

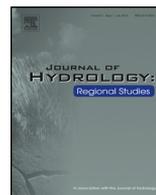


ELSEVIER

Contents lists available at ScienceDirect

Journal of Hydrology: Regional Studies

journal homepage: www.elsevier.com/locate/ejrh



Arsenic mobilization in an alluvial aquifer of the Terai region, Nepal



Jasmine Diwakar^a, Scott G. Johnston^{a,*}, Edward D. Burton^a,
Suresh Das Shrestha^b

^a Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

^b Central Department of Geology, Tribhuvan University, Kirtipur, Kathmandu, Nepal

ARTICLE INFO

Article history:

Received 3 March 2014

Received in revised form 25 September 2014

Accepted 5 October 2014

Available online 11 November 2014

Keywords:

Arsenic

Fluoride

Manganese

Nepal

Groundwater

ABSTRACT

Study Region: A shallow (<50 m) alluvial aquifer in the Terai region of Nepal.

Study Focus: We examine the hydrogeochemical characteristics of a shallow alluvial aquifer system in the Terai region (Nawalparasi district) to identify possible mechanisms and controls on geogenic As mobilization in groundwater. Groundwater and river water samples from a topo-gradient flow-path and floodplain of a minor river draining the Siwalik forehills were analyzed for physico-chemical parameters.

New Hydrological Insights for the Region: The aquifer is characterized by Ca-HCO₃ type water and is multi-contaminated, with the WHO guideline values exceeded for As, Mn and F in 80%, 70% and 40% of cases respectively. The middle portion of the floodplain was heavily contaminated with As, predominantly as As(III). The river water displayed some evidence of reductive processes in the hyporheic zone contributing As, Fe and Mn to baseflow and also had elevated fluoride. The generally sub-oxic conditions, dominance of As(III) and Fe²⁺ species and positive correlation between As and both NH₃ and UV-absorbance at 254 nm suggests that oxidation of organic matter coupled with microbial mediated reductive processes are important for mobilizing As in the aquifer. The apparent decoupling between As(III)_(aq) and Fe²⁺_(aq) may be explained by precipitation of siderite, but further work is required

* Corresponding author. Tel.: +61 66203407.

E-mail address: scott.johnston@scu.edu.au (S.G. Johnston).

to resolve this unambiguously. Along with reductive processes, other geochemical mechanisms including silicate weathering and precipitation/dissolution of carbonate minerals, control the solute and major ion composition of groundwater.

© 2015 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

Elevated geogenic arsenic (As) concentrations in alluvial aquifers of the Gangetic plain is an important human health concern (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009; Fendorf et al., 2010a; Michael and Voss, 2008; Mukherjee et al., 2015). The Terai region of Nepal is part of the upper Gangetic plain and almost half of Nepal's population resides in this region. Residents of the region are highly reliant on groundwater for drinking and other household purposes (Kansakar, 2005). The Terai is the most agriculturally productive region of Nepal and groundwater is also used for irrigating cultivated land (Gurung et al., 2005).

The presence of arsenic in groundwaters of the Terai region was first identified by Department of Water Supply and Sewerage (DWSS) and the World Health Organization (WHO) in 1999. Recent studies have confirmed the presence of elevated As concentrations ($>6.7 \mu\text{M}$) in alluvial aquifers within the Terai region (Bhattacharya et al., 2003; Gurung et al., 2005; van Geen et al., 2008). Various agencies tested 737,009 tubewells of the Terai region for As and approximately 9% of wells exceeded the WHO guideline value (GLV) of $0.13 \mu\text{M}$ (Thakur et al., 2011). These broad-scale well testing programs have identified the most affected districts are Rautahat, Nawalparasi, Parsa and Bara (NRCS, 2005). There is considerable spatial and temporal heterogeneity in As concentrations in the Terai aquifers (Brikowski et al., 2004, 2013; Weinman, 2010), similar to other As contaminated regions of the Gangetic Plain. People exposed to elevated groundwater As on the Terai display symptoms of arsenicosis, including diseases such as skin lesions and skin cancer (Bhattacharya et al., 2003; Pokhrel et al., 2009).

The thin alluvial aquifers of the Nawalparasi district are some of the most severely As contaminated in the Terai region (Maharjan et al., 2005). Alluvial sediments comprising the Terai aquifers in this district are derived from two main sources, (i) sediments deposited by large rivers that erode the upper-Himalayan crystalline rocks (Brikowski et al., 2004; Weinman, 2010), (ii) weathered meta-sediments carried by smaller rivers originating in the Siwalik forehills (Weinman, 2010).

There has been considerable international research effort aimed at understanding the scale of As contamination and the primary hydrogeochemical drivers of As mobilization in the middle and lower part of the Gangetic plain (e.g. Ahmed et al., 2004; Bhattacharya et al., 1997; Fendorf et al., 2010a; Harvey et al., 2002; Lawson et al., 2013; McArthur et al., 2011; Michael and Voss, 2008; Mukherjee et al., 2012; Nath, 2012; Swartz et al., 2004; van Geen et al., 2006b; Mahanta et al., 2015). However, groundwater arsenic contamination in the Terai region has received comparatively scant research attention.

A variety of competing hypotheses have been proposed to explain the mobilization and distribution of As in the aquifers of the Terai region. Bhattacharya et al. (2003) suggested possible oxidation of organic matter coupled with reductive dissolution of Fe and Mn-bearing minerals releasing As-oxyanions associated with these minerals. Gurung et al. (2005) also suggested a chemically reduced environment in the aquifer triggers desorption of As from As-bearing iron oxides. Bisht et al. (2004) identified the use of cowdung during tubewell drilling as a possible source of organic matter driving reductive processes and subsequent As release in groundwater, however this has not been independently verified. Weinman (2010) also identified reduction of As-bearing Fe-oxides as a source of As mobilization in Nawalparasi floodplain sediments and further suggested that groundwater As was mainly associated with sedimentary facies derived from large rivers (i.e. the Narayani/Gandaki) carrying sedimentary material eroded from the upper Himalaya crystalline basement rocks.

In contrast to this, Williams et al. (2004, 2005) suggested that As contamination in the Terai region may be the result of oxidation of authigenic As-bearing sulfides derived from the Siwalik meta-sediments, rather than reductive-dissolution of As-bearing Fe-oxides. Furthermore, an analysis

performed by Kansakar (2004) on 18,000 tubewells of the Terai region suggested greater As release from the Siwalik-derived sediment than sediments from the large first and second grade rivers such as the Narayani/Gandaki. Khadka et al. (2004) found concentrations of As increased downstream in waters of the Jharia, a minor river which originates from the Siwalik foothills near Nawalparasi. These studies suggest that the main source of geogenic As in the Terai alluvial aquifers may be sediments derived from erosion of the Siwalik foothills.

The sedimentary origins of As and the precise mechanism(s) responsible for As mobilization in alluvial aquifer sediments of the Nawalparasi district are yet to be unequivocally determined. Given the gaps in present understanding, it is important to further investigate the geochemical characteristics of groundwater in alluvial aquifers of this region. This study aims to explore the geochemical characteristics of groundwater and river water along the topo-gradient flow path of a minor river draining from the Siwalik foothills. The objective of the study is to examine the geochemical evidence for various arsenic release mechanisms within the alluvial aquifer in the Nawalparasi district, Nepal.

2. Materials and methods

2.1. Study site hydrogeology

The Nawalparasi district is located in the Terai alluvial plain, the Western Development Region, Nepal. It has a population of about 650,000 (CBS, 2012) and covers an area of 2162 km² (Bhattacharya et al., 2003). It is surrounded by Rupandehi, Chitwan and Palpa districts in east, west and north respectively, while India lies to the south. The elevation of the district ranges from 93 to 1491 m above mean sea level (msl). It is situated in a subtropical zone and is subjected to monsoonal rainfall with an average annual precipitation of about 1400 mm (Shrestha, 2007).

The district has three distinct hydrogeological zones: (1) the Siwalik Hills, (2) the Bhabar recharge zone and (3) the Terai plain unconsolidated Holocene floodplain sediments. The northern part of the district is bounded by the steeply sloped Siwalik Hills which are composed of sedimentary rocks such as sandstone, siltstone, mudstone, shale, and conglomerates. Immediately south lies the Bhabar zone, which is composed of unconsolidated sediments that are porous and coarse such as gravel, cobbles and boulder material, thereby making the Bhabar zone highly permeable, with an average transmissivity ~5000 m² per day and a hydraulic conductivity of ~200 m per day (Kansakar, 2004; Shrestha, 2007).

A major river, the Narayani/Gandaki, which descends from the Higher Himalaya, flows along the eastern boundary of the Nawalparasi district and has had a major influence on the underlying unconsolidated Holocene fluvial deposits that comprise the floodplain aquifer system (Weinman, 2010). Small local rivers originating in the Siwalik Hills, including the Turia, Jharia and Bhaluhi, dissect the floodplain in a North-South orientation (Pathak and Rao, 1998). The plain is situated on the Rapti-Gandaki interfan region and is mainly comprised of Holocene alluvium (NASC, 2004). Unlike other regions of Terai, where finer of sediments typically increase toward the south, fines predominate in the north and sand and gravels are found near the Nepal-India border (Shrestha et al., 2004). In the areas with fine grained sediments, elevated concentrations of As are typically recorded (Brikowski et al., 2004, 2013).

2.2. Water sampling, collection and preservation

All glass and plasticware used during sampling and laboratory analysis were soaked in 5% HCl for 24 h and then rinsed with deionized water (Milli-Q) for at least 24 h. All reagent solutions were prepared with Milli-Q water having a resistivity of 18.2 MΩ/cm.

In October 2012, tubewell water samples were collected along the floodplain of the Bhaluhi River, Nawalparasi district (Fig. 1). The sampling area was divided into three topo-gradient regions along the flow path of the Bhaluhi River referred herein as (i) the Upper region, (ii) the Middle region and (iii) the Lower region. The upper region lies on the edge of the Bhabar zone, while the middle and lower region are situated on the Terai plain. This division was based on the recognition that geomorphic and landform features can exert a vital control on aquifer stratigraphy and corresponding geochemistry and As concentrations (McArthur et al., 2011; Nath, 2012; Shamsudduha et al., 2008; Weinman et al.,

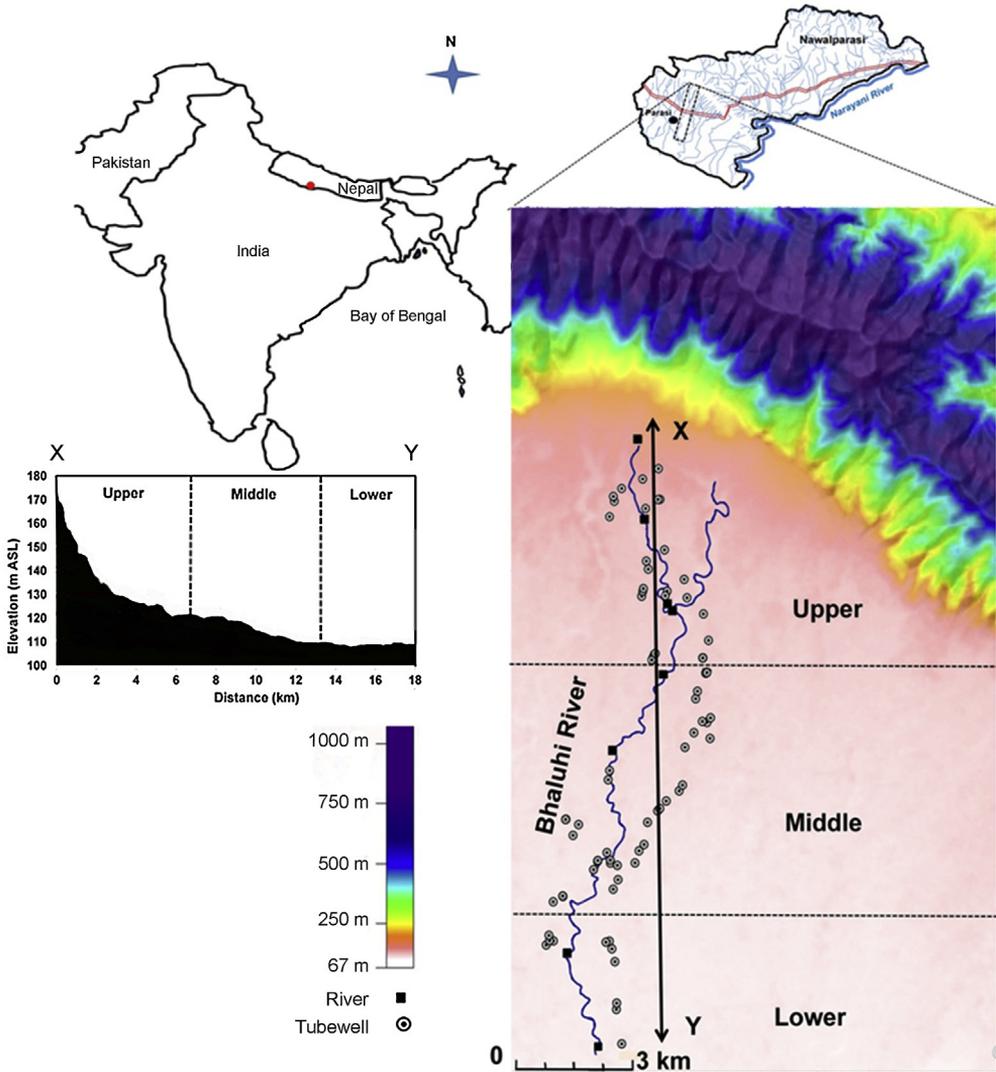


Fig. 1. Study site tubewell and river sampling locations and elevation profile along the flow-path of the Bhaluhi River.

