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Assessment of geochemical processes in the unconfined and confined aquifers in the Eastern Ganges Basin: a geochemical approach

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Abstract Groundwater quality is gaining more importance in groundwater management due to rapid growth in population, agriculture and industrial sectors worldwide. The goal of the present study is to evaluate the groundwater chemistry and to identify the geochemical processes governing the water chemistry in the shallow unconfined and deeper confined aquifers in the Eastern Ganges Basin using geochemical methods. Groundwater samples were analysed for major ions and metals (Fe, Mn, Zn, Cu, Pb and As). Shallow wells are found to have high pH, EC, TDS, Ca, Mg, Cl and SO_4, and low HCO_3/Cl ratio compared to the deep wells. However, the average concentration of Na, HCO_3, NO_3, PO_4, F and Mn is not significantly varied with depth which indicates that the variation in the water chemistry between unconfined and confined aquifers is not only due to the natural processes but also indicates that surface contamination sources could have affected the water chemistry in the unconfined aquifer. In the unconfined aquifer, processes like wastewater infiltration, denitrification, reverse ion exchange and mineral weathering govern the water chemistry. The water chemistry in the confined aquifer is regulated by weathering of silicate and carbonate minerals and regional flow.

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Introduction

The Eastern Ganges Basin (EGB), which spans across India (states of Bihar and West Bengal), Bangladesh and Nepal (Terai), has a population of 391.26 million (Rajmohan and Prathapar 2013). In the EGB, groundwater is a major source of water for drinking, domestic and agriculture use. The groundwater quality is questionable in some regions because of natural processes and man-made activities (Rajmohan and Prathapar 2013 and references therein). In the EGB, the high concentration of arsenic, fluoride, iron, manganese, zinc, chloride, nitrate and other metals in the groundwater has been reported and discussed by many studies (Yadav et al. 2015; Rajmohan and Prathapar 2013, 2014 and references therein). In Bihar, the Central Groundwater Board (CGWB) and the Public Health Engineering Department (PHED 2005) reported that 57 blocks in 15 districts are affected by arsenic contamination based on a blanket survey of $\sim$82,000 samples (Saha et al. 2009; Rajmohan and Prathapar 2014). In Bihar, PHED (2015) reported that fluoride and iron contaminations in the groundwater are encountered in 11 and 9 districts, respectively. Thus, a detailed knowledge of the source of contaminants, contamination levels and relevant geochemical processes will help to protect this resource from further pollution.

The concentrations of dissolved ions in the groundwater are governed by many factors, namely residence time, groundwater flow, lithology, aquifer materials, unsaturated zone thickness, mineral water interaction, geochemical

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reactions and process, and human activities (Bhatt and Saklani 1996; Karanth 1987; Nisi et al. 2008; Schot and Van der Wal 1992; Nagarajan et al. 2010; Xiao et al. 2015). In the agricultural regions, irrigation return flow, excessive applications of fertilizers and manures result in high nitrate, phosphate, potassium, chloride and salinity of groundwater. In urban and residential areas, the potential sources of groundwater contamination are infiltration of wastewater from septic tanks, pit latrines, landfills, sewage disposal sites, leachate from cattle farm wastes and increasing pumping, to name a few.

Groundwater contamination is highly dependent on aquifer material and geology. Though the vadose zone acts as a filter for most of the contaminants, groundwater in the unconfined aquifer is more susceptible to contamination due to shallow water tables, and high permeability and porosity of soil in the vadose zone (Nolan et al. 2002; Davraz et al. 2009; Jiang et al. 2009). In contrast, groundwater in the confined aquifer is protected naturally by impermeable soil layers against contamination (Ebraheem et al. 1997; Conboy and Goss 2000). Hence, water chemistry is not homogenous in both unconfined and confined aquifers within the same region. Many studies employed the major ion concentrations to study and evaluate the water chemistry, contamination assessment, aquifer connectivity, heterogeneity, geochemical processes controlling water chemistry, etc. (Hem 1989; Rajmohan and Elango 2004, 2006; Güler et al. 2002; Chenini and Khmiri 2009; Ruiz et al. 2015; Xiao et al. 2015). Further, few studies have documented the relation between well depth and water quality. Shi et al. (2013) assessed the suitability of deep well water for various uses by using a groundwater quality index (GQI) in North China. Zhai et al. (2013) characterized the groundwater renewability and evolution of the aquifer in the North China Plain using major ions and environmental tracers. They concluded that the shallow groundwater was vulnerable to contamination, which would probably further extend to the deep groundwater due to vertical flow. In India, Dash et al. (2010) correlated the well depth and water quality through spatial maps. In the city of Varanasi, Nandimandalam (2012) documented that groundwater in the shallow aquifer has high TDS (629 mg/l) and nitrate than the deep aquifers (TDS 423 mg/l, average). Sinha and Saxena (2006) studied the groundwater quality in Hasanpur, Uttar Pradesh. They reported that the groundwater from shallow domestic hand pumps (HPs) has high EC, TDS, TH, Ca, Mg, Cl, F, free CO_2 (>43 mg/l) and less DO (<3 mg/l) compared to deeper HPs. Hence, the objectives of this study are to evaluate the groundwater chemistry and to identify the geochemical processes governing the water chemistry in the shallow unconfined (first) and deeper confined (second) aquifers in Vaishali district, Bihar, in the EGB. In this study,

geochemical (major ion ratios, ion activity ratios, saturation indices and stability diagram) and statistical (correlation analysis) methods are employed.

