



Mineralogical profiling of alluvial sediments from arsenic-affected Ganges–Brahmaputra floodplain in central Bangladesh

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ABSTRACT

Mineral assemblages (heavy and light fractions) and sedimentological characteristics of the Quaternary alluvial aquifers were examined in the central Bengal Basin where As concentrations in groundwater are highly variable in space but generally decrease downward. Chemical compositions of sediment samples from two vertical core profiles (2–150 m below ground level, bgl) were analyzed along with groundwater in moderately As-enriched aquifers in central Bangladesh (Manikganj district), and the As mobilization process in the alluvial aquifer is described. Heavy minerals such as biotite, magnetite, amphibole, apatite and authigenic goethite are abundant at shallow (<100 m below ground level (mbgl)) depths but less abundant at greater depths. It is interpreted that principal As-bearing minerals were derived from multiple sources, primarily from ophiolitic belts in the Indus-Tsangpo suture in the north-eastern Himalayan and Indo-Burman Mountain ranges. Authigenic and amorphous Fe-(oxy)hydroxide minerals that are generally formed in river channels in the aerobic environment are the major secondary As-carriers in alluvial sediments. Reductive dissolution (mediated by Fe-reducing bacteria) of Fe-(oxy)hydroxide minerals under anoxic chemical conditions is the primary mechanism responsible for releasing As into groundwater. Authigenic siderite that precipitates under reducing environment at greater depths decreases Fe and possibly As concentrations in groundwater. Presence of Fe(III) minerals in aquifers shows that reduction of these minerals is incomplete and this can release more As if further Fe-reduction takes place with increased supplies of organic matter (reactive C). Absence of authigenic pyrite suggests that SO₄ reduction (mediated by SO₄-reducing bacteria) in Manikganj groundwater is limited in contrast to the southeastern Bengal Basin where precipitation of arsenian pyrite is thought to sequester As from groundwater.

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1. Introduction

Arsenic enrichment in drinking water-supplies poses a serious concern for the public health in many countries around the world including the Ganges–Brahmaputra–Meghna (GBM) Delta in Bangladesh and West Bengal, India where tens of millions of people are currently exposed to dangerous levels of the As (Bhattacharya et al., 1997; Acharyya et al., 2000; Smith et al., 2000; BGS and DPHE, 2001; Stüben et al., 2003; van Geen et al., 2003; Ahmed et al., 2004; Shamsudduha et al., 2008). Although As-enrichment in groundwater is common in many other countries such as Argentina, Cambodia, China, Mexico, Nepal, Pakistan, Taiwan, USA and Vietnam (Smedley and Kinniburgh, 2002; World Bank, 2005; van Geen et al., 2008), the health-affect of As poisoning is felt more severely in Bangladesh due to its high population density (~1000 person per km², BBS, 2008). Studies of groundwater As over the last

few decades (BGS and DPHE, 2001 and references therein; Ahmed et al., 2004) have brought researchers to a general consensus that the occurrence of elevated As (>50 µg/L; Bangladesh drinking water standard is 50 µg/L) in alluvial aquifers in the Bengal Basin is geogenic and reductive dissolution of Fe(III)-oxyhydroxide minerals due to microbial metabolism releases As into groundwaters (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001, 2004; Islam et al., 2004; Zheng et al., 2005; Saunders et al., 2005; Shamsudduha et al., 2008). Many others have suggested that elevated As in aquifers can occur by other processes such as chemical weathering and dissolution of phyllosilicate minerals (Pal et al., 2002; Pal and Mukherjee, 2009), for example, dissolution of biotite (Sengupta et al., 2004; Shamsudduha, 2007; Seddique et al., 2008), reduction of magnetite (Pal et al., 2002; Swartz et al., 2004; Shamsudduha, 2007), and dissolution of apatite (Shamsudduha, 2007), or redox disequilibrium between phases (Mukherjee et al., 2008). High-As concentrations in sediments at very shallow depths (<50 m below ground level, bgl) are found to be associated with sulfide minerals such as pyrite (Polizzotto

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et al., 2005; Lowers et al., 2007). Some suggest that Fe-oxyhydroxides (Pal and Mukherjee, 2009) and sulfide minerals (Saunders et al., 2008) in aquifer sediments act as potential sinks for As. Release of As in groundwaters and its mobilization depends on a number of factors including redox conditions in aquifers, abundance of As-enriched minerals, organic matter (Rowland et al., 2007) to drive reduction of Fe minerals (e.g., Fe-oxy(hydroxides)), and groundwater flow (BGS and DPHE, 2001; McArthur et al., 2004, 2008; Ravenscroft et al., 2005; Harvey et al., 2006; Shamsudduha et al., 2009; Neumann et al., 2010; Burgess et al., 2010).

Identification of primary and secondary mineral sources of As in groundwater has been a topic of multi-faceted investigations in Bangladesh and West Bengal, India since the discovery of elevated

As in groundwater in the 1980s (e.g., BGS and DPHE, 2001; Pal et al., 2002; Shamsudduha et al., 2008). Most of these studies focused on the association between elevated As concentrations in groundwater and sediments (e.g., BGS and DPHE, 2001; Swartz et al., 2004; Lowers et al., 2007) and were mainly limited to shallow depth (<60 mbgl) in the aquifer. No study has provided any detailed mineralogical profiling (i.e., detrital and authigenic phases) of the As-enriched alluvial aquifers to highlight the heterogeneity in mineral assemblages and its influence on the spatially patchy distribution of As in aquifers. This study focuses on detailed mineralogical profiling of sediment core samples collected as deep as 152 mbgl from the central part of the Bengal Basin where aquifers are moderately enriched with dissolved As. The main objective of this



Fig. 1. Simplified geological and geomorphological map of the Bengal Basin and location of the study area in Manikganj district in Bangladesh.

study includes identification of detrital and authigenic mineralogical assemblages within As-enriched shallow aquifers (<100 mbgl) and As-safe deep aquifers (>100 mbgl), and potential carriers of As in aquifers and source areas in the Bengal Basin.

2. Bengal Basin: geology and geomorphology

The part of the Bengal Basin in Bangladesh is a large delta-dominated basin that comprises the proximal, eastern portion of the immense, asymmetric foredeep of the Himalayas (Uddin and Lundberg, 2004). The basin is bounded by the Himalayas to the distant north, the Shillong Plateau, a Precambrian massif, to the immediate north, the Indo-Burman ranges to the east, the Indian Craton to the west, and the Bay of Bengal to the south (Fig. 1; Uddin and Lundberg, 1998a). Formed by crustal loading during the Himalayan collision, this basin is over 20 km deep and spreads over 130,000 km² (Imam and Shaw, 1985; Allison, 1998), and is filled by synorogenic Cenozoic and Tertiary sequences derived

from both the eastern Himalayas and the Indo-Burman ranges (Allison, 1998; Uddin and Lundberg, 1998a,b; Mukherjee et al., 2009; Uddin et al., 2010). Geomorphologically, the Bengal Basin comprises of lowland river floodplains and delta plains, and is surrounded by the Tertiary hills of various origin (Goodbred and Kuehl, 2000). Within the basin, the Madhupur and Barind tracts, and the Lalmai hills comprise the Pleistocene inliers composed of highly mottled, deeply weathered and oxidized clays (Morgan and McIntire, 1959). Three major rivers, Ganges, Brahmaputra and Meghna drain through the basin to the Bay of Bengal in the south, where sediment is transported further south of the basin by turbidity currents to the Bengal deep-sea fan, the largest submarine fan in the world (Curry and Moore, 1971; Goodbred and Kuehl, 2000). Although much of the delta remains buried, marginal uplift has exposed stratigraphic sequences representing most of its depositional history.