2008; Winkel et al., 2008) and the distribution of As concentrations in the aquifer derived from prior testing of the region. Seventy-three water samples from tube wells and eight samples from the Bhaluhi River were collected for detailed aqueous phase characterization (Fig. 1).

Most of the investigated tube wells were currently used by local people for domestic drinking or irrigation purposes. Information such as depth, age, screen interval, method of drilling and construction of tube well were collected via interview with the owner or nearest household user of the well. Each tube well was subjected to 5–10 min of continuous pumping, during which time the redox potential, pH, temperature, dissolved oxygen (DO) (luminescence probe) and electrical conductivity of the water was measured with HACH multimeters (HQd) and freshly calibrated probes. After 5–10 min of pumping and stabilization of physico-chemical parameters, water samples were collected into a clean high-density polyethylene (HDPE) bottle flushed with sample water three times and filled without any headspace.

Each 250 mL sample was immediately (within 5 min of collection) transferred to a mobile field-lab for filtration via 0.45 μm enclosed syringe filter unit and aliquots transferred to colourimetric reagents or subject to appropriate acid preservation. For on-site separation of As(III) species about ~ 50 mL of 0.45 μm -filtered water was passed through solid arsenic-speciation cartridges (Metalsoft) and preserved with concentrated HCl. The cartridge contains highly selective aluminosilicate that adsorbs As(V) and allows only As(III) to pass through the column (Le et al., 2000). For cations and trace metals, 50 mL of filtrate was preserved with 0.3 mL of concentrated HNO_3^- . For anions, the filtrate was pre-treated with 2 g per 50 mL of cation exchange resin [BioRad AG50W-XB (142–1421)] to prevent metal precipitation and subsequent scavenging of anions. All the water samples were protected from sunlight and stored at 4 °C until further analysis.

Spectrophotometric analysis was performed on the same day of sample collection for dissolved Fe^{2+} and total Fe (Fe^{Tot}) by the 1,10 Phenanthroline method (APHA, 2005); sulfide by the methylene blue method (Cline, 1969); alkalinity by the bromophenol blue method (Sarazin et al., 1999); phosphate by the ammonium molybdate method (Murphy and Riley, 1958); and ammonia by the salicylate method (Chemetrics® vacuvials kits). Additional UV–visible spectra were collected on a filtered aliquot of each sample using an ocean optics portable spectrophotometer equipped with a 10 mm path length quartz cell (Dahlen et al., 2000).

2.3. Laboratory analysis

2.3.1. Water samples

Arsenic was analyzed by Hydride Generation Atomic Absorption Spectrophotometry (HG-AAS; AA280FS, VARIAN Australia Pty Ltd, Australia) (McCleskey et al., 2004) with a detection limit of 3.4 nM and a precision within 5%. Individual samples were analyzed in quadruplicate and data presented are means. Major cations, anions and trace elements were analyzed at the Environmental Analysis Laboratory (EAL), Southern Cross University (SCU). Cations (Na, K, Ca, Mg), trace elements (arsenic, manganese, boron, molybdenum, vanadium, silver, mercury, silicon, iron, lead, chromium, cobalt, zinc, nickel, copper, barium, cadmium, aluminum and selenium) and anions (chloride, sulfur, phosphorus and bromide) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer ELAN-DRCe). For the purposes of this study, sulfur was assumed to be primarily SO_4^{2-} , as S(-II) was below detection limits. Nitrate, nitrite and fluoride were analyzed by flow injection analysis (FIA) (LCHAT QuikChem 8000).

2.4. Geochemical modeling and statistical analysis

Saturation indices (SI) were calculated using PHREEQC-2 for Windows V 2.15.06 (Parkhurst and Appelo, 1999) with stability constants derived from the Minteq database.

3. Results

3.1. Groundwater chemistry

Tubewell geochemical data are summarized in Table 1 and presented in relation to the depth of tubewell in Fig. 2. The groundwater is circum-neutral with pH (6.7–7.5) and the redox potential (pE) between 0.9 and 4.1 indicating the groundwaters are predominately moderately reducing and suboxic. Groundwater had a high amount of HCO_3^- (5.6–14.7 mM), variable concentrations of Cl^- (0.2–6.2 mM) and other major cations, Ca^{2+} (1.2–4.8 mM), Mg^{2+} (0.5–2.6 mM), Na^+ (0.2–7.3 mM) and K^+ (0.01–5.7 mM). The groundwater displayed low concentrations of SO_4^{2-} (0.0–1.5 mM), PO_4^{3-} (0–9.7 μM), NH_3^+ (0–2.8 μM), NO_2^- (0–0.2 μM) and negligible amounts of nitrate and sulfide below detection limits.

A piper plot (Fig. 3) indicates that shallow groundwater of Nawalparasi is Ca- HCO_3 dominant. Anions are clearly dominated by HCO_3^- . Ca^{2+} dominated cations in the upper and lower region and a localized increase in Na^+ was observed in the middle region.

Table 1

Summary of aqueous geochemistry of tubewell and river water sample collected along the flow path of the Bhaluhi River, Nawalparasi, Nepal.

	Upper (n = 25)			Middle (n = 37)			Lower (n = 11)			River (n = 8)		
	\bar{x}	Max	Min	\bar{x}	Max	Min	\bar{x}	Max	Min	\bar{x}	Max	Min
Depth (m)	10.6	19.8	0.6	19.3	45.7	5.5	14.8	21.3	2.7	<1	<1	<1
Temperature (°C)	25.5	27.3	24.3	25.6	26.7	24.6	25.3	25.7	25	26.3	30.7	23.9
pH	7	7.3	6.7	7.1	7.5	6.7	7.1	7.3	7.0	8.0	8.2	7.3
pE	1.9	4.1	0.9	1.6	4.1	0.9	1.5	3.1	1.1	2.2	4	0
DO	23.2	151.3	0	24.7	105.6	0	29.5	103.8	0	223.5	310.6	136.3
EC ($\mu\text{S cm}^{-1}$)	884	2230	632	894	1834	629	849	1294	553	537	724	459
HCO_3^-	8.94	14.72	6.78	9.98	13.42	7.94	8.18	12.53	5.58	5.7	7.44	4.77
Fe^{2+}	54.38	121.55	bdl	41.77	216.47	bdl	42.29	87.64	2.69	–	–	–
Fe^{Tot}	54.89	121.55	0.02	42.41	224.33	1.6	43.17	87.64	5.79	0.51	0.87	0.15
As(III)	0.44	1.64	bdl	2.33	6.87	bdl	0.54	2.26	bdl	0.03	0.07	0.001
As _{Tot}	0.49	1.75	bdl	2.58	bdl	bdl	0.59	2.48	0.003	0.04	0.10	0.002
NH_3^+	0.46	1.85	bdl	1.15	2.69	0.19	0.44	2.29	bdl	0.01	0.04	bdl
NO_3^-	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
NO_2^-	93	203	bdl	77	159	bdl	91	159	29	62	116	bdl
PO_4^{3-}	2.99	9.67	bdl	4.60	19.78	bdl	4.23	8.35	0.97	bdl	bdl	bdl
S(-II)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
SO_4^{2-}	0.17	1.54	0.03	0.11	0.89	0.03	0.24	0.85	0.03	0.12	0.15	0.09
Cl^-	1.12	6.16	0.29	0.82	5.92	0.17	1.23	3.87	0.28	0.37	0.47	0.25
Na^{++}	1.05	3.95	0.25	2.61	7.3	0.66	1.21	2.31	0.35	0.38	0.39	0.36
Ca^{2++}	3.02	4.65	1.59	2.61	4.78	1.25	3.19	4.64	2.33	1.81	2.65	1.39
Mg^{2++}	1.29	2.55	0.88	1.22	1.97	0.71	0.89	1.65	0.47	1.15	1.38	1.05
K^{++}	0.41	5.71	0.01	0.09	2.09	0.01	0.14	0.45	0.03	0.07	0.09	0.06
Si^*	0.31	0.41	0.21	0.53	0.82	0.23	0.57	0.76	0.38	0.22	0.25	0.21
Abs ₂₅₄	0.047	0.124	0.003	0.098	0.181	0.009	0.064	0.106	0.024	0.013	0.02	0.004
Al	0.21	4.61	0.001	0.15	1.96	0.01	0.09	0.56	0.01	0.39	3.18	0.01
B	2.02	9.76	0.72	6.85	16.66	1.38	2.01	5.22	0.76	0.69	0.73	0.64
Ba	3.81	9.83	1.27	1.74	4.46	0.66	1.02	2.04	0.62	2.39	3.28	2.11
Br	0.59	3.28	0.04	1.28	4.97	0.3	1.37	4.51	0.09	0.01	0.08	bdl
Co [#]	4	18	1	3	15	1	2	6	1	bdl	bdl	bdl
Cu [#]	13.53	50.37	5.99	12.48	41.51	3.56	15.16	21.04	9.69	15.23	20.33	11.41
F ^{-*}	0.09	0.2	0.04	0.06	0.13	0.01	0.09	0.13	0.01	0.13	0.15	0.07
Mn	8.33	45.41	0.04	3.01	19.93	0.15	8.36	24.98	1.44	0.26	0.58	0.01
Mo [#]	16	55	1	75	234	4	16	39	1	3	4	1
Ni [#]	5	43	1	7	34	1	4	1	bdl	bdl	3	bdl
Pb [#]	0.19	1.11	0.01	0.23	1.09	0.02	0.28	1.08	0.07	0.28	0.62	0.09
Se [#]	2	22	1	2	11	1	2	8	3	3	6	2
V [#]	1	9	1	1	8	1	1	5	2	4	6	2
Zn [#]	99	377	24	260	1470	15	124	596	5	39	207	18

All units in (μM) except where mentioned, * = mM, # = nM, bdl = below detection level.

