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# Evaluation of hydrogeochemical processes in the Pleistocene aquifers of Middle Ganga Plain, Uttar Pradesh, India

Janardhana Raju Nandimandalam

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**Abstract** Evaluation of major ion chemistry and solute acquisition process controlling water chemical composition were studied by collecting a total of fifty-one groundwater samples in shallow (<25 m) and deep aquifer (>25 m) in the Varanasi area. Hydrochemical facies, Mg-HCO<sub>3</sub> dominated in the largest part of shallow groundwater followed by Na-HCO<sub>3</sub> and Ca-HCO<sub>3</sub> whereas Ca-HCO<sub>3</sub> is dominated in deep groundwater followed by Mg-HCO<sub>3</sub> and Na-HCO<sub>3</sub>. High As concentration (>50 µg/l) is found in some of the villages situated in northeastern parts (i.e. adjacent to the concave part of the meandering Ganga river) of the Varanasi area. Arsenic contamination is confined mostly in tube wells (hand pump) within the Holocene newer alluvium deposits, whereas older alluvial aquifers are having arsenic free groundwater. Geochemical modeling using WATEQ4F enabled prediction of saturation state of minerals and indicated dissolution and precipitation reactions occurring in groundwater. Majority of shallow and deep groundwater samples of the study area are oversaturated with carbonate bearing minerals and under-saturated with respect to sulfur and amorphous silica bearing minerals. Sluggish hydraulic conductivity in shallow aquifer results in higher mineralization of groundwater than in deep aquifer. But the major processes in deep aquifer are leakage of shallow aquifer followed by dominant ion-exchange and weathering of silicate minerals.

**Keywords** Hydrochemistry · Groundwater · Pleistocene aquifers · Hydrochemical facies · Middle Ganga Plain · Arsenic · Saturation index

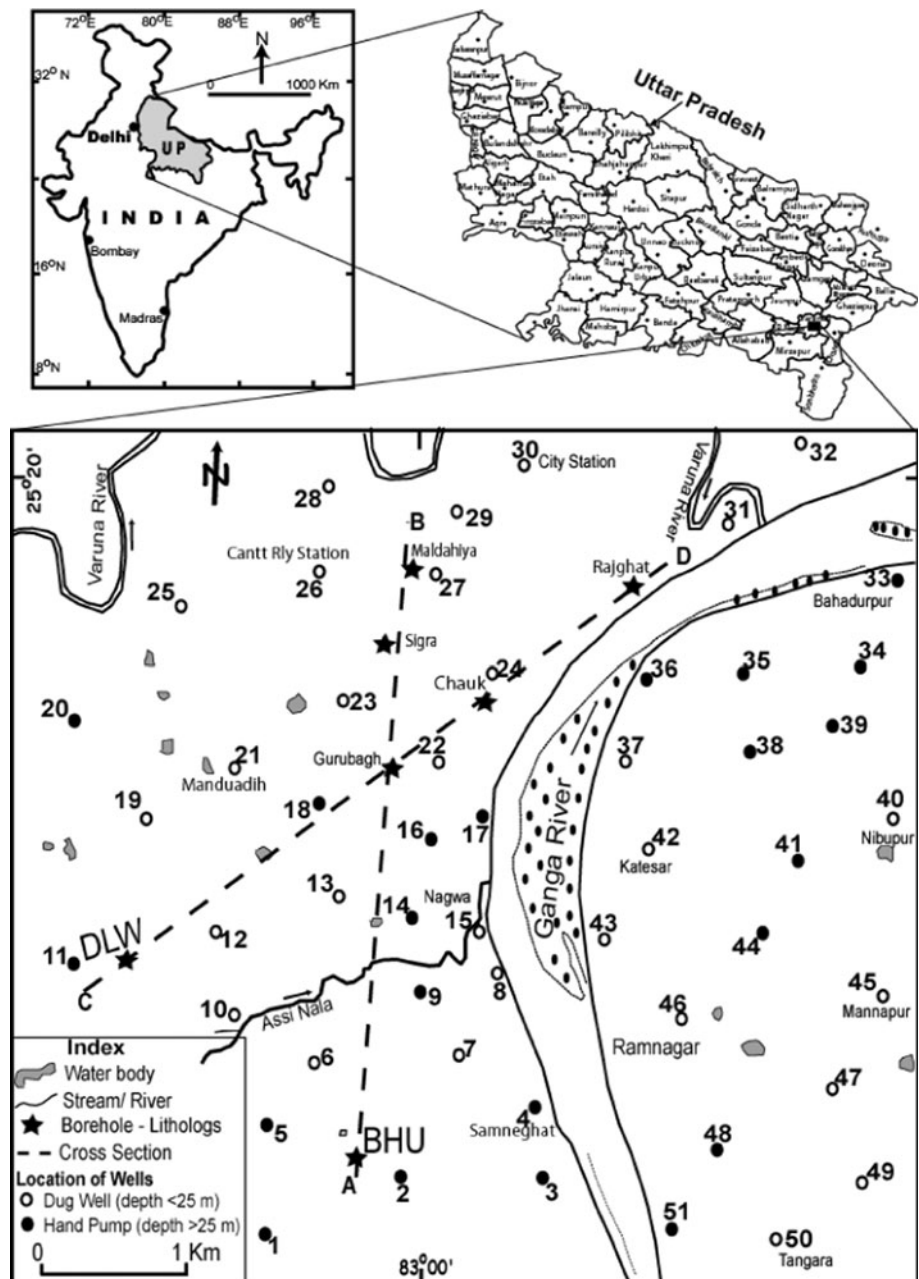
## Introduction

Water is an essential and vital component for our life support system. In tropical regions, groundwater plays an important role with context to fluctuating and increasing contamination of groundwater. Groundwater forms the major source of water supply for drinking and irrigation in most parts of India. With rapid increase in population and growth of industrialization, groundwater quality is being increasingly threatened by agricultural chemicals and disposal of urban and industrial wastes (Raju et al. 2011). It has been estimated that once pollution enters the subsurface environment, it may remain concealed for many years and rendering groundwater supplies unsuitable for consumption and other uses. Rate of depletion of groundwater levels and deterioration of groundwater quality is of immediate concern in major cities and towns of the country (Naidu et al. 1998; Meenakumari and Hosmani 2003; Dhindsa et al. 2004; Raju 2006, 2007; Umar and Ahmed 2007; Raju and Reddy 2007; Shah et al. 2008; Singh et al. 2008; Sahu and Sikdar 2008; Raju et al. 2009a, 2009b; Jain et al. 2010) and elsewhere (Nativ and Smith 1987; Fisher and Mulican 1997; Offiong and Edet 1998; Saleh et al. 1999; Geuo and Wang 2004; Jalali 2005, Jalali and Kolahchi 2008; Anku et al. 2009; Unsal and Celik 2010). Aquatic geochemistry is concerned with the chemical reactions and processes affecting the distribution and circulation of chemical species in natural waters.

The Quaternary alluvial deposits of the Ganga alluvial plain act as a life-line for socio-economic development supplying the needs of people to almost the entire domestic and irrigation demands (Singh 1987). Varanasi city lies between the latitude 25°15'0"N–25°20'22"N and 82°56'44"E–83°4'10"E; it is located in the middle Ganga plain of Indian Sub-continent (Fig. 1). Its climate is

J. R. Nandimandalam (✉)  
School of Environmental Sciences,  
Jawaharlal Nehru University, New Delhi 110 067, India  
e-mail: rajunj7@yahoo.com

**Fig. 1** Map showing Varanasi city and groundwater sample locations



tropical with a marked monsoonal effect. In summer, the maximum temperature rises to 45°C and in winter the minimum temperature drops to 4°C, and the average annual temperature being 24°C. The study area receives about 80% of its annual rainfall of 1,020 mm from the southwest monsoon during the month of July and August. Hydrogeological characters of the Pleistocene deposits in the middle Ganga plain have been studied in detail by various workers (Shukla and Raju 2008; Shah 2010; Raju et al. 2011). The paper attempts to evaluate the hydrogeochemical process controlling the water composition in shallow and deep aquifer conditions in the middle Ganga Pleistocene deposits of Varanasi area, Uttar Pradesh.

### Geomorphology, Geology and Hydrogeology

Ganga is the major river of Varanasi and drains at right side of the city area from south to north direction. Varanasi city is situated in the middle of the Indo-Gangetic plain at an average height of about 76.19 m above the mean sea level with even topography; it lies between peninsular India and the Siwalik range, which represents alluvial deposits filling the Himalayan foreland. Majority of sediments deposited in the foreland basin have their source in the Himalaya, where sediment production is attributed to the episodic tectonic activity and climate variability (Srivastava et al. 2003; Singh et al. 2007). According to Tandon et al. (2006),

Ganga plain lies within one of the world’s most active tectonic and southwest monsoon dominated regions of the world. Climatic and tectonic changes with the time have caused the development of various geomorphic surfaces and features, which are regionally persistent in the plain (Singh 2004).

At Varanasi, Ganga River has the narrowest valley which is just 1–2 km wide, though the active channel is only about 1 km wide and is totally confined between cliff walls. Varanasi city is located on the western cut side of the meander bend on an escarpment which is 8–17 m high. The escarpments are made of upland terrace surface (Older Alluvium) comprising beds of fine sand, yellowish-buff silt, grey-clayey silt and differentially ferruginized-silty clay. The drainage system of Varanasi environs is mainly controlled by Varuna River and Assi Nala (Khan et al. 1988). At Varanasi, Ganga River carries a mixed sediment load derived both from Himalaya and peninsular craton including Vindhyan rocks (Shukla and Raju 2008). Wherever the river valley is wide, dissected valley terrace (T<sub>1</sub>) (Newer Alluvium) (Shukla et al. 2001) is also developed and exhibits features like ponds, abandoned channels and meander scars. The study area is a part of the middle Ganga plain and the Vindhya Supre groups form its basement. The alluvial deposits can be subdivided into older and newer alluvium (Table 1). Newer alluvium is confined to river channels and the vicinity of the low-land areas. It is generally inundated by floods during the monsoon. Alluvium in the Varanasi region consists of alternate beds of sand and clay with occasional inter beds of calcareous concretions (i.e. kankar). Granular zones consist of various sand grades varying from fine through medium to coarse sands.

Hydrogeological cross sections, A–B and C–D (Fig. 2) are distributed across the maximum study area, in which A–B runs from north to south and C–D runs from southwest to northeast direction. These sections show broadly two-layered aquifer system up to 220 m in depth. In section A–B, the clay bed starts attaining thickness from south to north direction. The thin clay layer at southern part of cross

section occurs at about 80–90 m depth gradually mixed with the main clay horizon in the northern side. Maximum thickness of clay zone (~100 m) occurs in the Sigra area (Pandey 1993). The calcareous concretions are common feature and widely spread within the clay layers in the study area. Few coarse sand patches are occurring within the clay horizon in the northern side of the cross section. Fine/medium sand zone is separating the clay layer in the southern part of the area and these two clay layers are joining in the northern side of the area. A two-tier aquifer system is indicated in the southern side of area but the presence of two-coarse sand bodies in the northern side indicates three-tier aquifer systems. In the cross section C–D, clay layer thickness is increasing from the southwest to northeast direction and repeated clay lenses are found to occur in the southwestern part of the section. Section C–D shows a single layer aquifer system down to a depth of 200 m towards northeastern side but a two-tier aquifer system is observed in southwestern side. In general, it can be seen in the cross sections that granular zone increases thickness due to northeast side of Ganga River.