Sediment deposition in the Bengal Basin has taken place in a variety of environments (Uddin and Lundberg, 1999; Goodbred and Kuehl, 2000) ranging from predominant fluvial (channels,

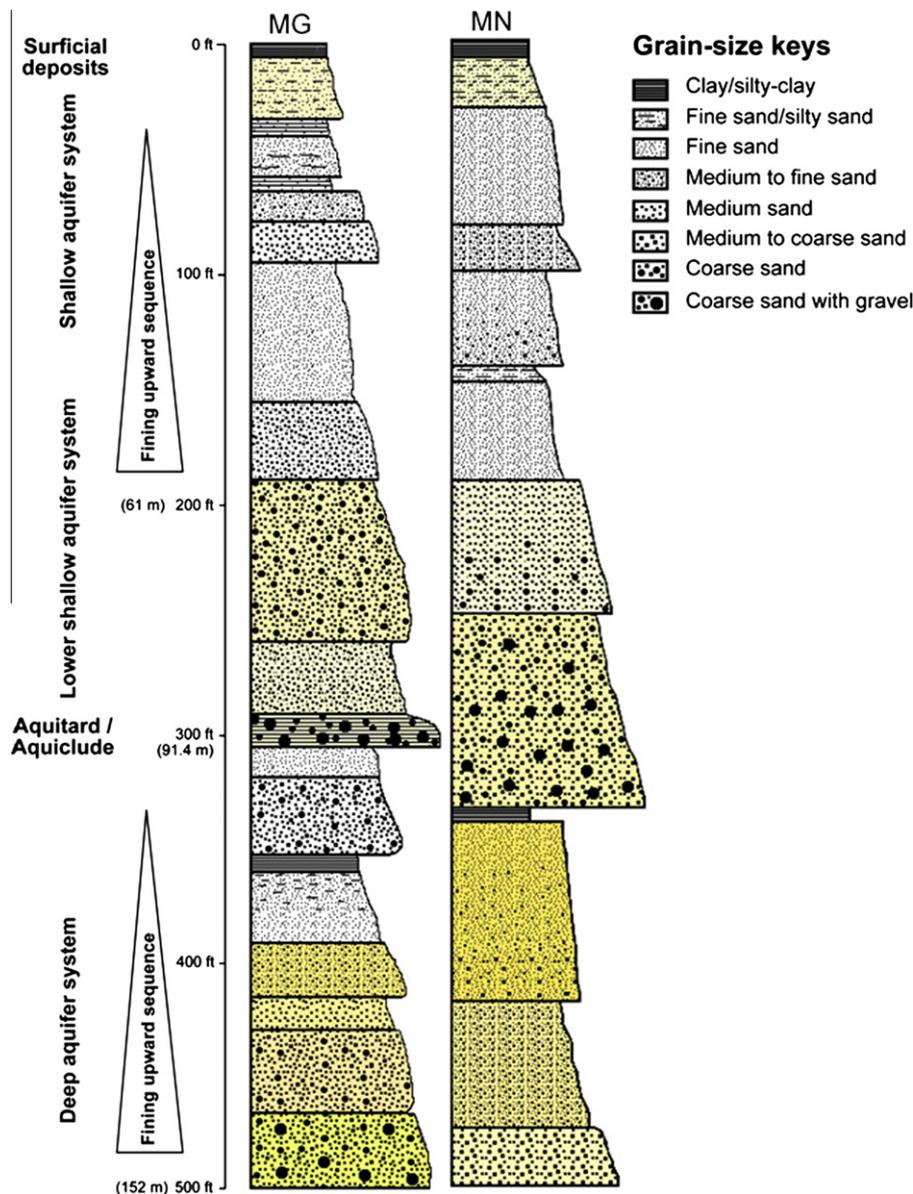


Fig. 2. Stratigraphic column at two drilled-core sites (MG and MN) in the Manikganj study area, showing sediment grain sizes and color with depth. Fining-upward sequences are observed on both columns. Depth-distribution of aquifers is also delineated in the stratigraphic context. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

floodplains, natural levees, back swamps, oxbow lakes) and paralic (e.g., mangrove forests, tidal flats, distributary channels, beaches), and a few deep marine (trench slope, deep-sea fan). Many deposits can be categorized as mixed as a result of changes in regional tectonics, climate change and sea-level oscillations (Goodbred and Kuehl, 2000; Uddin and Lundberg, 2004; Shamsudduha and Uddin, 2007). Several studies have suggested that the sea level rose to a maximum of about 3.0–3.5 m relative to present-day sea level during the Holocene high system tracts and encroached on most of the southern parts of the Bengal Basin (Islam and Tooley, 1999; Woodroffe and Horton, 2005). The depositional environments thus migrated back and forth between the Pleistocene inliers and the position of the present-day shoreline, leaving behind their characteristic sedimentary features, now buried beneath the recent sedimentary cover.

3. Study area

3.1. Location, geology, and hydrogeology

The study area (approximately 40 km²), covering the entire Manikganj town and its surrounding areas, is located approximately 70 km NW of the capital city of Dhaka (Fig. 1). Geographically, the study area is confined within 23.80–23.90°N latitude, and 89.95–90.05°E longitude. The area is covered mostly by recent alluvium deposited by the Ganges–Brahmaputra river system. Tectonically, the study area is positioned in the central part of the Bengal Basin. The surface geology of the area is characterized by alluvial silt and clay, alluvial silt, and marsh peat and clay deposits (Shamsudduha et al., 2008). The geomorphology of the study area is typically fluvial which is characterized by several active channels, abandoned channels, natural levees, backswamps, and

floodplains. Distribution of the geomorphic features and surface geology suggests that these landforms were formed mostly during the late Quaternary period (GRG and HG, 2002). Presence of broad and well-developed natural levee deposits associated with abandoned channels suggests that this region was fluvially very active in the recent past (Shamsudduha, 2007).

Several fining-upward sedimentary sequences characterize the subsurface geology and formation of various aquifers in the study area (Fig. 2). The color of the sediment varies from dark gray to orange-brown. Shallow (10–60 mbgl) sediments are generally gray to dark gray indicating reducing conditions, whereas, deeper (>60 mbgl) sediments are mostly yellowish-brown to orange indicating oxidizing conditions. A detailed description of sedimentary facies and petrography of the study area can be found in Shamsudduha et al. (2008). Aquifers are broadly classified into two groups: (1) the shallow aquifer system is encountered at ~10 mbgl and extends down to a depth of 90 mbgl, is composed of fine to medium gray to pale-yellowish sand and silt in the upper 50 mbgl and the bottom part of the aquifer is composed of medium to coarse sand with some gravels; and (2) the deep aquifer system occurring at >100 mbgl is composed of fine to medium grained yellowish-brown to bright orange-brown sands. The bottom part of the deep aquifer system is composed of medium to coarse grained sands. Sediment characteristics, color, and composition suggest that deep aquifers are composed of sediments equivalent to the Dupi Tila Formation of the Pliocene–Pleistocene age (BGS and DPHE, 2001; Shamsudduha et al., 2008).

3.2. Groundwater arsenic distribution

Arsenic concentrations in 84 groundwater samples (Fig. 3) collected from the study area range from 0.25 to 191 µg/L with a mean concentration of 33 µg/L and median of 17 µg/L. A detailed