Bivariate plots of major ion ratios may help to identify the relative importance of processes such as silicate weathering, carbonate weathering and evaporite dissolution on the concentration of major cations and anions in groundwater (e.g. Mukherjee and Fryar, 2008). The Na normalized Ca versus HCO_3^- plot [after Gaillardet et al. (1999) and Mukherjee and Fryar (2008)] (Fig. 4a) suggests that the tubewell water samples range from being influenced by silicate weathering to carbonate dissolution. The ratio of Na normalized Mg:Ca [after Gaillardet et al. (1999) and Mukherjee and Fryar (2008)] (Fig. 4b) suggests that the source of Mg is mostly by carbonate dissolution and partly by silicate weathering. A bivariate plot of Ca + Mg versus HCO_3^- [after Mukherjee and Fryar (2008)] (Fig. 4c) displays a broader scatter and suggests that the source of HCO_3^- is mostly carbonate dissolution or organic matter oxidation (Mukherjee and Fryar, 2008). Average (Ca + Mg)/ HCO_3^- of tubewell water samples of the upper region were found to be 0.48, middle region was 0.38 and the lower region was 0.50. The molar ratio of (Na + K) to Cl was greater than 1 for 59 tubewell water samples, which suggests silicate weathering is an important process (Mukherjee and Fryar, 2008; Stallard and Edmond, 1983), especially in the middle region. A bivariate plot of (Na + K)/Cl and Si suggests that these cations relative

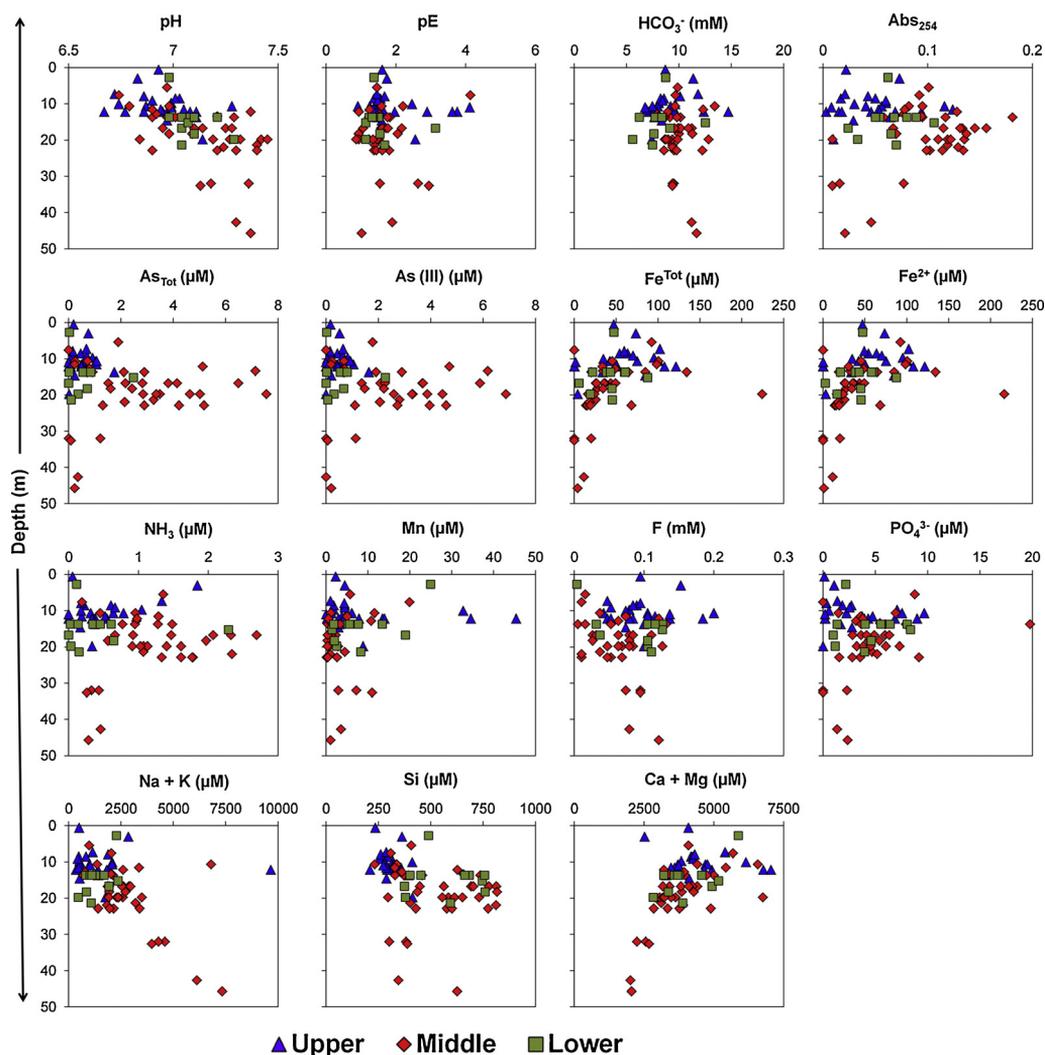


Fig. 2. Depth-profiles of water quality parameters.

to Cl increase as Si becomes $>250 \mu\text{M}$ (Fig. 4d), which is an indicator of significant silicate weathering (Mukherjee and Fryar, 2008). Si also generally increased along the flow-path of the aquifer (Fig. 5).

3.2. As, Fe, Mn and other trace elements

Aqueous geochemistry is summarized in Table 1 and bivariate plots of As_{Tot} and other species are shown in Fig. 6. The concentration of As_{Tot} in the filtered water samples from tubewells in the upper region ranged from below detection limits (BDL) to $1.7 \mu\text{M}$ with an average of $0.5 \mu\text{M}$. Eighteen groundwater samples exceeded the WHO limit in this region. The aqueous speciation of As is dominated by As(III). The concentration of $\text{Fe}_{(\text{aq})}$ varied from BDL to as high as $121.6 \mu\text{M}$ with mean of $54.9 \mu\text{M}$. Fe aqueous speciation is dominated by Fe^{2+} which varied from 0.0 to $121.6 \mu\text{M}$ with an average of $59.2 \mu\text{M}$. Manganese concentrations are also high and varied from BDL to $45.5 \mu\text{M}$ with an average of $8.3 \mu\text{M}$. There were also other major trace elements (Table 1) in groundwater of this

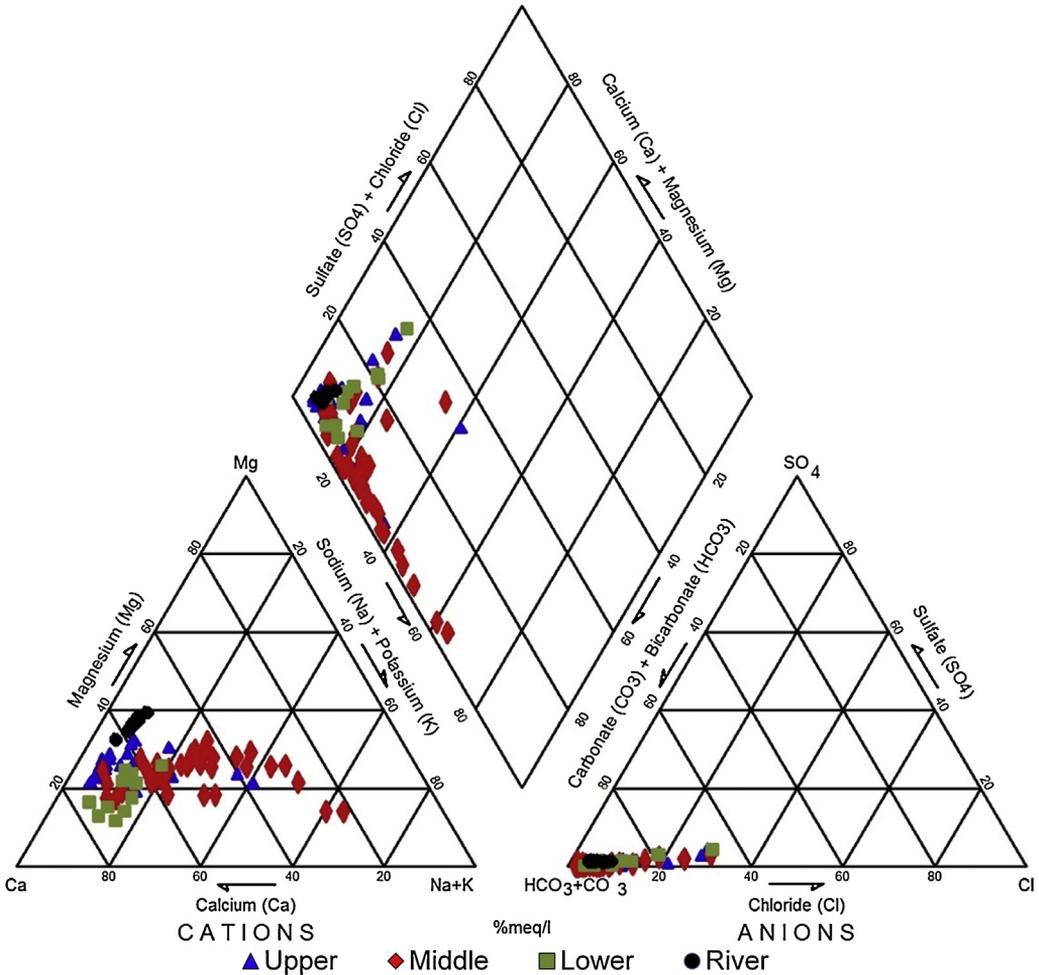


Fig. 3. Piper plot and the hydrochemical facies distribution of groundwater and river water samples.

region such as Si (0.2–0.4 mM), Al (<0.01–4.6 μM), Zn (0.02–0.4 μM), B (0.7–9.8 μM), Mo (1–100 nM), Ba (1.3–9.8 μM), and Br (4–3300 nM). The concentrations of Cu, Ni, Pb, Se, V and Co were very low. The mean fluoride level was 0.09 μM .

As_{Tot} concentrations peaked in the middle region and ranged from BDL to 7.6 μM with an average of 2.6 μM . Thirty-four out of thirty-seven groundwater samples in this region exceeded the WHO limit for As. As speciation was also dominated by As(III). Concentrations of $\text{Fe}_{(\text{aq})}$ were highest in this region, exceeding 200 μM with an average of 42.2 μM and aqueous speciation was dominated by Fe^{2+} . Manganese concentration was the lowest in this region and varied from 0.1 to 19.9 μM with an average of 3 μM . The other major trace elements detected in this region (see Table 1) were Si (0.2–0.8 mM), Al (0.01–2.0 μM), Zn (0.02–1.5 μM), B (1.4–16.7 μM), Mo (4–200 nM), Ba (0.7–4.5 μM) and Br (0.3–5.0 μM). The concentration of Cu, Ni, Pb, Se, V and Co was very low. Fluoride concentrations were mostly <0.1 μM .

In the lower region the average concentration of As_{Tot} was 0.6 μM with a maximum of 2.5 μM (Table 1). As(III) was dominant (Fig. 7). The concentration of $\text{Fe}_{(\text{aq})}$ varied from 5.8 μM to 87.6 μM with

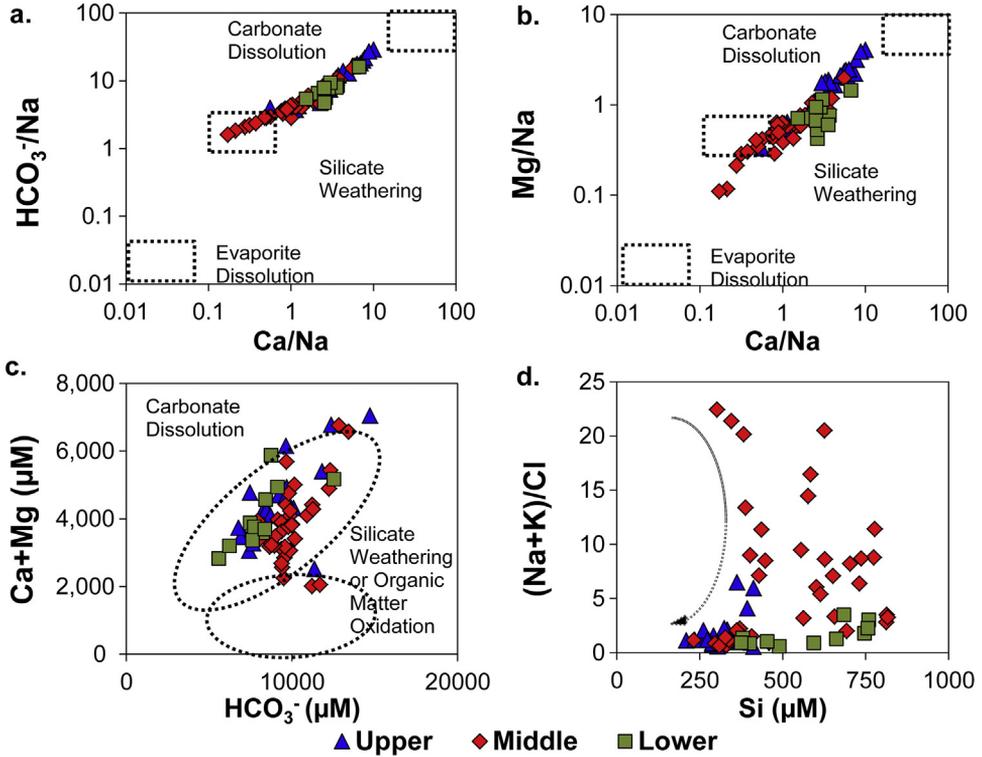


Fig. 4. Bivariate plots of major solutes. The dashes boxes represent the ranges of approximate compositions of the three main sources end members (evaporites, silicates, and carbonates) without any mixing (dashed line boundaries derived from Mukherjee and Fryar, 2008).

an average of 43.2 μM with Fe^{2+} as the dominant species. Manganese concentration varied from 1.4 to 25 μM with an average of 8.4 μM . Other trace elements detected in this region were Si (0.4–0.8 mM), Al (0.01–0.6 μM), Zn (<0.01–0.6 μM), B (0.8–5.2 μM), Ba (0.6–2 μM) and Br (0.1–4.5 μM). The concentrations of Mo, Cu, Ni, Pb, Se, V and Co were very low. Fluoride values did not exceed 0.15 μM .

