractionation of As, Fe and Mn into different host phases in the aquifer sediment of site 1 and site 2. The extraction scheme was adopted from Eiche et al. (2008), where F1: ionically bound, extracted with 0.05 M (NH₄)₂SO₄; F2: strongly adsorbed, extracted with 0.5 M NaH₂PO₄; F3: Co-precipitated with acid volatile sulfides, carbonates, Mn-oxides, very amorphous Fe oxides, extracted with 1 M HCl; F4: Co-precipitated with amorphous Fe oxides, extracted with 0.2 M NH₄-oxalate/oxalic acid; F5: Co-precipitated with crystalline Fe oxyhydroxides, extracted with DCB: 0.5 M Na-citrate + 1 M NaHCO₃ + 0.5 g Na₃PO₄ H₂O; F6: Co-precipitated with silicate, extracted with 10 M HF + 5 g H₃BO₃ and F7: co-precipitated with sulphides and organic matter, extracted with 16 M HNO₃ + 30% H₂O₂.

The corresponding position of piezometric head in the wells of two sites over the monitoring period have been shown in Fig. 12. At each site, the variation of piezometric head over the monitoring period was very much similar in all the wells, reflecting that the wells are installed within a single hydrostratigraphic unit. At both sites, the piezometric head declined continuously with the progress of the dry season in both years being lowest in the month of April. Then it started to increase again at the onset of the monsoon and became highest in the month of October (Fig. 12). Though, the piezometric head responded to the precipitation events quite instantaneously at the early stage of monsoon, there was a time lag between peak precipitation events and piezometric head.

**Fig. 12.** Cumulative rainfall between two successive sampling events and variation in piezometric head in the wells at site 1 and site 2 over the monitoring period.
monsoon and highest elevation of piezometric head at both the sites (Fig. 12). It is further revealed that the highest elevation of piezometric head during wet period was similar (~1.0 m bgl) at both sites, while the declination in the dry period was ~0.5 m higher for site 1 compared to site 2 (Fig. 12). Another interesting feature in the variation is that at both sites the declination of piezometric head was ~0.5 m higher in 2010 (site 1: ~5.50 m bgl, site 2: ~4.70 m bgl) compared to 2009 (site 1: ~5.00 m bgl, site 2: ~4.30 m bgl) (Fig. 12).

4.6.4 Distribution of $^2$H and $^{18}$O in rain water, pond water and groundwater of the study area (Paper III)

The values of $^2$H and $^{18}$O in the collected monthly composite samples of rain water vary between (-24.6‰ to 14.0‰) and (-4.38‰ to 0.46‰) respectively. The highest value of $^2$H and $^{18}$O represents the sample that was collected at the early stage of monsoon. The isotopic compositions of the rain waters, measured in the present study are then compiled with the available data for rain water of the whole western Bengal Basin, reported in Kumar et al. (2010), Sengupta and Sarkar (2006) and Mukherjee et al. (2007b) to construct the local meteoric water line (LMWL) by linear regression fit (Fig. 13). The resulting LMWL is defined by the equation of $^2$H = 8.03 $^{18}$O + 8.27 (Kumar et al., 2010), $^2$H = 7.88 $^{18}$O + 8.93 (Sengupta and Sarkar, 2006), and $^2$H = 7.20 $^{18}$O + 7.7 (Mukherjee et al., 2007b), estimated by fitting their individual data sets. The LMWL also follows very well to the GMWL, constructed by Rozanski et al. (1993), with a signature of slight evaporation (Fig. 13). The values of $^2$H and $^{18}$O in the collected pond water samples vary within (-34.1‰ to -18.0‰), median: -28.9‰ and (-4.54‰ to -2.03‰), median: -3.88‰) respectively. The linear regression fitting to these data defines the pond evaporation line (PEL) of the area as $^2$H = 6.02 $^{18}$O – 5.87 (R$^2$ = 0.94), indicating that pond water has experienced strong evaporation after accumulation (Fig. 13).

\[
y = 7.8631x + 8.4199
\]
\[
y = 6.0178x - 5.8658
\]
\[
R^2 = 0.9648
\]
\[
R^2 = 0.94
\]

Fig. 13. The variation of $^2$H and $^{18}$O in the wells at site 1 and 2 and their comparison to local meteoric water line (LMWL) and pond evaporation line (PEL). The LMWL has been constructed by linear regression fit to the compiled rain water data set of present study, Kumar et al. (2010), Mukherjee et al. (2007b) and Sengupta and Sarkar (2006). The depth profiles of $^2$H and $^{18}$O in the aquifer at two sites have been shown in inset.
The values of $\delta^2$H and $\delta^{18}$O in all the collected groundwater samples vary within (-32.2‰ to -3.68‰, median: -25.9‰) and (-4.65‰ to -1.34‰, median: -3.88‰) respectively for site 1 and (-35.8‰ to -3.88‰, median -29.6‰) and (-4.75‰ to 5.13‰, median: -4.41‰) respectively for site 2. The groundwater samples from both sites are mostly clustered between LMWL and PEL providing the signature of evaporation before recharge and the extent of evaporation is to some extent higher at site 1 compared to site 2 (Fig. 13). Further, the groundwater samples from well A & B at site 1 are significantly more enriched for $^2$H and $^{18}$O compared to other 3 wells (Fig. 13), reflecting the vertical stratification of two groundwater bodies within the aquifer. However, such vertical stratification of groundwater is absent at site 2, reflected by similar depth distribution of $\delta^2$H and $\delta^{18}$O for all the wells (Fig. 13).

4.6.5. Vertical distribution of major ions, As and other redox parameters in groundwater of two monitoring sites (Paper III)

In all the groundwater samples collected from both sites, Ca$^{2+}$ appears as the dominating cation, successively followed by Mg$^{2+}$, Na$^+$ and K$^+$, while HCO$_3^-$ is the major anion followed by Cl$^-$. Consequently, the groundwater samples of the two sites are of Ca-Mg-HCO$_3$ type to Ca-HCO$_3$ type having circum-neutral pH (Appendix Table A.1 and Table A.2 of Paper III). The depth profiles of major ionic constituents indicate that at site 1, the concentration of all the major ions is relatively high in the shallowest well A & B and considerably decreases in the wells C, D & E (Fig. 14); again reflecting vertical stratification of groundwater within the aquifer. The vertical variation of concentration is very low to negligible for most of the constituents in the wells of site 2.
Fig. 15. Depth profiles of dissolved As and other aqueous redox parameters in the aquifer at site 1 (filled symbols) and site 2 (open symbols). The depth profiles have been constructed taking the median values of time series data for each parameter in the wells at two sites. Error bar represents the standard deviation (SD) of the corresponding parameter over the monitoring period.

(Fig. 14), in agreement with the depth distributions of $\delta^2$H and $\delta^{18}$O (Fig. 13). Except the concentration of $K^+$ for the deepest 3 wells of site 2, the concentration of all other ions is considerably higher in the wells of site 1, compared to site 2 (Fig. 14). The depth profile of the EC in groundwater closely follows these distribution patterns of the major ions in the wells of two sites (Fig. 14), reflecting the higher extent of water-sediment interactions in the aquifer of site 1.

The depth profiles of As and other important aqueous redox parameters for both the sites represent that following the extent of variation in major ionic composition, the variations in As and other aqueous redox parameters are also considerably higher at site 1, compared to site 2 (Fig. 15). At site 1, the concentration of
dissolved As in groundwater samples collected from all the wells exceeds the WHO provisional drinking water guideline of 10 µg/L. Initially, the As concentration increases with increasing depth and being highest at well C, it decreases again in the deeper part of the aquifer producing typical “bell shaped” (Harvey et al., 2005) vertical profile of As distribution within aquifer (Fig. 15). Interestingly in well C, the concentration of dissolved As is highest where the concentration of Fe is lowest (Fig. 15). The speciation of dissolved As and Fe further shows that though, in all the wells the concentration of As(III) and Fe(II) mostly dominate over the concentration of As(V) and Fe(III) respectively, the extents of prevalence are considerably lower in well C (Fig. 15). In accordance with the spatial distribution over the study area, the vertical distribution of Mn in groundwater just follows the opposite trend of Fe, being the concentration highest at well C (Fig. 15). The concentration of dissolved organic carbon (DOC) is highest at well A and decreases over the depths (Fig. 15). The concentrations of NH$_4^+$ and PO$_4^{3-}$ mostly follow each other, being highest at the deeper part of the aquifer (Fig. 15). The concentration of SO$_4^{2-}$ is considerably high at well A & B, while the concentration is nearly BDL at the deeper part of the aquifer (Fig. 15). The value of Eh does not change considerably throughout the depths of the aquifer (Fig. 15).

At site 2, the concentration of dissolved As in groundwater collected from all the wells also exceeds 10 µg/L, being lowest at well A, highest at well B and then decreasing slightly with increasing depth (Fig. 15). Similar to site 1, the depth distributions of Fe and Mn are opposite to each other (Fig. 15). The speciation of dissolved As and Fe again shows that they are almost exclusively present in the lower oxidation states of As(III) and Fe(II) and do not show any variation over the depth (Fig. 15). The concentration of DOC also broadly decreases with increasing depth, except for well D (Fig. 15). The vertical distribution of NH$_4^+$ and PO$_4^{3-}$ closely follow each other at this site also, being the concentrations highest at well B and then decrease over the depth. The concentration of SO$_4^{2-}$ is mostly BDL throughout the aquifer at this site (Fig. 15). The value of Eh is relatively higher at well A and does not vary significantly over depths in the deeper part of the aquifer (Fig. 15). Over the entire depth of the aquifer at both sites, the concentration of NO$_3$ is mostly BDL.

### 4.6.6. Temporal variation of As and other aqueous solutes over the monitoring period (Paper III)

The temporal variation of dissolved As, other aqueous solutes, Eh and isotopic composition of δ$^{18}$O in the wells of two sites over the monitoring period has been shown in Fig. 16. The extent of variation has been statistically assessed by calculating the percentage of relative standard deviation (%RSD) (Appendix Table A.1 and Table A.2 of Paper III).