Availability of groundwater in Ganga alluvial zones is controlled by the presence of thickness of sand and clay zones. The alternating sand and clay layers have created multi-tier aquifer system in the Varanasi area (Shukla and Raju 2008). The top 25 m of the alluvial deposits is dominated by clay, silt, and sandy clay with thin lenses of sands, and the groundwater in this zone occurs under phreatic conditions. The sand beds with or without kankar in the area form main aquifer zones of multi-tier aquifer system. Groundwater is extracted through dug wells, hand tube wells and deep bore wells. Depth of water level varies between 5 and 29 m bgl. Dug wells and shallow tube wells (hand pumps) mainly tap the unconfined aquifers. General depth of deep bore wells ranges from 60 to 250 m bgl and at deeper levels aquifer occurs in semi-confined to confined conditions. Due to the fast urbanizing and intensive pumping for domestic and irrigation use, the water level shows lowering trends in some parts of the study area (Fig. 3).

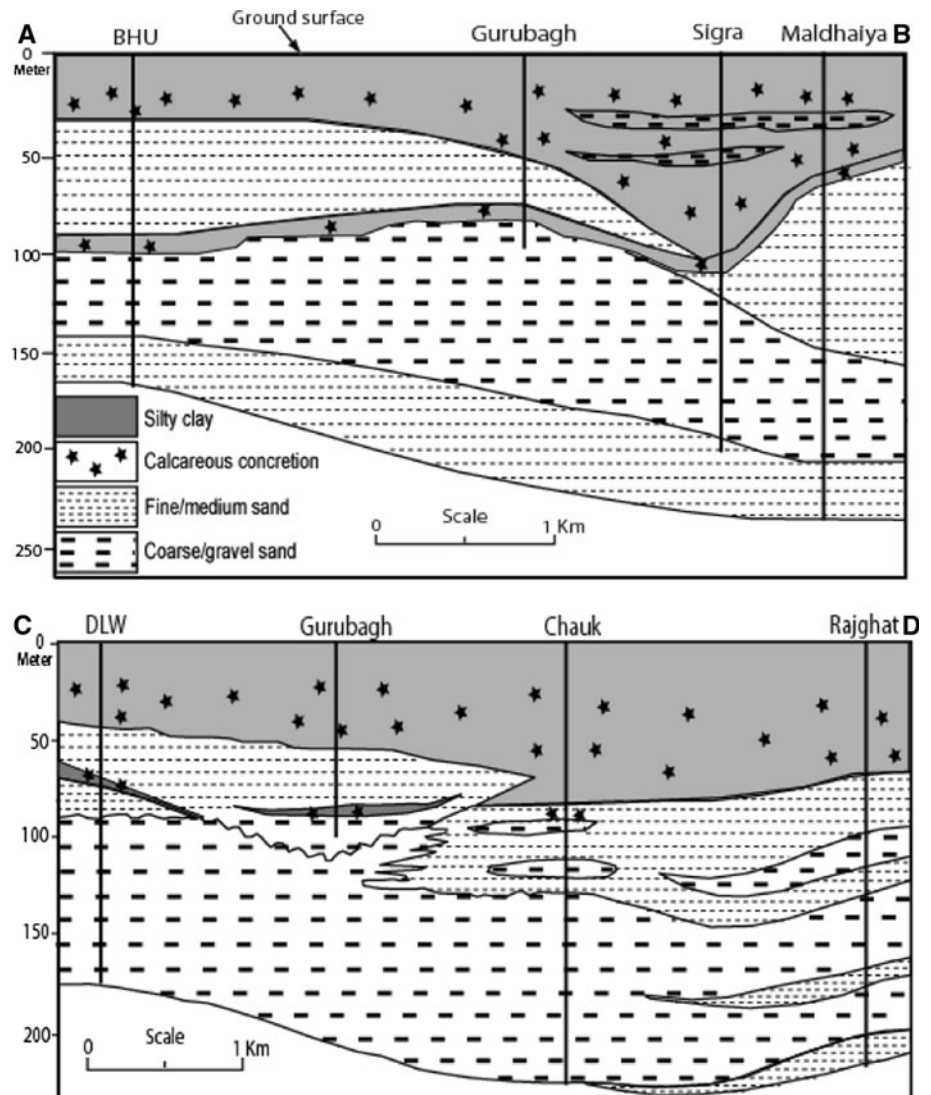
**Table 1** Geological succession of the middle Ganga plain in the Varanasi area

Age	Formation	Lithology
Upper Pleistocene to Recent	Newer alluvium	Unconsolidated sand, silt and clay
Middle to Upper Pleistocene	Older alluvium	Fairly consolidated clay with kankar, fine to medium sand with some gravel
Unconformity		
Upper Vindhyan	Kaimur sandstone	Sandstone and arkose

**Methodology**

A total of fifty-one groundwater samples from dug wells and hand pumps (Fig. 1) of the study area were collected between March and May 2007, and analyzed to understand the chemical variations of groundwaters. Samples collected were filtered using 0.45 μm pore size membrane and stored in polyethylene bottles which are initially washed with 10% of HNO<sub>3</sub> and rinsed thoroughly with distilled water. Another set was collected and acidified to pH <2 by adding ultra pure concentrated HNO<sub>3</sub> for heavy metal measurements.

**Fig. 2** Geological cross sections, using borehole lithologs along transect BHU-Maldhaiya (*a–b*) and DLW-Rajghat alluvium (*c–d*)



Physico-chemical characteristics of groundwater samples were determined using the standard analytical methods (APHA 1995). Physical parameters like pH and electrical conductivity were measured with portable ion meters (Elico Model). Total hardness and calcium were estimated by EDTA titrimetric method, and magnesium estimated by the difference of the hardness and calcium. Total alkalinity, carbonate and bicarbonate, and chloride were estimated by titrimetric method. Sodium and potassium were estimated by flame photometer (Elico Model CL-378). Sulphate estimations were done by the gravimetric method. Nitrate and iron were analyzed by the UV-spectrophotometer (Lab India Model UV 3000). Total dissolved solids (TDS) were estimated using calculation method. Fluoride was measured using an ion analyzer (Orion Model 4 star) with an ion selective electrode. Total arsenic in groundwater was determined by flow-injection-hydride generation atomic absorption spectrometry (FI-HG-AAS) (Perkin Elmer). The

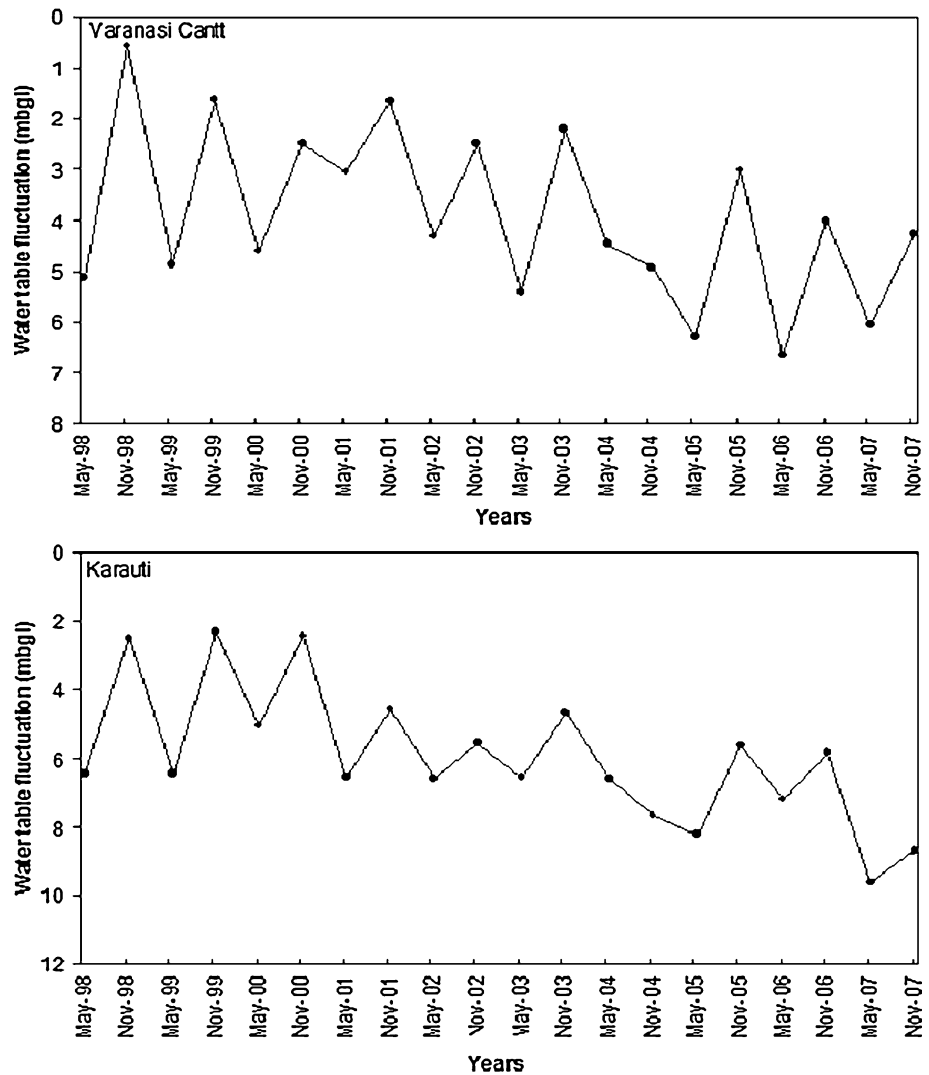
accuracy of the analytical method using FI-HG-AAS was verified for arsenic by analyzing standard reference materials from USEPA Environmental Monitoring and Support Laboratory, Cincinnati, OH, USA. The analytical precision for the measurement was determined by calculating the ionic balance error, which is generally found to be within  $\pm 5\%$ . Ion speciation in groundwater was calculated using computer code WATEQ4F program (Ball and Nordstrom 1992).

