Water Qual Expo Health (2011) 3:119–126
DOI 10.1007/s12403-011-0049-4

Multivariate Statistical Approach to Deduce Hydrogeochemical Processes in the Groundwater Environment of Begusarai District, Bihar

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Received: 19 August 2011 / Revised: 7 September 2011 / Accepted: 10 September 2011 / Published online: 29 September 2011

Abstract This work gives us an overview of the groundwater quality and problems pertaining to the occurrence of arsenic (As) and other chemical contaminants in the groundwater of Begusarai district of Bihar, India. The total As concentration in the analyzed water samples varies between 21.5–94.3 µg/L. Through the saturation index using PhreeqC, it was found that most of the samples are saturated for mineral goethite, calcite and dolomite. It was observed that mobilization of arsenic from the alluvial aquifers is mainly affected through the means of reductive dissolution of the iron oxyhydroxides within the sediments. Reductive dissolution of iron oxyhydroxide present as coatings on and around clay layer seems to be the main process responsible for the release of As into groundwater. Close to the Gangetic flood plain most of the tube wells (shallow aquifers) are affected. Groundwater is characterized by slightly alkaline pH with a moderate to strong reducing nature. The water type mainly falls in two categories i.e. Ca–HCO_3 and Ca–Cl (with contribution of 75 and 25% of total water type, respectively). Enrichment of NO_3^- at few locations is an indicator of agriculture practice well supported by effluent leaching.

Keywords Arsenic · Gangetic plain · PhreeqC · Groundwater

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Introduction

The presence of arsenic (As) in groundwater of sedimentary aquifers has emerged as a worldwide problem (Kumar et al. 2010). Most estimates of arsenic pollution are focused on the predominance of arsenic poisoning in the groundwater of West Bengal (India) and Bangladesh (Ahmed et al. 2004), which has been thought to be limited to the Ganges Delta (i.e. the lower Gangetic plain). Much arsenic in the groundwater of Lower Gangetic plain of Bangladesh and West Bengal was reported by Bhattacharya et al. (1997). Contaminated drinking water is the chief source of chronic human intoxication (Gebel 2000; Smith et al. 2000; Avtar et al. 2011), which results in skin ailments such as hyper pigmentation and keratosis, and leads progressively to cancer and ultimately death (WHO 1993; National Academy Press 2001). The current safe limit for drinking water quality guideline in case of arsenic is 10 µg/L (WHO 1993).

Management of arseniferous groundwater used for human consumption and irrigation, along with treatment or avoidance, is clearly an issue of global concern. The occurrence of arsenic in the groundwater of the upper and the central Gangetic plains are fairly new. In northern Indian states (Bihar, Jharkhand and Uttar Pradesh), considerable load of As is present in groundwater (Srivastava et al. 2008). Chakraborti et al. (2003) reported that for Bhojpur and Buxar districts of Bihar, As concentration in groundwater samples in 107 out of 152 villages exceeded the WHO and the national drinking water standards. Very recently As contamination in the groundwater of Bhagalpur district of Gangetic plain in northern India was reported by Kumar et al. (2010). The World Health Organization has repeatedly insisted that lack of ready access to clean drinking water adversely influences the general health and life expectancy of a population in many developing countries.