At site 1, the calculation of %RSD indicates that As varied considerably over the monitoring period in all wells (RSD ≥10%), and the extent of variation was substantially stronger in the shallowest part of the aquifer (well A & B), which is also directly visible in Fig. 16. In well A, a general trend of continuous increase of As over the monitoring period was observed. However, no seasonal pattern was prominent, except very small peak in concentration at the beginning of monsoon in each year (Fig. 16). High degree of seasonal change in As concentration was observed for well B (Fig. 16). From the starting of monitoring (December 2008) to the end of dry season (April 2009) As concentration was decreasing continuously. In the following period up to November 2009, when regular monitoring was stopped for pumping experiment, As concentration did not change considerably. When the monitoring was started again in January 2010, As concentration increased close to the value observed in December 2008. In the following dry period the change in As concentration was similar to the previous year. However unlike to the previous year, this time As concentration started to

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*Arsenic geochemistry in the alluvial aquifers of West Bengal, India*
Fig. 16. Temporal variation of As and other aqueous solutes in the wells at site 1 and site 2 over the monitoring period of 20 months (December 2008 – August 2010). Blue shaded area and white area in the figure represents monsoon period and dry period respectively. Green line and red line represents the time of pumping experiment at site 1 and bio-stimulation experiment at site 2 respectively.
increase just from the beginning of monsoon and when monitoring was stopped in July 2010 As concentration again went back to the value observed in January 2010 (Fig. 16). Arsenic(III) was always the predominating species and the extent of prevalence did not change markedly over the time (Fig. 16), indicating that change in As concentration actually represented the change in As(III) concentration. The seasonal change in PO$_4^{3-}$ concentration very closely followed the pattern of As (Fig. 16). However, the seasonal change in Fe, Mn, sum of major cations (SMC: Ca$^{2+}$ + Mg$^{2+}$ + Na$^+$ + K$^+$), HCO$_3^-$, Cl and SO$_4^{2-}$ concentration markedly decoupled from the seasonal behavior of As, being the concentrations increased in the dry period and decreased in the monsoon, especially in the year of 2010 (Fig. 16). Arsenic concentration also varied cyclically in well C in 2010 (Fig. 16). Similar to well B, the As concentration was decreasing when monitoring was started in January 2010 after pumping experiment and eventually became lowest at the end of dry season. Interestingly in well C, the percentage of As(III) was also decreased largely reaching to the value of 12.2% and change in Fe strongly coupled to the change in As being the concentration lowest to 0.07 mg/L at the end of dry season (Fig. 16). Phosphate showed similar behavior to As in this well also. The concentration of SO$_4^{2-}$ was increased just prior to the decrease of As and Fe concentration, while Mn, SMC, HCO$_3^-$ and Cl did not show any specific trend at that period (Fig. 16). Similar type of seasonal variations were absent in the year 2009 (Fig. 16). No seasonal variation in As concentration was observed in well D & E over the monitoring period (Fig. 16). In all the wells, Eh showed increasing trend during dry period in both years, however due to unavailability of data the trend during monsoon period could not be examined (Fig. 16).

At site 2, a strong seasonal variation in As concentration was observed in well A only (Fig. 16), where As concentration varied between 17.6 – 132 µg/L with a RSD of 50.6% (Appendix Table A.2 of Paper III). In contrast to variation in well B and C at site 1, here As concentration notably increased during the dry season both in 2009 and 2010. After passing through the maximum, the concentration decreased to the lowest value at the early stage of monsoon and no significant variation was observed in the following part of monsoon (Fig. 16). It is worthwhile to mention that though, in the early stage of bio-stimulation experiment As concentration was increased considerably (Neidhardt, 2012), it had returned to the baseline value before starting of regular monitoring in January 2010 (Fig. 16), indicating that peak in As concentration during the dry period of 2010 was not due to the effect of bio-stimulation experiment. Here also, the variation in As concentration actually represented the variation in As(III) concentration and was accompanied by the similar variation in PO$_4^{3-}$ concentration (Fig. 16). However, other parameters such as Fe, Mn, SMC and HCO$_3^-$ did not show any seasonal trend over the monitoring period, except the variation in Cl and SO$_4^{2-}$ concentration, which showed opposite trend to the variation in As (Fig. 16). Similar to site 1, in all the wells of site 2, Eh was also increasing during dry period in both years (Fig. 16). No considerable temporal variation in As and other aqueous solutes concentration was observed in other wells at site 2 (Fig. 16), except during the period of bio-stimulation experiment, when the concentrations were increased considerably (Neidhardt, 2012). Though, As concentration in all the wells at site 2 had returned to the base line before starting of monitoring in January 2010, other parameters, which increased considerably during experiment took few weeks to return to the base line value (Fig. 16). It is further worth to note that the composition of δ$^{18}$O did not change considerably in the wells at both sites over the monitoring period, except in well A at site 1, where similar to As, a general trend of continuous increase was observed (Fig. 16). The variation of As(V) also did not show any specific trend over the monitoring period for any well of
both the sites. Similar type of site and/or well specific trends of temporal variation in As and other aqueous solutes, limited only to the shallowest part of the aquifer have been reported from Araihazar of Bangladesh (Cheng et al., 2005; Dhar et al., 2008).

4.6.7. Application of SCMs in Predicting Temporal Variability of As (Paper IV)

In order to investigate the role of different surface complexation reactions onto aquifer materials in the As mobilization in ground-water, it was attempted to model the temporal variability in As(III) and As(V) concentrations by the application of D&M and CD-MUSIC SCMs (Fig. 17 and Fig. 18). The comparison of model-predicted concentration with the measured value indicates that though the performance of the CD-MUSIC SCM in predicting As(III) concentration in the wells of site 1 is fairly good, the predictions of the D&M SCM are even closer to the measured trends (Fig. 17). In site 2, the As(III) concentration predicted by

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**Fig. 17.** Measured and predicted (with the D&M and CD-MUSIC SCMs) temporal variability in the concentration of aqueous As(III) for the piezometers of site 1 & 2. The significance of blue and white shaded area and green and red line has been reported in Fig. 16.
both D&M and CD-MUSIC SCMs closely follows the measured concentration until the end of November 2009, when the sampling was stopped for one month for the bio-stimulation experiment (Fig. 17). In the post-experiment period, the CD-MUSIC SCM largely under-predicts the As(III) concentration, whereas the concentration predicted by the D&M SCM still quite closely follows the measured value until the end of the monitoring (Fig. 17). The estimation of root mean square error (RMSE) of the logarithm of dissolved As(III) concentration to assess the goodness of model fits statistically, also supports the above inferences (Paper IV). The poor performance of both SCMs in predicting As(III) concentration for the well B and well A of site 1 and 2 respectively (Fig. 17), might be due to the fact that for these wells the total As content in the system did not remain constant over the monitoring period as the hypothesis, because of seasonal mixing of groundwaters with distinct As...
concentrations from different depths and/or location.

For As(V), the predicted concentration by both SCMs approximately follows the scattered peaks observed in the measured concentration over the monitoring period (Fig. 18). However, the estimation of RMSE indicates that the performance of the D&M SCM is to some extent better than that of the CD-MUSIC SCM, indeed both models provide better estimations for As(III) than for As(V) (Appendix Table A.4 of Paper IV).

4.6.8. Modeled Surface Speciation of the Aquifer Sediment (Paper IV)

An attempt was also made to investigate the extent of formation of the different complexes at the surface of sorbent considered in the two SCMs. Well E from site 1 was selected for this investigation, based on the low estimated RMSE values for both SCMs for the prediction of As(III) concentration in groundwater (Appendix Table A.4 of Paper IV). The pattern of surface speciation of the weak sites, where As is also adsorbed, predicted by the two SCMs fairly well resembles each other (Fig. 19). According to both SCMs, the surface complexes of PO$_4^{3-}$ are the major adsorbing species, covering 35% and 58% of the weak surface sites of ferrihydrite and goethite, respectively. For ferrihydrite, the D&M SCM further predicts that PO$_4^{3-}$ adsorption is successively followed by proton binding (26%) and Fe(II) species adsorption (14%), while the CD-MUSIC SCM for goethite predicts higher adsorption of Fe(II) (22%) compared to proton binding (9%) (Fig. 19). Though HCO$_3^-$ is the major anion in groundwater, very low to negligible surface occupancy is estimated by both SCMs. According to the D&M SCM it only covers 10% of the surface sites similar to the adsorption of H$_4$SiO$_4$ species, while the CD-MUSIC SCM estimates <1% of the surface coverage to be due to the complexes of the HCO$_3^-$ and H$_4$SiO$_4$ species (Fig. 19). Following the large predominance of As(III) concentration over As(V) in groundwater, both SCMs predict higher average concentration of As(III) surface complexes compared to As(V) complexes (Fig. 19). The previous study by Jessen et al. (2012) also reported similar surface speciation for the Vietnam aquifer sediment by the simulation of CD-MUSIC SCM for goethite, the only difference being a higher adsorption of As(V) compared to As(III). However, the estimation by the D&M SCM for

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**Fig. 19.** The average D&M and CD-MUSIC SCMs predicted surface speciation of the weak adsorption sites, estimated by the equilibration of groundwater samples, collected from the well E of site 1. The percentage of site coverage by a component is calculated by adding all the surface complexes formed by the specific component with weak adsorption sites.
ferrhydrite in the present study significantly differs from the composition of surface complexes, previously calculated by the simulation of the D&M SCM for Bangladesh (Swartz et al., 2004), and for Vietnam aquifer sediment (Postma et al., 2007; Jessen et al., 2012), where H$_2$SiO$_4$ and HCO$_3^-$ were reported to be the major adsorbing species with a relatively low surface coverage by PO$_4$$^{3-}$. Further, in agreement with the findings of Jessen et al. (2012) the CD-MUSIC SCM predicts the binding As(III) to goethite exclusively by forming the As(III)-Fe(II) ternary surface complex (Fe$_{\text{uniOAs(OH)}}$$_3$$^{Fe_{0.5}}$). The formation of such a complex may explain the under-prediction of As(III) concentration by the CD-MUSIC SCM in the post-bio-stimulation experiment period for the wells at site 2. It should be mentioned here that due to the bio-stimulation in the aquifer by injecting degradable organic matter, the local groundwater composition was changed drastically for several days, including an elevation in As and Fe concentration (Neidhardt, 2012). When the regular monitoring was started again in January 2010, the As concentration had returned to the baseline value in all five piezometers (Fig. 17), while the Fe concentration remained elevated until the end of the monitoring (Neidhardt, 2012; Paper II).

4.7. Tubewell platform color as a rapid screening tool for As and Mn in drinking water wells (Paper V)

4.7.1. Classification of TWs according to platform color

According to well platform color, 423 TWs were classified into three color categories, viz. black, mixed and red (Fig. 20). Of the 423 sampled TWs, 353 TW platforms (83%) were assigned a particular color, either as black (n = 171, 40%) or red (n = 182, 43%). In 50 TWs (12%), platforms were classified as mixed colored (both black and red coloration), while in 20 TWs (5%) color was
not recognizable due to undeveloped well platform, regular cleaning of the platform, formation of bio-films and/or algal growth. The age of well platform is also an important factor for the development of color, because newly built platforms are less likely to develop color irrespective of elevated Mn or Fe concentration. The mixed colored stain on the well platform may develop because of simultaneous enrichment of groundwater with high Fe and Mn (McArthur et al., 2011) as a consequence of overlapping redox zone for Mn and Fe oxyhydroxides reduction in the aquifer (Mukherjee et al., 2008; Nath et al., 2009).