## Results and discussion

### Chemical quality of groundwater

In order to know the chemical quality of groundwater, 51 water samples have been collected, out of which 29 are from dug wells or shallow wells (depth <25 m) tapping shallow aquifers and remaining 22 are from hand pumps or

**Fig. 3** Long term water level fluctuations in the study area (1998–2007). (Source Central Groundwater Board)



bore wells tapping deep aquifers (depth >25 m) (Fig. 1). The summarized results of chemical analysis of major ions and arsenic of shallow and deep groundwaters are presented in Table 2. Overall, the groundwaters of the study area show slightly alkaline nature with a pH ranging from 7.0 to 8.2. About 96% of the samples are fresh with TDS <1,000 mg/l. Remaining groundwater samples are brackish (TDS between 1,000 and 2,000 mg/l). Groundwater from shallow aquifer (shallow groundwater) was observed to be more mineralized (average TDS 628.6 mg/l) than from deep aquifers (deep groundwater) (average TDS 423.2 mg/l). There is a considerable difference in the spatial distribution of TDS between shallow and deep groundwater (Fig. 4). High TDS concentrations in shallow groundwaters are found in the northern and eastern parts whereas in case of deep waters, it is in central portion of the study area. Among the cationic concentrations, sodium (mean 95.2 mg/l) is dominant ion followed by calcium (mean 63.7 mg/l), magnesium (mean 55.3 mg/l) and

potassium (mean 11 mg/l) ions in shallow waters whereas calcium (mean 62.3 mg/l) is dominant ion followed by sodium (mean 50.7 mg/l), magnesium (mean 33.8 mg/l) and potassium (mean 8.2 mg/l) ions in the deep groundwaters of the study area. Among anionic concentrations, bicarbonate (mean 403 and 346 mg/l) is dominant ion followed by chloride (mean 119 and 65.6 mg/l), sulphate (mean 55.2 and 30.7 mg/l) and nitrate (mean 33.2 and 10 mg/l) ions in shallow and deep groundwaters, respectively (Table 2). Bicarbonate and Ca<sup>2+</sup> are the dominating anion and cation, in terms of total reacting values, constituting about 65 (59% in shallow water and 70% in deep waters) and 36% (30% in shallow waters and 40% in deep waters) of total anions and cations, respectively. Mg<sup>2+</sup> and Na<sup>+</sup> constitute 34.5 (34% in shallow and 35% in deep waters) and 28% (33% in shallow and 23% in deep waters) of total cations, whereas Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> constitute 24 (26% in shallow and 22% in deep waters) and 8% (9% in shallow and 6% in deep waters) of total anions, in terms of meq

**Table 2** Chemical quality of shallow and deep groundwater in the Varanasi environs

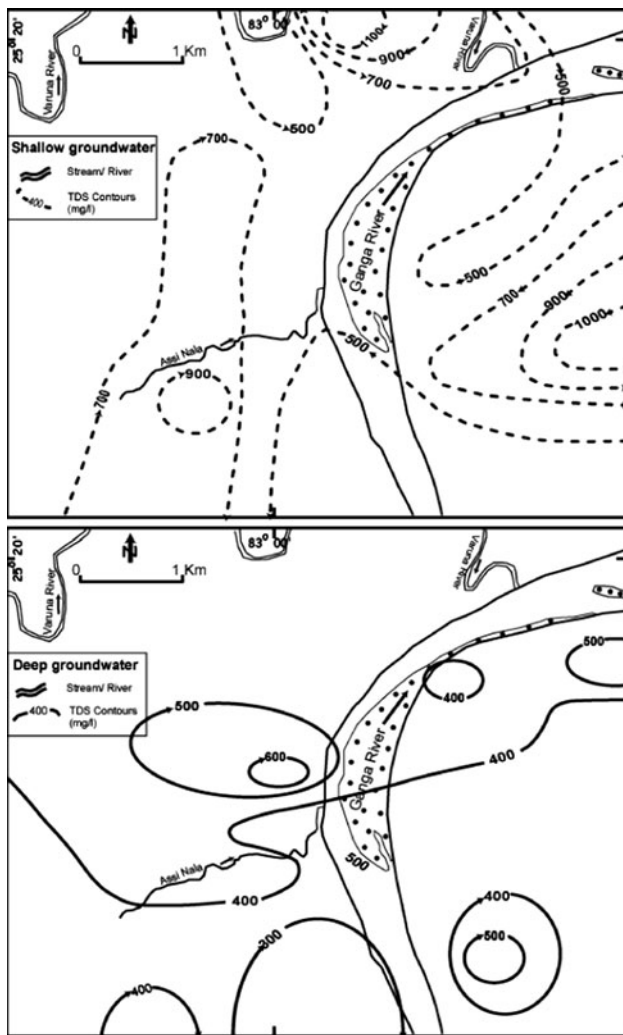
Sl. no	Parameter	Range		Mean		Standard deviation	
		Shallow	Deep	Shallow	Deep	Shallow	Deep
1	pH	7.0–8.2	7.1–8.2	7.5	7.66	0.37	0.34
2	TDS (mg/l)	343–1,175	277–688	628.6	423.2	203.23	103.19
3	EC ( $\mu$ S/cm)	600–2,150	478–1,166	1,134	716.8	384.79	166.57
4	Ca (mg/l)	10–145	10–183	63.7	62.3	37.64	30.15
5	Mg (mg/l)	8.2–127	3.1–69.3	55.3	33.8	28.58	19.33
6	Na (mg/l)	20.4–252	15.1–131	95.2	50.7	53.16	35.29
7	K (mg/l)	0.8–75	0.6–53.3	11.0	8.2	15.02	12.09
8	HCO <sub>3</sub> (mg/l)	145–720	264–447	403.9	346	138.33	54.97
9	SO <sub>4</sub> (mg/l)	2.5–180	2.5–120	55.2	30.7	48.68	32.01
10	Cl (mg/l)	12–397	26–138	119	65.6	81.30	29.39
11	NO <sub>3</sub> (mg/l)	0.82–106	1.2–62	33.2	10	34.75	13.88
12	F (mg/l)	0.31–1.34	0.4–1.2	0.74	0.70	0.26	0.17
13	Fe (mg/l)	0.1–3.5	0.2–6.8	0.8	1.4	0.48	0.39
14	As ( $\mu$ g/l)	<3–31	<3–80	5.8	16	13.6	24.9
15	Hardness (mg/l)	226–825	190–520	408.7	312	145.95	63.64
16	pCO <sub>2</sub> (atm)	$2 \times 10^{-3}$ – $4 \times 10^{-2}$	$1.69 \times 10^{-3}$ – $2.3 \times 10^{-2}$	$1 \times 10^{-2}$	$6.45 \times 10^{-3}$	–	–

values. Nitrate ions constitute about 3% (5% in shallow and 1% in deep waters) of total anionic concentrations. Cation chemistry is dominated by Ca<sup>2+</sup> and Mg<sup>2+</sup> which have equal percentage concentration in respect to total reacting values.

Magnesium in shallow groundwater is 1.5 times higher concentration than deep groundwaters. The abundance of calcium carbonate (i.e. kankar) in the alluvial basin and dissolution of other carbonate minerals will add significant amounts of Ca<sup>2+</sup> and Mg<sup>2+</sup> to groundwaters of the study area. However, much greater number of calcium bicarbonate water suggests that calcite and dolomite weathering are the dominant processes. There is almost two times higher Na<sup>+</sup> concentration in shallow waters when compared to deep groundwaters. But variation in Ca<sup>2+</sup> and K<sup>+</sup> content is not as pronounced as Na<sup>+</sup> and Mg<sup>2+</sup> in both shallow and deep groundwaters of the study area. A part of Ca<sup>2+</sup> and K<sup>+</sup> may also have been derived from mineral dissolution process in the alluvium. The study area is marked by wide variation of Cl<sup>−</sup> concentration which is nearly two times higher in shallow groundwaters than in deep groundwaters (Table 2). Considering that saline water and Cl<sup>−</sup> rich minerals are not found in the Varanasi area, high Cl<sup>−</sup> content in groundwater is likely to originate from anthropogenic pollution sources. Cl<sup>−</sup> may be derived from the pollution sources such as domestic effluents, fertilizers, septic tanks, dissolution of fluid inclusions and Cl<sup>−</sup> bearing minerals (Ritzi et al. 1993). Analogous to Cl<sup>−</sup> distribution, SO<sub>4</sub><sup>2−</sup> concentration in shallow groundwaters is much higher than deep groundwaters. Sources of SO<sub>4</sub><sup>2−</sup> include rainfall, fertilizers and dissolution of sulfide bearing

minerals present in alluvium. Nitrate content in shallow groundwater is at about three times higher when compared to deep groundwaters.

Maximum nitrate content in shallow groundwater is 106 mg/l. Agriculture and urbanization are dominant land use in the studied area and improper sewage collection and application of nitrate fertilizers clearly have an impact on the shallow groundwaters. In comparison to the WHO's drinking water guideline (WHO 1993) of 50 mg/l for NO<sub>3</sub>, 31% of shallow and 4% of deep groundwater samples showed higher nitrate concentration in the study area. In 55 and 91% of the shallow and deep groundwater samples, NO<sub>3</sub> concentration was low (<20 mg/l) and the remaining samples indicate above 20 mg/l of NO<sub>3</sub> concentration. Groundwater with NO<sub>3</sub> concentration exceeding the threshold of 13 mg/l is considered contaminated due to human activities (Burkart and Kolpin 1993, Eckhardt and Stackelberg 1995). About 45 and 9% of the shallow and deep groundwater samples showed NO<sub>3</sub> concentrations above permissible limits (WHO 1993). High-nitrate concentrations mainly occurred in densely populated (density of population is around 0.4 million) western, northern and a small pocket in the southeastern parts of the study area, which may be due to the sources from chemical fertilizers, septic tank and sewage discharges. Marked increase in N fertilizer applied to agricultural soils causes N to be leached below rooting zone (Pratt 1985; Hallberg 1989). Jalali and Kolahchi (2008) reported that 75% of the water samples showed NO<sub>3</sub> concentrations above permissible limit, while more than 12.5% exceeded the maximum acceptable level (50 mg/l NO<sub>3</sub>) in northern Malayer,

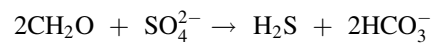
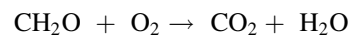


**Fig. 4** Distribution of total dissolved solids in shallow and deep groundwaters

western Iran. Hydrogeological investigations show that nitrate levels are high in sandy soil than in clayey soil, because of low water holding capacity and high permeability of pollutants like chloride and nitrate. Nitrate reacts with other chemicals (amines and amides) in human body to form carcinogenic compounds (*N*-nitroso-compounds) (Shih et al. 1997). Nitrate, after conversion to nitrite, oxidizes ferrous ion of haemoglobin to ferric state, forming methemoglobin. Repeated boiling of nitrate rich water for feeding, high-nitrate water used for preparing dried milk powder, weaning with nitrate rich vegetables e.g. spinach in children cause increase in nitrate toxicity.