Study area

The study was carried out in and around Mukundpur village, Vaishali district, Bihar, India (Fig. 1). The geographical area of the Vaishali district is 2015.37 km². The district is bound in the south and west by the river Ganges and the river Gandak, respectively, and in the north and east by Muzaffarpur and Samastipur districts, respectively. The total population is about 3.5 million (Census of India, 2011), and 93.35 % of the populace lives in the rural areas. Vaishali district is located in the EGB and has two sub-basins, namely Gandak and Burhi Gandak. The main river is the Gandak, and it flows in the south-easterly direction and disgorges into the Ganges River near Hajipur (CGWB 2007). The temperature in this district ranges from 4 to 40 °C, and the climate is subtropical and sub-humid. The average annual rainfall is 1168 mm, and this district receives 85 % of the total rainfall during the south-west monsoon (June–September). The Vaishali district is plain and formed by alluvium brought by the rivers Ganges, Gandak and their tributaries. Geomorphologically, the district is classified into three broad categories, namely Hazipur surface (yellow-brown to brownish-grey compact clay), Vaishali surface (ash-grey silt/silt–clay/clayey silt and overlies the Hazipur surface) and Diara surface (youngest geomorphic unit). The district is characterized by a wide variety of soils, which can be broadly classified into two categories: entisols and inceptisols. Entisols is rich in potash and lime, while inceptisols is a calcareous alluvial soil enriched with potash, lime and kanker. Paddy and wheat are the principle crops grown in this district, while both groundwater and canal water are the common water sources for irrigation.

Vaishali district is formed by Quaternary alluvial deposits comprised of alternative layers of sand, silt, clay and gravel, which form prolific unconfined and confined aquifer systems (CGWB 2007). The sand layers with parting thin clay layers are identified up to 60–70 mbgl depth, which form the unconfined aquifer. In the shallow depth, the clay layers are not regionally extensive. The transmissivity and specific yield of this aquifer vary from 1000 to 5000 m²/day and from 8 to 12 %, respectively. The groundwater flows in the south-east direction towards the river Ganges. The depth to groundwater level ranges from 3 to 9 mbgl during pre-monsoon season and from <1 to 5 mbgl during post-monsoon season, respectively. According to the CGWB (2007), the aquifer is semi-confined to confined in nature due to impervious clay layers at greater depths. The transmissivity and storativity values of the

Fig. 1 Location map of the study area with sampled groundwater wells. *SW* shallow wells, *DW* deep wells, *SH* state high way
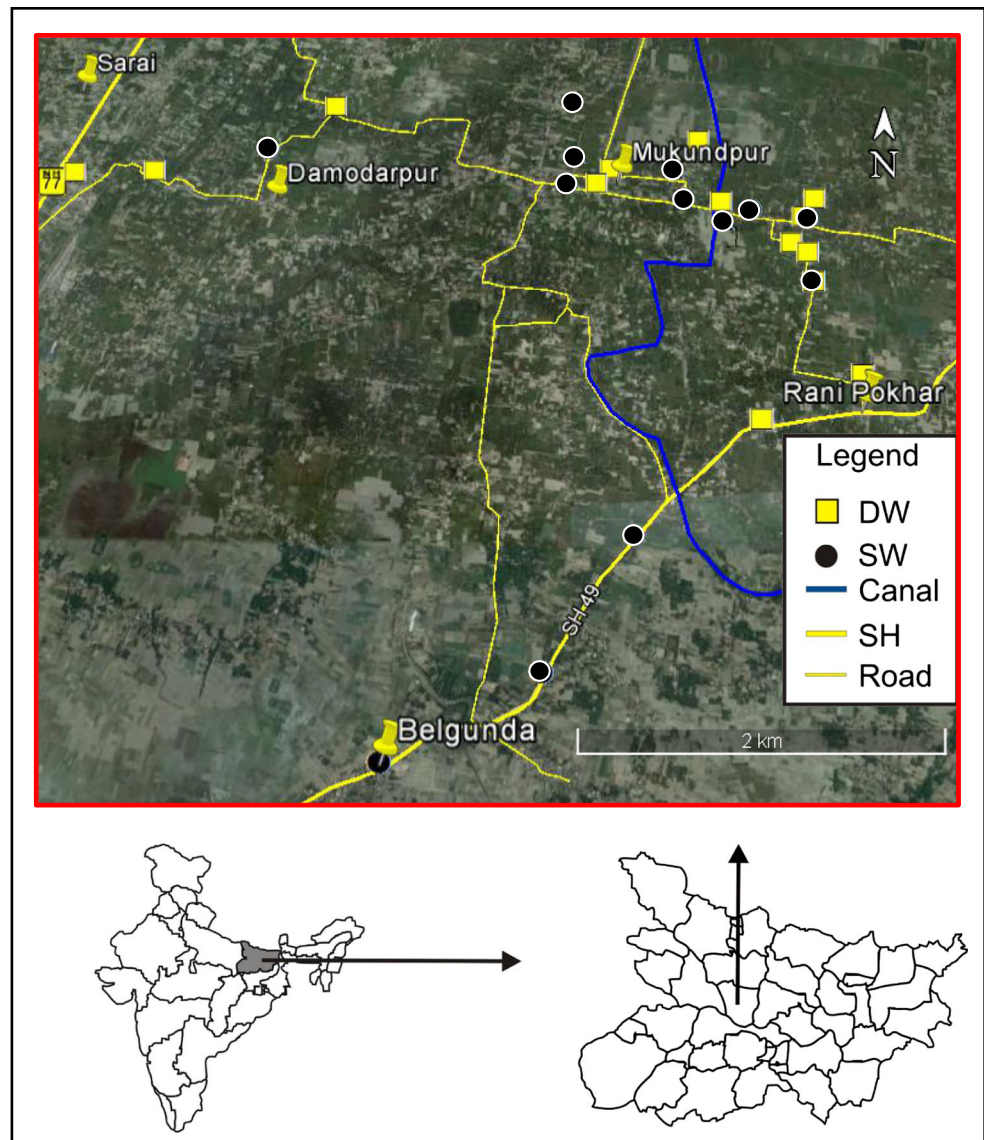
deeper confined aquifer range from 621 to 5163 and 0.13×10^{-7} m^2/day, respectively (CGWB 2007). Due to huge thickness of the confined aquifer, high discharge (200 m^3/h) is possible in the deeper wells (300 m).