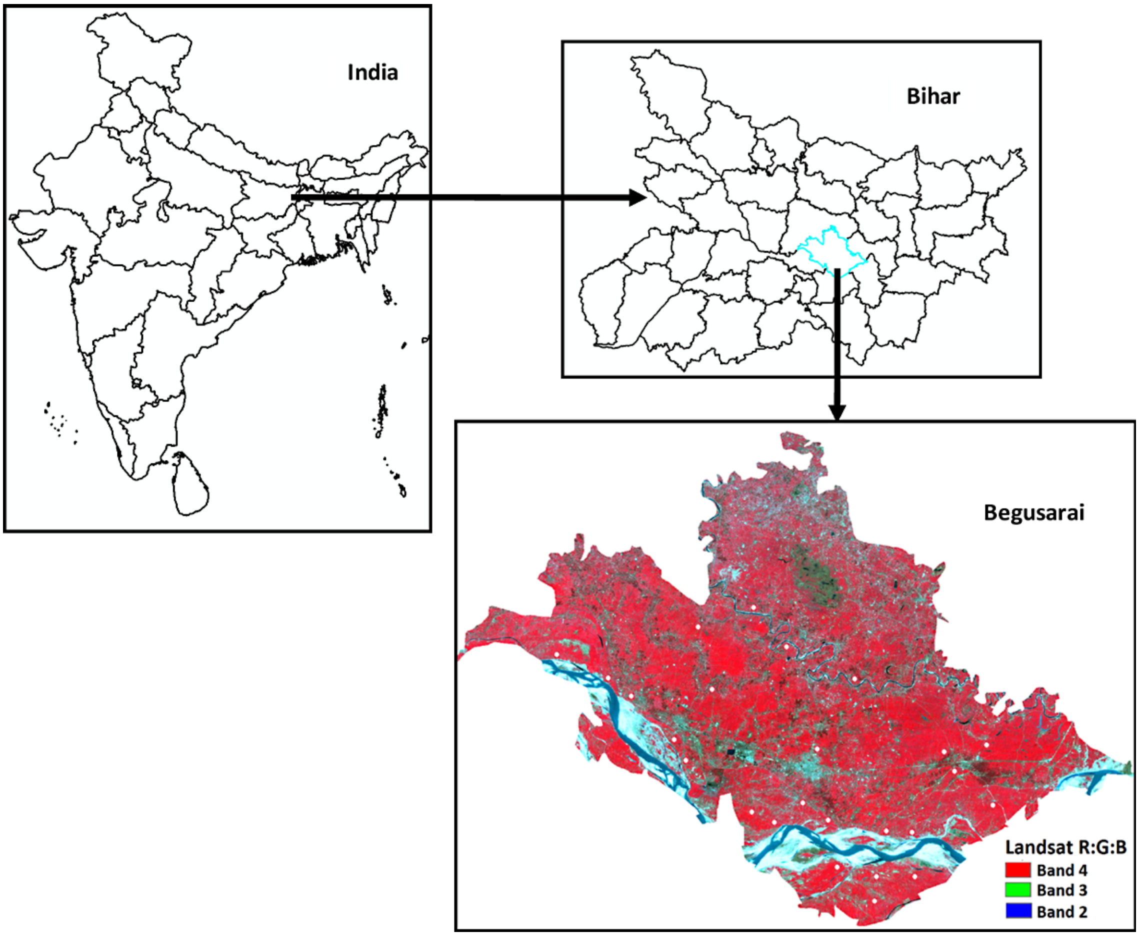

Fig. 1 Map of the area studied, showing the groundwater sampling location

Still a very small amount of literature is available on the water quality as evident from the above review, especially on arsenic pollution in this region, therefore this work is carried out to integrate and interpret chemical data with statistical techniques to delineate geochemical processes regulating groundwater quality of the Begusarai district, Bihar.

Study Area

Study area (Begusarai district, Bihar), is situated in a part of Middle Gangetic plains, locally known as North Bihar plains (Fig. 1). In general, it is a low-lying flat terrain (MSL 32–45 m) having a southerly to southeasterly slope. This factor governs the flow of streams. The Ghagra–Gandak interfluves, the Gandak–Kosi interfluves and the western Kosi fan belt dominate its fluvial geomorphology from west to east. The mid-Gangetic plains can be broadly divided into a number of major geomorphic units. The northernmost part is the region of the Siwalik ranges and is followed by the piedmont fan surface fringing the foothills, 10–30 km wide, built up by coalescing fan surfaces of major Himalayan rivers. This surface includes both the bhabar and tarai land. Built upon these surfaces are fluvial regimes classified into megafans (f) and interfluves characterized by upland terraces (T2), river valley terraces (T1) and active flood plain (T0) surfaces. The entire district of Begusarai falls in this T0 surface (Singh 2004). The district is drained by a number of rivers, viz. the Ganga, Burhi Gandak, Bagmati and Balan rivers.