The concentration of  $\text{HCO}_3^-$  ranges between 143–720 mg/l in shallow and 264–447 mg/l in deep groundwaters. Concentration of bicarbonate is high in shallow groundwaters and showing wide variations in comparison to deep groundwaters. Anthropogenic  $\text{CO}_2$  gas should be considered as a potential source of bicarbonate in urban

groundwater and ranges of partial pressure of the carbon dioxide ( $\text{pCO}_2$ ) values are shown in Table 2. High log  $\text{pCO}_2$  values in shallow wells observed in the northern and southern parts of the study area whereas high values in deep wells are observed in the central part of the study area. This may be due to accumulation of unorganized domestic wastewater as pools in local depressions. It could be expected that a great part of  $\text{HCO}_3^-$  originated from dissolution of carbonate rocks and lime kankar in the aquifer through the action of percolating waters enriched in  $\text{CO}_2$  after being in contact with the atmosphere (Appelo and Postma 1993). Potential sources of  $\text{CO}_2$  gas are municipal wastes within unlined landfill sites, due to the oxidation of organic materials leaked from old latrines and open sewage systems in some parts of Varanasi area and dissolved  $\text{HCO}_3^-$  ion from sulfate reduction of organic materials in the aquifer (Clark and Fritz 1997):



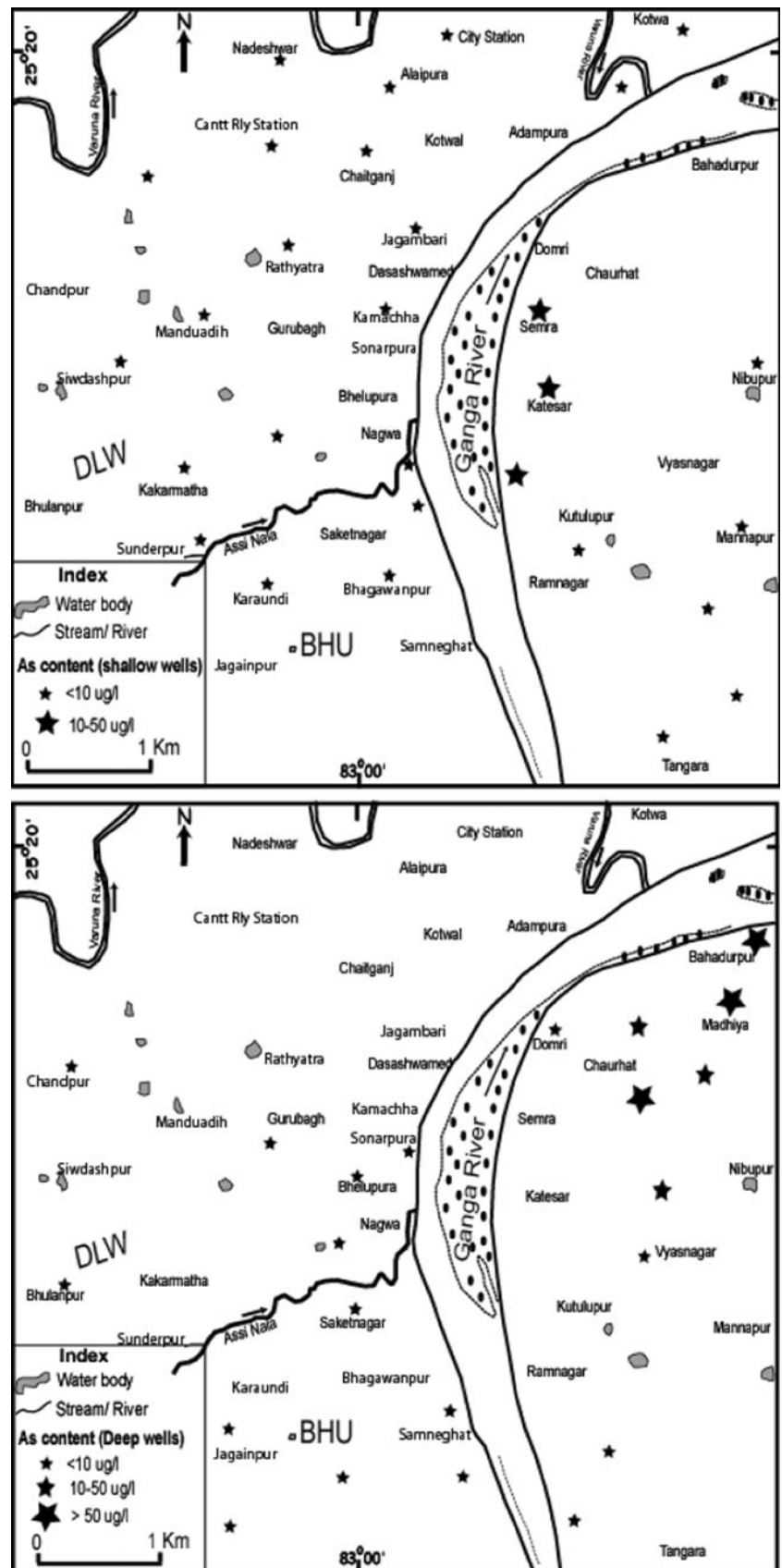
A few shallow groundwaters of high bicarbonate concentrations are likely to be influenced by anthropogenic carbon dioxide. In order to obtain more detail on its source within shallow and deep groundwater,  $\text{pCO}_2$  in groundwater samples was calculated using WATEQ4F program (Ball and Nordstrom 1992). The computed  $\text{pCO}_2$  of shallow and deep groundwater samples in the Varanasi area ranges from  $2 \times 10^{-3}$  to  $4 \times 10^{-2}$  atm and  $1.69 \times 10^{-3}$  to  $2.3 \times 10^{-2}$  atm, respectively (Table 2). The common range of  $\text{CO}_2$  pressures of  $10^{-1.5}$ – $10^{-2.5}$  atm is found in open system soil layers (Appello and Postma 1993).  $\text{CO}_2$  is generated in soils by decay of organic material and by root respiration. In case of  $\text{CO}_2$  pressure  $< 10^{-2.5}$  atm,  $\text{CO}_2$  gas was consumed through mineral dissolution in a closed groundwater system. Municipal wastes in unlined landfill sites, leaky sewage and latrine are likely organic pollution sources in urbanized parts of the study area.

#### Arsenic distribution in groundwater

The study area exhibits arsenic concentration in a wide range (below detection limit to 80  $\mu\text{g/l}$ ) and ranges of shallow and deep groundwater arsenic concentrations are presented in Table 2. Arsenic content in shallow groundwater samples indicates that 10% of the samples are exceeding 10  $\mu\text{g/l}$ , whereas in case of deep groundwater samples 18 and 13% samples are exceeding 10 and 50  $\mu\text{g/l}$  (Fig. 5), respectively. In about 90% ( $n = 29$ ) of shallow and 68% ( $n = 22$ ) of deep groundwater samples arsenic remained below detection limit (BDL). The limit for human consumption for arsenic prescribed by WHO (1993)



**Fig. 5** Spatial distribution of arsenic in shallow and deep groundwaters in the study area



is 10 µg/l, which is endorsed by the Bureau of Indian Standards (BIS 2003). Nevertheless, in the states of Bihar and Uttar Pradesh, drinking water with As contamination up to 50 µg/l is still being considered acceptable (CGWB and PHED 2005). High As concentration is found in some of the villages situated in northeastern parts (eastern side of the Ganga River) of the Varanasi area (Fig. 5). Some of the hand tube wells in Bahadurpur, Madhiya and Bhojpur are having arsenic more than 50 µg/l where as Ratanpur, Semra, Jalilpur, Kateswar, Bhakhara and Kodupur depict arsenic content more than 10 µg/l which are situated adjacent to concave part of the meandering Ganga River in the Varanasi area. Wide spatial variation is observed in arsenic concentration and even within the same village, variation as high as 30 times has been found. Smith et al. (1999) reported that life time risk of dying from cancer (lung, kidney or bladder) while drinking 1 l of water per day with 50 µg/l of arsenic. The remaining part of the study area i.e. mainly western side of Ganga River shows <10 µg/l of arsenic content, which indicates arsenic free groundwaters in shallow and deep wells. This may be due to lack of rich organic content for the reduction of iron oxides which helps for releasing of arsenic content in groundwater in western part of the study area. Arsenic contaminated aquifers are confined within low-land organic rich, clayey deltaic sediments in the Bengal basin and locally within similar facies in narrow entrenched river channels and flood plains particularly in its abandoned meander belts of middle Ganga plains.

Groundwater in the Varanasi city area (i.e. western side of Ganga River) is virtually arsenic safe due to its position in older alluvial upland surfaces whereas villages located in Holocene newer alluvium sediments (i.e. eastern side of Ganga River) in entrenched channels and flood plains of Ganga River have arsenic contaminated groundwater. Even within arsenic affected areas in Uttar Pradesh, most of the dug wells are found to be arsenic safe because of their oxygenated nature. In general, it is observed that often arsenic contaminated tube wells (hand pumps) in Uttar Pradesh are being used for drinking water, whereas dug wells with arsenic-safe water are poorly maintained and used unhygienically for other domestic purposes. Present study reveals that sources of As in the fluvial environment of the Ganga plain must lie within alluvial plain sediments and river sediments. The present data and other recent studies (Shah 2010; Singh et al. 2010) suggest upslope migration of arsenic crisis from the Bengal Delta region through the lower and middle Ganga plain to the upper Ganga plain.

#### Saturation index

Saturation indices (SI) describe quantitative deviation of water from equilibrium with respect to dissolved minerals. If

water is exactly saturated with dissolved mineral, SI equals to zero. Positive values of SI indicate saturation, and negative ones indicate under-saturation (Appelo and Postma 1993; Drever 1997). SI can be expressed in terms of ion activity product (IAP) and equilibrium constant ( $K$ ) as follows:

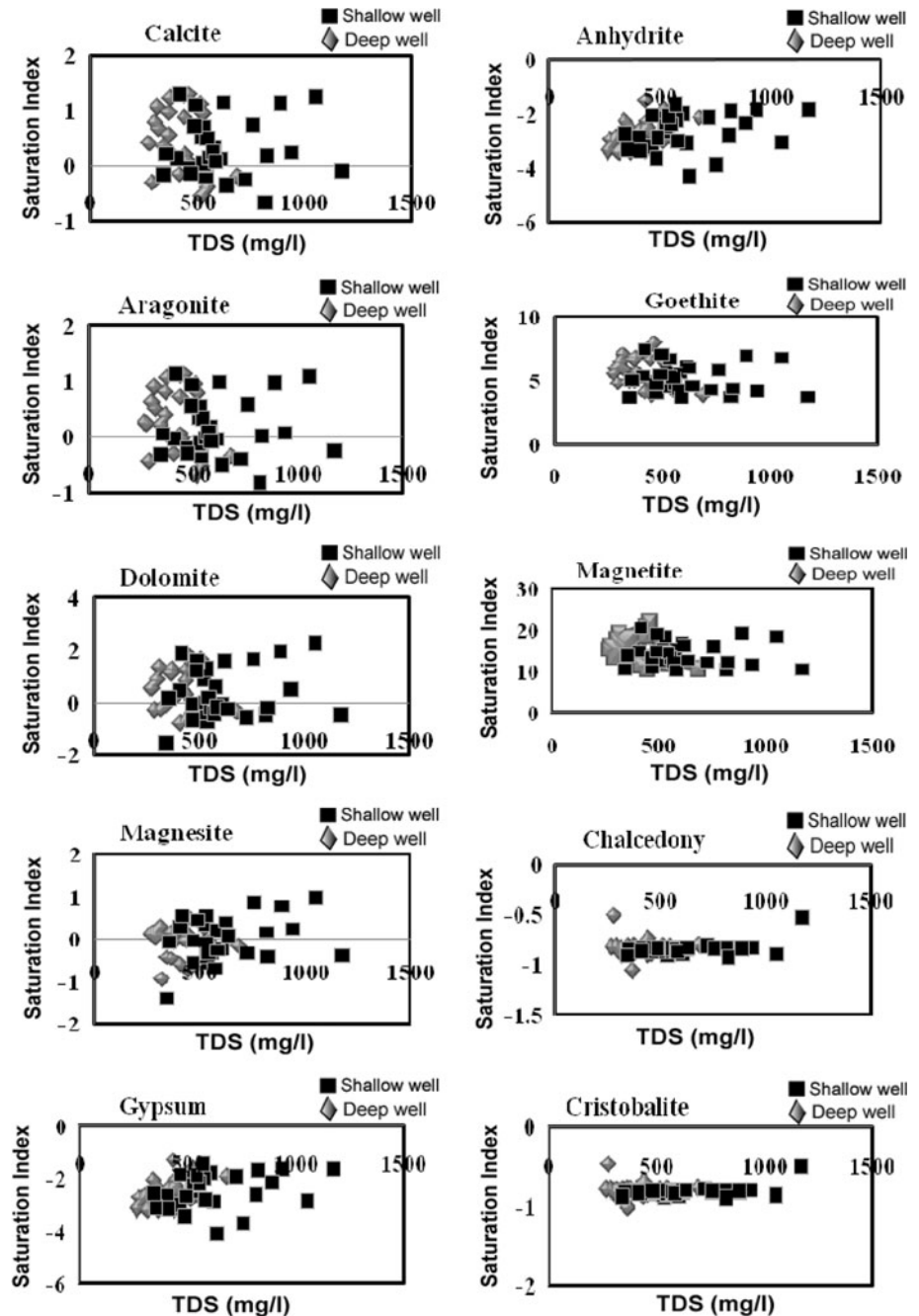
$$SI = \log IAP/K = 0 \text{ – equilibrium state}$$

$$SI = \log IAP/K < 0 \text{ – undersaturation state} \\ \times (\text{mineral dissolution condition})$$

$$SI = \log IAP/K > 0 \text{ – oversaturation state} \\ \times (\text{mineral precipitation condition})$$