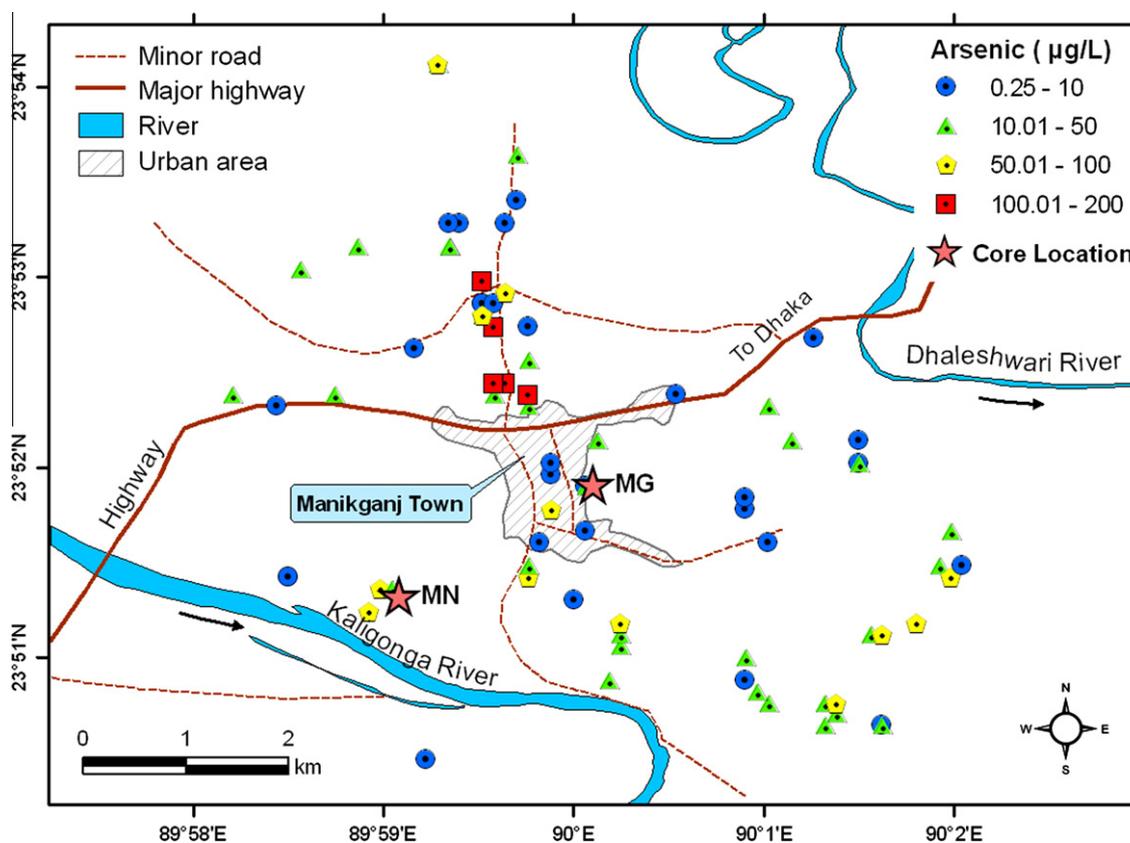


Fig. 3. Arsenic concentrations in groundwater samples in the study area. Locations of two drill-core sampling sites are shown on the map.

description of groundwater sampling and analytical procedures can be found in Shamsudduha et al. (2008). Higher concentrations of As in groundwater are found to the north of Manikganj town. Considerable spatial variability in As concentrations is observed in the study area although there is no obvious pattern in groundwater samples. High-As tubewells are generally located within abandoned channels or natural levees whereas low-As tubewells are found within the floodplain of the major rivers in the area. Overall, As concentrations decrease with depth with greatest concentrations ($>100 \mu\text{g/L}$) found at two depths, 15 mbgl and 35 mbgl. Low-As ($<50 \mu\text{g/L}$) tubewells are found within areas of elevated ground surface and high-As concentrations ($>50 \mu\text{g/L}$) are located in topographically low-lying areas which is consistent with similar associations observed at the national-scale study (Shamsudduha et al., 2009).

4. Field sampling and analytical methods

4.1. Core drilling and litho-sampling

Sediment core samples from two boreholes (Fig. 2 and 3) were collected by a split-spoon sampler made from a 0.6 m section of PVC pipe (internal diameter of 5 cm) with a rotary drill rig operated by the Bangladesh Water Development Board. The first set of sediment core samples ($n = 47$) were collected in January 2001 from the MG core site in Manikganj town by GRG and HG (2002). More sediment samples ($n = 100$) were collected from a second site (MN Core) in Manikganj drilled between 25th December 2005 and 8th January 2006 with a total length of 152 mbgl. Sediment samples were collected from the MN site with a continuous recovery from the top 30 mbgl, and discontinuously (sampling intervals of 3 m from 30 to 90 mbgl, and 6 m from 100 to 152 mbgl) collected to the bottom of the borehole. Samples were collected in plastic PVC tubes with a maximum length of 60 cm but the average length was ~ 30 cm. Both ends of the core tube were wax-sealed on site immediately after the recovery from the drill-hole. Both MG and MN core samples were collected following the same procedure.

4.2. Sediment geochemistry analysis

A total of 32 samples were selected from both MG and MN cores based on the information on groundwater As concentrations at various depths in the study area. Samples were collected at each selected depth from the core in a way that each one is representative of the entire length (mean ~ 30 cm) of the core tube. Samples were dried in an oven at approximately 50°C for 24 h. Approximately 20 g of dried sediment for each sample was crushed with a mortar and pestle. Powdered sediment samples were sent to the ACME Laboratories Ltd. in Vancouver, Canada for analysis (Group 1DX). In the laboratory, 0.50 g sample was leached with 3 mL 2-2-2 HCl-HNO₃-H₂O (hot Aqua Regia extraction) at 95°C for 1 h and diluted to 10 mL and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). A total of 36 major and trace elements including As were determined in all sediment samples.

4.3. Heavy mineral separation: gravity settling and magnetic susceptibility

Heavy mineral assemblages from 16 sediment samples were separated by a gravity settling method with tetrabromoethane (Br₂CHCHBr₂, density 2.89–2.96 gm/cc) (Uddin and Lundberg, 1998a). Dry samples were weighed and added to the heavy liquid in a separating funnel for 24 h. The mixture was stirred periodically to ensure that grains were thoroughly mixed with the solution. Heavy minerals then gradually accumulated at the bottom

of the funnel and were collected on filter paper. The lighter fraction was drained into a new funnel. Both fractions were washed thoroughly with acetone and put into an oven for drying. The fraction of heavy minerals was weighed and magnetically separated in two stages by (1) a hand magnet, and (2) an isodynamic magnetic separator (Frantz magnetometer). Heavy minerals were separated to produce four fractions of different magnetic susceptibility. These four fractions were (1) strongly magnetic (SM), (2) moderately magnetic (MM), (3) weakly magnetic (WM), and (4) poorly magnetic or non-magnetic (PM) with an order of decreasing magnetic susceptibility/intensity.

4.4. Petrographic analysis: mineral identification and imaging

Unconsolidated sand was sieved and fractions coarser than 0.063 mm were epoxied into plugs for thin-section preparation. Petrographic analysis of polished thin-sections was performed under a petrographic microscope (Nikon E600 POL) with a photomicrographic setup. Sixteen thin-sections were prepared from core samples at various depth intervals. Thin-sections were stained for both K and plagioclase feldspars following techniques modified from Houghton (1980) to aid identification under the microscope. Minerals were identified with a petrographic microscope using their optical properties (Uddin and Lundberg, 1998b).

The Energy Dispersive Spectroscopy (EDS) technique was also used to identify minerals in sediment samples. Polished thin-sections of minerals from MG core and several concretions from both MG and MN cores were used for the EDS analysis. Sediment grains exhibiting secondary mineral overgrowths, extracted from the MG core, were imaged using a field-emission Backscattered Scanning Electron Microscope (BSEM). EDS is a procedure performed in conjunction with a BSEM for identifying the elemental composition of samples. EDS with a standard (Princeton Gamma-Tech, Inc.) and automatic spectrum report was used to identify each mineral grain or concretion. Electron beams with 20 kV and a beam current of 2 nA were used for identifying elements present in each mineral grain or concretion.

4.5. Electron microprobe analysis

Electron microprobe (EPMA) analysis provides (1) a quantitative chemical analysis of microscopic volumes of solid materials through X-ray emission spectral analysis; and (2) high-resolution scanning electron and scanning X-ray images. There are two types of scanning electron images used in EPMA analysis: backscattered electron (BSE) images, which show compositional contrast; and secondary electron (SE) images, which show enhanced surface and topographic features. Samples were analyzed with a JEOL 8600 electron microprobe using a 15 keV accelerating voltage and 15 nA beam current. Mineral grains were qualitatively identified using a Noran Microtrace energy dispersive spectrometer (EDS) equipped with a SiLi detector and controlled by a PGT Avalon 4000 multichannel analyzer and run with the eXcalibur software. Quantitative analyses of some mineral grains/crystals were performed with wavelength dispersive spectrometers (WDS) automated with Geller Micro-analytical Laboratory's dQANT software using natural and synthetic mineral standards.