Geology and Soil

The geology of the area constitutes the highest alluvial plain in the domain of the Himalayan Rivers to the north of the Ganga. The basin was formed during late Paleocene–Neocene period and is related to the upheaval of the Himalayas vis-a-vis flexural downwarp of the Indian lithosphere under the supracrustal load of the Himalayas (Wadia 1981). The entire segment abounds in buried faults and grabens. The Quaternary sediments of the Indo-Gangetic plains have been traditionally subdivided into the older and younger alluvium and locally called Bhanger and Khader. Entire area of Begusarai falls in the domain of "Khader" sediments. The soil of this land unit is primarily unaltered allu-

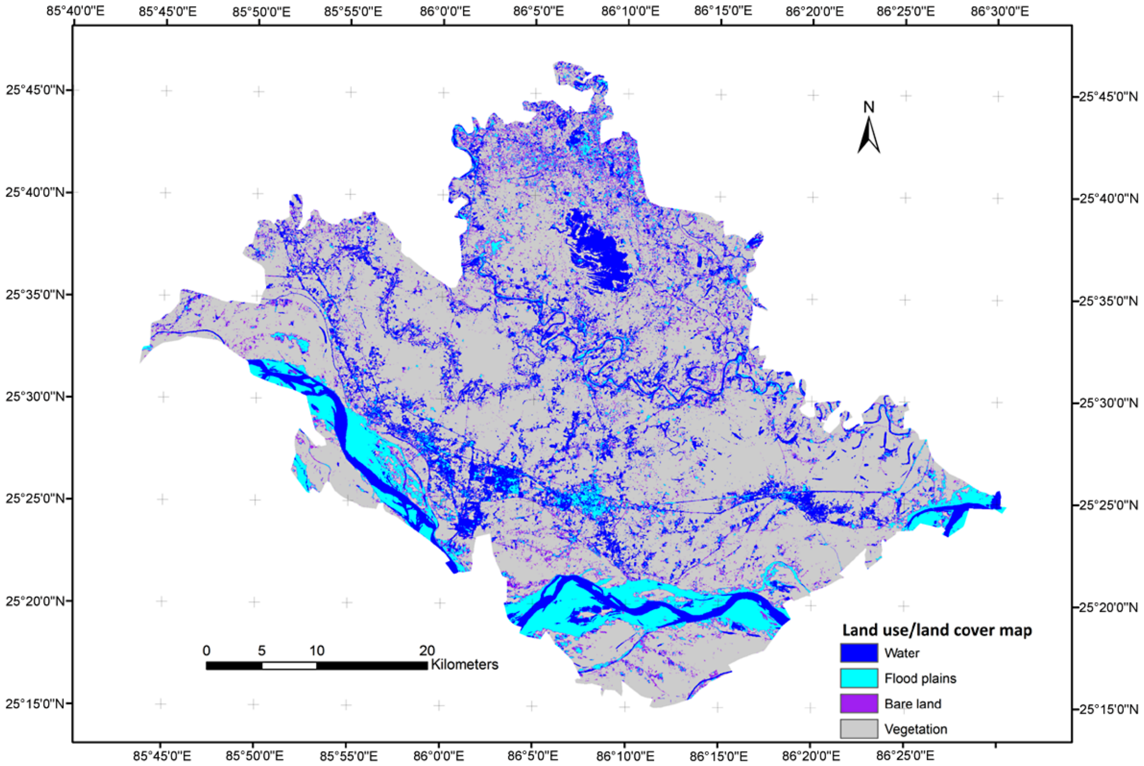

Fig. 2 Land use/land cover map of the area (based on Landsat TM data of November 05, 2005)

vium, which is yet to undergo pedogenesis (process of soil formation). Texturally it varies from sandy loam to loam in the meander scroll and levee (the upland bounding the flood plains of the river) areas, to silty loam and silt in flood basin areas of the Himalayan rivers and from loam in the levees of Ganga to clayey loam and clay in the basin of Burhi Gandak and Bhagmati river.

Land Use Land Cover Map of the Area

Landsat Thematic Mapper (TM) satellite data of November, 05, 2005 and topographic maps were used to prepare the land use and land cover (LULC) map of the study area using unsupervised classification technique in ERDAS Imagine 9.0. The study area was classified into four major land use categories viz. water, vegetation, flood plains and bare land (Fig. 2). Most of the area is covered by vegetation followed by water body and flood plains. The agriculture land along the river side is covered by rice and wheat crops (Rabi crop) because for the winter season (November) most of the farmers sow these crops in October month.