Aqueous speciation computed with WATEQ4F program (Ball and Nordstrom 1992) was used to better define the possible chemical reactions in the aquifer system to assess the state of equilibrium between groundwater and minerals present. The WATEQ4F program is an equilibrium speciation code, which can calculate complexes, activity coefficients and equilibrium with minerals and gas pressure, all as a function of temperature and for all kinds of hydrochemical conditions. Graphs of SI of gypsum, calcite and dolomite with TDS in groundwater in the study area are shown in Fig. 6. Approximately 75 and 25% of the shallow water samples and 77 and 23% of the deep water samples show over-saturation and under-saturation, respectively, with respect to calcite mineral, while 55 and 45% of the shallow water samples and 64 and 36% of the deep water samples show oversaturation and undersaturation with respect to dolomite mineral (Fig. 6) in the study area. Water samples of shallow and deep aquifers are under-saturated with respect to sulfur-bearing minerals (gypsum and anhydrite) in the study area. Water samples were saturated with goethite, magnetite and hematite and under-saturated with respect to sepiolite, fluorite, chalcedony, cristobalite and silica gel. Summary statistics of mineral saturation index of groundwaters calculated by WATEQ4F are presented in the Table 3. Dissolution of silicate minerals is generally a very slow process that does not produce significant variations in water chemistry (Condeso de Melo et al. 1999). Study of saturation indices reveals that majority of shallow and deep groundwater samples of the study area are oversaturated with calcite, aragonite, dolomite and magnesite minerals, whereas all samples are under-saturated with gypsum and anhydrite minerals. Carbonate minerals show higher saturation in groundwater of the study area because surface water percolates into subsurface zone and enrich carbonate concentration by the dissolution of carbonate minerals. Water samples which are saturated to oversaturated with these carbonate minerals indicated that the excess input of Ca and Mg ions are mainly from carbonate weathering processes. Precipitation of carbonate minerals, calcite and dolomite can also be assessed in terms of a SI using a simple thermodynamic approach (Garrels and

**Fig. 6** Plots of saturation indices with respect to different minerals against total dissolved solids



Christ 1965). About 77% of the shallow and deep groundwaters of the study area are oversaturated and rest of the samples is under-saturated with respect to calcite mineral, whereas 52 and 64% of shallow and deep groundwater samples, respectively are oversaturated and 48 and 36% are under-saturated with respect to dolomite mineral (Fig. 7).

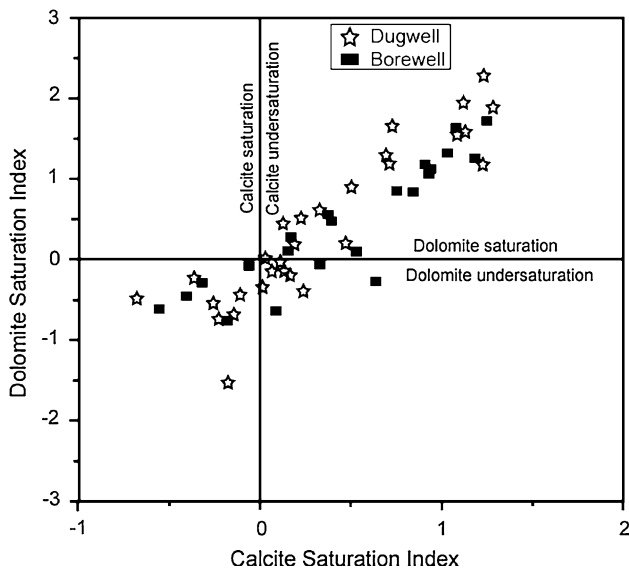
#### Hydrochemical facies

A study of litho-facies distribution based on lithologies of the sediments for shallow aquifers (0–25 mbgl) and deep aquifers (25–70 mbgl) depicts interesting phenomenon in

relation to hydrochemical facies distribution. Hydrochemical facies are water masses that have different geochemical attributes and are helpful for comparing the origins and distribution of groundwater masses (Lloyd and Heathcote 1985). Based on the relative dominance of major cations and anions, in terms of their reacting values, nine hydrochemical facies have been identified in the study area. In case of a clear dominance of a particular cation or anion (>50% of the total cations or anions), facies have been identified based on dominant constituents (e.g. Ca-HCO<sub>3</sub> facies). In case of no clear cut dominance of ions, 33% is taken as minimum cut off value to classify facies e.g. if a

**Table 3** Summary statistics of mineral saturation index of groundwater calculated by WATEQ4F

Mineral phase	Magnesite	Dolomite	Calcite	Anhydrite	Gypsum	Aragonite	Fluorite
Shallow groundwater							
Minimum	-1.399	-1.5469	-0.679	-4.3131	-4.093	-0.8222	-2.247
Maximum	0.9913	2.2568	1.284	-1.6528	-1.433	1.1404	-0.79
Average	0.00052	0.34425	0.298	-2.6696	-2.45	0.15433	-1.578
Deep groundwater							
Minimum	-0.9499	-0.7646	-0.56	-3.421	-3.201	-0.703	-2.344
Maximum	0.4877	1.7301	1.246	-1.572	-1.352	1.1017	-0.549
Average	-0.0957	0.4154	0.452	-2.772	-2.552	0.3079	-1.454
Mineral Phase	Chalcedony	Cristobalite	Silica gel	Goethite	Magnetite	Hematite	Sepiolite
Shallow groundwater							
Minimum	-0.9255	-0.8897	-1.459	3.652	10.188	9.3121	-8.8369
Maximum	-0.5255	-0.4898	-1.059	7.4593	20.461	16.927	-2.0266
Average	-0.8343	-0.79852	-1.368	5.1903	14.314	12.389	-4.7384
Deep groundwater							
Minimum	-1.0571	-1.0213	-1.5903	3.816	10.5321	9.6407	-6.733
Maximum	-0.5318	-0.496	-1.065	7.863	21.7725	17.7343	-2.64
Average	-0.8391	-0.8033	-1.3723	5.661	15.58012	13.33106	-4.503



**Fig. 7** Saturation indices of calcite versus dolomite

sample having cations  $Ca^{2+}$  18%,  $Mg^{2+}$  44%,  $Na^+$  35%,  $K^+$  1% and anions as  $HCO_3^-$  34%,  $SO_4^{2-}$  16%,  $Cl^-$  37%,  $NO_3^-$  11% and  $F^-$  0.2%, is classified as  $Mg-Na-Cl-HCO_3$  facies. A total of 51 groundwater samples (29 shallow and 22 deep waters) have been classified into nine hydrochemical facies which are  $Ca-HCO_3$  (5 shallow and 10 deep water);  $Ca-Na-HCO_3$  (2 shallow and 2 deep waters);  $Mg-Na-HCO_3$  (5 shallow waters);  $Mg-HCO_3$  (6 shallow and 5 deep waters);  $Mg-Ca-HCO_3$  (3 deep waters);  $Na-Mg-HCO_3$  (4 shallow and 2 deep waters);  $Na-HCO_3$

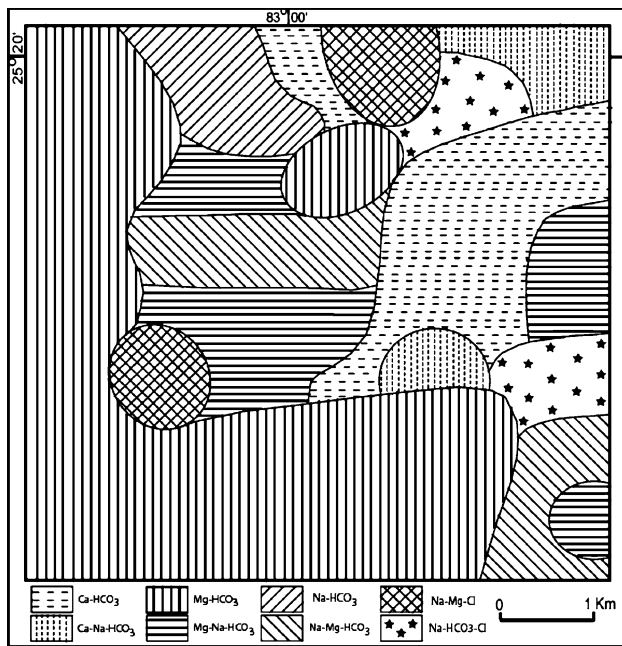
(3 shallow waters);  $Na-Mg-Cl$  (2 shallow waters) and  $Na-HCO_3-Cl$  (2 shallow waters) (Table 4).

Magnesium dominated facies are widely distributed in shallow groundwaters when compared to deep groundwaters. Ca-dominated facies are more generally spread in deep groundwaters and comparatively less in shallow groundwaters. Out of nine facies, two have been identified and occur more frequently in shallow aquifers as Mg-dominated facies i.e.  $Mg-HCO_3$  and  $Mg-Na-HCO_3$  (Fig. 8), whereas in deep groundwaters Mg-dominated facies are less frequently observed. Ca-dominated facies i.e.  $Ca-HCO_3$  and  $Ca-Na-HCO_3$  are more widely distributed in deep aquifer, whereas Mg-dominated facies are restricted to south-central parts of the study area (Fig. 9). The average chemical composition and percent content of masses of different hydrochemical facies are presented in Table 4. The  $Ca-HCO_3$ ,  $Mg-HCO_3$  and  $Na-Mg-HCO_3$  each represents 29, 21 and 12% of the total number of groundwater samples analyzed, while  $Ca-Na-HCO_3$  and  $Mg-Na-HCO_3$  each represents 9% of the total number of water samples analyzed. The other  $Mg-Na-HCO_3$  and  $Na-HCO_3$  each represents 6%, while  $Na-Mg-Cl$  and  $Na-HCO_3-Cl$  each represents 4% of the total number of water samples analyzed. The  $Ca-HCO_3$  type water is dominated in the most part of the studied area with Ca ranges from 2.59 to 9.13 meq/l, while  $HCO_3^-$  ranges from 4.33 to 7.33 meq/l (Table 4). Average TDS value for the  $Na-Mg-Cl$  and  $Na-HCO_3-Cl$  water types is 892 and 939 mg/l, respectively. The  $Ca-HCO_3$  (average TDS = 408 mg/l),  $Ca-Na-HCO_3$  (average TDS = 493 mg/l) and  $Mg-Ca-HCO_3$