5. Results

5.1. Petrography and sediment characteristics

Representative photomicrographs of sands collected from the MG core site are shown in Fig. 4 (see Supplementary Fig. S1 for a high-resolution version). Variations in framework minerals,

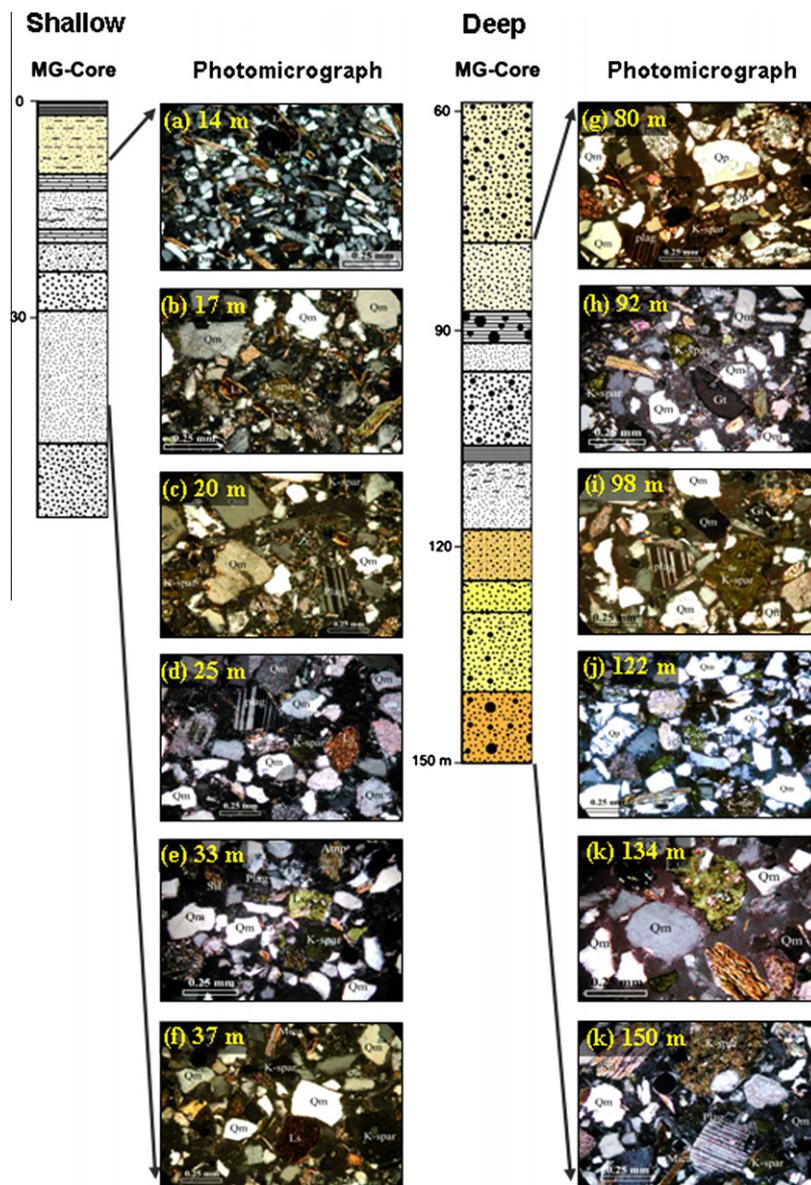


Fig. 4. Representative photomicrographs of sands in shallow and deep sediments in Manikganj. Relative position in the stratigraphic column (depth in mbgl) for each plate is provided. Mineral key: Qm – Monocrystalline Quartz; Qp – Polycrystalline Quartz; K-spar – Potassium feldspar; Plag. – Plagioclase feldspar; Ls – Sedimentary lithic fragment; Lv – Volcanic (plutonic) lithic fragment; Lm – Metamorphic lithic fragment; Gt – Garnet; Sil – Sillimanite; Bt – Biotite; Amp – Amphibole; Zr – Zircon.

texture, and grain size in sediments with the increasing depth are well illustrated in these photomicrographs. Grain shapes in core samples range from angular to sub-angular in shallow sediments, and broadly varies from sub-angular to sub-rounded shapes in sediment of deeper sequences. Minerals in the shallow aquifer are comparatively smaller in size than those of the deeper aquifers in the core profile. Most of the shallow sediments are floodplain or channel-fill deposits and composed of gray sand, silts and silty clay in the upper part and relatively coarser particles toward the bottom of the shallow aquifer system (Shamsudduha et al., 2008). The intensity of gray varies from light (with muscovite) to dark (with dark heavy mineral contents) in the stratigraphic sequence. With an increase in the grain size to medium and coarse sand with occasional gravels, gray to yellowish-brown sediments towards the deeper core samples are composed mostly of quartz and feldspars with some heavy minerals. A gravel-rich layer of medium to coarse grained sands, which is found between the two fining-upward sequences, is thought to have formed under a high-energy deposition environment with channels with steep

hydraulic gradients (Shamsudduha, 2007). Typical yellowish-brown to bright orange-brown medium to coarse sands of the Pleistocene Dupi Tila Formation (BGS and DPHE, 2001) are found in the lower fining-upward sequence indicating highly oxidizing condition in sediments due to an extensive period of weathering in an oxic environment (Shamsudduha et al., 2008).

Petrographic data from 11 thin-sections from various depths suggest that the sand in the Quaternary alluvium in Manikganj is mainly of arkose to subarkose types. Sands in core samples are dominated by quartz, feldspar, mica (muscovite), lithic fragments, and numerous heavy minerals although relatively stable, heavy minerals (e.g., zircon, rutile and tourmaline) are not abundant in young Quaternary sands analyzed in this study. A detailed description of heavy mineral assemblages and their variations with depth in the stratigraphic sequence is discussed in the following section.

The mean percentage of quartz in sands is approximately 60%, which is mostly dominated by monocrystalline type. The mean percentage of polycrystalline quartz is $\sim 7\%$ in the bulk sediment composition which increases with depth (Shamsudduha, 2007).

The mean percentages of feldspar and lithic fragments are about 25% and 15%, respectively. Potassium feldspar is the dominant species of the feldspar group with a mean percentage of approximately 19% of the bulk composition. The ratio between plagioclase and K feldspar ranges from 0.2 to 0.86 with an average of 0.47. Sedimentary lithic fragments are the predominant lithic framework of Quaternary sands in the study area (e.g., shale, mudstone, argillite and siltstone). The percentage of sedimentary lithic fragments is approximately 5% of the sand composition. The percentage of metamorphic lithic fragments (e.g., phillites and schists) is ~3% of the bulk composition, and <2% for volcanic lithic fragments.

Sands at shallow depths (<100 m bgl) are dominated mainly by monocrystalline quartz with very little polycrystalline quartz but the percentage increases in sands at greater depth (Fig. 4). Quartz grains mostly shows both straight and undulose extinctions in all samples. However, undulosity in quartz grains increases from slight to highly undulose as the depth increases. Framework grains at shallow depths are relatively smaller in size than the deeper

sediments. Some overgrowth texture in quartz is also observed in several thin-sections. Inclusions are also common in quartz grains that are mostly zircon, tourmaline and pyroxene minerals. The K feldspars are mainly fresh and unaltered throughout the vertical core profile. Plagioclase feldspars predominantly show polysynthetic twinning. Potassium feldspars are mostly orthoclase, and microclines are rarely found in these Quaternary sediments. Inter-growth structures (both perthitic and myrmekitic) are observed. Average sorting of minerals in sands is moderate to fair suggesting variations in the depositional energy during the Quaternary period in the central part of the Bengal Basin.

5.2. Heavy mineral assemblages

The average concentration of heavy minerals in two different core sequences ranges from approximately 4.36 wt.% to 7.34 wt.% whereas the maximum and the minimum concentrations are 10.28 wt.% and 2.44 wt.%, respectively, in sediment samples.



Fig. 5. Representative photomicrographs of heavy minerals from Manikganj. Key: Gt – Garnet; Ky – Kyanite; Sil – Sillimanite; Bt – Biotite; Amp – Amphibole; Zr – Zircon; FeO – Iron oxide; Gth – Goethite; Cpx – Clinopyroxene; Ep – Epidote; St – Staurolite; Ap – Apatite; Zs – Zoisite; Sid – Siderite; Sph – Sphene; Chld – Chloritoid.