4.7.2. Evaluation of platform color as a tool for screening As in TWs

The distribution of As among the surveyed TWs (n = 423) without considering platform color, shows that 61% TWs (n = 258) exceeded WHO drinking water guideline value of 10 µg/L, while 28% (n = 117) exceeded national drinking water standard of 50 µg/L. Whereas platform color-wise distribution indicates that, 73% (n = 125) of the TWs with black colored platform (n = 171) had safe level of As and 84% (n = 153) of the TWs with red colored platform (n = 182) were enriched with As in TW water, compared to WHO guideline value (Fig. 21a). This result is comparable to the earlier observation (McArthur et al., 2011), that both black and red colored platform with 90% certainty can respectively identify a safe and As enriched TW, following WHO guideline value. With 50 µg/L standard, black and red colored platform in 93% (n = 159) and 38% cases (n = 70) correctly identify safe and unsafe TWs respectively (Fig 21b). Thus for 20% (n = 34) and 46% (n = 83) cases, black and red colored platform indicates TWs had As concentration ranging between 10 to 50 µg/L. Again when TWs with mixed colored platform were considered, 80% TWs (n = 40) contained As above 10 µg/L and 42% TWs (n = 21) above 50 µg/L (Paper V). Thus from public health perspective, TWs with mixed colored platform could be considered as As contaminated wells.

4.7.3. Effectiveness of platform color as a tool for screening As in TWs

The TW platform color to be effective as a screening tool, it should have high probability of true-positive and negative values and reasonably low probability of false-positive and negative values (for details see supporting information of Paper V) with respect to a particular drinking water standard. Figure 21 shows comparison of the respective true-positive and negative and false-positive and negative values for As at WHO drinking water guideline and national standard. The

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</tr>
<tr>
<td>Efficiency</td>
<td>$[(A+D)/(A+B+C+D)]$</td>
<td>79</td>
<td>-</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>Positive Predictive Value (PPV)</td>
<td>$A/(A+B)$</td>
<td>84</td>
<td>78</td>
<td>89</td>
<td>38</td>
</tr>
<tr>
<td>Negative Predictive Value (NPV)</td>
<td>$D/(C+D)$</td>
<td>73</td>
<td>66</td>
<td>79</td>
<td>93</td>
</tr>
</tbody>
</table>

Table 3. Assessment of the effectiveness of TW platform color as a screening tool for As in TWs.
sensitivity, specificity, efficiency and predictive values (positive and negative) are summarized in Table 3. The results show that at WHO guideline, the positive predictive value (PPV) of red colored platform is 84%, while the negative predictive value (NPV) of black colored platform is 73%. The respective efficiency, sensitivity and specificity of the tool are 79%, 77% and 81%. This signifies that platform color can be regionally used as an initial screening tool to evaluate As in groundwater. While if 50 µg/L standard is considered, the platform color tool is moderately efficient (65%) to screen low and high As in TW water. However, the NPV of black colored platform to identify As safe TW is very high (93%) compared to PPV (38%) of red colored platform to identify As enriched TWs. Thus the sensitivity (85%) of the tool is acceptably higher compared to the specificity (59%) (Table 3). This indicates that at the national standard, despite having moderate efficiency of the tool, black colored platform can still be used as an excellent indicator to screen safe TWs for As rather than to identify unsafe wells by red colored platforms.

**4.7.4. Evaluation and effectiveness of platform color as a tool for screening Mn in TWs**

The distribution of Mn in the surveyed TWs (n = 423), without considering platform color, shows that 55% TWs (n = 231) exceeded national guideline for Mn in drinking water. Whereas platform color-wise distribution indicates that, 78% (n = 134) of the TWs containing black colored platform (n = 171) would be enriched with Mn, while 64% (n = 117) of the TWs containing red colored platform (n = 182) would be Mn free (Fig. 22). The efficiency, sensitivity and specificity of the tool are 71%, 67% and 76 respectively (Table 4). This suggests that both black and red colored platforms are effective to screen TWs for high and low Mn in well water at the national drinking water standard for India.

**4.7.5. Predictive value and prevalence**

The prevalence of As and Mn enrichment in TWs of a region may affect the performance of platform color tool to screen contaminants in well water. Bayesian model was used to evaluate this effect at different cut-off levels (Fig. 23). The figure indicates that for both As and Mn at different permissible limits, the PPV increases with increase in prevalence. This means, in a particular region, with increase in the extent of As and Mn enrichment in TWs, the performance of the tool to identify unsafe TW increases, while with decrease in the extent of As and Mn enrichment in TWs, the performance of identifying safe TW increases.

**5. Discussion**

**5.1. Evolution of the shallow hydro-stratigraphic framework in the central western Bengal Basin (Paper I)**

The previous studies, conducted mostly in Bangladesh and southwestern part of West Bengal, have discussed in detail about the basin fill history and evolution of different landforms of Bengal Basin in the late Quaternary period (e.g. Umitsu, 1987, 1993; Goodbred and Kuehl, 2000; Allison et al., 2003; Goodbred et al., 2003; McArthur et al., 2008; Mukherjee et al., 2009a; Sarkar et al., 2009). Here an attempt has been made to correlate the different stratigraphic units identified within shallow depth of the study area to that reported by these previous studies to extrapolate the current under-
standings of basin fill history also for the area of central western Bengal Basin, which is still barely investigated.

The lowest hydrostratigraphic unit, aquifer-3 and the overlying brown clay layer correspond to the lower unit of Umitsu (1993) and oxidized facies of Goodbred and Kuehl (2000). The brown color of the sand of aquifer-3 and overlying clay layer indicates that these units were exposed to extensive atmospheric weathering (Umitsu 1993; Goodbred and Kuehl, 2000; von Brömssen et al., 2007; McArthur et al., 2008; Pal and Mukherjee, 2009). However, there is some disagreement regarding the time of deposition of these sediments and subsequent sub-aerial oxidation. Because of paucity of the suitable dating materials only a few dates are available from these units. Near Khulna, Umitsu (1987) dated a plant fragment from the uppermost part of these oxidized units as ~12 ka, while in Diamond Harbour of southern West Bengal, Stanley and Hait (2000) dated organic rich mud as ~14 ka. Additionally, Umitsu (1993) reported the deposition of 10 m thick sandy gravel bed at the base of these oxidized units and inferred that this sandy gravel bed was deposited during last glacial maximum (LGM) (around 18 – 20 ka), when the rivers were dissecting the former surfaces and designated this unit as lowest late Quaternary unit of this region. He further hypothesized that the oxidized units were deposited in the following period of LGM, but prior to 12 ka, when the glaciers at the Himalaya were retreating and sea level was rising rapidly and sub aerial oxidation occurred in the period of 10 – 12 ka probably because of temporal sea level regression. The alternative hypothesis, proposed by Goodbred and Kuehl (2000) and more detailed by McArthur et al. (2008) is that these oxidized units were deposited prior to LGM and oxidation occurred during low stand of the sea level (around 18 – 20 ka), following the maximum epoch of the glaciation. McArthur et al. (2008) have tried to provide the ages of these units indirectly. They found similar major and trace elemental compositions in the bottom part of the palaeo channel sand adjacent to the oxidized sand and inferred that during the period of LGM, when sea level was approaching minimum (120 m below present level), the oxidized sand unit was deeply incised and deposited as reworked sand in the incised valley. They determined the OSL age of quartz from this incised valley sand unit as 17 – 23 ka and concluded that being the parent materials the age of the oxidized sand unit would be considerably higher than 23 ka. Further, they have proposed that the brown colored clay layer at the top of the oxidized sand unit was deposited no later than 20 ka and termed this clay layer as “Last Glacial Maximum Palacosols (LGMP)”. In an accompanying investigation in the same boreholes, Sarkar et al. (2009) have hypothesized that the

Table 4. Assessment of the effectiveness of TW platform color as a screening tool for Mn in TWs.

<table>
<thead>
<tr>
<th>Indices for validation of well platform color tool (in %)</th>
<th>Basis for calculation (Formula × 100)</th>
<th>Mn National Standard (300 µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>A/(A+C)</td>
<td>Estimated Value: 67</td>
</tr>
<tr>
<td>Specificity</td>
<td>D/(B+D)</td>
<td>95% confidence interval: 60</td>
</tr>
<tr>
<td>Efficiency</td>
<td>(A+D)/(A+B+C+D)</td>
<td>Lower limit: 74</td>
</tr>
<tr>
<td>Positive Predictive Value (PPV)</td>
<td>A/(A+B)</td>
<td>Upper limit: -</td>
</tr>
<tr>
<td>Negative Predictive Value (NPV)</td>
<td>D/(C+D)</td>
<td></td>
</tr>
</tbody>
</table>

40
Fig. 23. Plot showing the relationship of positive predictive values (PPV) with prevalence of TWs with a. As concentration of ≥10 µg/L and ≥50 µg/L, b. Mn concentration of ≥300 µg/L.

sediment succession of marine clay unit (underneath the brown sand), brown sand unit and brown clay were deposited in the period of Oxygen Isotope Stage (OIS) of 5 (pre 80 ka), 3 (50 – 30 ka) and 2 (around LGM) respectively. It is worth to mention here that the period of deposition and subsequent weathering of the oxidized units can have important consequences on their regional distributions. For example, McArthur et al. (2008) have forecasted that as glacial maximum and subsequent sea level low stand occurred globally, these oxidized units are possibly present throughout the basin and elsewhere in the world under similar environment. However, if these units were deposited in the following period of LGM and oxidation occurred during temporal sea level regression of 10 – 12 ka, because of its less extent compared to LGM, the distribution of the oxidized units might be limited to some patches only. In order to conclude this debate, the present study has determined the age of the two quartz samples, retrieved from brown sand unit by OSL dating and results indicate that they were deposited around 70 ka (Table 1), closely supporting the speculation of Sarkar et al. (2009). The lower part of aquifer-1 corresponds to the grey sand unit of Goodbred and Kuehl (2000). As mentioned before, this unit was probably deposited by reworked sand of the older oxidized units due to incision during LGM (Goodbred and Kuehl, 2000; McArthur et al., 2008; Sarkar et al., 2009).