Material and Method

A total of thirty groundwater samples were collected from Begusarai District in June, 2007. Sampling wells were selected in such a way that they cover different geological formations and land use patterns at varying topography of the area. Groundwater samples were collected in clean polyethylene bottles. In-situ measurements for EC, pH and Eh were taken using a portable Orion Thermo water analyzing kit (Model Beverly, MA, 01915) and total arsenic was analyzed with the help of Digital Arsenator (Wagtech Company, UK). Following collection, the samples were brought to JNU, New Delhi and stored at 4°C before the analysis for minimizing its chemical alterations. Groundwater samples were filtered by 0.45 μm Millipore filter paper and acidified with 2 $NHNO_3$ (Ultra pure Merck) for cation analysis and HBO_3 acid was used as a preservative for nitrate analysis. Iron was analyzed in the laboratory by an Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6800). Concentrations of As were cross checked on acidified samples using Graphite-Furnace (GF) AAS in absorption mode using chemical standards with detection limit of 2 μg/L. All cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were analyzed by EEL Flame Photometer (APHA 1995). The concentration of HCO_3^- was determined by acid titration. Other anions Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} were analyzed by the Dionex Ion-Chromatography DX-120. High purity reagents (Merck) and milli-Q water (Model Milli-Q, Biocel) were used for all the analysis.

Hounslow (1995) approach (also called source-rock deduction method), which is derived from a simplistic mass balance based on water quality data, is used here to find or confirm the possible origin of the quality of the water. Schematic flow chart showing the logic of water quality elucidation using this technique is shown in Fig. 3. To apply this technique, the concentration of the various constituents must be expressed in meq/L, except for silica (which is in mmol/L) to be able to combine various ions in a chemically meaningful way. The ion balance must be within ±5%, and pH must not be less than 5 because it is not applicable to acid water. Speciation calculations were performed using the program PhreeqC (Parkhurst and Appelo 1999) and thermodynamic data compiled from databases of minteq.dat and llnl.dat.

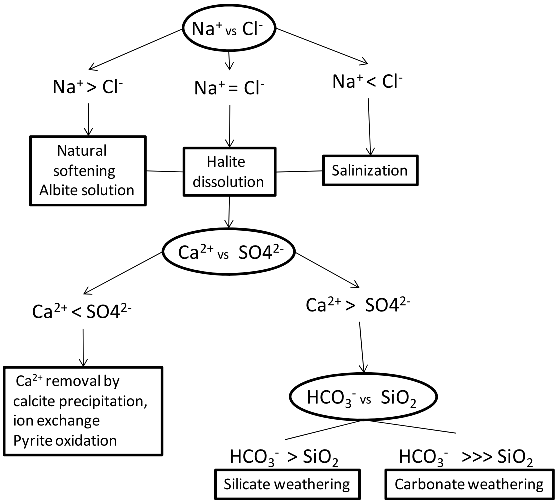

Fig. 3 Schematic diagram showing the logic of the quality of the water interpretation using simple mass balance method (Hounslow 1995)

Result and Discussion

Water quality data were analyzed by use of Piper diagrams and we found that water mainly falls in two categories, i.e. Ca–HCO_3 (about 75%) and Ca–Cl (about 25%) (Fig. 4). Finally, among the anions bicarbonate is the dominant species, while the trend of the average value found was $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$, while the trend for cations was $Ca^{2+} > Na^+ > Mg^{2+} > K^+$.

The groundwater was alkaline with an average value of pH was 8.0 (Table 1). The high pH suggests that the soils/sediments are very reactive, which eventually enhances dissolution (Subramanian and Saxena 1983). The large variation in EC (from 350.9 to 1126 µS/cm), suggests the high concentration of dissolved solids and/or high ionic strength of groundwater, local variation in soil type, multiple aquifer system and agricultural activities in the area.