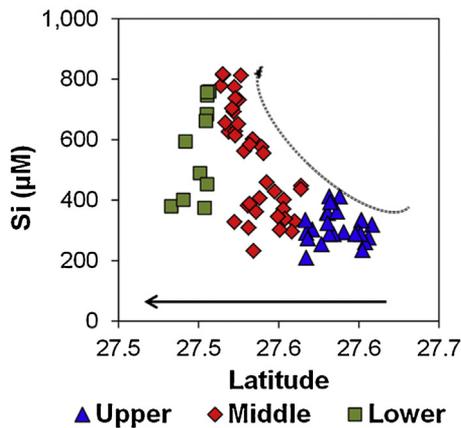


Fig. 5. Distance along the flow path of the Bhaluhi River (expressed as latitude) versus tubewell Si concentrations.

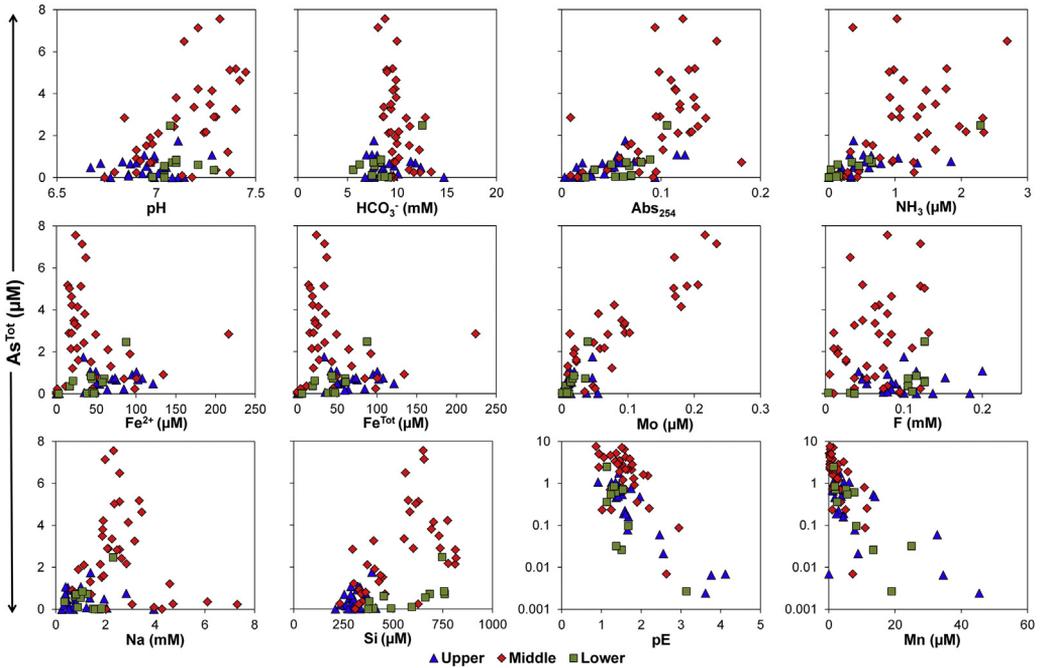


Fig. 6. Bivariate plots showing relationships between As and other parameters.

Significant positive correlations were observed between As_{Tot} and NH_3 ($r^2 = 0.37$, $\alpha = 0.01$), As_{Tot} and Mo ($r^2 = 0.84$, $\alpha = 0.01$), and As_{Tot} and Abs_{254} ($r^2 = 0.44$, $\alpha = 0.01$) (Fig. 6). Strong significant positive correlation was also observed for NH_3 and Abs_{254} ($r^2 = 0.53$, $\alpha = 0.01$) (Fig. 8).

3.3. River water chemistry

All river samples were circum-neutral to slightly alkaline (7.3–8.3) (Table 1). The river water chemistry along the river flow-path is presented in Fig. 9. There are increases in the concentration of As, Fe, Mn, Abs_{254} and Mo evident in the middle region of the flow-path. Khadka et al. (2004) also reported that the Jharia River (adjacent to the Bhaluhi River) displayed increasing As concentrations downstream. However, the concentration of arsenic in the Bhaluhi River was lower than that reported by

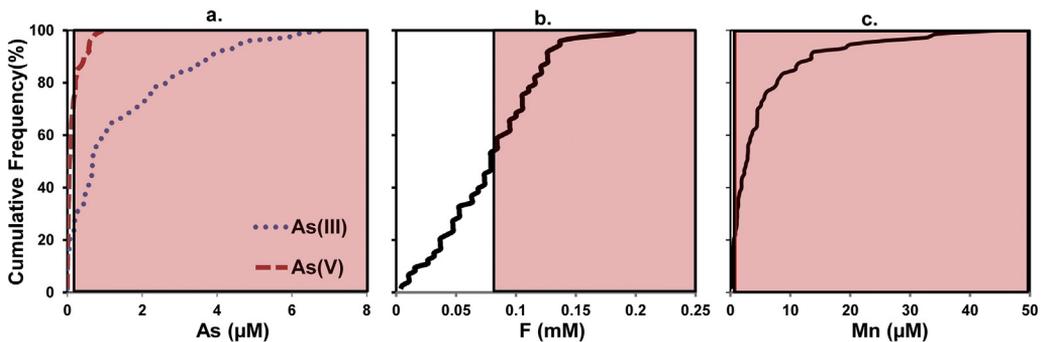


Fig. 7. Cumulative frequency distribution (% of total) of As, F and Mn (the shaded part represents exceeding the WHO GLV for the respective element). The WHO GLV for As = 0.13 μ M, F = 0.08 mM and Mn = 0.91 μ M.

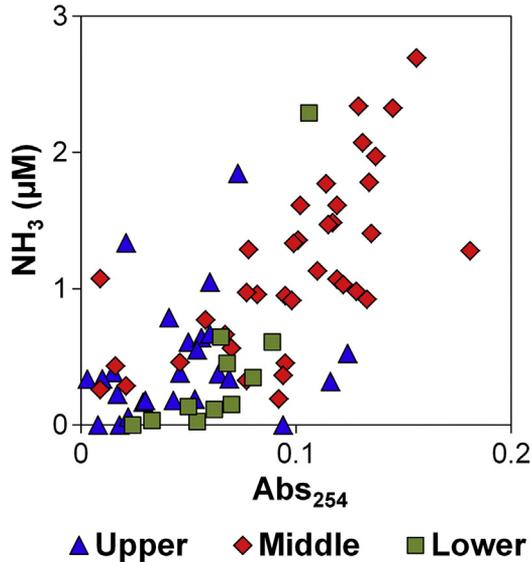


Fig. 8. Bivariate relationship between NH_3 and Abs_{254} .

Khadka et al. (2004) for the Jharia River. Manganese concentrations peaked initially at the middle region and then displayed a sharp decline, suggesting precipitation of Mn. However, the concentrations of other major ions such as HCO_3^- , Ca, Mg, K, Si, F and Br generally decrease along the flow path of the Bhaluhi River. Fluoride in rivers water exceeded the WHO GLV of $0.07 \mu\text{M}$ except at sampling point 3.

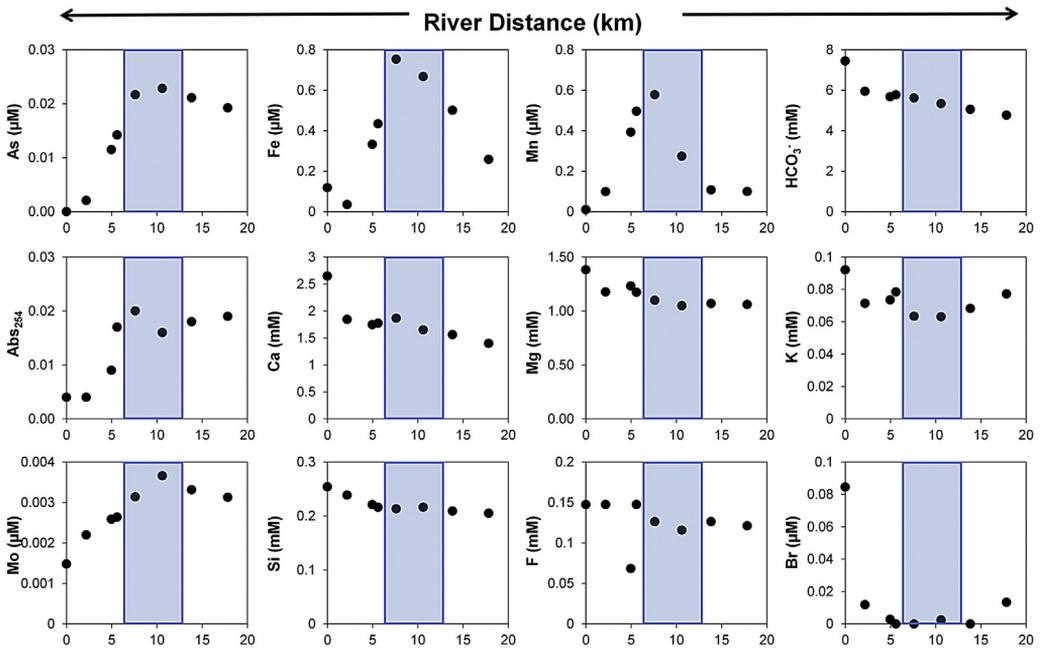


Fig. 9. Bhaluhi River water chemistry along the river flow-path. The shaded portion represents middle region of the Bhaluhi River floodplain.

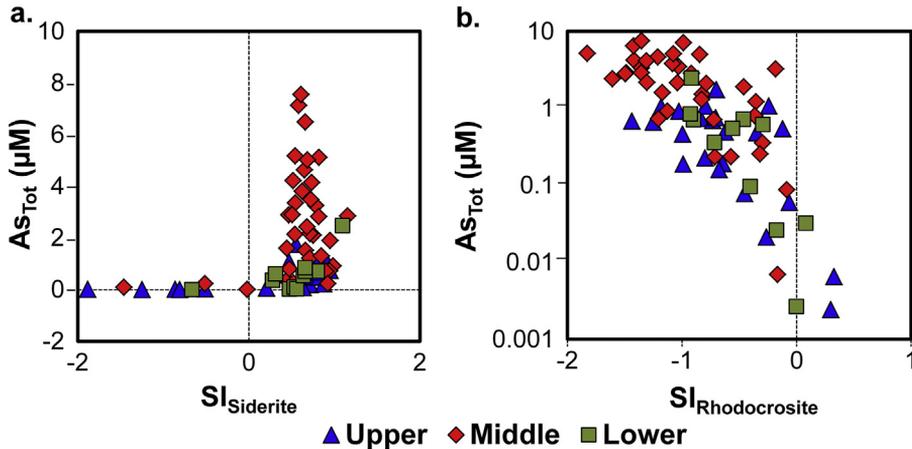


Fig. 10. Relationship between As and saturation indices of (a) Siderite and (b) Rhodocrosite.