In the following period of LGM to early of the Holocene, when sea level was transgressing very rapidly, sedimentation was mostly confined in the palaeo channel in the form of estuarine valley fill (Sarkar et al., 2009). The 14C age of 9.5 ka of the peaty clay layer at the top of the oxidized units (Table 1) indicates that around that time a major change in the depositional environment had occurred in the study area, when the oxidized surfaces were back flooded and the extensive peaty clay layer was developed (Goodbred and Kuehl, 2000; Sarkar et al., 2009). This time probably represents the age of initiation of the early Holocene delta formation in the area (Sarkar et al., 2009). During drilling, wood and shell fragments were occasionally observed within this peaty clay layer, particularly along the eastern margin of the study area (BH-4) (Fig. 3), possibly indicating marine influence (Umitsu, 1993; Goodbred and Kuehl, 2000). In the following period up to 7.21 ka, the sedimentation rate was very high (4.6 m/ka), as a response to the intensified southwest monsoon, which resulted in tremendous river sediment discharge of ~ 2.5 × 10^8 t/yr (Goodbred and Kuehl, 2000; Goodbred, 2003), depositing the thick section of the overbank silty clay in the central floodplain of the study area. This unit corresponds to the middle unit of Umitsu (1993) and lower delta mud of Goodbred and Kuehl (2000). The deposition of sand in the channel was continued at that time also (Sarkar et al., 2009), forming the continuous thick channel deposition of aquifer-1. However, much
younger $^{14}$C age (5.63 ka at depth of 33.4 – 34.8 m bgl of BH-6) of the inter-bedded clay layer within channel sand (Table 1) might indicate post depositional erosion due to river avulsion and deposition of the reworked sand afterwards. After 7 ka, the rate of sea level increase slowed down, the mode of delta formation was changed from aggradational to progradational phase (Goodbred and Kuehl, 2000; Sarkar et al., 2009) and colonization of mangrove reappears locally forming upper sub-layer of peat (Sarkar et al., 2009). In the following period the sedimentation rate largely decreased (1.09 m/ka) and sand was dispersed throughout the floodplain because of increased fluvial activity (Goodbred and Kuehl, 2000; Sarkar et al., 2009), forming the aquifer-2 at the top of the overbank deposits. This unit possibly represents the upper unit of Umitsu (1993) and muddy sand unit of Goodbred and Kuehl (2000). The formation of the scattered peaty clay layer, which dated as 2.99 ka at the top of the aquifer-2 at BH-2 borehole (Table 1) indicates the developments of local swampy condition in the study area at that period (Sen and Banerjee, 1990; Goodbred and Kuehl, 2000). The top most sandy clay layer, distributed throughout the study area, represents modern overbank deposit and corresponds to uppermost unit and thin mud of Umitsu (1993) and Goodbred and Kuehl (2000) respectively. By conducting a geophysical survey Métral et al. (2008) and Nath et al. (2010) have reported the occasional presence of sand windows, which outcrop to the surface, within this surface unit of the study area and concluded that this surface sandy clay layer plays a key role to maintain reducing condition in the underlying aquifer by regulating the mode of recharge. From the same study area, Neidhardt et al. (2013a) have also reported the higher enrichment of trace elements like As, Cu, Ti, Zn, which are commonly associated with Fe and Mn oxyhydroxides, in the water table fluctuating zone within the surface unit and inferred that this higher enrichment is probably due to the re-oxidation of anoxic groundwater, enriched with dissolved elements, when rose to the oxic vadose zone.

5.2. Source of recharge to the As rich shallow aquifer (Paper III)

The origin of groundwater recharge at the As rich shallow aquifers of Bengal Basin is still a controversial issue. The different possibilities that are explored by the previous researchers include: i) the recharge of groundwater by evaporation influenced surface water through ponds, wetlands, and agricultural paddy fields, where the rate of recharge is largely controlled by the scale of groundwater abstraction (Harvey et al., 2002, 2005; Neumann et al., 2010; Lawson et al., 2013) and ii) direct meteoric recharge, without having contribution from the evaporated surface water (Sengupta et al., 2008; Datta et al., 2011). These very different inferences were drawn from the site specific studies, conducted at different locations of the basin. However, by comparing the isotopic signature of $\delta^2$H and $\delta^{18}$O over the whole western Bengal Basin, comprising the present study area also, Mukherjee et al. (2007b) have suggested that though regionally the groundwater recharge is mostly of meteoric origin, the contribution of evaporated surface water to the recharge of shallow aquifers cannot be ruled out. Further, they have suggested that Bhagirathi-Hooghly river can also be the source of recharge, particularly for the river bank aquifers. The isotopic compositions of $\delta^2$H and $\delta^{18}$O in the monitoring samples from two sites and their comparison to the LMWL and PEL (Fig.13) indicate that wetland and constructed pond do have some role in the groundwater recharge in the study area. The recharge through pond and wetland can contribute DOC in the shallowest part of the aquifer (Harvey et al., 2002; Neumann et al., 2010; Lawson et al., 2013; Mailloux et al., 2013), which is also consistent with the depth profile of DOC at both the sites (Fig.15). It is worth to mention here that Lawson et al. (2013) from the same study area have identified the presence of DOC, which is younger than the sedimentary
Fig. 24. Bivariate plot of Na⁺ normalized \( \text{HCO}_3^- \) and \( \text{Mg}^{2+} \) versus Na⁺ normalized \( \text{Ca}^{2+} \) to identify prevailing minerals weathering in groundwater of study area.

organic carbon even at depth >100 m. They concluded that the drawdown of surface derived organic matter through pond and wetland because of groundwater extraction is the origin of this younger DOC in groundwater. By comparing with the findings of previous studies mentioned above, it seems that the origin of groundwater recharge to the sub-surface shallow aquifers is site specific and largely controlled by the local lithology. For example, by conducting the study in an area of Barasat-1 Block of North 24 Parganas, West Bengal, where the surface silty clay layer is extended down to 9 – 24 m bgl (McArthur et al., 2004), Sengupta et al. (2008) has rejected the possibility of recharging evaporated surface water to the groundwater. Similar conclusion was also made by Datta et al. (2011). The study area of Datta et al. (2011) was distributed over 6 blocks, in the district of Murshidabad, West Bengal. In 5 out of 6 blocks, the surface silty clay layer is extended down to more than 9 m and consequently, groundwater samples, collected from these blocks plotted along the LMWL. Interestingly, in the 6th block, where the surface silty clay layer is limited within just 3 m, a significant number of the groundwater samples plotted along the local PEL (Datta et al., 2011), indicating the recharge from surface water. Similar to the 6th block of Datta et al. (2011), at both sites of the present study and at the study area of Harvey et al. (2002) and Neumann et al. (2010) in Munshiganj District of Bangladesh, the surface silty clay layer just extends down to 3 m, where the signature of recharge from pond and rice fields is evident. Furthermore, as mentioned before the sandy lenses within surface aquitard may also act as a conduit for evaporative surface water recharge to the shallow aquifers (Métral et al., 2008; Nath et al., 2010). Thus, considering the complexity and heterogeneity in the formation of subsurface shallow aquifers in Bengal Basin, it can be concluded that any prediction of the origin of groundwater recharge to the As rich shallow aquifers for whole basin could be over-simplified; rather it should be considered as a site specific phenomenon.

5.3. Evolution of major ion composition in groundwater (Paper II & III)

5.3.1. Regional evolution (Paper II)

The geochemical evolution of groundwater in Bengal Basin is mainly regulated by carbonate mineral dissolution, silicate weathering and ion exchange processes with the aquifer materials (Dowling et al., 2003; Mukherjee and Fryar, 2008). The concentration of \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) and \( \text{HCO}_3^- \) is mainly controlled by the carbonate mineral dissolution, while the weathering of silicate minerals and ion exchange primarily is responsible for \( \text{Na}^+ \) and \( \text{K}^+ \) in groundwater. The relative contribution of these processes to the evolution of major aqueous chemistry largely depends on the bulk mineralogy of the aquifer sediment as well as kinetics of the chemical weathering processes (Tardy, 1971; Faure, 1998). Possibly the longer groundwater residence time in Bengal Basin as a consequence of low hydraulic gradient (1.00 - 0.01 m/km from northern to southern part) and extended flow path is
responsible for silicate weathering and ion exchange despite of slow kinetics (Mukherjee et al., 2007a, 2009b). Mukherjee and Fryar (2008) and Mukherjee et al. (2009b, 2011) have documented in details about the interplay of these processes for the deeper part of Sonar Bangla aquifer of western Bengal Basin, which also encompasses the present study area. In the present study as suggested by Mukherjee et al. (2009b), solute mass-balance approaches have been adopted to demonstrate the extent of these chemical processes occurring in BSA and GSA.

On the bivariate plot of Na\(^+\)-normalized Ca\(^{2+}\) versus Na\(^+\)-normalized HCO\(_3\) and Mg\(^{2+}\) (Fig. 24), groundwater samples from two aquifers are clustered between the zone of global average silicate and carbonate weathering, which indicates that both carbonate mineral dissolution and silicate weathering are concurrently occurring in the two aquifers. However, the trend of the groundwater samples to fall along the y = 2x line on the bivariate plot of Ca\(^{2+}\) + Mg\(^{2+}\) versus HCO\(_3\)\(^-\) together with high ratio of HCO\(_3\)\(^-\) to Na\(^+\) + K\(^+\) in the groundwater of BSA and GSA (Fig. 25) suggests that carbonate mineral dissolution is more prevailing in the two aquifers. The relative enrichment of P\(_{CO_2}\) in the aquifers compared to atmospheric P\(_{CO_2}\) and equilibria of groundwater with respect to the calcite and dolomite minerals are further consistent with the prevailing carbonate mineral dissolution in the aquifers. To explore the extent of active cation-exchange in the aquifers, HCO\(_3\) and SO\(_4\)\(^2-\) corrected Ca\(^{2+}\) + Mg\(^{2+}\) (to exclude the contribution of Ca\(^{2+}\) and Mg\(^{2+}\) from carbonate and silicate weathering) was plotted against Cl\(^-\) versus HCO\(_3\) (to exclude the Na\(^+\) input from atmospheric deposition) (Fig. 26). Jankowski et al. (1998) have reported that for the aquifer with active cation exchange between Na\(^+\) and Ca\(^{2+}\) + Mg\(^{2+}\), the slope of this equivalent bivariate plot would be -1 (i.e. y = -x). Thus the slope of -0.65 and -0.86 respectively for BSA and GSA indicates that cation-exchange is also to some extent responsible for the observed groundwater compositions in both aquifers, while the
extent is more prominent in the GSA. Notwithstanding the higher extent of cation exchange in GSA, the concentration of Na\(^+\) is relatively higher (although not very significantly) in the groundwater of BSA (median, BSA: 27.2 mg/L and GSA: 22.4 mg/L). This small enrichment of Na\(^+\) in BSA might be due to the chemical weathering of NaAlSi\(_2\)O\(_6\) as indicated by factor 3. The higher extent of cation-exchange in GSA might also contribute to the relative enrichment of K\(^+\) in the groundwater (Mukherjee et al., 2009b). To trace the origin of Cl\(^-\) enrichment in the groundwater of GSA, Cl\(^-\) was plotted against Na\(^+\) (Fig. 27). The previous mineralogical studies of aquifer sediment from the study area by Gault et al. (2005), Nath et al. (2005, 2008a) and Charlet et al. (2007) did not report the presence of Cl\(^-\) in the sediment. In absence of any potential source of Cl\(^-\) within the aquifer sediment, the Cl\(^-\) content in groundwater might be due to atmospheric deposition and mixing with connate sea water. In Bangladesh, von Brömssen et al. (2007) have reported the enrichment of Cl\(^-\) and higher EC in the BSA due to mixing with connate sea water. However in the present study area, the enrichment of Cl\(^-\) in shallow GSA compare to deeper BSA discards the possibility of mixing with connate sea water. Furthermore, if Cl\(^-\) content in groundwater is entirely of meteoric origin, it should be balanced by equivalent Na\(^+\). However, the bivariate plot of Na\(^+\) versus Cl\(^-\) indicates that despite higher extent of cation-exchange in the GSA, in some groundwater samples the ratio of Cl\(^-\) to Na\(^+\) is greater than 1 and this ratio is always less than 1 for the groundwater of BSA. This might indicate that the enrichment of Cl\(^-\) in groundwater of GSA is of anthropogenic origin such as agricultural return flow, septic tank, domestic waste water etc (Jacks et al., 1999; Rajmohan and Elango, 2006; Nath et al., 2008c; McArthur et al., 2012a). By doing an isotopic study Lawson et al. (2008) have already reported the recharge of evaporated surface water, which might get an input from domestic waste water as well as agricultural return flow (Charlet et al., 2007; Mukherjee et al., 2007b), to the shallow aquifers of this study area.