Among anions HCO_3^- is the main source of alkalinity in the water samples. The higher value of Cl^- and SO_4^{2-}, which acts as a source of secondary salinity might come from sewage effluent, breakdown of organic material and agriculture runoff carrying unutilized SO_4^{2-} (Anderson 1979). In water samples, NO_3^- varied significantly from 1.3

Fig. 4 Piper diagram showing ground water quality for the Begusarai district

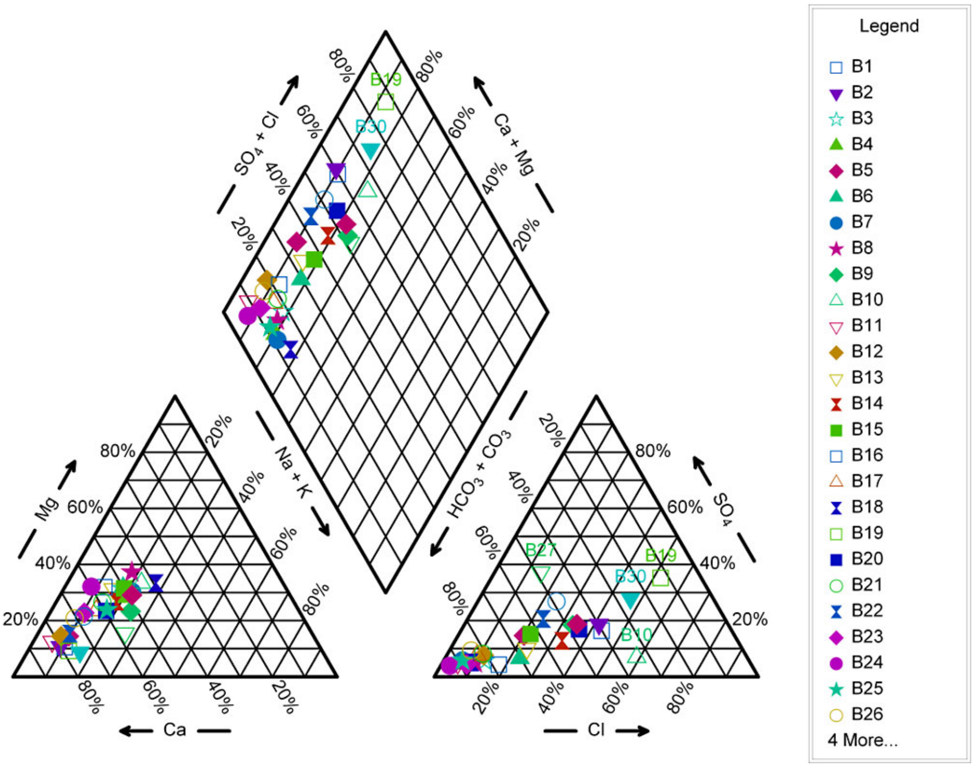

Table 1 Statistical analysis of water samples from Begusarai ($n = 30$)

Variables	Unit	Minimum	Maximum	Average
Depth	(ft)	33.0	130.0	76.9
Ph		7.8	8.3	8.0
ORP	mv	8.0	129.0	60.6
EC	µs/cm	350.9	1126.0	569.3
Na^+	mg/L	4.4	29.7	12.9
K^+	mg/L	1.07	5.2	2.1
Ca^{2+}	mg/L	20.7	143.0	56.7
Mg^{2+}	mg/L	9.0	11.1	10.4
HCO_3^-	mg/L	61.7	331.9	153.0
Cl^-	mg/L	2.6	288.5	49.6
NO_3^-	mg/L	1.3	76.8	21.3
SO_4^{2-}	mg/L	4.1	156.1	32.6
PO_4^{3-}	mg/L	2.2	5.2	3.46
SiO_2	mg/L	12.0	42.2	25.9
Fe	mg/L	0.4	1.9	1.1
As(tot)	µg/L	21.5	94.3	48.6

to 76.8 mg/L (Table 1), which indicates sporadic contact of groundwater to agricultural activities, microbial mineralization and landfill leaching (Kumar et al. 2010). The concentration of PO_4^{3-} found in water samples mainly indicates input of fertilizers in farmlands to enhance the paddy and wheat productivity in rainy season. It also acts as secondary leachates.

Among cations, average high concentration of Ca^{2+} may come from weathering of carbonaceous sandstone, plagioclase feldspar minerals commonly found in alluvial flood plains (Bhattacharya et al. 1997). The significant amount of Na^+ in the water samples can be associated with the weathering of albite mineral and ion exchange with clay, dissolution of rock salt (Tirumalesh et al. 2010). The concentration of SiO_2 varied from 12.0 to 42.2 mg/L, which mainly comes from possible alumino-silicate weathering.