3.4. Geochemical modeling

Saturation indices (SI) values of some minerals that may influence the geochemistry of shallow groundwater and the Bhaluhi River in Nawalparasi are shown in Table 2. The groundwater is highly undersaturated with respect to As (e.g. arsenolite), Mn oxide phases (e.g. birnessite, bixbyite, hausmannite, manganite, nsutite and pyrolusite) and sulfate phase (e.g. gypsum), indicating that aqueous As, Mn and S are unlikely to precipitate as these mineral phases (Mukherjee and Fryar, 2008). A minority of groundwater samples (15/73 or 21%) were highly to moderately supersaturated with respect to Fe(III) (oxyhydr) oxide phases like ferrihydrite, hematite, lepidocrocite, goethite, maghemite, and Mg-Ferrite. This means those minerals might be present in the aquifer at those locations. Groundwater and river water is near equilibrium with respect to slightly undersaturated with respect to fluoride phase (e.g. fluorite). Groundwater is mostly saturated with respect to siderite (Fig. 10a) and also near equilibrium or undersaturated with respect to other Fe(II) minerals like melanterite and greenalite, as well as carbonate phases (e.g. aragonite, calcite, dolomite). There is a negative correlation between AS_{Tot} and rhodocrosite (Fig. 10b).

4. Discussion

4.1. Major ion composition

The groundwater chemistry is predominately moderately reducing and suboxic with circum-neutral pH and high concentrations of Ca^{2+} and HCO_3^- . High concentrations of Ca^{2+} and HCO_3^- is a common feature in South and Southeast Asia floodplain aquifers (Berg, 2001; Bhattacharya, 2002; Bhattacharya et al., 2002; Buschmann et al., 2007; Mukherjee et al., 2012; Mukherjee and Fryar, 2008; Postma et al., 2007) and highlights the important role of carbonate dissolution and generation of bicarbonate in the hydrochemical evolution of groundwater facies and subsequent trace metal mobilization (Mukherjee et al., 2008). Similar hydrochemical facies have also been observed in deeper aquifer samples (>150 m) from the highly As contaminated region in the Bhagirathi sub-basin, Bangladesh (Mukherjee et al., 2008).

Concentrations of HCO_3^- are higher than expected based on the stoichiometry of calcium carbonate weathering, suggesting that HCO_3^- is being generated from other processes in addition to carbonate dissolution (i.e. silicate weathering or organic matter mineralization), or that some Ca^{2+} is being lost in either cation exchange reactions or precipitation of Ca-bearing minerals (e.g. Sharif et al., 2008). Groundwater is mostly saturated with respect to carbonate phases such as calcite and dolomite, further

Table 2

Saturation indices (SI) calculated using PHREEQC for tubewell and river water samples collected along the flowpath of Bhaluhi River, Nawalparasi, Nepal.

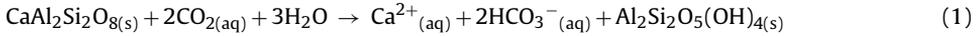
	Upper (n = 25)			Middle (n = 37)			Lower (n = 11)			River (n = 8)		
	\bar{x}	Max	Min	\bar{x}	Max	Min	\bar{x}	Max	Min	\bar{x}	Max	Min
^a Arsenolite [As ₄ O ₆]	-22.6	-20.4	-25.2	-20.3	-17.9	-25.2	-22.3	-19.8	-25.2	-25.4	-25.3	-25.4
Aragonite [CaCO ₃]	0.1	0.4	-0.2	0.3	0.5	0.0	0.2	0.4	0.1	0.8	0.9	0.3
Calcite [CaCO ₃]	0.2	0.5	-0.1	0.4	0.6	0.1	0.3	0.6	0.2	0.9	1.1	0.5
Dolomite [CaMg(CO ₃) ₂]	0.1	0.9	-0.3	0.5	1.2	-0.1	0.2	0.9	-0.1	1.8	2.0	0.7
Gypsum [CaSO ₄ ·2H ₂ O]	-2.5	-1.3	-3.1	-2.8	-1.5	-3.3	-2.3	-1.4	-3.0	-2.5	-2.3	-2.7
^b Siderite [FeCO ₃]	0.3	0.9	-2.0	0.6	1.1	-0.5	0.5	1.1	-0.7			
^c Magnetite [Fe ₃ O ₄]	18.5	20.7	16.9	19.2	21.1	16.6	19.6	20.4	18.6			
^b Melantherite [FeSO ₄ ·7H ₂ O]	-6.7	-5.8	-9.1	-6.8	-5.1	-7.8	-6.4	-5.6	-6.9			
^c Ferrihydrite [Fe(OH) ₃]	2.0	2.6	1.7	1.8	2.5	0.6	2.1	2.3	1.9			
^c Hematite [Fe ₂ O ₃]	17.9	19.1	17.2	17.3	18.8	15.0	18.1	18.5	17.5			
^c Lepidocrocite [FeOOH]	5.6	6.1	5.2	5.3	6.0	4.1	5.7	5.9	5.4			
^c Goethite [FeOOH]	6.4	7.0	6.1	6.2	6.9	5.0	6.5	6.7	6.3			
^c Maghemite [Fe ₂ O ₃]	7.5	8.6	6.7	6.9	8.4	4.6	7.7	8.1	7.1			
^c Mg-Ferrite [MgFe ₂ O ₄]	8.0	9.0	7.4	7.9	9.7	4.8	8.2	8.8	7.7			
^b Greenalite [Fe ₃ Si ₂ O ₅ (OH) ₄]	-0.3	2.3	-7.1	1.5	3.1	-1.3	1.1	2.7	-3.0			
^d Birnessite [MnO ₂]	-17.8	-12.3	-20.2	-17.9	-13.6	-20.1	-17.8	-14.3	-19.1	-12.9	-10.3	-16.0
^d Bixbyite [Mn ₂ O ₃]	-16.3	-9.6	-19.8	-16.5	-12.0	-19.5	-15.9	-12.1	-17.8	-10.2	-8.1	-12.9
^d Hausmannite [Mn ²⁺ Mn ³⁺ ₂ O ₄]	-19.0	-11.3	-23.6	-19.3	-14.3	-23.1	-18.3	-14.2	-20.8	-11.5	-8.4	-14.2
^d Manganite [MnOOH]	-8.2	-4.9	-10.0	-8.3	-6.1	-9.8	-8.0	-6.1	-9.0	-5.2	-4.2	-6.5
^d Nsutite [MnO ₂]	-17.2	-11.8	-19.6	-17.3	-13.0	-19.6	-17.2	-13.7	-18.5	-12.3	-9.8	-15.4
^d Pyrolusite [MnO ₂]	-15.5	-10.1	-17.9	-15.6	-11.3	-17.9	-15.5	-12.1	-16.8	-10.5	-7.7	-13.8
^d Rhodochrosite [MnCO ₃]	-0.7	0.3	-1.9	-0.9	-0.1	-1.8	-0.5	0.1	-0.9	-0.9	-0.5	-1.3
Fluorite [CaF ₂]	-0.4	0.3	-1.1	-1.0	-0.2	-2.8	-0.6	-0.1	-3.0	-0.3	0.0	-0.8
Quartz [SiO ₂]	0.5	0.6	0.3	0.7	0.9	0.4	0.7	0.9	0.6	0.3	0.4	0.2

Blank fields indicate values not available. SI < 0: undersaturation; SI > 0: supersaturation.

^a Upper (n = 19), middle (n = 34), lower (n = 8) and river (n = 2).^b Upper (n = 25), middle (n = 33) and river (n = 0).^c Upper (n = 3), middle (n = 8), lower (n = 4) and river (n = 0).^d Upper (n = 25) and river (n = 7).

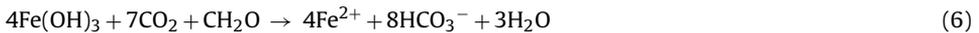
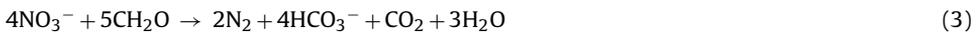
suggesting that carbonate dissolution alone does not contribute to the high bicarbonate in the aquifer of Nawalparasi.

Our data clearly indicate that silicate weathering is also contributing to the major ion solute composition of the groundwater. Bicarbonate can also be derived by weathering of primary silicate minerals such as Ca- or Na-feldspar, as represented the following equations (Eqs. (1) and (2)).



The elevation gradient of the aquifer is from north to south (Fig. 1), hence there is likely to be a generally southward flow in the aquifer system. The plot of Si against latitude (Fig. 4) reveals that the concentration of Si in groundwater generally increases downstream (southward), which is consistent with increased Si weathering along the topo-gradient flow-path of the aquifer. Elevated concentrations of Ca^{2+} and Na^+ in the shallow wells of Nawalparasi may suggest evaporative concentration or a higher degree of active weathering in the redox transitions zones (e.g. Kocar et al., 2008).

However, HCO_3^- may be also be generated by root respiration (Mukherjee and Fryar, 2008) and anaerobic oxidation of organic matter (Bhattacharya et al., 2002; Mukherjee and Fryar, 2008; Sharif et al., 2008). There are multiple pathways of anaerobic carbon metabolism that generate HCO_3^- (or consume protons), including those involving N, Mn, Fe and SO_4^{2-} as terminal electron acceptors, according to the following equations (Eqs. (3)–(7)).



The generally low redox potential of tube well waters combined with the abundance of reduced species of various redox sensitive elements (i.e. Fe^{2+} , As(III), NH_3) clearly indicates that reductive processes are important controls on aquifer geochemistry in the study area. For example, the presence of ammonia in groundwater indicates some degree of dissimilatory nitrate reduction. Ammonia could be sourced from sewage input or agricultural areas (Nath et al., 2008) or may be derived from nitrate reduction coupled with organic matter decomposition. Low nitrate and high ammonia concentration in the groundwater results suggests dissimilatory nitrate reduction is an important pathway of carbon metabolism in the aquifer (Bhattacharya et al., 2003). The reducing conditions observed here are broadly consistent with the previous studies of Bhattacharya et al. (2003), Gung et al. (2005) and Khadka et al. (2004) in the Nawalparasi district. Based on $\text{Fe}^{2+}:\text{Fe}^{\text{Tot}}$ ratios, Fe^{2+} is the dominant Fe species (Fig. 6) in the tubewell water samples. The dominance of Fe^{2+} in the groundwater samples of Nawalparasi clearly indicates prevalence of Fe(III)-reducing conditions in the aquifer (McArthur et al., 2001; Kocar et al., 2008; Winkel et al., 2008; Ravenscroft et al., 2009).

4.2. Potential sources of arsenic in groundwater

Concentrations of As in this study area varied from 0.0 to 7.6 μM and As(III) was clearly the dominant species in most samples (Fig. 6). This result is consistent with the findings of Bhattacharya et al. (2003) for this region. The significance of the predominance of As(III) species is twofold, (i) As(III) is more toxic and generally more mobile than As(V) and (ii) it is consistent with reductive processes being an important mechanism of As mobilization (Bhattacharya, 2002; Smedley and Kinniburgh, 2002). Groundwater is highly undersaturated with respect to major As phases which indicates As is unlikely to precipitate as discrete As-bearing minerals after mobilization (Mukherjee et al., 2008).

While the middle region of the study area had generally higher concentrations of As_{Tot} , overall there was a high degree of spatial heterogeneity. A heterogeneous distribution of As is consistent with the complex aquifer stratigraphy that has been reported in the Nawalparasi region previously

(Weinman, 2010; Brikowski et al., 2013). A high degree of spatial heterogeneity in As is also commonly reported in Gangetic floodplain aquifers and various mechanisms have been proposed to explain it. For example, McArthur et al. (2011) proposed that the absence or presence of a palaeo-weathering surface was a key control on As heterogeneity at their study site in West Bengal, India. McArthur et al. (2011) suggested that a palaeo-weathering surface formed during the last glacial maximum protects the underlying Pleistocene aquifer from contamination with DOC and As enriched water (McArthur et al., 2011). Spatial heterogeneity of arsenic creates difficulties for predicting the location of safe aquifers and hampers efforts to protect local people health from arsenic contamination or to identify aquifers suitable for development.