5.3.2. Site specific vertical evolution (Paper III)

The bulk mineralogical investigation at the two piezometer installation sites indicates the abundance of carbonate and silicate minerals in the aquifer sediment further supporting their role in controlling major ion composition of the groundwater. However, considerably higher enrichments of Ca\(^{2+}\), Mg\(^{2+}\) and HCO\(_3\) over Na\(^+\) and K\(^+\) in groundwater at both sites again indicates that carbonate minerals dissolutions are prevailing in the aquifers. The calculation of SI for calcite and dolomite further support this inference, as groundwater at both sites is at near equilibrium to slightly supersaturate with respect to these minerals (Paper III).

As mentioned before, the concentrations of the major ions are relatively high in groundwater of well A & B and decrease with increasing depth at site 1 (Fig. 14) reflecting that minerals dissolutions are extensive in the upper most part of the shallow aquifer. Now the question is which factors are responsible for this increased rate of minerals dissolutions in well A & B. In aquifers, the rate of carbonate and silicate minerals dissolution is controlled by the availability of the mineral content in the aquifer sediment and supply of proton (H\(^+\)) in the aquifers (Appelo and Postma, 2005). As mineralogical investigation indicates that these minerals are abundant in the aquifer sediments, probably the availability of H\(^+\) is
the rate limiting for the minerals dis- solutions. Two different possibilities can be accounted for the supply of H⁺ in the aquifers. First possibility is the enrichment of Pₐₒ₂ in the aquifer either through degradation of the OC, which is usual in the reducing aquifers (Harvey et al., 2002; Postma et al., 2007) or by root respiration, which is essentially confined only to the soil horizon (Appelo and Postma, 2005). However, the concentration of NH₄⁺, which is often considered as the bio-indicator for the degradation of OC (Bhattacharyya et al., 2002; Harvey et al., 2002; Bhattacharyya et al., 2003; McArthur et al., 2004), is relatively high in the deeper part of the aquifer (Fig. 15), where the concentration of major ionic constituents is comparatively low (Fig. 14). Such decoupling possibly nullifies the link between organic matter degradation and enhanced minerals dissolution in the aquifer of study site, at least in the shallowest part. It seems that the downward diffusion below water table or transportation of CO₂ with recharge water from the soil horizon might accelerate the minerals dissolution in the shallowest part of the aquifer (Appelo and Postma, 2005). Since, the agricultural activities are intensive in the study sites; the accumulation of CO₂ in the soil horizon is very much likely (Appelo and Postma, 2005). The second possibility is that the availability of H⁺ can be coupled to the pyrite oxidation as follows (Appelo and Postma, 2005):

\[ \text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]

\[ \text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \frac{5}{2} \text{H}_2\text{O} = \text{Fe(OH)}_3 + 2\text{H}^+ \]

Though, the mineralogical investigation did not indicate the presence of detrital pyrites in the sediment, it can be formed authigenically during seasonal redox cycling of SO₄²⁻ as reported by Cheng et al. (2005). Possibly, in the period of dry season with the progressive lowering of piezometric head O₂ front enters into the aquifer and causes pyrite oxidation producing SO₄²⁻ and H⁺. In the period of monsoon, when anoxic condition develops in the aquifer SO₄²⁻ gets reduced and precipitates authigenic pyrites, which is again oxidized in the next dry season period. The time series data for Eh in groundwater also reflects the development of less reducing to oxidizing condition in the aquifer with the progress of dry season (Fig. 16). The possibility of pyrite oxidation and its relation to the increased carbonate and silicate minerals dissolution is reflected by the occurrence of comparatively high concentrations of SO₄²⁻ in well A and B (Fig. 15) and similar temporal variation of major cations, HCO₃⁻ and SO₄²⁻ in well B (Fig. 16).

The calculation of molar ratio of Cl⁻ to Na⁺ indicates that the ratio is predominantly >1 in groundwater of well A (range: 0.64 – 1.82, median: 1.40) & B (0.23 – 1.99, 1.38) and this ratio is mostly <1 for other wells (C: 0.40 – 1.03, 0.69; D: 0.25 – 0.77, 0.65; E: 0.18 – 1.26, 0.92) at site 1. This again supports that the relatively high Cl⁻ concentration in the shallowest part of aquifer is of anthropogenic origin (Jacks et al., 1999; Rajmohan and Elango, 2006; McArthur et al., 2012a). The recharge with surface water either through the pond at the immediate vicinity of piezometer installation site, which also gets input of domestic waste waters and agricultural run-off from the nearby paddy field or through sandy outcrops within surface aquitard at nearby site can be the potential source of Cl⁻ in these two wells. This is also consistent with the higher enrichment of ²H and ¹⁸O in the wells A & B of this site (Fig. 13). The higher enrichment of ²H and ¹⁸O in the wells A & B might indicate another possibility that evaporation/evapotranspiration could enrich the concentration of major ions in these wells over the dry period. However, the temporal variation of δ¹⁸O did not show any specific enrichment pattern over the dry periods for these wells (Fig. 16).

The similar concentrations of the major ions at different depths of the aquifer at site 2 (Fig. 14) possibly indicate that the rate of recharge at this site is relatively faster to make the aquifer homogeneous with respect to these ions. As mentioned in the section 2.2, a high yielding irrigation well is installed at depth of 24 m, around 75 m from the well installation site. It is very much likely that
the monitoring wells are within the influence zone of groundwater abstraction by this irrigation well, which increases the rate of vertical recharge and hence decreases the groundwater residence time substantially at this study site (Stute et al., 2007). The absence of any inter-bedded clay layer has further ensured the aquifer system to be easily homogenized. However, at present no groundwater dating is available from the study site to verify this hypothesis. Such inter-bedded clay layer neither presents at site 1 also (Fig. 10). Nevertheless, because of absence of any high yielding irrigation well at immediate vicinity, the natural groundwater flow system in the studied aquifer is mostly unperturbed at this site, ensuring vertical layering of groundwater composition in aquifer. The higher rate of recharge at site 2 is also consistent with the lower extent of water-sediment interactions, reflected by the lower concentration of the total dissolved solutes and EC (Fig. 14), and comparatively lower enrichment of $^2$H and $^18$O in groundwater of site 2, compared to site 1 (Fig. 13).

5.4. Mobilization of As, Fe and Mn in shallow aquifers (Paper I, II, III & IV)

5.4.1. Sedimentological controls on the spatial distribution of As, Fe and Mn (Paper I & II)

The dissolved concentration and distribution of As, Fe and Mn in the aquifers is primarily controlled by a series of different terminal electron accepting processes (TEAPs), coupled to the oxidative degradation of organic matter (Stumm and Morgan, 1981; Appelo and Postma, 2005). In the sequence of TEAPs, DO and NO$_3^-$ are reduced at first and subsequently redox status passes through the stages of Mn and Fe oxyhydroxides reduction, SO$_4^{2-}$ reduction to methanogenesis respectively (Fig. 6) (Stumm and Morgan, 1981). The reductive dissolution of Mn oxyhydroxides possibly releases both Mn as well as As into groundwater. Nevertheless, the released As is readily readsorbed onto Fe oxyhydroxides in the aquifer sediment (Stüben et al., 2003; Hasan et al., 2007). Only when the redox status reaches the stage of Fe oxyhydroxides reduction As is mobilized into groundwater together with Fe and retained in the aqueous phase (Bhattacharya et al., 1997; Nickson et al., 1998; McArthur et al., 2004; Mukherjee and Fryar, 2008; Biswas et al., 2011). In the transition period of redox status from Mn oxyhydroxides to Fe oxyhydroxides, Mn is often immobilized through precipitation of secondary mineral phases such as MnCO$_3$ and MnHPO$_4$ formed in presence of high HCO$_3^-$ and PO$_4^{3-}$ respectively, commonly found in reducing aquifers (Ahmed et al., 2004; Stollenwerk et al., 2007; von Brömssen et al., 2008). Furthermore, in anoxic groundwater Mn can also be immobilized by adsorption and/or co-precipitation onto siderite and calcite by forming metastable solid solutions (FeCO$_3$ – MnCO$_3$; CaCO$_3$ – MnCO$_3$), which further recrystallizes to pure mineral phases (Wersin et al., 1989; Saunders and Swann, 1992). A considerable amount of Mn incorporation into the carbonate mineral phases has been found in the aquifer sediments of two monitoring sites and different parts of Bengal Basin (Bhattacharya et al., 2001; Ahmed et al., 2004; Stollenwerk et al., 2007). Thus, in groundwater the enrichment of As often couples to enrichment of Fe and decouples to the enrichment of Mn (McArthur et al., 2008, 2011). In presence of high HCO$_3^-$ and PO$_4^{3-}$, Fe can also be immobilized through precipitation of FeCO$_3$ and Fe$_3$(PO$_4$)$_2$ respectively (von Brömssen et al., 2008), decoupling Fe and As enrichment in groundwater, which has been discussed in the following section. The equilibria of groundwater with respect to MnCO$_3$, MnHPO$_4$, FeCO$_3$ and Fe$_3$(PO$_4$)$_2$ also support the cycling of Mn and Fe in the aquifers of study area.