Shallow sediments tend to have more heavy minerals (average 5.2 wt.%) than deeper sediments (average 3.1 wt.%) as revealed from MG cores. Heavy minerals were identified by their optical properties under the petrographic microscope and, occasionally, by their chemical composition and backscattered imaging. As many as 30 different heavy mineral species were identified in the Quaternary sediments in the study area, Fig. 5 (see Supplementary Fig. S2 for a high-resolution version) shows heavy mineral assemblages at various depths in the stratigraphic sequence in the MG core.

Heavy minerals are separated and presented according to their magnetic susceptibility (i.e., strong to poor magnetic susceptibility).

Strongly magnetic (SM) minerals in the core samples are identified as magnetite, hematite, biotite (with inclusions of magnetic minerals), goethite, ferrihydrite and other Fe-oxides minerals. The moderately magnetic (MM) fraction includes biotite, ilmenite, garnet, olivine and chloritoid. The weakly magnetic (WM) fraction of the heavy mineral assemblages includes hornblende, epidote, chlorite, tourmaline, spinel, staurolite, muscovite, zoisite and

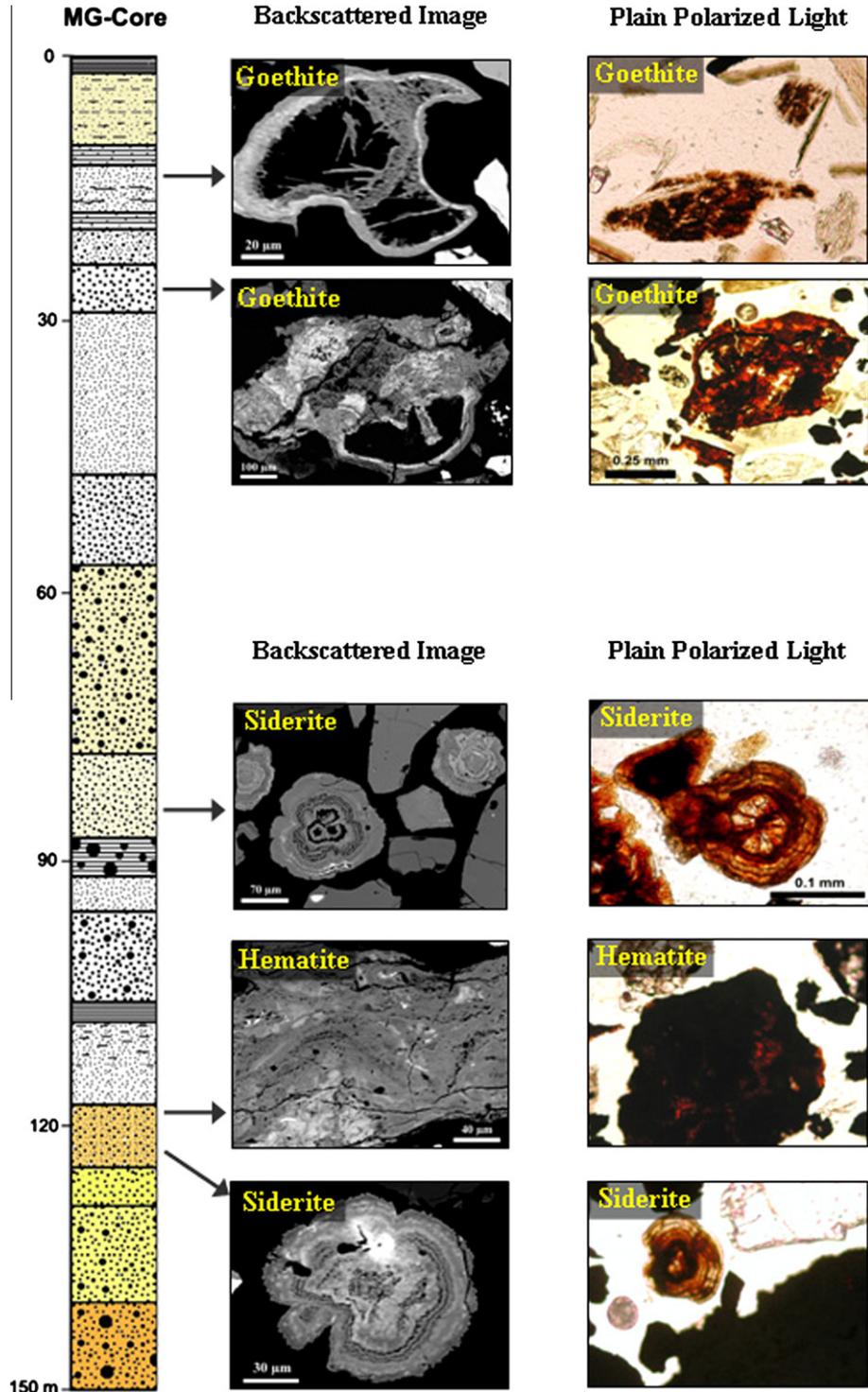


Fig. 6. Backscattered and plain-polarized light images of some authigenic minerals such as Fe-oxyhydroxides (Goethite), Fe-oxides (Hematite) and siderite (FeCO₃) found at various depths in Manikganj aquifer sediments.

clinozoisite. The rest of the heavy minerals were classified as poorly magnetic (PM) or non-magnetic. This group includes slightly magnetic heavy minerals such as sphene, apatite, and monazite, and non-magnetic minerals like zircon, rutile, pyrite, kyanite and sillimanite.

Sediments at shallow depths are represented by abundant magnetite, goethite, biotite, hornblende, chlorite, kyanite, epidote, sillimanite, epidote, garnet, and other Fe-oxides (Fig. 5). Stable heavy minerals (e.g., zircon, rutile and tourmaline) are not abundant in shallow sediments. However, some less commonly found minerals like apatite, monazite, olivine, rutile and pyrite (detrital) are found in shallow sediments. The deeper sediments are abundant in garnet, amphiboles, pyroxene, kyanite, sillimanite and sphene with some tourmaline, rutile, zircon, corundum and zoisite. Iron-oxide minerals are less common in deeper sediments, and are primarily hematite with few goethites.

5.3. Authigenic minerals and their geochemistry

Several authigenic minerals are found within the sediment core samples from Manikganj (Fig. 6). Energy Dispersive Spectroscopy (EDS) with backscattered imaging on polished thin-sections confirmed the presence of authigenic Fe-oxides and Fe-carbonates in sediment samples. In MN core samples, at a depth of ~4 mbgl, some brown-colored concretions of Fe-oxide were found within a dark-gray layer of silty clay. This sediment layer has the highest As (Aqua-Regia extractable) concentration (8.8 mg/kg). Numerous Fe-oxyhydroxide minerals (goethite and ferrihydrite) were found in core samples identified by the EDS spectrum and electron microprobe analysis. Backscatter images reveal the texture of these authigenic Fe-oxides present in sediments. Sediments at shallow depths under moderately reducing conditions mostly host these goethite and other FeOOH minerals, but at deeper depths these Fe-oxides were found primarily as hematite in oxidized brown sediments. Electron microprobe (EPMA) analysis was performed on some of these goethite grains at various spots to determine major chemical (as oxides-wt.%) compositions (Table 1). For most samples, As concentrations were found to be below the regular detection limit (~500 mg/kg) of the EPMA measurement. However, in one specific case, EPMA analysis on a particular goethite grain/crystal extracted from a shallow (25 mbgl) sediment layer revealed As concentration of approximately 340 mg/kg with a modified (reduced) minimum detection limit of ~300 mg/kg.