There are multiple processes that may be evoked to explain the elevated As concentrations in the study site aquifer, including weathering of primary minerals like apatite (e.g. Mailloux et al., 2009), sulfide oxidation (e.g. Williams et al., 2004, 2005) or reductive dissolution of As-bearing Fe(III) phases. Other studies of the Terai region aquifers have suggested sulfide oxidation may be an important mechanism of As mobilization (Williams et al., 2004, 2005). However, the low concentrations of nitrate, sulfate and absence of acidic water observed in our studies does not support the hypothesis of sulfide mineral oxidation being a major source of As (Dowling et al., 2002). The fact that S(-II) was generally below detection limits ($4\ \mu\text{M}$) also clearly indicates that the groundwater has not attained sulfidic conditions (Mukherjee and Fryar, 2008) and thus thiolated As species are unlikely to be important under these conditions. In addition, the low phosphate content in our samples suggests phosphate is unlikely to be a major competitor for anion adsorption sites on mineral surfaces (Dowling et al., 2002).

The reductive mobilization hypothesis (i.e. reductive dissolution of As-bearing Fe-oxides) is commonly evoked as a primary mechanism to explain As mobilization in Gangetic floodplain aquifers (e.g. Bhattacharya et al., 1997; McArthur et al., 2001; Mukherjee and Bhattacharya, 2001; Smedley and Kinniburgh, 2002; Dowling et al., 2002; Zheng et al., 2004; Nath et al., 2008; Seddique et al., 2008; Fendorf et al., 2010a). Iron oxide minerals are common in sediments of the Gangetic plain (Acharyya, 2005; Mukherjee, 2012) and the Bengal Deltaic plain (McArthur et al., 2001). These minerals are strong sorbents for As (Kocar et al., 2009). Arsenic may be desorbed from the surface of the dissolving Fe oxide, or released from within the mineral structure itself (Harvey et al., 2002; McArthur et al., 2004). Only a minority of groundwater samples at our study site were saturated with respect to Fe(III) (oxyhydr)oxide phases like ferrihydrite, hematite, lepidocrocite, goethite, maghemite, and Mg-Ferrite. However, this suggests that precipitation of Fe(III) phases from groundwater is thermodynamically favorable at these locations.

4.2.1. Decoupling between As and Fe

McArthur et al. (2001) observed a positive correlation between As(III) and Fe^{2+} in West Bengal and suggested they are coupled via reductive dissolution of As-bearing Fe(III) minerals. The study of Bhattacharya et al. (2003) in the aquifer of the Nawalparasi district also observed a positive correlation between As and Fe ($r^2 = 0.59$).

However, in this study As concentrations displayed poor correlation with most major cations (Mn, Ca and Na) including Fe (Fig. 5), which is consistent with the studies of Khadka et al. (2004) in the Nawalparasi district. There was also weak correlation between aqueous As(III) and HCO_3^- , which may be a consequence of local baseline alkalinity being generated mainly by carbonate mineral weathering and nitrate reduction (Nath et al., 2008).

Weak correlation between aqueous As and Fe in Gangetic plain aquifers has also been observed by others (Dowling et al., 2002; van Geen et al., 2006a) and may indicate decoupling between mobilization of As and Fe^{2+} . The behavior of Fe(III) oxides under reducing conditions is complex and although Fe(III) oxides are important host phases for As, during either reductive dissolution or Fe(II)-catalyzed mineral transformation, the degree of As mobilization depends on the affinity of the original and transformed minerals for the arsenic species (e.g. Dixit and Hering, 2003). A variety of studies have shown that Fe(II)-catalyzed transformation of poorly crystalline Fe(III) oxides into more thermodynamically stable crystalline phases can retard As mobilization (e.g. Fendorf et al., 2010b; Pedersen et al., 2006). In addition, the release of As during reductive dissolution of ferrihydrite can be substantially delayed compared to Fe^{2+} , as As(V) continues to adsorb to residual ferrihydrite until surface sites are saturated,

only then releasing As to the aqueous phase (Pedersen et al., 2006). This can have the effect of causing an apparent decoupling between Fe^{2+} and As mobilization.

Decoupling between Fe^{2+} and As may also result from sorption of Fe^{2+} to other surfaces (i.e. clays) or precipitation of Fe(II) minerals, such as siderite. Groundwater in Nawalparasi is near saturated with respect to siderite in most samples (Fig. 7). This suggests that aqueous Fe^{2+} in the groundwater may precipitate as siderite, vivianite or hydroxycarbonates (McArthur et al., 2001; Ahmed et al., 2004), which is consistent with the groundwater chemistry being strongly regulated by the precipitation/dissolution of carbonate minerals (Bhowmick et al., 2013). The fact that conditions are thermodynamically favorable for precipitation of siderite within the aquifer sediments provides a plausible explanation for the apparent decoupling between As and Fe observed in Fig. 6.

4.3. Other contaminants

Seventy-seven percent of groundwater samples exceeded the United States Environmental Protection Agency (USEPA) GLV for Mn of $0.91 \mu\text{M}$ (Fig. 6). Exposure to elevated Mn in drinking water is associated with neurotoxic effects in children and diminished intellectual function (Wasserman et al., 2006). Mn oxides, found in soils and sediments, are highly reactive and strong scavengers of heavy metals and trace elements (Post, 1999), including As. The presence of manganese oxides decreases As availability and As mobilization both by the oxidation of arsenite and sorption of arsenate (Lafferty et al., 2011). This behavior is consistent with the observed negative correlation between As and Mn evident in Fig. 5.

Groundwater was slightly saturated to undersaturated with respect to rhodocrosite. Slightly to undersaturated groundwater with respect to rhodocrosite has also been observed in the Bengal Basin (e.g. Mukherjee et al., 2008). Precipitation of rhodocrosite may occur in reducing environments and removes Mn(II) from groundwater (Mukherjee et al., 2008). The negative correlation observed between As_{Tot} and rhodocrosite (Fig. 7b) tentatively suggests that rhodocrosite may be a potential host phase of As. However, further work would be required to confirm this suggestion.

In addition to As and Mn contamination, about 40% of samples had fluoride concentrations exceeding the WHO GLV of $0.07 \mu\text{M}$ (see Fig. 6). Khadka et al. (2004) also detected F in the tubewell water of Nawalparasi. However, they also reported a positive correlation between F and As concentrations, a feature which was not observed by this study. A desorption/adsorption study of Kim et al. (2012) indicated that if Fe(III) (oxyhydr)oxide is the host for both As and F^- , then co-contamination may be induced by the reductive dissolution of the Fe(III) (oxyhydr)oxide in reducing aquifers. Exposure to elevated arsenic and fluoride in drinking water (>WHO GLV) can cause endemic arsenicosis and endemic fluorosis, affect the immune system, reduce IQ levels and decrease intellectuality of children (Wang et al., 2006; Wasserman et al., 2004; Rocha-Amador et al., 2009, 2011). Dissolution and precipitation of Ca minerals (such as fluorite and calcite) regolith weathering (Hallet et al., 2015) and F-adsorption–desorption typically control fluoride in groundwater (Guo et al., 2012). The majority of the groundwater samples here are saturated with CaCO_3 and undersaturated with respect to CaF_2 . Undersaturation of CaF_2 might be due to CaCO_3 precipitation, preventing it by lowering Ca^{2+} activity and allowing more CaF_2 to dissolve (Rafique et al., 2008).

There was no correlation observed in between As and other trace elements except Mo. Mo occurs as an oxyanion and its aqueous behavior is somewhat similar to As oxyanions (Dowling et al., 2002), therefore a positive correlation between them is not surprising.

4.4. Organic matter

Natural organic matter in aquifer sediments and groundwater is of crucial concern, as it is a primary source of electron donors driving reductive geochemical processes that can mobilize As (Islam, 2004; Lawson et al., 2013). High concentrations of electron donors or chelating ligands derived from natural organic matter may act as a catalyst for the dissolution of iron oxides (Fendorf et al., 2010b). UV absorbance at 254 nm (Abs_{254}) is a proxy for dissolved organic matter content in natural waters and is also positively correlated with aromatic carbon content (Junquet, 2010; Mrkva, 1983; Weishaar et al.,

2003). A positive correlation observed in between NH_3 and Abs_{254} in the middle and lower region (Fig. 8) is consistent with nitrate reduction induced by the anaerobic oxidation of organic matter.

The positive correlations between As_{Tot} and NH_3 , as well as As_{Tot} and Abs_{254} observed in the groundwater of Nawalparasi are consistent with microbial activity, reducing conditions and a sufficient supply of organic matter as being important factors contributing to As mobilization (Dowling et al., 2002). Bhattacharya et al. (2003) also reported a positive correlation between arsenic and ammonia in groundwater of the Nawalparasi district. However, Khadka et al. (2004) did not observe any correlation between them in their studies of the same region. Dowling et al. (2002) also observed a positive correlation between As and NH_3 and Mo in the groundwater of the Bengal Basin.

There may be a variety of different sources of organic matter in the aquifer sediments. Oxbow lakes formed by channel meandering are common in the low-lying topography of the floodplain and form organic-rich wetland areas. The anaerobic environment that prevails within the shallow sediments of such wetlands can encourage microbial induced reductive dissolution of As-bearing Fe (hydr)oxide minerals (e.g. Kocar et al., 2008) such as ferrihydrite and goethite (Winkel et al., 2008), thereby mobilizing As in groundwater. In other systems, such reductive mobilization of As has been reported as continuing with increasing depth until depletion of labile As or exhaustion of labile carbon (Kocar et al., 2008). Other sources of carbon could include young labile carbon derived from organic-rich recharge waters (i.e. constructed ponds and flooded rice fields) and encouraged by anthropogenic changes in land use or aquifer abstraction patterns (Harvey et al., 2006; Kocar et al., 2008; Lawson et al., 2013). For example, recent studies of Lawson et al. (2013) in regions of Cambodia and West Bengal with intensive pumping of groundwater showed that pond-derived organic carbon can be transported to the 50–100 m depth in the underlying arsenic-contaminated aquifers. Further work is required to ascertain the possible origin(s), age and characteristics of DOC in Terai aquifers.

4.5. River water chemistry

The river water chemistry (increase in concentrations of As, Fe, Mo and Abs_{254}) are broadly consistent with the spatial patterns in groundwater chemistry. Although As concentrations in the Bhaluhi River water were below the WHO GLV, there was a general increase in concentrations downstream, with a peak corresponding to the middle region of the sampling area where groundwater As concentration were also highest. The higher concentration of As in the river water might be due to baseflow from shallower, more As-enriched groundwater (Mukherjee and Fryar, 2008) or localized reductive processes in the hyporheic zone. This is consistent with Brikowski et al. (2013), who suggested that groundwater in this region made a significant contribution to stream baseflow during the dry season. The decrease in concentration of Mn in the middle region suggests precipitation or loss of Mn via sorption. The elevated concentrations of fluoride suggest fluoride is also being released in the river water via groundwater baseflow.

4.6. Further research

This study extends the work of Bhattacharya et al. (2003) and Weinman (2010) and suggests that, along with carbonate and silicate weathering, microbial mediated oxidation of organic matter coupled with reductive dissolution of FeOOH is likely to be an important process responsible for release of high concentrations of aqueous As(III) and Fe(II) in the shallow aquifer at Nawalparasi. The apparent decoupling between As and Fe may be explained by the formation of siderite, but further investigation is required to confirm this suggestion. Contrary to Williams et al. (2004, 2005), we found no evidence to suggest sulfide oxidation was a major source of contemporary As. Further work is required to ascertain the origin(s), role and age of organic carbon in the aquifer systems.

However, there are important limitations in using well-based collection methods to resolve aquifer geochemical processes. This is particularly the case in environments with complex stratigraphy where the screened zone of tube wells may span multiple, contrasting sedimentary facies. Future work that collects depth-resolved sediments and porewaters simultaneously and integrates sediment mineralogy with aqueous characterization would be of great benefit in helping unambiguously identify key geochemical processes controlling aquifer As mobilization in the Terai.

5. Conclusions

In the shallow aquifer of the Nawalparasi district, groundwaters display reducing/sub-oxic conditions with circum-neutral pH and are characterized by Ca-HCO₃ type water. The concentration of aqueous As [mainly As(III)] exceeded the WHO limit (0.13 μM) for safe drinking water in 59 (80%) out of 73 sampled wells. The aquifer is also contaminated with manganese and fluoride, with 77% and 40% of samples above WHO guidelines respectively. Groundwater chemistry is largely controlled by carbonate minerals. While the hydrogeochemical data are broadly consistent with microbially mediated reductive dissolution of Fe(III) oxyhydroxides being an important mechanism releasing As into the aquifer, further work is required to unambiguously resolve the mechanism(s) and definitively explain the apparent decoupling with Fe²⁺. Other geochemical processes, e.g., silicate weathering and carbonate dissolution, are primarily responsible for distribution of solutes in groundwater.