The close overlapping of spatial distribution of factor score of As mobilization and Mn immobilization factor (factor 2) with the distribution of GSA in the study area (Fig. 9a) and the positive loadings of As, Fe, NH$_4^+$ and PO$_4^{3-}$ together with negative loadings of Eh and Mn for this factor suggest that in GSA the redox status is lowered beyond the stage of Mn oxy-
hydroxides reduction. Currently reductive dissolution of Fe oxyhydroxides, possibly coupled to microbially mediated oxidation of organic matter is the prevailing redox processes, which causes high As groundwater in this aquifer. The high concentration of NH$_4^+$ and PO$_4^{3-}$ was produced during oxidation of organic matter (Harvey et al., 2002; Bhattacharyya et al., 2003). The PO$_4^{3-}$ in groundwater could also be released during reductive dissolution of Fe oxyhydroxides as well (van Geen et al., 2008a; von Brömssen et al., 2008). However in BSA, high enrichment of Mn along with low concentration of NH$_4^+$, PO$_4^{3-}$ and Fe suggest that the redox status is mostly limited to the stage of Mn oxyhydroxides reduction. The comparison of observed pe values with calculated pe values of Fe(III)/Fe(II) redox couple (Fig. 6) further supports the distinct redox zonation in the two aquifers. The positive loadings of DOC and NH$_4^+$ in combination with negative loading of SO$_4^{2-}$ for factor 3 might represent that even in some locations of GSA redox status has reached to the stage of SO$_4^{2-}$ reduction. The notable odor of H$_2$S in some samples of GSA further supports the ongoing SO$_4^{2-}$ reduction process. This SO$_4^{2-}$ reduction may sequester dissolved As to some extent from groundwater by co-precipitation with authigenic pyrite as reported in the aquifer sediment of the study area (Nath et al., 2008a).

It is already mentioned that after deposition, the aquifer sands of BSA have been exposed to atmosphere and oxidized extensively. During this atmospheric oxidation, because of increased hydraulic gradient the BSA was further flushed with oxic water, which also maintains the comparatively higher redox status at BSA (McArthur et al., 2004; von Brömssen et al., 2007). The burial of BSA by the post oxidation stage Holocene sediments deposition could not even alter the redox status. In this context the olive to pale blue and brown colored clay layer, which caps the BSA might play a key role by protecting the underlying BSA from the vertical recharge of As and DOC rich groundwater from the overlying Holocene sediments, as discussed elsewhere in western Bengal Basin (McArthur et al., 2008; 2011). Relatively very high concentration of Mn, Fe and As in groundwater along the margin of BSA and GSA, is probably because of development of overlapping redox fronts of Mn and Fe oxyhydroxides reductions (Mukherjee et al., 2008) by lateral focused recharge of DOC rich groundwater to BSA through channel fill aquifer sand of GSA (McArthur et al., 2012b). At Barasat, the study by McArthur et al. (2012b) has further reported that the concentration of Mn in the interior of BSA is in the range of 200 – 400 µg/L. However in the present study area, the concentration of Mn often exceeds 400 µg/L in the interior of BSA (Fig. 5). Furthermore, though the number is very small, in few wells the concentration of Fe and As also exceeds 5 mg/l and 50 µg/L respectively in the interior of BSA (Fig. 5), reflecting that the overlapping redox condition is also sometimes prevailing even in the interior of BSA. Secondly, the As sorption ability of the aquifer materials of BSA could also play a key role in maintaining low As concentration in groundwater (Stollenwerk et al., 2007; Radloff et al., 2011; Robinson et al., 2011). However in the present study area, the BSA is being capped everywhere by impermeable brown clay layer, the sorption of As to aquifer materials might be limited along the margin only.

5.4.2. Vertical distribution of As in groundwater of shallow aquifer (Paper III)

The outcome of the geochemical characterizations of aquifer sediment that Fe oxyhydroxides are the predominant hosts of As in sediment of both the monitoring sites and the positive association of Fe and As in groundwater of most of the wells, where Fe(II) and As(III) are also prevailing species of dissolved Fe and As respectively (Paper III), further support the view that As is primarily mobilized into groundwater through the reductive dissolution of Fe oxyhydroxides (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; Bhattacharya, et al., 2002; Harvey et al., 2002; Stüben et al., 2003; McArthur et al., 2004). The enrichment of NH$_4^+$ and PO$_4^{3-}$ in ground-
water of the two sites (site 1 – range: 1.87 – 4.22 mg/L; median: 2.88 mg/L; site 2 – range: 0.54 – 3.26 mg/L; median: 2.39 mg/L) again indicates that the microbially catalyzed degradation of organic matter is closely related to the progress of these redox processes in the aquifer (Nickson et al., 2000; McArthur et al., 2001; Bhattacharyya et al., 2002; Bhattacharyya et al., 2003; McArthur et al., 2004). The vertical distribution of As is possibly related to the redox zonation within aquifer at the two sites. At both the sites, the overall decreasing trend of DOC with increasing depth and relatively higher enrichment of NH$_4^+$ and PO$_4^{3-}$ possibly reflects stronger reducing condition in the deeper part of aquifer, which might be responsible for relatively higher enrichment of As at this part of aquifer. Furthermore, the relatively low reducing condition in the shallower part of aquifer at site 1 is also reflected by the presence of high concentration of SO$_4^{2-}$ (Fig. 15). At both sites, the lowest enrichment of As in well A does not support the hypothesis that As is released in the water table fluctuation zone and then transported to the well screen depth, as proposed by previous studies in Bangladesh and Cambodia (Polizzotto et al., 2005, 2008). Rather as mentioned before, the high accumulation of As and other trace elements with the abundance of Fe and Mn oxyhydroxides in the water table fluctuation zone (site 1: 2.05 – 4.65 m; site 2: 1.45 – 3.85 m) indicates that this zone could be the potential sink instead of source at the study sites (Neidhardt et al., 2013a). The lower enrichments of As and most other aqueous redox parameters in groundwater of site 2 compared to site 1 (Fig. 14 and Fig. 15) is possibly the result of aquifer flushing and lower extent of sediment-water interactions, influenced by the groundwater abstraction (Stute et al., 2007; van Geen et al., 2008a).

It is of worth noting that at site 1, though, the groundwater in well A & B is comparatively more enriched with dissolved Fe, the concentration of As is relatively low; again in well C though, the concentration of As is highest among the five wells, the concentration of Fe is lowest (Fig. 15), apparently reflecting the decoupling of As and Fe release into groundwater in these wells (Horneman et al., 2004; van Geen et al., 2004, 2006). It is likely that in well A & B, the Fe oxyhydroxides reduction is not the sole processes responsible for Fe enrichment. The weathering of silicate minerals, specifically of biotite coupled to the pyrite oxidation (as discussed in the previous section), could be the additional source of dissolved Fe in groundwater (Seddique et al., 2008). This is also consistent with the results of sequential extraction, which indicate that Fe is largely associated with the silicate minerals in the aquifer sediments (Fig. 11). It should be mentioned here that during oxidation of pyrite some Fe could also be immobilized because of oxidation to Fe(III), however, it can contribute Fe(II) into groundwater, when oxidation is limited by the availability of O$_2$ in the aquifer (Appelo and Postma, 2005). Possibly, the measured concentration of Fe in groundwater of well A & B at site 1 is the net results of Fe oxyhydroxides reduction, pyrite oxidation coupled to silicate weathering and authigenic pyrite precipitation. It seems that the consideration of the presence of Fe(II) in groundwater as the indicator for ongoing Fe oxyhydroxides reduction in the aquifer is not always justified. Previous studies have also accounted the weathering of silicate minerals as the source of As in groundwater (Dowling et al., 2003; Charlet et al., 2005; Chakraborty et al., 2007; Charlet et al., 2007; Seddique et al., 2008; Chakraborty et al., 2011). However, as indicated by the sequential extraction, the concentration of As in the crystal lattice of silicate minerals is negligible (Fig. 11). Thus, weathering of silicate minerals does not significantly contribute to the As enrichment in groundwater in the study sites. This provides the explanation for the occurrence of comparatively low concentration of As in Fe rich groundwater of well A & B of site 1 (Fig. 15). In well C, though, the high As concentration in groundwater is accompanied with low Fe concentration, the variations of As and Fe are mutually
correlated very strongly and positively ($r = 0.81, n = 33$) (Paper III). Despite high concentration of Mn at this well, the correlation of As with Mn is not significant ($r = 0.28, n = 33$) (Paper III). This reflects that at this well As is also very likely mobilized through the reductive dissolution of Fe oxyhydroxides. As reported by Horneman et al. (2004) for the aquifer sediment of Araihazar, Bangladesh, possibly at this aquifer depth of site 1 also, the reduction of Fe oxyhydroxides mostly proceeds with the formation of new authigenic Fe(II) or Fe(II/III) phases, like magnetite, rather than releasing Fe(II) in groundwater and thus results in high As groundwater with low Fe content. In anoxic groundwater the concentration of Fe(II) can also be limited by precipitating secondary minerals like siderite and vivianite (van Geen et al., 2004; Postma et al., 2007; von Brömmssen et al., 2008). The calculation of SI for these minerals also reveals that their precipitations are thermodynamically favorable in the aquifer of both study sites (Paper III). Though, the mineralogical identification by XRD (detection limit: ~1%) does not indicate the presence of these minerals, the extraction with 1 M HCl releases second largest pool of Fe from the sediment samples at both sites (Fig. 11), indicating its association in some extent with the carbonate minerals in the aquifer. The precipitation of siderite in the aquifer of West Bengal has already been reported by Pal et al. (2002). Previous studies have reported that the precipitation of these secondary minerals can also immobilize As through adsorption (Islam et al., 2005). However, the sequential extraction results indicate that though for the sediments of site 2 the second largest pool of As is released in extraction with 1 M HCl, the amount is very low for the sediment of site 1 (Fig. 11). This reflects that in case of site 2 there is possibility of co-precipitation of As with these minerals, while at site 1 the precipitation of the secondary minerals to some extent might be responsible for decoupling of As and Fe enrichment in groundwater. Precipitation of these minerals resulting in decoupling of As and Fe in aqueous phase has already been reported both in laboratory and field studies (van Geen et al., 2004; Burnol et al., 2007; Burnol and Charlet, 2010).