Numerous siderite grains were found in sediment samples ranging in depth from 80 to 120 m in Manikganj area (Fig. 6). The chemical composition of siderite is given in Table 2. The mineral texture (botryoidal and concentrically-zoned spherulitic grains; Saunders and Swann, 1992) suggests that siderite minerals were authigenically formed (under reducing condition) within the alluvial aquifer. EDS analysis shows that these siderite concretions contain variable amounts of Fe (24–38%), O (32–40%) and C

Table 2

Chemical composition of siderite (FeCO_3) with some dolomite ($\text{CaMg}(\text{CO}_3)_2$) as revealed by electron microprobe analysis on some selected siderite concretions at several spots in one of the samples (MG-44 at 86 mbgl); CO_2 was calculated stoichiometrically for all the elements. Numbers of ions are shown on the basis of six Oxygens.

Oxides (wt.%)	MG-44(1)	MG-44(2)	MG-44(3)	MG-44(4)
CaO	4.13	29.08	29.07	3.82
MgO	0.16	16.28	16.27	0.20
FeO	52.59	7.41	7.41	57.82
MnO	4.17	1.54	1.54	2.17
SrO	0.00	0.03	0.03	0.03
BaO	0.03	0.00	0.00	0.04
CO_2	38.23	46.10	46.09	40.00
Total	99.32	100.44	100.41	104.07
Element	Major mineral			
	Siderite	Dolomite	Dolomite	Siderite
Ca	0.17	0.99	0.99	0.15
Mg	0.01	0.77	0.77	0.01
Fe	1.69	0.20	0.20	1.77
Mn	0.14	0.04	0.04	0.07
Sr	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00
C	4.00	4.00	4.00	4.00
Total	6.00	6.00	6.00	6.00

(10–13%), and minor amounts of Ca and Mg (2–3%) and Mn (1–2%) (Turner, 2006). Chemical composition of these siderite concretions varies from pure FeCO_3 to $(\text{Fe,Mn})\text{CO}_3$ and sometimes they contain traces of CaCO_3 and SiO_2 (Shamsudduha, 2007).

6. Discussion

6.1. Mineral phases in sediments and As in groundwater

Mineral association in sediments provides a strong clue to their parent source rocks and offers a tool for analyzing chemical changes in sediment and groundwater composition in the aquifer through their diagenetic alteration due to water–rock interaction. The association between elevated As in sediments, groundwater, and mineral assemblages in the alluvial aquifers of central Bengal Basin is discussed. Arsenic concentrations in sediments of Manikganj aquifers, groundwater samples, and weight percentages of heavy minerals of varying magnetic susceptibilities are compared along the vertical core profile in order to understand mineral–water interactions. Elevated (>50 $\mu\text{g/L}$) As concentrations in groundwater are observed between 10 and 40 mbgl in Manikganj where aquifer sediments are predominantly gray colored and moderate to highly reduced indicated by the redox potential (ORP) of groundwater samples which varies from –152 to 177 mV with an average value of –88 mV (Shamsudduha, 2007). Elevated

Table 1

Chemical composition of Fe-oxyhydroxide minerals (goethite and hematite) revealed by electron microprobe analysis at several spots (4 each) on some selected samples (MG-21 at 25 mbgl, and MG-50 at 122 mbgl) in MG core sediments.

Oxides (wt.%)	MG-21(1)	MG-21(2)	MG-21(3)	MG-21(4)	MG-50(1)	MG-50(2)	MG-50(3)	MG-50(4)
SiO_2	3.82	0.64	1.05	0.88	0.08	1.84	3.42	1.84
TiO_2	0.04	0.03	0.00	0.01	0.07	0.03	0.07	0.05
Al_2O_3	0.46	0.04	0.09	0.09	0.22	0.09	0.07	0.03
MgO	0.12	0.10	0.24	0.24	0.03	0.15	0.13	0.16
FeO	69.15	82.29	72.51	79.34	92.93	72.94	55.30	59.67
CaO	0.79	0.42	0.35	0.36	0.01	0.34	0.72	1.40
MnO	0.44	0.61	1.07	0.79	0.12	0.88	13.70	2.76
Cr_2O_3	0.23	0.14	0.00	0.12	0.03	0.00	0.00	0.02
NiO	0.15	0.02	0.00	0.20	0.00	0.00	0.00	0.10
P_2O_5	0.06	0.03	0.04	0.08	0.08	0.08	0.08	0.08

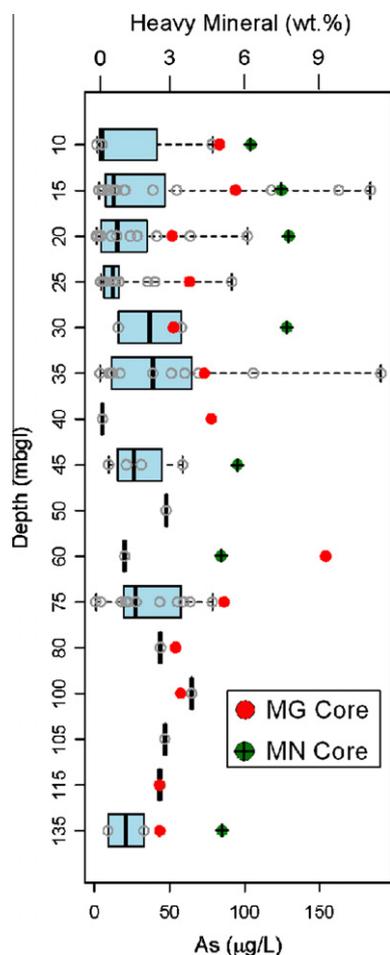


Fig. 7. Groundwater As and heavy mineral concentrations in Manikganj alluvial aquifers. Arsenic concentrations are grouped (shown as boxplots) according to the intake depth of the sampled tubewells into a common bin size of 5 m. There are some missing intervals between 50 and 135 mbgl. Data associated with each group are also shown with their generalized depths. Heavy mineral concentrations (wt.% of the sample) are plotted alongside groundwater As concentrations which show interesting association between them.

(>4 mg/kg) As concentrations in sediments are observed within the upper 15 m of the stratigraphic sequence just above the peak As concentration in groundwater. A strong association exists between elevated groundwater As and heavy mineral concentrations (wt.% of total minerals) in aquifers (Fig. 7) particularly with moderately magnetic mineral phases (Fig. 8). A correlation (Pearson) coefficient (r) of ~ 0.6 ($p = 0.2$) is observed between mean groundwater As and heavy mineral concentrations although the relationship is not statistically significant. High-As concentrations in magnetic minerals (magnetite, ilmenite, goethite, biotite and other Fe-oxides minerals) of alluvial aquifers have been reported in several studies (e.g., BGS and DPHE, 2001; Pal et al., 2002; Saunders et al., 2008). A few studies (Pal et al., 2002; Pal and Mukherjee, 2009) have reported the presence of high amounts (>20 mg/kg) of soil-phase As in fine-grained sediments and moderate to strongly magnetic minerals in the Holocene aquifers in the western Bengal Basin (West Bengal). Arsenic concentration as high as 7 mg/kg have been measured in biotite and 10 mg/kg in illite grains (Pal and Mukherjee, 2009). Seddique et al. (2008) found a positive correlation between As, Al and Fe concentrations and concluded that chemical weathering of biotite is the primary mechanism for As mobilization in groundwater and prevailing reducing conditions contribute to the expansion of As enrichment in Holocene aquifers in the central Bengal Basin. In the Manikganj area, low-As concentrations in

deep (>100 mbgl) stratigraphic sequences coincide with low amounts of heavy minerals (Shamsudduha, 2007). Concentrations of heavy minerals in these Quaternary sediments are higher than the older Cenozoic sediments in the Bengal Basin (Uddin and Lundberg, 1998a).