Arsenic Distribution and Its Chemistry

Total arsenic concentrations in the groundwater varied from 21.5 to 94.3 µg/L (Table 1). The assorted occurrence of it near the river is an elemental signature of alluvial plain aquifer, and it also suggests that the importance of depositional environment and geological age are the key factors controlling As mobilization. From the scatter plot for depth profile of arsenic distribution (Fig. 5), it was found that there is an inverse relation between concentration of As and the depth of wells. In general, the highest As concentration occurs 60–90 feet below the ground surface and decreases rapidly below about 120 feet, a finding similar to previous reports by Bhattacharya et al. (2009). For the depth between 60 to 90 feet, it is assumed that active terminal electron accepting processes (TEAPs) drive the arsenic mobilization (McArthur et al. 2001; Mukherjee et al. 2008; Dhar et al. 2008; Zheng et al. 2004). The high concentration of As is associated with low concentrations of iron (Fig. 6), which can be described by the reduction of arseniferous Fe-oxyhydroxides coupled to precipitation of Fe^{2+} as $FeCO_3$ when anoxic conditions develop during microbial oxidation of sedimentary organic matter (Srivastava et al. 2008; Bhattacharya et al. 1997). Biomediated reductive dissolution of hydrated iron oxide (HFO) by anaerobic heterotrophic Fe^{3+} reducing bacteria (IRB) also play a significant role in the release of sorbed As to groundwater (Nickson et al. 1998; Lovley and Chapelle 1995; Islam et al. 2004).

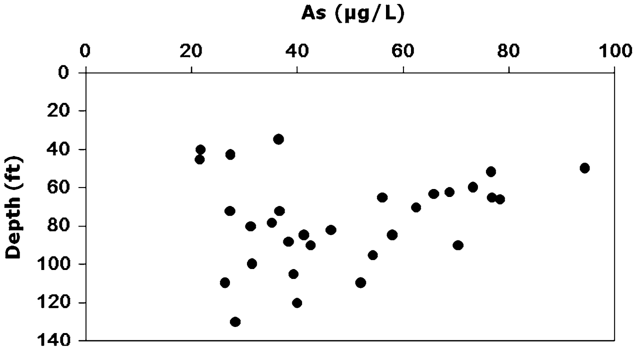

Fig. 5 Scatter plot showing arsenic distribution with depth in the Begusarai district

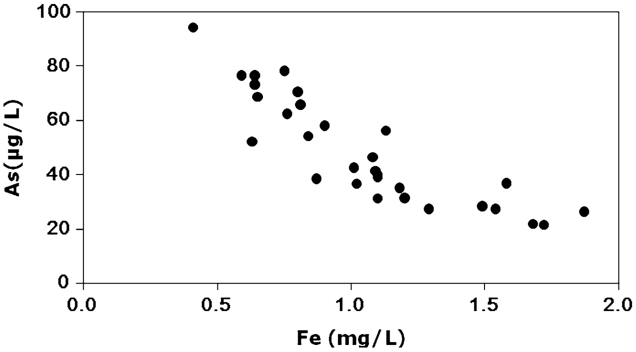

Fig. 6 Scatter plot showing relation between arsenic and iron

Geochemical Process Deduction Using Hounslow Method

First step is to compare the chloride and sodium contents (Fig. 7). Most of the groundwater samples have the relation of $Na^+ < Cl^-$, meaning the existence of salinization and for abnormal higher value of Cl^- can be attributed to the surface sources through the domestic wastewaters, septic tanks, infiltration of sewage effluents from the rural households and mixing of groundwater from different aquifers with variable Cl^- concentrations (Hasan et al. 2007). In the second