5.4.3. Processes regulating the seasonal variation of As in shallow aquifer (Paper III)

Two different possibilities can be accounted to explain seasonal variation of As in well B at site 1 and at present it is difficult to determine which one, if not both, is the predominating processes resulting in the observed variation. The first possibility is that the seasonal cycling of As is closely related to the cycling of SO$_4^{2-}$ as discussed by Cheng et al. (2005). In the dry period the pyrite oxidation leads to the formation of Fe oxyhydroxides, which immobilize As through adsorption. In the following period of monsoon with the recharge of groundwater again gradually anoxic condition develops in the aquifer. The development of anoxic condition leads two processes to occur simultaneously: i) remobilization of As through reductive dissolution of Fe oxyhydroxides and ii) precipitation of authigenic pyrites without sequestering As from the aqueous phase has already been reported in laboratory and field studies (Bostick et al., 2004; van Geen et al., 2004). However, it is not clear why it took longer time to develop anoxic condition following the monsoonal recharge in 2009 compared to 2010 (Fig. 16). One speculation is that the oxidizing condition in the shallowest part of the aquifer in 2009 was stronger compared to 2010, possibly because of air compression into the well A for well development after installation in November 2008. However, then another question should arise why the As concentration in well A did not response to the air compression. It is worth to recall here that As concentration in well A showed a trend of continuous increase over the monitoring period (Fig. 16). Such a steady increment in As concentration could be
linked to the gradual development of anoxia because of continuous seepage of organic rich evaporative surface water at this aquifer depth, as reflected by similar continuous enrichment of $^{18}$O over the monitoring period (Fig. 16). This gradual development of anoxia probably overruled the influence of $O_2$ during dry season in 2009 and 2010. Additionally, the evaporation/evapotranspiration could also play a role in the continuous increase in As concentration and $^{18}$O in well A.

The second plausible explanation for the observed seasonal variation of As concentration in well B is that in the dry period As is scavenged into the colloidal aggregates formed in presence of DOC at comparatively higher ionic strength caused by higher mineralization and during monsoon As is remobilized because of dispersion of the colloidal aggregates by dilution with recharge water (Planer-Friedrich et al., 2012). In well B, the decreasing trend of As with increasing trends for major cations and anions in the dry period (Fig. 16) supports this hypothesis. However, this hypothesis again cannot also explain why As concentration did not increase during wet period of 2009. Sometimes vertical displacement of groundwater layer has been also accounted for the seasonal variation of As in shallow aquifer (Cheng et al., 2005). However, the fact that As concentration in well B started to increase just at the onset of monsoon in 2010 (Fig. 16) discards the possibility that As was increasing due to upward shift of As rich groundwater layer from well C to the screen position of well B. Because in that case a time delay, which is necessary for 1 m (difference between two screen positions) upward shift of groundwater layer is expected between the starting of monsoon and increase of As concentration in well B. Further, in that case a similar increase in As concentration in well B after starting of monsoon was expected also in the year 2009. The fluctuation of redox conditions in the aquifer during dry and wet period and their control over the seasonal variation in As concentration is more evident in well C at site 1, where the concentration of total As, abundance of As(III) and concentration of Fe decreased drastically during the dry period and started to increase just at the onset of monsoon in 2010 (Fig. 16). It should be noted here that As concentration in well C did not show a similar seasonal variation in 2009. Possibly, the redox condition was relatively more oxidizing during the dry period in 2010 because of greater drawdown (~0.5 m) of groundwater table in this year (Fig. 12).

At site 2, the trend of As enrichment during dry period in well A (Fig. 16) was possibly linked to the increased groundwater abstraction by the nearby irrigation well at that period for the Boro rice cultivation. The increased groundwater abstraction could influence the As concentration either by migrating As plume from the nearby contaminated site (Charlet et al., 2007) or by perturbing the local redox equilibriums through mixing with organic rich water and thus triggering the As mobilization at this aquifer depth (Harvey et al., 2002). The concentration of As decreased at the onset of monsoon at both years possibly because of dilution with recharge water (Planer-Friedrich et al., 2012).

5.4.4. Relative roles of competing ions and pH on As mobilization in shallow aquifer (Paper IV)

In order to estimate the relative roles of competing ions and pH on the As mobilization, the sensitivity of the modeled aqueous As(III) and As(V) concentrations towards the changes in the concentration of competing ions and pH was investigated (Fig. 28). The sensitivity test was performed by the simulation of only the D&M SCM for the well E of site 1. The D&M SCM was chosen as it better predicts the temporal variation of As at both sites over the whole monitoring period. For the sensitivity test, only the concentration of the selected parameter of interest was varied (-100% to +100%, except for pH, which was varied -5% to +5%) in the simulation, while keeping concentration of other parameters fixed to the measured value. The results indicate that in the aquifer $PO_4^{3-}$ is the major competitor of As(III) and As(V) adsorption onto Fe...
Fig. 28. Sensitivity of the modeled aqueous As(III) and As(V) concentration towards the change in pH and concentration of competing ions. A sensitivity test was performed by the simulation of D&M SCM by equilibrating the groundwater samples of well E of site 1. In the sensitivity test only the value of selected parameter of interest was varied (-100% to +100%, except for pH, which was varied -5% to +5%), while keeping other parameters fixed to the measured value, in the simulation.

oxyhydroxides (Fig. 28) and the competition ability of the different ions decreases in the order PO_4^{3-} >> Fe(II) > H_2SiO_4 = HCO_3^-.

In the simulation, when dissolved concentration of PO_4^{3-} is set to zero, the modeled concentration of both As(III) and As(V) is reduced on average by 92.5%. However, a similar imposition for the concentration of Fe(II), H_2SiO_4 and HCO_3^- in the simulation only reduces the As(III) concentration by 12.2%, 7.40%, and 7.04% respectively (Table 5). Phosphate, Fe(II) and H_2SiO_4 appears to be equally effective to compete with both As(III) and As(V), while HCO_3^- competes more strongly with As(V) as compared to As(III) (Table 5). Though
previous studies have concluded that Fe(II) does not affect the re-sorption of As onto residual Fe oxyhydroxides (Appelo et al., 2002; Dixit and Hering, 2006), our results indicates a small but significant competition between Fe(II) and As for adsorption sites. It is further observed that the As concentration does not vary linearly with the change in PO$_4^{3-}$ concentration. Although, the As(III & V) concentration is reduced by 92.5% when the PO$_4^{3-}$ concentration is set to zero in the simulation, it is increased by only 31.4% when the PO$_4^{3-}$ concentration is doubled (Table 5). This demonstrates that in the aquifer the competition of PO$_4^{3-}$ with As for the adsorption sites might already reach close to maximum level. In contrast, the relations with the other competing ions are still linear (Table 5). Thus, the present study suggests that only the reductive dissolution of Fe oxyhydroxides cannot explain the observed high As concentration in the groundwater of Bengal Basin. In the absence of potential competition for the adsorption sites, the As released by the reductive dissolution of Fe oxyhydroxides would have been re-adsorbed onto the residual Fe phases. It appears that the reductive dissolution of Fe oxyhydroxides followed by competitive ion exchange with the aquifer sediment is the processes conducive for As enrichment in the sedimentary aquifers. The reductive dissolution of Fe oxyhydroxides coupled to the mineralization of organic matter leads to the release of As together with Fe(II) and PO$_4^{3-}$ (van Geen et al., 2008a; von Brömssen et al., 2008). The released PO$_4^{3-}$ and Fe(II) then compete with As for re-sorption onto the residual Fe-oxyhydroxides and thus maintain a high dissolved As concentration in the groundwater. This mobilization processes is consistent with the findings of high level of PO$_4^{3-}$-exchangeable As in the aquifer sediment at two monitoring sites. Additionally, this mobilization processes provides a satisfactory explanation for the observed high molar ratio of Fe to As in the aquifer sediment compared to that in the contacting As rich pore water in the reduced aquifer (Dixit and Hering, 2006).

Some studies have also concluded that Ca$^{2+}$ can enhance the adsorption of As(V) onto Fe oxyhydroxides significantly particularly at high pH, by reducing the surface negative charge (Stachowicz et al., 2008). In contrast, recently Saalfield and Bostick, (2010) have suggested that the adsorption of Ca$^{2+}$ or Mg$^{2+}$ together with HCO$_3^-$ can increase the desorption of As(V) from ferrihydrite to a greater extent compared to their individual competition. To this end a sensitivity test was performed by changing the concentrations of these ions in different combinations. The results indicate that the change in concentration of Ca$^{2+}$ and Mg$^{2+}$ together with HCO$_3^-$ affect the adsorption of both As(III) and As(V) to Fe.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Change in parameters (%)</th>
<th>Change in conc. of As(III) (%)</th>
<th>Change in conc. of As(V) (%)</th>
</tr>
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<td>-50.0</td>
<td>-23.3</td>
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<tr>
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<td>+50.0</td>
<td>+17.2</td>
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<td></td>
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</tr>
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<tr>
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<td>-50.0</td>
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<td></td>
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</tr>
<tr>
<td>HCO$_3^-$</td>
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<tr>
<td></td>
<td>+100</td>
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**Table 5.** Average change in modeled aqueous As(III) and As(V) concentration for the samples collected from well E of site 1 in response to the variation in pH and concentration of different competing ions. The '-' & '+' signs indicates the decrease and increase of the value respectively.
oxyhydroxides almost negligibly (Appendix Fig. A.3 of Paper IV).

The results further indicate that the pH value also has a strong influence on the mobility of As(III) and As(V) in the aquifer by changing their concentration oppositely to each other (Fig. 28). A 5% decrease in pH increases the As(III) concentration by 65.3% and decreases the As(V) concentration by 91.2% on average, representing greater influence on the As(V) mobility. The influence on the As(V) mobility becomes even more prominent during increase of pH (Table 5). The ease of formation of the major surface complexes for As(III) and As(V) determines their different behavioral pattern towards the change in pH. In the D&M SCM, the major surface complex for As(III) and As(V) are $\text{Fe}_\text{wH}_2\text{AsO}_3$ and $\text{Fe}_\text{wHAsO}_4^-$, respectively. With a decrease of pH the formation of these complexes and consequently the adsorption of As(III) and As(V) are constrained and favored respectively. Moreover, as reflected in the modeled speciation of surface complexes formed in the D&M SCM (Fig. 19), with a decrease of pH the protonation of the weak sites would be increased making them less available for As(III) adsorption. At the same time the protonation of the weak sites reduces the surface negative charge and consequently decreases the electrostatic repulsion during adsorption of negatively charged oxyanions of As(V). At high pH, this electrostatic repulsion becomes so prominent that the desorption of the oxyanions of As(V) increases drastically.

5.5. Targeting safe aquifer within shallow depth: consequences for drinking water supply (Paper I & II)

The subsurface lithological investigation of the present study indicates that BSA is distributed to a significant extent over the study area within drilling depth (<50 m bgl), targetable by locally available low-cost drilling technology. The concentration of As in groundwater from BSA rarely exceeds the WHO provisional drinking water guideline of 10 µg/L (Fig. 4). This indicates the possibility that installation of TWs at BSA can be an alternative source of As safe drinking water to the population in As affected regions of Bengal Basin. However, it is worth to recall here that though the concentration of dissolved As in groundwater of BSA is very low, the concentration of dissolved Mn is significantly higher than previous WHO drinking water guideline as well as Indian national drinking water standard (Fig. 4). It should be mentioned here that recently WHO has withdrawn the drinking water guideline for Mn by reasoning that worldwide commonly observed concentrations of Mn in drinking water sources are well below the health based guideline value of 400 µg/L (WHO, 2011). However, the results presented here contradict with the reason proposed by WHO and warrant re-evaluation of drinking water guideline for Mn in near future. Present study suggests that the underlying health risk of Mn in drinking water needs to be addressed more rigorously before considering mass scale exploitation of BSA for sustainable drinking water supply. However, considering the severity of As health risk in rural Bengal due to the limited availability of As safe drinking water sources, the BSA can be targeted temporarily for As safe drinking water with regular monitoring program until alternate As as well as Mn safe drinking water sources are explored and made available to the affected population.