6.2. Groundwater chemistry and mineral assemblages in aquifers

Mineral phases in aquifer sediments reflect the general chemistry of groundwater, oxidation–reduction potential, groundwater fluctuation and seasonal recharge to aquifers. Some detrital minerals are completely dissolved (oxidized) in the aerobic environment between source areas and the site of deposition during transport by river channels. A small number of such detrital minerals (pyrite, olivine, etc.) are found in sediments from the study area in Manikganj. Presence of such easily-soluble minerals and even prismatic quartz crystals in cored sediments suggests rapid transportation from nearby source terrains with relatively quick rates of burial. Presence of authigenic mineral phases in aquifer sediments indicates intensity of redox potential and general composition of groundwater. In Manikganj cored sediments the most abundant, authigenically formed minerals are Fe-bearing minerals such as goethite (FeOOH). Other Fe-bearing minerals are ferrihydrite (Fe₂O₃·0.5(H₂O)) and other Fe-oxides (such as magnetite, Fe₃O₄) that are found at shallow depths (<80 mbgl) whereas authigenic siderite (FeCO₃) grains are found at deeper depths (>80–150 mbgl). In a typical deltaic environment, primary (detrital) sulfide minerals are completely oxidized prior to deposition and, therefore, pyrite (FeS₂) grains that are generally found in aquifer sediments are mainly of authigenic origin (Saunders and Swann, 1992; McArthur et al., 2001). However, no authigenic pyrite was found in Manikganj cored samples. A very few detrital pyrite grains were observed and identified with backscattered imaging during the electron microprobe analysis. Absence of widespread authigenic pyrite in the Manikganj area suggests dominance of Fe-reducing condition in groundwater and lack of available S.

Below the discussion on presence of authigenic minerals and implications for As mobilization in alluvial aquifers in the Bengal Basin is extended. Authigenic Fe-(oxy)hydroxide minerals are commonly formed in situ as a result of the direct metabolic activity of bacteria (Fe-oxidizing) under oxic conditions which promotes the oxidation of Fe(II) to Fe(III) and the precipitation of Fe-oxides (goethite), also known as biogenic Fe-oxides (Saunders et al., 1997). Metalloids such as As are strongly adsorbed on Fe-oxyhydroxides which have greater specific surface area and strong affinity to metals. Goethite and other Fe-(oxy)hydroxides have a great capacity to sorb both As(III) and As(V) at pH < 8 and this is an important process which takes place during goethite transport to river floodplains (Saunders et al., 2005). Under the reducing subsurface environment (below the groundwater table), Fe-reducing bacteria (e.g., Geobacter) reduce Fe(III) to Fe(II) and release sorbed As into groundwater (Islam et al., 2004). Arsenic concentrations are found to be highest where reduction of Fe-(oxy)hydroxide minerals is complete and no reactive Fe(III) minerals are present (Swartz et al., 2004; Polizzotto et al., 2005). In Manikganj, the presence of authigenic Fe-(oxy)hydroxide suggests that microbial reduction of Fe(III) is ongoing or limited due to low available organic C in sediments. Authigenic Fe-(oxy)hydroxide minerals are not observed in reduced gray sediments collected from highly As-affected areas in Bangladesh such as Faridpur (mean As 96 µg/L), Lakshmipur (mean As 105 µg/L), and Chapai Nawabganj (mean As 146 µg/L) (BGS and DPHE, 2001) but observed in brown sediments (Lowers et al., 2007). The presence of authigenic siderite (FeCO₃) in Manikganj sediments suggests that Fe-rich groundwater at greater depths (>80 mbgl) comes into contact of HCO₃-rich groundwater and forms siderite. Formation of authigenic siderite can sequester As

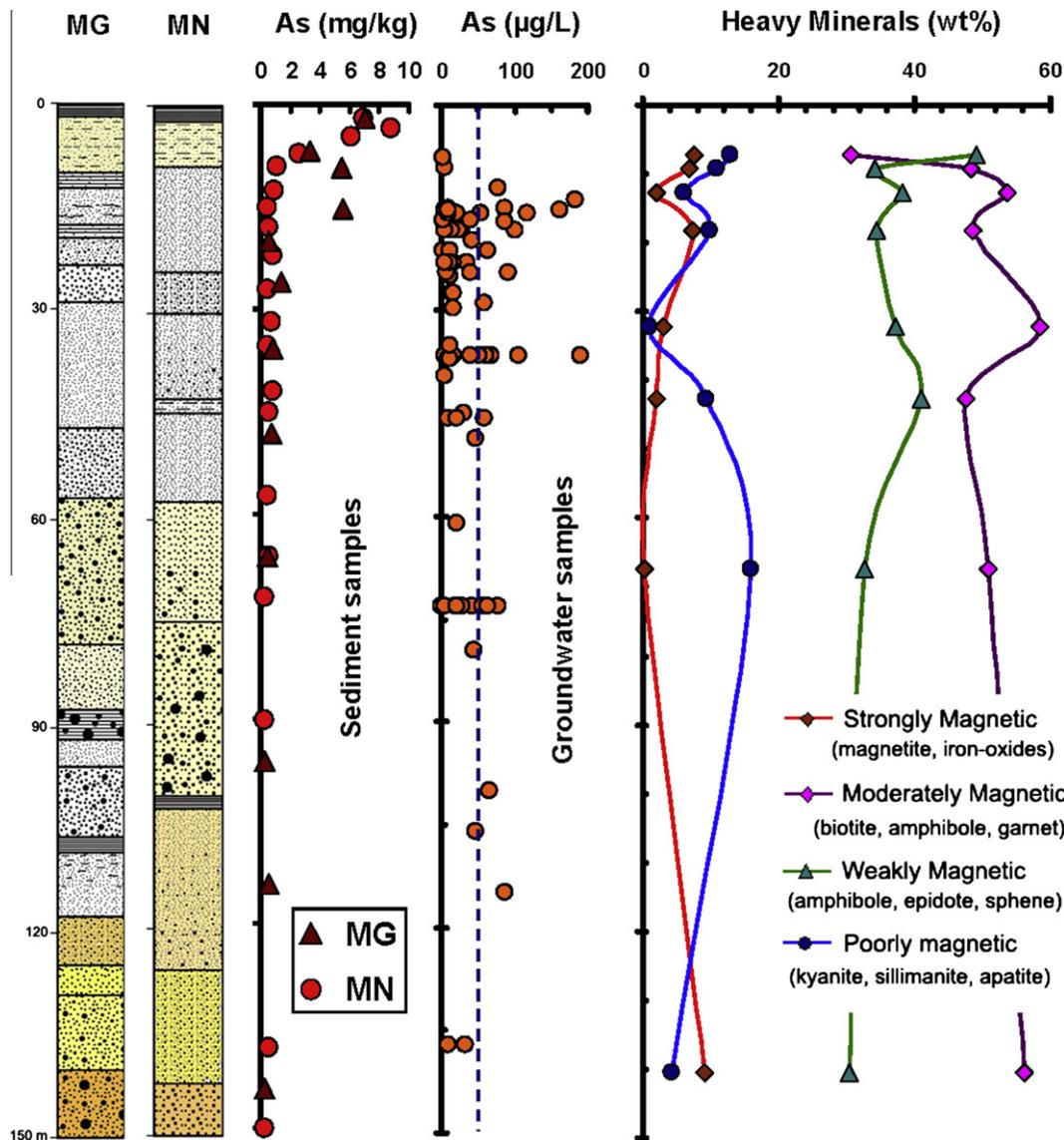


Fig. 8. Depth-wise As concentrations in sediments of MG and MN cores, and groundwater samples. Depth-wise variations of heavy mineral fractions (weight % of total heavy fraction) of different magnetic susceptibility in MN core samples are shown. High concentrations of As in groundwater coincide with the abundance of strongly magnetic (magnetite, Fe-oxides), and moderately magnetic (biotite, amphibole) in sediments. Dashed line in the panel for As in groundwater samples corresponds to 50 µg/L (Bangladesh drinking water standard).

from groundwater as it precipitates. Relatively stable Fe-oxides (hematite) that might have adsorbed considerable amounts of As in oxidized sediments, are found at greater depths in Manikganj.