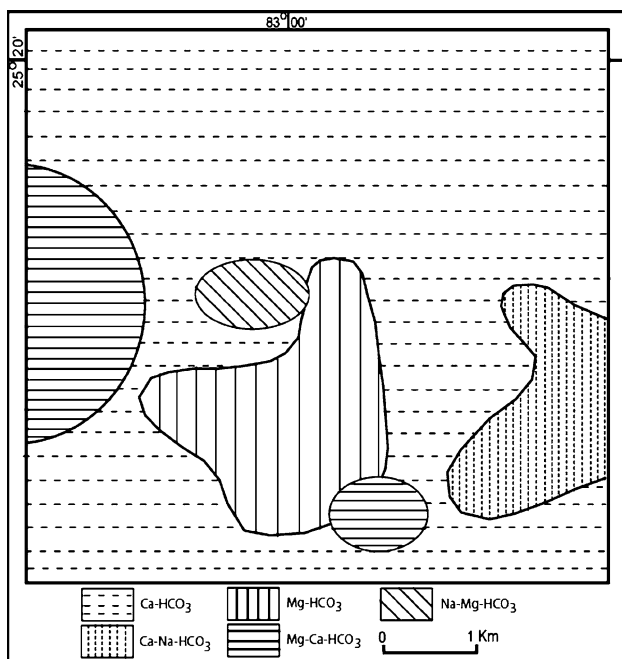
**Table 4** Average chemical composition of different hydrochemical facies ( $N = 51$ )

Sl. No	Facies	TDS (mg/l)	Ca (meq)	Mg (meq)	Na (meq)	K (meq)	HCO <sub>3</sub> (meq)	SO <sub>4</sub> (meq)	Cl (meq)	NO <sub>3</sub> (meq)	F (meq)	Sample numbers
1	Ca-HCO <sub>3</sub>											<b>1, 5, 8, 14, 29, 33,</b>
	Minimum	311	2.59	0.67	0.89	0.02	4.33	0.05	0.82	0.03	0.01	<b>34, 35, 36, 37, 38, 39, 42,</b>
	Maximum	573	9.13	3.72	1.83	0.16	7.33	2.08	3.24	0.15	0.15	<b>44, 51</b>
	Average	408	4.74	1.81	1.37	0.06	5.75	0.44	1.66	0.08	0.05	
	% content		59.39	22.68	17.16	0.75	72.05	5.51	20.8	1	0.62	
2	Ca-Na-HCO <sub>3</sub>											32, <b>41, 43, 48</b>
	Minimum	326	3.44	0.25	1.97	0.02	4.72	0.05	1.44	0.06	0.02	
	Maximum	623	5.34	2.81	4.23	0.09	9.65	2.08	2.23	1.08	0.05	
	Average	493	3.99	1.83	3.22	0.05	6.5	0.61	1.85	0.33	0.03	
	% content		43.89	20.13	35.42	0.55	69.74	6.54	19.84	3.54	0.32	
3	Mg-Na-HCO <sub>3</sub>											13, 15, 23, 40, 49
	Minimum	489	0.5	4.13	3.29	0.03	4.26	0.03	2.34	0.02	0.03	
	Maximum	818	2.64	9.81	6.54	0.19	11.8	2.5	4.77	1.48	0.12	
	Average	663	1.96	6.3	4.91	0.11	7.51	1.18	3.46	0.36	0.06	
	% content		14.75	47.43	36.97	0.82	59.74	9.38	27.52	2.86	0.47	
4	Mg-HCO <sub>3</sub>											<b>2, 4, 6, 7, 9, 10, 17, 19,</b>
	Minimum	285	0.8	3.48	0.66	0.06	4.39	0.21	0.73	0.01	0.02	<b>24, 25, 46</b>
	Maximum	940	6.14	10.4	4.83	1.36	9.38	3.75	6.35	1.03	0.2	
	Average	536	2.34	5.42	2.41	0.31	6.1	1.08	2.77	0.29	0.1	
	% content		22.32	51.71	22.99	2.95	59.1	10.46	26.8	2.81	0.96	
5	Mg-Ca-HCO <sub>3</sub>											<b>3, 11, 20</b>
	Minimum	277	2.3	2.72	0.74	0.08	5.08	0.1	0.99	0.09	0.04	
	Maximum	418	2.59	4.19	2.15	0.11	5.74	0.42	1.3	1.01	0.09	
	Average	360	2.49	3.41	1.25	0.09	5.37	0.24	1.14	0.55	0.06	
	% content		34.39	47.09	17.26	1.24	72.96	3.26	15.48	7.47	0.67	
6	Na-Mg-HCO <sub>3</sub>											<b>16, 18, 21, 22, 47, 50</b>
	Minimum	524	0.49	3.23	3.49	0.03	5.83	0.03	2.23	0.02	0.02	
	Maximum	688	2.94	5.7	7.81	0.73	8.97	2.5	3.89	1.23	0.06	
	Average	592	1.78	4.21	5.01	0.3	7.03	1.01	2.8	0.28	0.44	
	% content		15.75	37.25	44.33	2.65	62.93	9.04	25.06	2.5	3.8	
7	Na-HCO <sub>3</sub>											26, 27, 28
	Minimum	470	2.49	1.65	3.38	0.07	3.85	0.83	1.38	0.33	0.02	
	Maximum	555	3.79	2.69	5.62	0.21	7.05	1.87	3.39	1.08	0.07	
	Average	523	3.01	2.32	4.66	0.14	5.88	1.32	2.12	0.67	0.05	
	% content		28.22	23.38	46.97	1.41	58.56	13.14	21.11	6.67	0.49	
8	Na-Mg-Cl											12, 30
	Minimum	608	3.09	4.09	3.33	0.11	2.29	2.08	4.2	1.46	0.02	
	Maximum	1175	4.99	7.6	8.7	0.17	5.25	2.49	11.2	1.55	0.03	
	Average	892	4.04	5.85	6.02	0.14	3.77	2.29	7.7	1.51	0.03	
	% content		25.17	36.44	37.5	0.87	24.64	14.96	50.32	9.86	0.19	
9	Na-HCO <sub>3</sub> -Cl											31, 45
	Minimum	825	3.44	3.02	4	0.59	5.57	0.21	4.93	0.35	0.02	
	Maximum	1,053	3.94	5.27	10.98	1.92	11.37	2.08	7.81	1.48	0.06	
	Average	939	3.69	4.15	7.49	1.26	8.47	1.15	6.37	0.92	0.04	
	% content		22.24	25.01	45.14	7.59	49.97	6.78	37.58	5.42	0.23	

Bold sample numbers are deep wells, and remaining are shallow wells



**Fig. 8** Hydrochemical facies distribution in shallow groundwater



**Fig. 9** Hydrochemical facies distribution in deep groundwater

(average TDS = 360 mg/l) type waters are less mineralized than the other type of groundwaters.

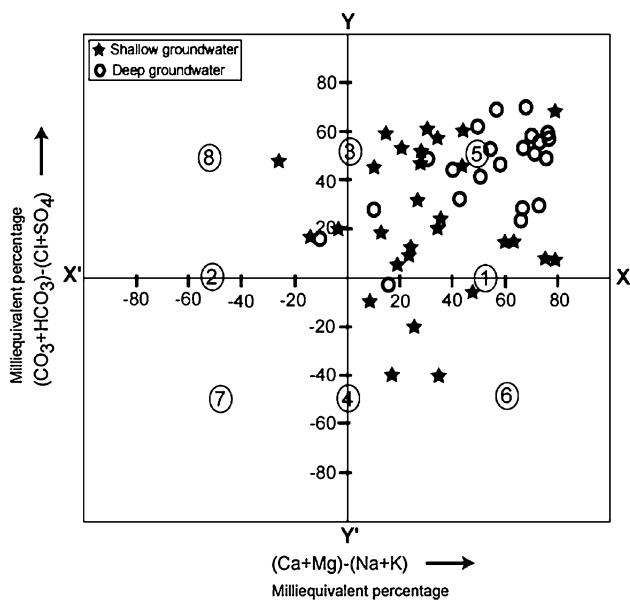
The sluggish movement of shallow groundwater results in higher mineralization in comparison to deeper groundwater aquifers. In shallow groundwater, ion-exchange is a less dominant process (mean ratio of  $Na^+/Ca^{2+}$  is 1.91). In shallow aquifer, the  $Ca^{2+}$  dominated hydrochemical facies (eastern and northeastern parts, Fig. 8) are confined mainly

to those areas marked by clayey sand or silty sand litho facies, whereas  $Na^+$  dominated facies (northern, central and eastern parts, Fig. 9) appeared to be common in areas with clay litho facies, which are finer in grain size resulting in sluggish groundwater movement. This is well supported by higher TDS of particularly the four main  $Na^+$  dominated hydrochemical facies i.e.  $Na-HCO_3$  (mean TDS value 523 mg/l),  $Na-Mg-HCO_3$  (mean value 592 mg/l),  $Na-Mg-Cl$  (mean value 892 mg/l) and  $Na-HCO_3-Cl$  (mean value 939 mg/l). The sluggish movement of groundwater in shallow aquifer, predominantly made up of clay, silty clay and sandy clay, indicates ion-exchange process, resulting in the formation of lime kankar and consequent increase of  $Na^+$  in groundwater. Another prominent process in the modification of shallow groundwater chemistry is infiltration of irrigation water charged with agricultural fertilizers and recharge from rainfall. A comparison between litho-facies and hydrochemical facies of deep aquifer also reveals that  $Na^+$  dominated facies are common in areas with clay or sandy clay litho-facies (in central parts of the study area) which is supported by TDS values of deep aquifer. Hydrogeochemistry is modified primarily by leakage of groundwater from shallow aquifer and ion-exchange process (mean ratio of  $Na^+/Ca^{2+}$  is 2.82), which is the most dominant process in deep groundwater aquifer. In general, weathering of silicate minerals in the alluvium remains to be the very important process in deep groundwater aquifer.

### Hydrogeochemical evolution

The process involved in geochemical facies evolution and interpretation of chemical data of groundwater is studied by analyzing chemical quality data by Chadha diagram (Chadha 1999). Facies are a function of lithology, solution kinetics and flow patterns of the aquifer. In the proposed rectangular diagram (Fig. 10), the difference in milliequivalent percentage between alkaline earths (Ca + Mg) and alkali metals (Na + K), expressed as percentage reacting values, is plotted on the X axis, and the differences in milliequivalent percentage between weak acidic anions ( $CO_3 + HCO_3$ ) and strong acidic anions ( $Cl + SO_4$ ) are plotted on the Y axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would be plotted in one of the four possible sub-fields of the rectangular diagram. The rectangular field describes the overall character of the water. In order to define the primary character of the water, the rectangular field is divided into eight sub-fields, each of which represents a water type. The results of chemical analyses were plotted on the proposed diagram to test its applicability for geochemical classification of groundwater and to understand the

hydrochemical processes shown in Fig. 10. Majority of shallow (73%) and deep (91%) groundwater samples in the study area fall under the subfield of alkaline earths and weak acidic anions that exceed both alkali metals and strong acidic anions (Ca–Mg–HCO<sub>3</sub> type); such waters may have temporary hardness. These types are generally more spread in deep groundwaters and comparatively less in shallow groundwaters. Around 17 and 10% of the shallow groundwater samples fall in the subfields of 6 (Ca–Mg–Cl water type) and 8 (Na–HCO<sub>3</sub> water type), respectively whereas 4.5% of the deep groundwater samples fall in 6 and 8 water types. This indicates that majority of deep



**Fig. 10** Geochemical classification and hydrochemical parameters of groundwater (after Chadha 1999)

groundwater samples may have temporary hardness when compared to the shallow groundwater which depicts the shallow aquifers have permanent hardness conditions in the study area (Table 5). Ca–Mg–Cl type waters have permanent hardness and do not deposit residual sodium carbonate in irrigation use and Na–HCO<sub>3</sub> type waters release residual sodium carbonate while irrigating and cause foaming problems when used for domestic purpose.