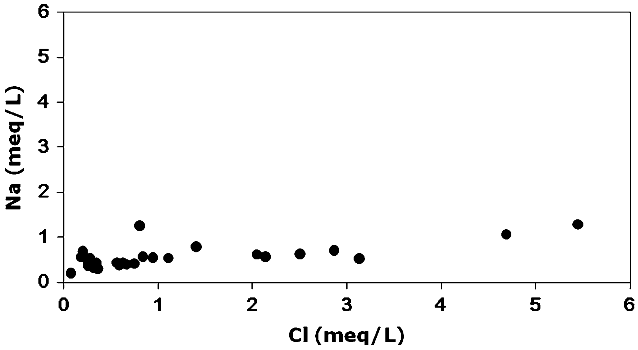

Fig. 7 Scatter plot showing relation between sodium and chloride

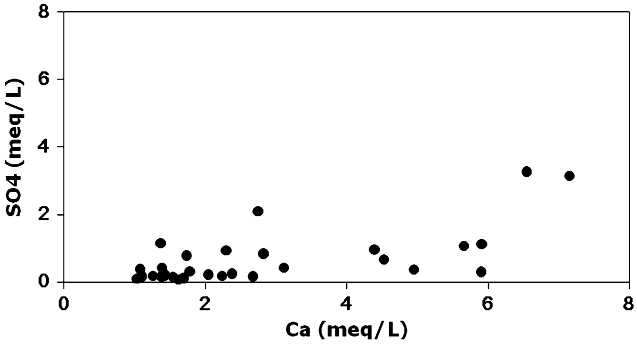

Fig. 8 Scatter plot showing relation calcium arsenic and sulphate

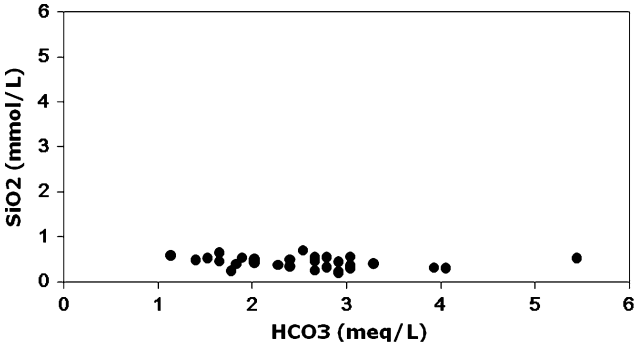

Fig. 9 Scatter plot showing relation between bicarbonate and silica

step, during the comparison of the sulfate and calcium contents, it was found that all the samples show the relation of $Ca^{2+} > SO_4^{2-}$, meaning that calcium sources of groundwater come from calcite, dolomite or silicate minerals other than gypsum (Fig. 8). The third step is to compare bicarbonate with silica to distinguish which type of weathering is occurring in these aquifers. Most of the sample had $HCO_3^- \ggg SiO_2$, suggesting that carbonate weathering is dominating here (Fig. 9). Higher HCO_3^- concentrations are because of weathering of carbonaceous sandstones might be supported by precipitation of HCO_3^- along with other cations.