5.6. Application of TW platform color as a rapid screening tool for As and Mn in drinking water wells (Paper V)

This study validates that TW platform colors are potential indicator for rapid screening of dissolved As and Mn in well water, that can be introduced at the policy level together with spot check measurement by field test kits, to tackle the problems regarding identifying safe drinking water supply. It can be used as a primary guide during regional screening of TWs for dissolved As and Mn in drinking water, to exclude a significant percentage of TWs at the preliminary stage from further rigorous groundwater testing.
Thus the effort, time and cost for the screening can be reduced significantly. The prime advantage of platform color tool is its simplicity. It does not require any expertise for the field application. The rural villagers, who practically have no access to laboratory or any field test kits, can apply this tool to identify their TWs as safe or unsafe. Accordingly people themselves can identify the patches of TWs with high and low As water. This may lead to reduce As exposure, at least in short term by switching drinking water source from unsafe to nearest safe TWs (van Geen et al., 2003). Platform color may also act as an indicator during the post TW switching period to monitor the level of As in the drinking water wells. Moreover local driller can use this tool to identify the BSA, which is primarily safe for As, for new TW installation (McArthur et al., 2011). Thus systematically low As aquifer can be targeted for sustainable drinking water supply.

6. Conclusions

6.1. Shallow hydrostratigraphic framework: sedimentological controls on the spatial distribution of As, Fe and Mn in groundwater (Paper I & II)

The drilling of 29 boreholes and subsequent hydrostratigraphic modeling has identified three aquifers within 50 m bgl. Aquifer-1 represents thick palaeo channel sequence, distributed in parallel to River Hooghly and Ichamati. Aquifer-2 is formed locally within overbank deposits in the central floodplain area and its vertical extension is strictly limited within 25 m bgl. Aquifer-3 is formed underneath of the floodplain overbank deposits and represents interfluvial aquifer of the area. Aquifer-3 is of Pleistocene age, while aquifer-1 and 2 essentially represents the Holocene deposits. The aquifer-3 is markedly separated from the overlying Holocene deposits by the successive upward sequences of brown and olive to pale blue impervious clay layers. The groundwater quality is very much similar in aquifer-1 and 2, where the concentration of As and Fe very commonly exceeds 50 µg/L and 5 mg/L respectively. Thus, because of grey color of the aquifer materials these two aquifers are jointly designated as GSA, which constitute 40% (1.84 × 10^5 m^3) of the total drilled volume. In aquifer-3, the concentration of As and Fe is very low, mostly <10 µg/L and 1 mg/L respectively. This aquifer has been designated as BSA because of brown color of the aquifer materials and represents 10% (4.8 × 10^4 m^3) of the total drilled volume. The detailed hydrogeochemical characterization indicates that despite close similarity in major ion composition, the redox condition is markedly different in groundwater of BSA and GSA. The redox condition in BSA is delineated to be Mn oxyhydroxides reducing, not sufficiently lowered for As mobilization into groundwater. Thus despite low concentration of As the concentration of Mn often exceeds 400 µg/L. In contrast, the enrichments of NH₄⁺, PO₄³⁻, Fe and As along with lower Eh in groundwater of GSA reflect reductive dissolution of Fe oxyhydroxides coupled to microbially mediated oxidation of organic matter as the prevailing redox process causing As mobilization into groundwater of this aquifer type. In some portions of GSA the redox status even has reached to the stage of SO₄²⁻ reduction, which to some extent might sequester dissolved As from groundwater by co-precipitation with authigenic pyrite.

6.2. Geochemical processes regulating vertical and temporal variation of As in shallow aquifer (Paper III)

A detailed sediment geochemistry has been combined to a high resolution hydrogeochemical monitoring study over 20 months at the two sets of piezometers (2 × 5) to explain geochemical processes that regulate vertical and temporal variation of As in shallow aquifer. The results indicate that the lithology, mineralogy and vertical profiles of major and trace elements in the aquifer sediment of two sites is mostly similar. At both sites As is mainly bound to the amorphous to crystalline Fe oxyhydroxides in the aquifer sediment and readily exchangeable with PO₄³⁻. The
determination of isotopic composition of δ²H and δ¹⁸O in groundwater of two sites indicates the recharge of evaporative surface water to the aquifer. The recharge of surface water could also transport DOC into aquifer, at least to the shallowest part. The site specific vertical distribution of major aqueous solutes, EC, δ²H and δ¹⁸O in the aquifer could be linked to the local geochemical and hydrological (extent of groundwater abstraction) conditions. This study supports the view that reductive dissolution of Fe oxyhydroxides coupled to the degradation of organic matter is the processes that mobilize As in the aquifer. However, the decoupling of As and Fe release into groundwater is evident in the shallowest part of aquifer (<24 m bgl). Such decoupling could be the consequence of Fe enrichment in groundwater by processes other than reductive dissolution of Fe oxyhydroxides, such as weathering of silicate minerals, especially of biotite, which does not release significant As in groundwater of study sites. Additionally, the precipitation of secondary mineral phases like siderite and vivianite and incomplete reduction of Fe oxyhydroxides leading to the formation of secondary Fe(II) or Fe(II/III) phases like magnetite can also be responsible for such decoupling of As and Fe in shallow groundwater. The vertical distribution of As within the aquifer can be explained in terms of redox zonation. The seasonal variations of As and other aqueous solutes are limited within the upper portion of aquifer only (<30 m bgl) and can be related to seasonal cycling of redox status, aggregation and dispersion of As scavenging colloids, local groundwater abstraction and monsoonal recharge.

6.3. Role of competing ions and pH on As mobilization (Paper IV)
This study has estimated that among the competing ions, PO₄³⁻ is the major competitor of As(III) and As(V) adsorption onto Fe oxyhydroxides and the competition ability decreases in the order PO₄³⁻ >> Fe(II) > H₃SiO₄ = HCO₃⁻. It is further revealed that a small change in pH can also have a significant effect on the mobility of As(III) and As(V) in the aquifers. A decrease in pH increases the concentration of As(III), while decreases the As(V) concentration and vice versa. The present study suggests that the reductive dissolution of Fe oxyhydroxides alone cannot explain the observed high As concentration in groundwater of the sedimentary aquifers. This study supports the view that the reductive dissolution of Fe oxyhydroxides followed by competitive sorption reactions with the aquifer sediment is the processes conducive for As enrichment in groundwater of Bengal Basin.

6.4. Recommendation for targeting safe aquifer within shallow depth for drinking water supply (Paper I & II)
The present study indicates that BSA, where the concentration of dissolved As is primarily <10 μg/L, is distributed to a significant extent over the study area within drilling depth (<50 m bgl), targetable by locally available low-cost drilling technology. However, despite low concentration of As, the concentration of Mn very often exceeds 400 μg/L, a health based guideline value. Thus, this study warrants rigorous assessment of attendant health risk for Mn prior to considering mass scale exploitation of the BSA for possible sustainable drinking water supply. However in the area, where no alternative As safe drinking water source is available, considering the severity of As toxicity BSA can be targeted temporarily for drinking water supply, until both As and Mn safe drinking sources are made available to the population.

6.5. Recommending TW platform color as a screening tool for As and Mn in well water (Paper V)
This study demonstrate that TW platform colors can be potentially used as a rapid screening tool for identifying TWs with elevated dissolve As and Mn in well water. Thus checking platform colors can be implemented as an initial screening tool to make TW screening for the contaminates more intensive and to prioritize As mitigation management by demarcating the safe aquifers regionally.
7. Future Scope of Research

Although, a critical understanding has been developed through the research undertaken in the present study, still few questions are open, which need to be addressed in future research in order to provide further insight of As mobilization and its distribution in the subsurface aquifers and for better management of groundwater resources in Bengal Basin. Some examples are as follows:

i) Few recent investigations have reported that not the quantity of organic matter, but the nature of organic matter is important in the As mobilization processes (Rowland et al., 2006, 2007, 2009; Lawati et al., 2012). In future research, it would be interesting to investigate how the nature of organic matter vary in the sites with high and low As concentration in groundwater, in other words the control of organic matter on the spatial distribution of As in groundwater. Furthermore, organic matter is known for playing dual role, as an electron donor and electron shuttle, in the As mobilization processes (Rowland et al., 2007; Mladenov et al., 2010). Few recent investigations indicate that organic matter can also form complex with As and Fe (Gustafsson et al., 2007; Sharma et al., 2010, 2011; Langer et al., 2012). It is worth for future research to investigate how the formation of these complexes affect the redox potential of the redox couples like Fe(III)/Fe/(II) and As(V)/As(III) and formation vis a vis stability of different colloids in the aquifer and their consequences on the As mobilization processes.

ii) The surface complexation modeling of the present study indicates that the competing ions especially $\text{PO}_4^{3-}$ do have role in the arsenic mobilization processes. In future research it would be of great interest to validate this modeling result by performing laboratory based mechanistic study of As desorption from sediments under different boundary conditions (e.g. availability and unavailability of $\text{PO}_4^{3-}$ and DOC and biotic and abiotic control).

iii) Two SCMs and the corresponding data bases used in the present study are originally developed for the sorbent of pure ferrihydrite and goethite Fe oxides. However, under field condition the actual adsorbent is not any pure mineral phases, but a composite one of multiple mineral phases, which could be impure and much more heterogeneous as well (Hiemstra et al., 2010; Jessen et al., 2012). So far only few studies (for e.g. Stollenwerk et al., 2007; Nath et al., 2009; Itai et al., 2010; Chakraborty et al., 2013) have investigated the adsorption of As to the natural aquifer sediments. Furthermore, the surface complexation data base for the modeling of adsorption of As and other metal and metalloids and anions to the natural soils and sediments is not well developed. Such development could ensure better prediction of contaminants transport in the soils and sub-surface aquifers and warrants future research.

iv) It would be of great interest also to study how groundwater composition evolves along the flow path, which could provide an insight of the spatial distribution of As in groundwater. Such kind of study is lacking in Bengal Basin.

v) Furthermore, substantial research is necessary for the identification of safe aquifers for the supply of drinking water, which would comply with the health based drinking water guideline for other contaminants (for e.g. Mn) as well with As. The assessment of long term sustainability of these aquifers for safe drinking water supply would also be of great interest.
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