Compositional relations among dissolved species can reveal the origin of solutes and the process that generated the observed water compositions. Correlation coefficient matrix (Tables 6, 7) for chemical parameters of shallow and deep groundwater samples indicates the existence of several groups of significantly related constituents at 0.01 and 0.05 confidence levels. The correlation coefficient between TDS and other major ions such as Mg<sup>2+</sup> ( $r = 0.698$  and  $0.464$ ); Na<sup>+</sup> ( $r = 0.757$  and  $0.694$ ); Cl<sup>-</sup> ( $r = 0.914$  and  $0.851$ ); SO<sub>4</sub><sup>2-</sup> ( $r = 0.395$  and  $0.715$ ) and HCO<sub>3</sub><sup>-</sup> ( $r = 0.42$  and  $0.63$ ) indicating a strong correlation in shallow and deep groundwaters, respectively (Tables 6, 7) in the study area. There is a significant negative correlation observed in between NO<sub>3</sub> and HCO<sub>3</sub> in shallow groundwater and Ca and Mg in deep groundwater. Ca and Mg exist as a negative correlation ( $r = -0.309$  and  $r = -0.673$  in shallow and deep groundwaters, respectively) (Tables 6, 7), indicating that the sources of ions are not in common. The correlation coefficient ( $r = -0.027$ ) between Ca and HCO<sub>3</sub> for shallow waters is not significant. This indicates that calcite may not be source of calcium. The most common weathering reaction for calcite is simple dissolution (Drever 1997). Thus, the dissolution of carbonate releases Ca<sup>2+</sup> into solution, yielding water of type Ca–HCO<sub>3</sub> as a final product. Natural processes such as dissolution of carbonate minerals and dissolution of

**Table 5** Geochemical classification of the shallow and deep groundwaters

Sub-field	Water type	Groundwater samples in different sub-fields		Percentage	
		Shallow	Deep	Shallow (%)	Deep (%)
1	Alkaline earths exceed alkali metals	–	–	–	–
2	Alkali metals exceed alkaline earths	–	–	–	–
3	Weak acidic anions exceed strong acidic anions	–	–	–	–
4	Strong acidic anions exceed weak acidic anions	–	–	–	–
5	Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively	21	20	73	91
6	Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions	5	1	17	4.5
7	Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions	–	–	–	–
8	Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions	3	1	10	4.5

**Table 6** Correlation matrix for the groundwater samples of shallow aquifers ( $N = 29$ )

Parameter	TDS	Ca	Mg	Na	K	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	F
TDS	1									
Ca	0.049	1								
Mg	0.698**	-0.309	1							
Na	0.757**	-0.307	0.441*	1						
K	0.292	-0.025	-0.025	0.117	1					
HCO <sub>3</sub>	0.420*	-0.027	0.360	0.538**	-0.022	1				
SO <sub>4</sub>	0.395*	0.128	0.403*	0.043	0.220	-0.315	1			
Cl	0.914**	0.168	0.632**	0.610**	0.225	0.177	0.409*	1		
NO <sub>3</sub>	0.333	0.012	0.010	0.146	0.255	-0.444*	0.171	0.413*	1	
F	0.023	0.264	0.005	0.003	-0.114	0.291	0.101	-0.013	-0.396*	1

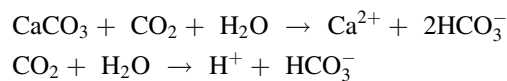
\* Correlation is significant at the 0.05 level (2-tailed)  
 \*\* Correlation is significant at the 0.01 level (2-tailed)

**Table 7** Correlation matrix for the groundwater samples of deep aquifers ( $N = 22$ )

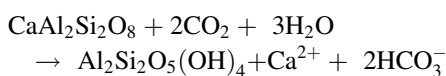
Parameter	TDS	Ca	Mg	Na	K	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	F
TDS	1									
Ca	-0.094	1								
Mg	0.464*	-0.673**	1							
Na	0.694**	-0.320	0.182	1						
K	0.461*	-0.450*	0.447*	0.278	1					
HCO <sub>3</sub>	0.630**	0.252	0.286	0.193	0.303	1				
SO <sub>4</sub>	0.715**	-0.396	0.476*	0.567**	0.412	0.053	1			
Cl	0.851**	-0.175	0.517*	0.547**	0.448*	0.457*	0.632**	1		
NO <sub>3</sub>	-0.125	-0.106	-0.023	-0.089	-0.124	-0.220	-0.134	-0.344	1	
F	0.073	0.148	-0.040	-0.048	-0.042	0.234	-0.198	0.087	-0.014	1

\* Correlation is significant at the 0.05 level (2-tailed)  
 \*\* Correlation is significant at the 0.01 level (2-tailed)

atmospheric and soil CO<sub>2</sub> gas could be mechanisms which supply HCO<sub>3</sub> to the groundwater:



A major part of Ca<sup>2+</sup> of groundwater may have been contributed by fertilizers like super phosphate. Dissolution of anorthite also can contribute to the Ca<sup>2+</sup> ions in groundwater. Dissolution of anorthite produces kalinite plus calcium:



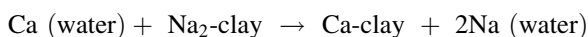
The positive correlation coefficient ( $r = 0.333$ ) of TDS and nitrate of shallow waters indicates that nitrates are soluble in water but not adsorbed by clay rich soils. Natural levels of nitrates in groundwater are low (<20 mg/l). This suggest that high NO<sub>3</sub><sup>-</sup> concentrations in the groundwaters relate to the removal of NO<sub>3</sub><sup>-</sup> from soils, since nitrogen

fertilizers represent the main source of NO<sub>3</sub><sup>-</sup> in this extensively farmed region. In the area studied, various anthropogenic activities such as intensive agriculture, vegetable production and horticulture have been going on for many years. Recharge from precipitation and irrigation may carry nitrogen compounds from the soil into the shallow aquifer, often resulting in elevated nitrate concentrations in shallow wells (Table 2). Important non-agricultural sources of nitrate in the studied area include municipal and industrial discharges containing nitrogen bearing effluent and atmospheric deposition. Fluoride is negatively correlated with NO<sub>3</sub> in shallow groundwaters and SO<sub>4</sub> in deep groundwaters, while it is positively correlated with HCO<sub>3</sub> in shallow and deep groundwaters of the study area. There is statistically very significant positive correlation exists between TDS and Cl in both shallow and deep groundwaters. High loading on Cl<sup>-</sup> indicates relatively long residence time due to sluggish movement of groundwater in clay dominating litho-facies. Cl<sup>-</sup> seems to be derived from anthropogenic sources such



as domestic wastewater, open disposal of excreta and irrigation return flow in the study area (Raju et al. 2011).

High positive correlation of  $\text{Na}^+$  ( $r = 0.694$ ) and negative correlation of  $\text{Ca}^{2+}$  ( $r = -0.094$ ) in deep groundwater with TDS, indicate ion-exchange of  $\text{Na}^+$  (in clay) for  $\text{Ca}^{2+}$  (in water), as per the following equation:



This process explains the deposition of lime kankar (caliche nodules) and ion-exchange, resulting enrichment of  $\text{Na}^+$  in groundwater. The cation exchange between  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  and  $\text{Na}^+$  may also explain the excess  $\text{Na}^+$  concentration (Stimson et al. 2001). Calcium and magnesium can exchange sodium sorbed on the exchangeable sites of clay minerals, resulting in the decrease of calcium and magnesium and increase sodium in groundwaters. Agricultural contamination is also responsible for the increase of  $\text{Na}^+$  in groundwater. Ferromagnesian minerals such as, amphibole, pyroxene and biotite present in the sediments react with the circulating groundwater and undergo dissolution, resulting in  $\text{Mg}^{2+}$  enrichment in groundwater. The high concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the groundwaters of the study area indicates the process of dissolution of feldspathic and ferro-magnesium minerals in the aquifer matrix.

A good correlation between  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.403$ , shallow and  $r = 0.476$ , deep water) suggests that a part of the  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  may also be derived by the weathering of  $\text{Mg}^{2+}$  sulfate mineral. High  $\text{SO}_4^{2-}$  levels, in combination with high  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations, have frequently been explained by weathering of reduced pyrite (Dalai et al. 2002). In general, high  $\text{SO}_4^{2-}$  concentrations may be derived either by sulfide or  $\text{SO}_4^{2-}$  weathering (Stallard and Edmond 1987). Pyrite weathering may contribute  $\text{SO}_4^{2-}$  load to groundwater in the study area. The correlation coefficient between Na and Cl ( $r = 0.610$ , shallow and  $r = 0.547$ , deep waters) indicates a strong correlation between them. However, the analytical chemical data indicating  $\text{Na}^+$  ions are also derived from other chemical processes. There is a positive correlation ( $r = 0.567$ ) between  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  for deep groundwaters indicating that the excess of  $\text{Na}^+$  in these samples mostly results from dissolution of sodium sulfate minerals. Among rock forming minerals involved in hydrolysis, sodium plagioclase is perhaps common and important mineral in the formation of sodium in groundwater. Silicate dissolution can be a probable source for  $\text{Na}^+$  in groundwater in the study area. The contribution of potassium to groundwater in these samples is modest. The low levels of potassium in natural waters are a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary mineral (Mathess 1982). The

positive correlation coefficient ( $r = 0.255$ ) of  $\text{K}^+$  and  $\text{NO}_3^-$  for shallow waters indicate infiltration of fertilizer rich irrigation water to the shallow groundwater regime (Handa 1975; Pandey and Mukherjee 1994).

## Conclusions

The present study indicates different paths of geochemical evolution of shallow and deep groundwaters in the Pleistocene tract of Middle Ganga Plain in the Varanasi environs. TDS of water samples indicate that shallow groundwater was observed to be more mineralized than deep groundwater. Major cations in the studied shallow and deep groundwater are in decreasing order as  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$  and  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  types, respectively whereas anionic concentrations for both waters belong to  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$  types. Based on major constituents, in general, dominant facies are Na- $\text{HCO}_3$  in shallow groundwater and Ca- $\text{HCO}_3$  in deep groundwater from the studied area. In the process of ion-exchange,  $\text{Na}^+$  from the aquifer matrix dominated by clays and sandy clays replaces  $\text{Ca}^{2+}$  in groundwater which results in formation of lime kankar (i.e. calcium nodules). The mobilization of sediment bond As may have a significant influence on future environmental quality of water resources that are heavily used by the domestic and agricultural sectors in eastern parts of the study region. The correlation coefficient between TDS and other major ions  $\text{Na}^+$  ( $r = 0.757$  and  $0.694$ ) and  $\text{Cl}^-$  ( $r = 0.914$  and  $0.851$ ) indicates a strong correlation in shallow and deep groundwaters, respectively in the study area. High loading of Cl and Na indicates relatively long residence time due to sluggish movement of groundwater in clay dominating litho-facies. The saturation index of the various minerals with TDS indicated that majority of shallow and deep groundwater samples of the study area are oversaturated with carbonate bearing minerals (calcite, aragonite, dolomite and magnesite) and undersaturated with respect to sulfur bearing minerals (gypsum, anhydrite) and amorphous silica minerals (chalcedony and cristobalite). Water samples which are saturated to over-saturated with these carbonate minerals indicated that excess input of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are mainly from carbonate weathering processes. In general weathering of silicate minerals in the alluvium remains to be the very important process in deep groundwater aquifers compared to shallow groundwater aquifer in the study area.