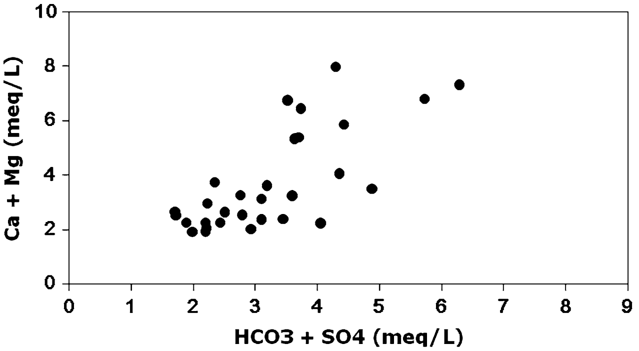

Fig. 10 Scatter plot showing relation between $HCO_3 + SO_4$ and $Ca + Mg$

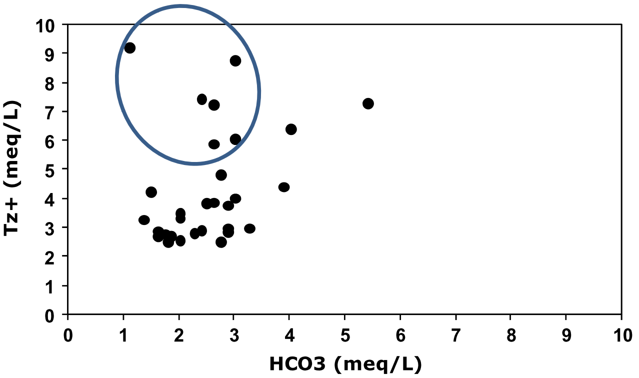

Fig. 11 Scatter plot showing relation between HCO_3 and Tz+

Other Supportive Test

In general for the plot of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$, most of the points will lie close to the 1:1 line if the dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system. In this case some of the sampling points which lie left of the equiline are located there because of the reverse ion exchange process dominating the quality of the water (Fisher and Mulican 1997) (Fig. 10). It was found that Ca^{2+} and Mg^{2+} are the dominant cations with their average contribution is 84% of the total cations, whereas HCO_3^- accounts for more than 60% of the total anions, which suggests that carbonate sandstone, dolomitic limestone and kankar are the major sources for carbonate in the area. The extent of contamination can be furthered probed from HCO_3^- vs. total cations (Tz+) plots as proposed by Kim (2003). The majority of sample points occupy the area above equiline and closer to *y*-axis (samples falling in the open circle), confirming that the water chemistry of the area is also influenced by secondary processes like anthropogenic activity (Fig. 11).

Speciation Modeling

With PhreeqC (Parkhurst and Appelo 1999) speciation modeling was done to confirm the possibility of solubility con-

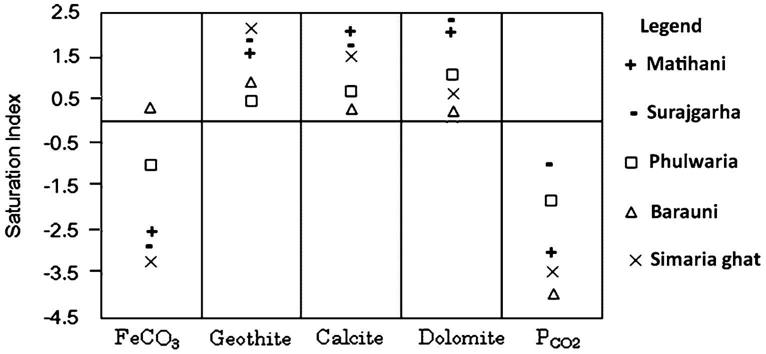

Fig. 12 Saturation Index variations with respect to five kinds of mineral for selected groundwater samples

trol for As and other species (Sracek et al. 2004). Five major factors ($FeCO_3$, Calcite, Geothite, Dolomite and P_{CO2}) were chosen to analyze their saturation index (Fig. 12) by using PhreeqC program. The result shows that the value for log P_{CO2} is low for most of samples. Most of the samples are supersaturated (saturation index >0.5) with goethite, calcite and dolomite, while only one sample was saturated with siderite. Saturation with goethite and siderite may be suggested as sink for dissolved iron. Precipitation of iron minerals may results in de-coupling of As and Fe (Mukherjee et al. 2008). However, the above results have to be described with care, because of uncertain redox status. Groundwater is strongly undersaturated with respect to any As-bearing phase, including $FeAsO_4{\cdot}2H_2O$, realgar and AsS (not shown). Combined with the geochemical composition, this study found that "oxyhydroxide reduction theory" is responsible for release of arsenic in the aquifer of the area of the study, i.e. Begusarai district, Bihar.

Conclusion

The groundwater shows a primary problem of arsenic followed by nitrate contamination (with highest value of 94.3 μg/L and 76.8 mg/L, respectively), which needs attention for taking timely precautionary measures. The weathering pattern of carbonate and silicate minerals is one of the most prominent processes occurring here which determine the quality of the water. Through the Hounslow method, it was found that the quality of the groundwater in this area is affected by natural as well as anthropogenic activities (mainly extensive agriculture practices and some of the industrial set up). Chemical results show that the distribution of moderately high arsenic mainly clustered around the river, mainly places named as Matihani, Surajgarha, Phulwaria etc. Mobilization of arsenic is governed by redox reactions at shallow depth, which supports the dissolution of arsenic from arseniferous iron oxyhydroxides, which was also firmly supported by speciation modeling.

Acknowledgements The author would like to thank to School of Environmental Sciences, Jawaharlal Nehru University, New Delhi for providing the Central Instrumentation Facility to complete all analytical works.

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