In nature, both Fe and SO_4 reduction can occur parallel to each other depending on the availability of reactive organic C, Fe and SO_4 in groundwater (Saunders et al., 2008). SO_4 concentration is generally low in Bangladesh groundwaters (BGS and DPHE, 2001). Under the SO_4 -reducing conditions, authigenic/biogenic pyrite is formed in aquifers that are generally associated with gray to dark-gray sediments (Saunders et al., 1997; McArthur et al., 2001). Authigenic framboidal pyrite in sediments is observed in many As-affected areas in the Bengal Basin (BGS and DPHE, 2001; Pal et al., 2002; Swartz et al., 2004; Polizzotto et al., 2005; Lowers et al., 2007). Lack of Fe-(oxy)hydroxide suggests that the Fe-reduction is exhausted in the aquifer sediment delivering all sorbed As and currently SO_4 reduction is forming biogenic pyrite which sequesters a fraction of the previously dissolved As. High rates of microbial SO_4 reduction decreases dissolved As concentrations locally in pore waters, where precipitation of As-rich sulfides

(authigenic pyrite) may occur heterogeneously in sediment pore spaces (O'Day et al., 2004). Arsenic incorporation in pyrite is dependent on the rate of S supplied by bacterial SO_4 reduction. In southeastern Bangladesh (As hot-spots), higher concentrations of solid-phase As are associated with slowly-developed massive pyrite at depth (>20 mbgl) in aquifers (Lowers et al., 2007).

6.3. Himalayan litho-tectonic belts and potential As sources

It is critical to review the regional tectonics and formation of the Bengal Basin and its surrounding terrains in order to understand the occurrence of high-As in the Holocene aquifers. The Bengal Basin is surrounded by two major orogenic belts in northern and eastern directions; the approximately 2500 by 300 km east–west elongated Himalayas (north) and 1500 by 230 km north–south oriented Indo-Burman ranges (east) (Fig. 9). The Himalayan orogenic belt is made up of 4 longitudinal litho-tectonic units juxtaposed along nearly north-dipping thrust faults. There are As-rich minerals associated with a range of igneous, metamorphic and sedimen-

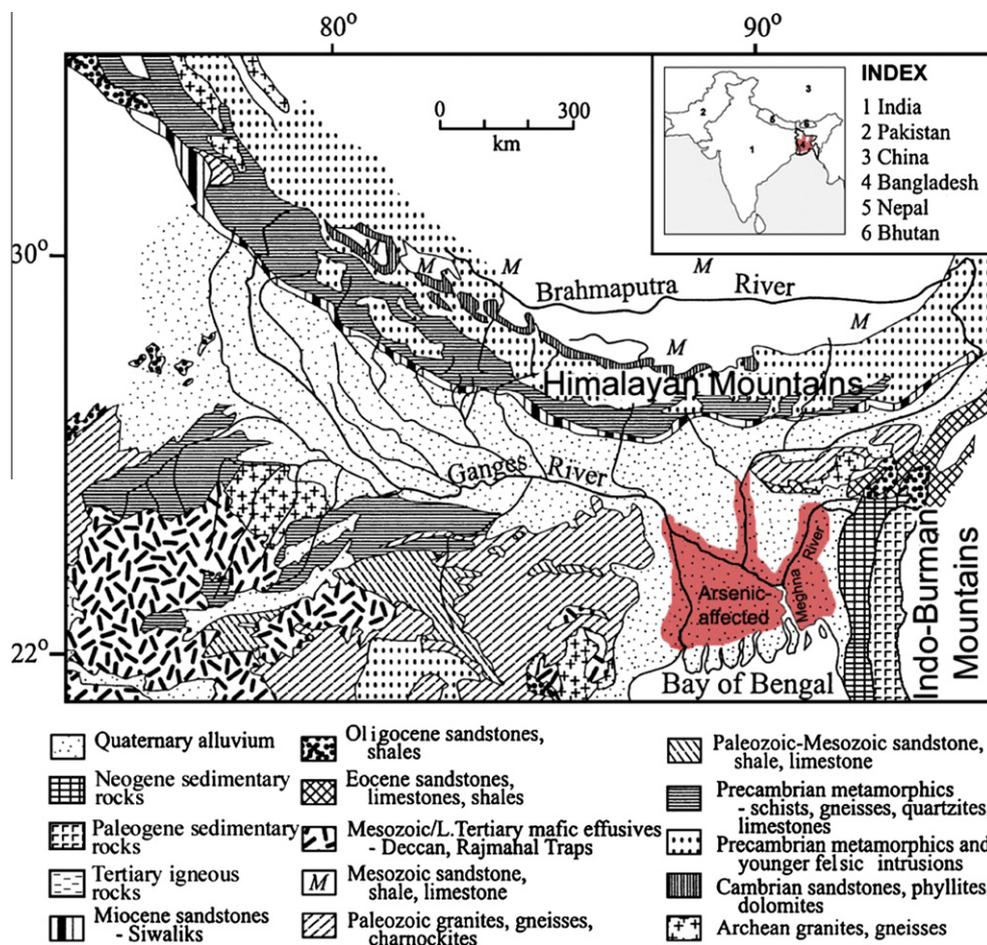


Fig. 9. Generalized geological map (modified after Heroy et al., 2003) of the Ganges, Brahmaputra and Meghna (GBM) drainage basins and the surrounding areas. The Ganges River drains the Indian Shield and southern slope of the Himalayas; the Brahmaputra River flows through the northern slope of the Himalayas, and the Meghna River drains the western slope of the Indo-Burman Mountain Ranges. Geographic extents of As-affected aquifers in the Bengal Basin are also shown.

tary rocks in these belts. Ascending from the Indo-Gangetic plain (Quaternary deposits), from south to north, these units are (1) the Sub-Himalaya, representing the Miocene to Pleistocene molasse deposits of the Siwalik belts (Fig. 9); (2) the Lower or Lesser Himalaya, composed of Precambrian and Paleozoic sedimentary rocks, crystalline rocks, and granites; (3) the Higher Himalaya, composed of schists, gneisses, and granites; and the (4) Tethys Himalaya and Trans-Himalaya, representing fossiliferous Cambrian to Eocene sedimentary rocks (shallow-water deposits, such as limestone, calcareous sandstone and dolomite), batholiths and volcanic rocks. The Indus-Tsangpo suture in northeastern India is marked by ophiolitic rocks, including olivine serpentinites (Guillot and Charlet, 2007). These ophiolites are composed of serpentinitized peridotite, layered mafic to ultramafic rock, volcanic and oceanic sediments that contain high-As. Based on mineral assemblages found in cored samples it is suggested that sediments in shallow As-affected aquifers in Manikganj were derived mostly from As-enriched ophiolitic and Siwalik belts, and also from Precambrian crystalline rocks in the Shillong Plateau and deposited primarily by the Brahmaputra river system.

7. Conclusions

A detailed mineralogical profiling of both heavy and light minerals in aquifer sediments from drilled cores of Manikganj district in central Bangladesh sheds lights on mineralogical heterogeneity and potential sources of As in Quaternary sediments

and groundwater in the Bengal Basin. Mineral assemblages reflect on the chemical composition of As-enriched groundwater at various depths along the stratigraphic sequence down to a depth of 150 m. Summarized below are the major findings of this study highlighting As sources and mobilization processes in Holocene aquifers in the Bengal Basin: (1) elevated dissolved As in shallow groundwater is primarily derived from reductive dissolution of secondary Fe-(oxy)hydroxide minerals (authigenic goethite, ferrihydrite, and amorphous Fe-(oxy)hydroxides) mediated by Fe-reducing bacteria; (2) other potential sources of As in shallow aquifers include detrital heavy mineral phases such as magnetite, biotite, olivine, and apatite derived from the Himalayan ophiolitic and Siwalik belts, and Precambrian crystalline rocks from the Shillong Plateau; (3) heavy mineral concentrations in shallow (<100 m) sediments are greater than deeper sequences indicating greater rates of weathering and unroofing of relatively fresh Himalayan sediments, and rapid transport and deposition in the Bengal Basin; (4) Highest (>4 mg/kg) As concentrations are observed in sediments at very shallow (<10 m) depths which do not coincide with high-As concentrations in groundwater occurring at depth (>15 m); this may suggest variable intensity and completeness of reductive dissolution of As-bearing Fe(III) minerals with depth (i.e., high-As concentrations in groundwater are associated with intensive and complete Fe-oxyhydroxides reduction); and (5) in the absence of S in Manikganj groundwater authigenic siderite is formed in sediments (>80 m) which might have precipitated As from solution and decreased As concentration.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2011.01.006.

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