Acknowledgements

This project was funded by Australian Research Council Future Fellowship (Grant no. FT110100130) and Southern Cross University. The authors would like to thank Mr. Makhan Maharjan (ENPHO) for providing blanket testing data of groundwater arsenic. We also appreciate the support of Environment and Public Health Organization (ENPHO), Nepal Red Cross Society (NRCS), Central Department of Geology (CDG) of Tribhuvan University, Department of Mines and Geology (DMG), Groundwater Resources Development Board (GRDB), HEMS Nepal and ASHA/Nepal for their kind cooperation. We acknowledge the invaluable contribution of Mr. Gyan Prakash Yadav, Ms. Lauren Hook and Er. Om Shrestha during the field study at Nawalparasi. We thank Barbara Harrison for assisting with sample quarantine and Environmental Analysis Laboratory for chemical analyses. We would like to thank anonymous reviewers for their suggestions. J. Diwakar was financially supported by the Australian Postgraduate Award/International Postgraduate Research Scholarship (APA/IPRS) provided by Australian Government. Salary support for Scott Johnston was provided by the Australian Research Council Future Fellowship (Grant no. FT110100130).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ejrh.2014.10.001](https://doi.org/10.1016/j.ejrh.2014.10.001).

References

- Acharyya, S.K., 2005. Arsenic levels in groundwater from Quaternary alluvium in the Ganga Plain and the Bengal Basin, Indian subcontinent: insights into influence of stratigraphy. *Gondwana Res.* 8, 55–66.
- Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A., Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Appl. Geochem.* 19, 181–200.
- APHA, 2005. Standards Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association – American Water Works Association, Baltimore, USA.
- Berg, M., 2001. Arsenic contamination of ground and drinking water in Vietnam: a human health threat. *Environ. Sci. Technol.* 35, 2621–2626.
- Bhattacharya, P., Chatterjee, D., Jacks, G., 1997. Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: options for safe drinking water supply. *Int. J. Water Resour. Dev.* 13, 79–92.
- Bhattacharya, P., 2002. Arsenic contaminated groundwater from the sedimentary aquifers of South-East Asia. In: Bocanegra, E., Martinez, D., Massone, H. (Eds.), *Groundwater and Human Development*, Proceedings of the XXXII IAH and VI ALHSUD Congress, Mar del Plata, Argentina, pp. 357–363.
- Bhattacharya, P., Jacks, G., Ahmed, K.M., Khan, A.A., Routh, J., 2002. Arsenic in groundwater of the Bengal delta plain aquifers in Bangladesh. *Bull. Environ. Contam. Toxicol.* 69, 538–545.
- Bhattacharya, P., Tandukar, N., Neku, A., Valero, A.A., Mukherjee, A.B., Gunnar, J., 2003. Geogenic arsenic in groundwater from Terai Alluvial Plain of Nepal. *J. Phys. IV France* 107, 173–176.
- Bhowmick, S., Nath, B., Halder, D., Biswas, A., Mondal, P., Chakraborty, S., Nriagu, J., Bhattacharya, P., Iglesias, M., Roman-Ross, G., Mazumder, D.G., Bundschuh, J., Chatterjee, D., 2013. Arsenic mobilization in the aquifers of three physiographic settings of West Bengal, India: understanding geogenic and anthropogenic influences. *J. Hazard. Mater.* 262, 915–923.
- Bisht, S.B., Khadka, M.S., Kansakar, D.R., Tuinhoff, A., 2004. Study of arsenic contamination in irrigation tube wells in the Terai, Nepal. In: Kansakar, D.R. (Ed.), *Proceeding of the Seminar on Arsenic Study in Groundwater of Terai and Summary Project Report. Arsenic Testing and Finalization of Groundwater Legislation Project*. His Majesty's Government, Ministry of Water

- Resources, Department of Irrigation/Groundwater Resources Development Project, Bank, Netherland Water Partnership Program, The World Bank, Kathmandu, pp. 48–55.
- Brikowski, T.H., Smith, L.S., Shei, T.C., Shrestha, S.D., 2004. Correlation of electrical resistivity and groundwater arsenic concentration, Nawalparasi, Nepal. *J. Nepal Geol. Soc.* 30, 99–106.
- Brikowski, T.H., Neku, A., Shrestha, S.D., Smith, L.S., 2013. Hydrologic control of temporal variability in groundwater arsenic on the Ganges floodplain of Nepal. *J. Hydrol.* (in press).
- Buschmann, J., Berg, M., Stengel, C., Sampson, M.L., 2007. Arsenic and manganese contamination of drinking water resources in Cambodia: coincidence of risk areas with low relief topography. *Environ. Sci. Technol.* 41, 2146–2152.
- CBS, 2012. National Population and Housing Census 2011 (Village Development Committee/Municipality). Central Bureau of Statistics, National Planning Commission Secretariat, Government of Nepal, Kathmandu.
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454–458.
- Dahlen, J., Karlsson, S., Backstrom, M., Hagberg, J., Petterson, J., 2000. Determination of nitrate and other water quality parameters in groundwater from UV/Vis spectra employing partial least squares regression. *Chemosphere* 40, 71–77.
- Dixit, S., Hering, J.C., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implication for arsenic mobility. *Environ. Sci. Technol.* 37, 4182–4189.
- Dowling, C.B., Poreda, R.J., Basu, A.R., Peters, S.L., Aggrawal, P.K., 2002. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. *Water Air Soil Pollut.* 38, 1173.
- Fendorf, S., Michael, H.A., van Geen, A., 2010a. Spatial and temporal variations of groundwater arsenic in south and Southeast Asia. *Science* 328, 1123–1127.
- Fendorf, S., Nico, P.S., Kocar, B.D., Masau, Y., Tufano, K.J., 2010b. Arsenic chemistry in soils and sediments. In: *Developments in Soil Science*. Elsevier, pp. 357–378.
- Gaillardet, J., Dupre, B., Louvat, P., Allegre, C.J., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Guo, H., Zhang, Y., Xing, L., Jia, Y., 2012. Spatial variation in arsenic and fluoride concentrations of shallow groundwater from the town of Shahai in the Hetao basin, inner Mongolia. *Appl. Geochem.* 27, 2187–2196.
- Gurung, J., Ishiga, H., Khadka, M., 2005. Geological and geochemical examination of arsenic contamination in groundwater in the Holocene Terai Basin, Nepal. *Environ. Geol.* 49, 98–113.
- Hallet, B., Dharmagunawardhane, H.A., Atal, S., Valsami-Jones, E., Ahmed, S., Burgess, W.G., 2015. Mineralogical sources of groundwater fluoride in Archaed bedrock/regolith aquifers: mass balances from southern India and north-central Sri Lanka. *J. Hydrol.: Reg. Stud.* 4, 111–130.
- Harvey, C.F., Swartz, C.H., Badruzzan, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science* 298, 1602–1606.
- Harvey, C.F., Ashfaq, K.N., Yu, W., Badruzzaman, A.B.M., Ali, M.A., Oates, P.M., Michael, H.A., Neumann, R.B., Beckie, R., Islam, S., Ahmed, M.F., 2006. Groundwater dynamics and arsenic contamination in Bangladesh. *Chem. Geol.* 228, 112–136.
- Islam, F.S., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68–71.
- Junquet, P., 2010. Role of DNOM Photo-Degradation on Eutrophication in Freshwater Lakes. Department of Chemistry, University of Oslo, Oslo, Norway.
- Kansakar, D.R., 2004. Geologic and geomorphologic characteristics of arsenic contaminated groundwater areas in Terai, Nepal. In: Kansakar, D.R. (Ed.), *Proceeding of the Seminar on as Study in Groundwater of Terai and Summary Project Report. Arsenic testing and Finalization of Groundwater Legislation Project*. His Majesty's Government, Ministry of Water Resources, Department of Irrigation/Groundwater Resources Development Project, Bank – Netherland Water Partnership Program, The World Bank, Kathmandu, pp. 31–46.
- Kansakar, D.R., 2005. Understanding groundwater for proper utilization and management in Nepal. In: Sharma, B.R., Villhoth, K.G., Sharma, K.D. (Eds.), *Groundwater Research and Management: Integrating Science into Management Decisions*. International Water Management Institute (IWMI), Groundwater Governance in Asia. IWMI-TATA Water Policy Program and National Institute of Hydrology Roorkee, India, pp. 95–104.
- Khadka, M.S., Kansakar, D.R., Bisht, S.B., Regmi, S., Vaidya, M.P., Singh, M.P., Singh, T.B., Tuinoff, A., 2004. Study of arsenic in groundwater in and around Parasi Bazaar, Nawalparasi District, Nepal. In: Kansakar, D.R. (Ed.), *Proceeding of the Seminar on Arsenic Study in Groundwater of Terai and Summary Project Report. Arsenic Testing and Finalization of Groundwater Legislation Project*. His Majesty's Government, Ministry of Water Resources, Department of Irrigation/Groundwater Resources Development Project, Bank, Netherland Water Partnership Program, The World Bank, Kathmandu, pp. 57–71.
- Kim, S.H., Kim, K., Ko, K.S., Kim, Y., Lee, K.S., 2012. Co-contamination of arsenic and fluoride in the groundwater of unconsolidated aquifers under reducing environments. *Chemosphere* 87, 851–856.
- Kocar, B.D., Polizzotto, M.L., Benner, S.G., Ying, S.C., Ung, M., Ouch, K., Samreth, S., Suy, B., Phan, K., Sampson, M., Fendorf, S., 2008. Integrated biogeochemical and hydrologic processes driving arsenic release from shallow sediments to groundwaters of the Mekong delta. *Appl. Geochem.* 23, 3059–3071.
- Kocar, B.D., Borch, T., Fendorf, S., 2009. Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite. *Geochim. Cosmochim. Acta* 74, 980–994.
- Lafferty, B.J., Ginder-Vogel, M., Sparks, D.L., 2011. Arsenite oxidation by a poorly-crystalline manganese oxide. 3. Arsenic and manganese desorption. *Environ. Sci. Technol.* 45, 9218–9223.
- Lawson, M., Polya, D.A., Boyce, A.J., Bryant, C., Mondal, D., Shantz, A., Ballentine, C.J., 2013. Pond-derived organic carbon driving changes in arsenic hazard found in Asian groundwaters. *Environ. Sci. Technol.* 47, 7085–7094.
- Le, X.C., Yalcin, S., Ma, M., 2000. Speciation of submicrogram per liter levels of arsenic in water: on-site species separation integrated with sample collection. *Environ. Sci. Technol.* 34, 2342–2347.
- Mahanta, C., Enmark, G., Nordborg, D., Sracek, O., Nath, B.N., Nickson, R.T., Herbert, R., Jacks, G., Ramanathan, A.L., Mukherjee, A., Bhattacharya, P., 2015. Understanding distribution, hydrogeochemistry and mobilization mechanism of arsenic in groundwater in a low-industrialized homogeneous part of Brahmaputra river floodplain, India. *J. Hydrol.: Reg. Stud.* 4, 154–171.