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## References

- Anku YS, Yakubo BB, Asiedu DK, Yidana SM (2009) Water quality analysis of groundwater in crystalline basement rocks, Northern Ghana. *Environ Geol* 58:989–997
- APHA (1995) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, Washington
- Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. AA Balkema, Rotterdam
- Ball JW, Nordstrom DK (1992) User's manual for WATEQ4F with revised thermodynamic database and test cases for calculating speciation of minor, trace and redox elements in natural waters. US Geol Surv Open File Rep 91–183:189
- Bureau of Indian Standards (BIS) (2003) Indian Standards: drinking water specification (1<sup>st</sup> revision, Amendment no. 2). Bureau of Indian Standards, New Delhi
- Burkart MR, Kolpin DW (1993) Hydrologic and land use factors associated with herbicides and nitrates in near surface aquifers. *J Environ Qual* 22:646–656
- Clark I, Fritz P (1997) Environmental isotopes in Hydrology. Lewis Boca Raton, New York
- CGWB, PHED (2005). A report on status of arsenic contamination in groundwater in the state of Bihar and action plan to mitigate it. Central Ground Water Board, Govt. of India and Public Health Engineering Dept. Govt of Bihar
- Chadha DK (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol J* 7:431–439
- Condesso de Melo MT, Marques da Silva MA, Edmunds WM (1999) Hydrochemistry and flow modelling of the Aveiro multilayer cretaceous aquifer. *Phys Chem Earth. Part B: Hydrol, Oceans Atmos* 4:331–336
- Dalai TK, Krishnaswami S, Sarin MM (2002) Barium in the Yamuna River system in the Himalaya: sources, fluxes, and its behaviour during weathering and transport. *Geochem Geophysics Geosystems* 3:1076
- Dhindsa SS, Bheel P, Musturia Y (2004) Hydrochemical study of groundwater quality variation in Tonk district, Rajasthan. *Indian J Environ Ecoplanning* 8(1):129–136
- Drever JI (1997) Geochemistry of natural waters, 2nd edn. Eagle Wood Cliffs, Prentice Hall, p 388
- Eckhardt DAV, Stackelberg PE (1995) Relation of groundwater quality to land use on Long Island, New York. *Groundwater* 33:1019–1033
- Fisher RS, Mulican WF III (1997) Hydrogeochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the northern Chihuahuan desert, Trans Pecos, Texas, USA. *Hydrogeol J* 10(4):455–474
- Garrels RM, Christ JC (1965) Solutions, minerals and equilibria. Freeman, Cooper, San Francisco
- Geuo H, Wang Y (2004) Hydrogeochemical processes in shallow quaternary aquifers from the northern part of the Datong basin, China. *Appl Geochem* 19:19–27
- Hallberg GR (1989) Nitrate in groundwater in the United States. In: Follee RF (ed) Nitrogen management and groundwater protection. Elsevier, Amsterdam, pp 35–138
- Handa BK (1975) Environmental pollution, occurrence of high nitrate ion concentration in groundwater from some parts of India. *Int Assoc Hydrogeol Congr, de Montpellier* 10:80–85
- Jalali M (2005) Major ion chemistry in the Bahar Area, Hamadan, Western. Iran *Environ Geol* 47:763–772
- Jalali M, Kolahchi Z (2008) Groundwater quality in an irrigated, agricultural area of northern Malayer, western Iran. *Nutr Cycl Agroecosyst* 18(1):95–105
- Jain CK, Bandyopadhyay A, Bhadra A (2010) Assessment of groundwater quality for drinking purpose, District Nainital, Uttarkhand, India. *Environ Monit Assess* 166:663–676
- Khan AA, Nawani PC, Srivastava MC (1988) Geomorphological evolution of the area around Varanasi, U.P. with the aid of aerial photographs and LANDSAT imageries. *Geol Surv India Rec* 113:31–39
- Lloyd JW, Heathcote JA (1985) Natural inorganic hydrochemistry in relation to groundwater. Clarendon Press, Oxford, p 294
- Mathes G (1982) The properties of groundwater. Wiley, New York
- Meenakumari HR, Hosmani SP (2003) Physico-chemical and biological quality of groundwater in Mysore city, Karnataka. *Indian J Environ Ecoplanning* 7(1):79–82
- Naidu MN, Srinivas N, Prasada Rao PV (1998) Urban water quality in north coastal Andhra Pradesh. *Indian J Environ Prot* 18(4):273–277
- Nativ R, Smith A (1987) Hydrogeology and geochemistry of the Ogallala aquifer southern high plains. *J Hydrol* 91:217–253
- Offiong OE, Edet AE (1998) Water quality assessment in Akpabuyo, Cross River basin, South-Eastern Nigeria. *Environ Geol* 34:167–174
- Pandey DS (1993) Groundwater pollution studies in urban settlements of Varanasi city, UP. Annual work programme report 1992–1993. Central Groundwater Board, Allahabad, p 35
- Pandey DS, Mukherjee S (1994). Nitrate contamination in groundwater in Varanasi city and its environs, Uttar Pradesh. Proc Reg Workshop Environ Aspects Groundwater Dev. Kurekshetra University, Kurukshetra 123–130
- Pratt PF (1985). Agriculture and groundwater quality. CAST Report, 103
- Raju NJ (2006) Seasonal evaluation of hydrogeochemical parameters using correlation and regression analysis. *Curr Sci* 91(6):820–826
- Raju NJ (2007) Hydrogeochemical parameters for assessment of groundwater quality in the upper Gunjanaeru River basin, Cuddapah district, Andhra Pradesh, South India. *Environ Geol* 52:1067–1074
- Raju NJ, Ram P, Dey S (2009a) Groundwater quality in the lower Varana River basin, Varanasi district, Uttar Pradesh, India. *J Geol Soc India* 73:178–192
- Raju NJ, Dey S, Das K (2009b) Fluoride contamination in groundwaters of Sonbhadra district, Uttar Pradesh, India. *Curr Sci* 96(7):979–985
- Raju NJ, Reddy TVK (2007) Environmental and urbanization affect on groundwater resources in a pilgrim town of Tirupati, Andhra Pradesh, South India. *J Appl Geochem* 9(2):212–223
- Raju NJ, Shukla UK, Ram P (2011). Hydrogeochemistry for the assessment of groundwater quality in Varanasi: a fast urbanizing center in Uttar Pradesh, India. *Environ Monit Assess*. doi: 10.1007/s10661-010-1387-6
- Ritzi RW, Wright SL, Mann B, Chen M (1993) Analysis of temporal variability in hydrogeochemical data used for multivariate analyses. *Groundwater* 31:221–229
- Sahu P, Sikdar PK (2008) Hydrochemical framework of the aquifer in and around east Kolkata wetlands, West Bengal, India. *Environ Geol* 55:823–835
- Saleh A, Al-Ruwaihi F, Shehata M (1999) Hydrogeochemical processes operating within the main aquifers of Kuwait. *J Arid Environ* 42:195–209
- Shah D, Dhar YR, Sikdar PK (2008) Geochemical evolution of groundwater in the Pleistocene aquifers of south Ganga plain, Bihar. *J Geol Soc India* 71:473–482

- Shah BA (2010) Arsenic contaminated groundwater in Holocene sediments from parts of middle Ganga plain, Uttar Pradesh, India. *Curr Sci* 98(10):1359–1365
- Shukla UK, Singh IB, Sharma M, Sharma S (2001) A model of alluvial megafan sedimentation: Ganga Megafan. *Sediment Geol* 144:243–262
- Shukla UK, Raju NJ (2008) Migration of Ganga River and its implication on hydrogeological potential of Varanasi area. *UP. J Earth Syst Sci* 117(4):489–498
- Shih RD, Marcus SM, Gnense CA (1997) Methemoglobinemia attributable to nitrate contamination of potable water through boiler fluid additives—New Jersey, 1992 & 1996. *Morb Mortal Wkly Rep* 46:202–204
- Singh UK, Kumar M, Chauhan R, Jha K, Ramanathan AL, Subramanian V (2008) Assessment of the impact of landfill on groundwater quality: a case study of the Pirana site in western India. *Environ Monit Assess* 141:309–321
- Singh IB (1987) Sedimentological history and Quaternary deposits in Gangetic plain. *Indian J Earth Sci* 14:272–282
- Singh IB (2004) Late Quaternary history of the Ganga Plain. *J Geol Soc India* 64:431–454
- Singh M, Singh IB, Muller G (2007) Sediment characteristics and transportation dynamics of the Ganga River. *Geomorphology* 86:144–175
- Singh M, Singh AK, Swati, Srivastava N, Singh S, Chowdhary AK (2010) Arsenic mobility in fluvial environment of the Ganga Plain, northern India. *Environ Earth Sci* 59:1703–1715
- Smith AH, Biggs ML, Moore L, Haque R, Steinmaus C, Chung J, Hernandez A, Lopepero P (1999). In: Chappell WR, Abernathy CO, Calderon RL(eds) *Arsenic exposure and health effects*, Elsevier Science, Oxford pp 191–200
- Srivastava P, Singh IB, Sharma M, Singhvi AK (2003) Luminescence chronometry and Late Quaternary geomorphic history of the Ganga Plain India. *Palaeogeogr Palaeoclim Palaeoecol* 197:15–41
- Stallard RF, Edmond JM (1987) Geochemistry of the Amazon 3. Weathering chemistry and limits to dissolved inputs. *J Geophys Res* 92:8293–8302
- Stimson J, Frape S, Drimmie R, Rudolph D (2001) Isotopic and geochemical evidence of regional-scale anisotropy and inter-connectivity of an alluvial fan system, Cochabamba Valley, Bolivia. *Appl Geochem* 16:1097–1114
- Tandon SK, Gibling MR, Sinha R, Singh V, Ghazanfari P, Dasgupta A, Jain M, Jain V (2006) Alluvial valleys of the Ganga Plain, India: timing and causes of incision. *SEPM Spec Publ* 85:15–35
- Umar R, Ahmed I (2007) Hydrochemical characteristics of groundwater in parts of Krishni-Yamuna Basin, Muzaffarnagar district, UP. *J Geol Soc India* 69:989–995
- Unsal N, Celik M (2010) Hydrogeochemistry and water quality evaluation along the flow path in the unconfined aquifer of the Duyce plain, North-western, Turkey. *Acta Geol Sinica* 84(1):213–222
- WHO (1993) *Water and sanitation. Guidelines for drinking water quality*, vol. 1, 2nd edn. WHO, Geneva