- Maharjan, M., Watanabe, C., Ahmand, A., Ohtsuka, R., 2005. Arsenic contamination in drinking water and skin manifestations in lowland Nepal: the first community-based survey. *Am. J. Trop. Med. Hyg.* 73, 477–479.
- Mailloux, B.J., Alexandrova, E., Keimowitz, A.R., Wovkulich, K., Freyer, G.A., Herron, M., Stolz, J.F., Kenna, T.C., Pichler, T., Polizzotto, M.L., Dong, H., Bishop, M., Knappett, P.S.K., 2009. Microbial mineral weathering for nutrient acquisition releases arsenic. *Appl. Environ. Microbiol.* 75, 2558–2565.
- McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwal, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.* 37, 109–117.
- McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem.* 19, 1255–1293.
- McArthur, J.M., Nath, B., Banerjee, D.M., Purohit, R., Grassineau, N., 2011. Palaeosol control on groundwater flow and pollutant distribution: the example of arsenic. *Environ. Sci. Technol.* 45, 1376–1383.
- McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic (III/V) determinations: an evaluation of the literature and new analytical results. *Appl. Geochem.* 19, 995–1009.
- Michael, H.A., Voss, C.I., 2008. Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. *Proc. Nat. Acad. Sci. U. S. A.* 105, 8531–8536.
- Mrkva, M., 1983. Evaluation of correlations between absorbance at 254 nm and COD of river waters. *Water Res.* 17, 231–235.
- Mukherjee, A.B., Bhattacharya, P., 2001. As in groundwater in the Bengal Delta Plain: slow poisoning in Bangladesh. *Environ. Res.* 9, 189–220.
- Mukherjee, A., Fryar, A.E., 2008. Deeper groundwater chemistry and geochemical modeling of the arsenic affected western Bengal basin, West Bengal, India. *Appl. Geochem.* 23, 863–894.
- Mukherjee, A., von Brömsen, M., Scanlon, B.R., Bhattacharya, P., Fryar, A.E., Hasan, M.A., Ahmed, K.M., Chatterjee, D., Jacks, G., Sracek, O., 2008. Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the Western (Bhagirathi sub-basin, India) and Eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin. *J. Contam. Hydrol.* 99, 31–48.
- Mukherjee, A., 2012. Controls on distribution of arsenic in the Central Gangetic basin (including the river Kosi fan). In: Ramanathan, A.L., Mukherjee, A., Nath, B., Johnston, S. (Eds.), *Indo-Australian Workshop on Arsenic*. Jawaharlal Nehru University, New Delhi, India, pp. 13–16.
- Mukherjee, A., Scanlon, B.R., Fryar, A.E., Saha, D., Ghosh, A., Chowdhuri, S., Mishra, R., 2012. Solute chemistry and arsenic fate in aquifers between the Himalayan foothills and Indian craton (including central Gangetic plain): influence of geology and geomorphology. *Geochim. Cosmochim. Acta* 90, 283–302.
- Mukherjee, A., Saha, D., Harvey, C.F., Taylor, R.G., Ahmed, K.M., 2015. Groundwater systems of the Indian sub-continent. *J. Hydrol.: Reg. Stud.* 4, 1–14.
- Murphy, J., Riley, J.P., 1958. A single-solution method for the determination of soluble phosphate in sea water. *J. Mar. Biol. Assoc. U.K.* 37, 9–14.
- NASC, 2004. *The State of Arsenic in Nepal-2003*. ENPHO/USGS, Kathmandu.
- Nath, B., Stuben, D., Malik, S.B., Chatterjee, D., Charlet, L., 2008. Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic: Part I. Comparative hydrochemical and hydrogeological characteristics. *Appl. Geochem.* 23, 977–995.
- Nath, B., 2012. Sedimentological controls on the distribution and heterogeneity of arsenic concentrations in the lower Gangetic plain, West Bengal, India. In: Ramanathan, A.L., Mukherjee, A., Nath, B., Johnston, S. (Eds.), *Indo-Australian Workshop on Arsenic*. Jawaharlal Nehru University, New Delhi, India, pp. 10–12.
- NRCS, 2005. *Drinking Water Quality Improvement Programme (2000–2005)*. An Overview. Nepal Red Cross Society, New Baneshwar, Kathmandu.
- Parkhurst, D.L., Appelo, C.A.J., 1999. *User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One Dimensional Transport and Inverse Geochemical Calculation*. U.S. Geological Survey, Denver.
- Pathak, D., Rao, G.K., 1998. Groundwater recharge to the confined aquifer system in the Terai plain of Nawalparasi district, western Nepal: a hydrochemical approach. *J. Nepal Geol. Soc.* 17, 37–44.
- Pedersen, H.D., Postma, D., Jakobsen, R., 2006. Release of arsenic associated with the reduction and transformation of iron oxides. *Geochim. Cosmochim. Acta* 70, 4116–4129.
- Pokhrel, D., Bhandari, B.S., Viraraghavan, T., 2009. Arsenic contamination of groundwater in the Terai region of Nepal: an overview of health concerns and treatment options. *Environ. Int.* 35, 157–161.
- Post, J.E., 1999. Manganese oxide minerals: crystal structures and economic and environmental significance. *Proc. Nat. Acad. Sci. U. S. A.* 96, 3447–3454.
- Postma, D., Larsen, F., Minh Hue, N.T., Duc, M.T., Vie, P.H., Nhan, P.Q., Jessen, S., 2007. Arsenic in groundwater of the Red River floodplain, Vietnam: controlling geochemical processes and reactive transport modeling. *Geochim. Cosmochim. Acta* 71, 5054–5071.
- Rafique, T., Naseem, S., Bhangar, M.I., Usmani, T.H., 2008. Fluoride ion contamination in the groundwater of Mithi sub-district, the Thar Desert, Pakistan. *Environ. Geol.* 56, 317–326.
- Ravenscroft, P., Brammer, H., Richards, K., 2009. *Arsenic Pollution – A Global Synthesis*. RGS-IBG Book Series. Wiley-Blackwell, Chichester.
- Rocha-Amador, D., Navarro, M., Trejo-Acevedo, A., Carrizales, L., PérezMaldonado, I., Díaz-Barriga, F., Calderón, J., 2009. Use of the Rey-Osterrieth complex figure test for neurotoxicity evaluation of mixtures in children. *Neurotoxicology* 30, 1149–1154.
- Rocha-Amador, D.O., Calderon, J., Leticia, C., Costilla-Salazar, R., Perez-Maldonado, I.N., 2011. Apoptosis of peripheral blood mononuclear cells in children exposed to arsenic and fluoride. *Environ. Toxicol. Pharmacol.* 32, 399–405.
- Sarazin, G., Michard, G., Prevot, F., 1999. A rapid and accurate spectroscopic method for alkalinity measurements in sea water samples. *Water Resour.* 33, 290–294.
- Seddique, A.A., Masuda, H., Mitamura, M., Shinoda, K., Yamanaka, T., Itai, T., Maruoka, T., Uesugi, K., Ahmed, K.M., Biswas, D.P., 2008. As release from biotite into a Holocene groundwater aquifer in Bangladesh. *Appl. Geochem.* 23, 2236–2248.

- Shamsudduha, M., Uddin, A., Saunders, J.A., Lee, M.-K., 2008. Quaternary stratigraphy, sediment characteristics and geochemistry of arsenic-contaminated alluvial aquifers in the Ganges–Brahmaputra floodplain in central Bangladesh. *J. Contam. Hydrol.* 99, 112–136.
- Sharif, M.U., Davis, R.K., Steele, K.F., Kim, B., Kresse, T.M., Fazio, J.A., 2008. Inverse geochemical modeling of groundwater evolution with emphasis on arsenic in the Mississippi river valley alluvial aquifer, Arkansas (USA). *J. Hydrol.* 350, 41–55.
- Shrestha, R., 2007. Report on Impact Study of Nawalparasi District Sunwal-Swathi Cluster. Groundwater Resources Development Project, Babarmahal, Kathmandu.
- Shrestha, S.D., Brikowski, T.H., Smith, L.S., Shei, T.C., 2004. Grain size constraints on arsenic concentration in shallow wells of Nawalparasi, Nepal. *J. Nepal Geol. Soc.* 30, 93–98.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.* 17, 517–568.
- Stallard, R.F., Edmond, J.M., 1983. Geochemistry of Amazon 2. The influence of geology and weathering environment on the dissolved load. *J. Geophys. Res.* 88, 9671–9688.
- Swartz, C.H., Blute, N.K., Badruzzaman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004. Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization. *Geochim. Cosmochim. Acta* 68, 4539–4557.
- Thakur, J.K., Thakur, R.K., Ramanathan, A.L., Kumar, M., Singh, S.K., 2011. Arsenic contamination of groundwater in Nepal – an overview. *Water* 3, 1–20.
- van Geen, A., Aziz, Z., Horneman, A., Weinman, B., Dhar, R.K., Zheng, Y., Goodbred, S., Versteeg, R., Seddique, A.A., Hoque, M.A., Ahmed, K.M., 2006a. Preliminary evidence of a link between surface soil properties and the arsenic content of shallow groundwater in Bangladesh. *J. Geochem. Explor.* 88, 157–161.
- van Geen, A., Zheng, Y., Cheng, Z., Aziz, Z., Horneman, A., Dhar, R.K., Mailloux, B., Stute, M., Weinman, B., Goodbred, S., Seddique, A.A., Hoque, M.A., Ahmed, K.M., 2006b. A transect of groundwater and sediment properties in Araihaazar, Bangladesh: further evidence of decoupling between As and Fe mobilization. *Chem. Geol.* 228, 85–96.
- van Geen, A., Radloff, K., Aziz, Z., Cheng, Z., Huq, M.R., Ahmed, K.M., Weinman, B., Goodbred, S., Jung, H.B., Zheng, Y., Berg, M., Trang, P.T.K., Charlet, L., Metral, J., Tisserand, D., Guillot, S., Chakraborty, S., Gajurel, A.P., Upreti, B.N., 2008. Comparison of arsenic concentrations in simultaneously-collected groundwater and aquifer particles from Bangladesh, India, Vietnam, and Nepal. *Appl. Geochem.* 23, 3244–3251.
- Wang, S.-X., Wang, Z.-H., Cheng, X.-T., Li, J., Sang, Z.-P., Zhang, X.-D., Han, L.-L., Qiao, X.-Y., Wu, Z.-M., Wang, Z.-Q., 2006. Arsenic and fluoride exposure in drinking water: children's IQ and growth arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin County, Shanxi Province, China. *Environ. Health Perspect.* 115, 643–647.
- Wasserman, G.A., Liu, X., Parvez, F., Ahsan, H., Factor-Litvak, P., van Geen, A., Slavkovich, V., Lolocono, N.J., Cheng, Z., Hussain, I., Momotaj, H., Graziano, J.H., 2004. Drinking water arsenic exposure and children's intellectual function in Araihaazar, Bangladesh. *Environ. Health Perspect.* 112, 1329–1333.
- Wasserman, G.A., Liu, X., Parvez, F., Ahsan, H., Levy, D., Factor-Litvak, P., Kline, J., van Geen, A., Slavkovich, V., Lolocono, N.J., Cheng, Z., Zheng, Y., Graziano, H., 2006. Water manganese exposure and children's intellectual function in Araihaazar, Bangladesh. *Environ. Health Perspect.* 114, 124–129.
- Weinman, B., Goodbred, S., Zheng, Y., Aziz, Z., Steckler, M., van Green, A., Singhvi, A., Nagar, Y., 2008. Contributions of floodplain stratigraphy and evolution to the spatial patterns of groundwater arsenic in Araihaazar, Bangladesh. *Geol. Soc. Am. Bull.* 120, 1567–1580.
- Weinman, B., Unpubl. Ph.D. Thesis 2010. The Evolution of Aquifers and Arsenic in Asia: A Study of the Fluvio-Deltaic Processes Leading to Aquifer Formation and Arsenic Cycling and Heterogeneity in Bangladesh, Vietnam and Nepal. Vanderbilt University, Nashville, TN.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fuji, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37, 4702–4708.
- Williams, V., Breit, G.N., Whitney, J., Yount, J., Amatya, S.C., 2004. Preliminary observations on the geology and geochemistry of arsenic-bearing sediments in Nawalparasi District, Nepal. In: Kansakar, D.R. (Ed.), *Proceeding of the Seminar on Arsenic Study in Groundwater of Terai and Summary Project Report. Arsenic testing and Finalization of Groundwater Legislation Project.* His Majesty's Government, Ministry of Water Resources, Department of Irrigation/Groundwater Resources Development Project, Bank, Netherland Water Partnership Program, The World Bank, Kathmandu, pp. 73–83.
- Williams, V.S., Kansakar, D.R., Ghimire, B., 2005. Nepalese groundwater contamination is related to Siwalik source rock. Abstracts with programs. *Geol. Soc. Am.* 37, 170.
- Winkel, L., Berg, M., Stengel, C., Rosenberg, T., 2008. Hydrogeological survey assessing arsenic and other groundwater contaminants in the lowlands of Sumatra, Indonesia. *Appl. Geochem.* 23, 3019–3028.
- Zheng, Y., Stute, M., van Geen, A., Gavrieli, I., Dhar, R., Simpson, H.J., Schlosser, P., Ahmed, K.M., 2004. Redox control of arsenic mobilization in Bangladesh groundwater. *Appl. Geochem.* 19, 201–214.