Materials and methods

Groundwater sampling and analysis

The groundwater sampling was carried out in and around Mukundpur village in Vaishali district, Bihar, India during October 2013 (Fig. 1). Groundwater wells inventory survey were carried out before the groundwater sampling campaign in order to select the representative groundwater wells for sampling. During this survey, electrical conductivity (EC) and pH were measured in the field and well total depth details were collected from the well owners. The groundwater samples were collected from 26 wells tapping either shallow unconfined (first) or deeper confined (second) aquifer. The groundwater samples were analysed for major ions, nutrients and trace metals using standard methods (APHA 1995). The analysis was carried out in the PHED, Patna, Bihar, India. The trace metals (Fe, Mn, Zn, Cu, Pb and As) were analysed using atomic absorption spectrophotometer (Perkin-Elmer AA700). The measurement repeatability and precision for each analysis were less than 2 %. The analytical precision for the total measurements of ions was checked again by calculating the ionic balance errors and was found to be generally within ±5 %.

Data analysis

PHREEQC (version 2.18), a geochemical computer program, with thermodynamic database Phreeqc.dat was used to calculate the distribution of aqueous species, ion activities and saturation indices of mineral phases (Parkhurst and Appelo 1999). The details of calculation methods are given in Parkhurst and Appelo (1999). The saturation indices were calculated using the relation, $SI = log(IAP/Ks)$ where IAP is ion activity product and Ks is the solubility product of the mineral. Pearson correlation analysis was performed to identify the associations between the chemical constituents using SPSS (v 16.0) software.

Results and discussion

General water chemistry

The survey of the groundwater wells was carried out to select the representative wells for sampling, and EC and pH were measured in the surveyed wells. In the surveyed wells ($n = 63$), the depth varies from 6.1 to 53.3 m with an average value of 28.7 m. In the surveyed wells ($n = 63$), EC and pH range from 282 to 2500 μS/cm and from 7.2 to 8.3 with a mean value of 907 ± 388 μS/cm (mean $\pm$ SD) and 7.7 ± 0.25, respectively (Fig. 2). High standard deviations in depth and EC indicate that wells do not tap the same aquifer and water chemistry is not homogenous. Based on this information, 26 representative wells were selected for sampling and analysis.

The descriptive statistics of the physical and chemical parameters analysed in the water samples ($n = 26$) are reported in Table 1. EC varies from 578 to 1394 μS/cm with an average of 866 ± 227 μS/cm ($n = 26$). Likewise, total dissolved solids (TDS) ranges between 370 and 892 mg/l with a mean value of 554 ± 145 mg/l. In the study site, TDS is less than 1000 mg/l in the water samples and therefore is classified as freshwater (Freeze and Cherry 1979). The dominance of anions is in the order $HCO_3 > Cl > SO_4$ except for two samples ($HCO_3 > SO_4 > Cl$; $Cl > HCO_3 > SO_4$). In the case of cations, dominance orders $Mg > Na > Ca > K$, $Mg > Ca > Na > K$, $Ca > Na > Mg > K$ and $Ca > Mg > Na > K$ are noticed in 11, 10, 2 and 3 samples, respectively. The trace metals such as As, Cu, Pb, Fe, Mn and Zn were analysed in the water samples. The concentrations of As, Cu and Pb are below detection limit (BDL). The concentration of iron varies from 0.14 to 2.11 mg/l with an average of 0.53 mg/l. The concentrations of Mn and Zn range from 0.02 to 0.09 mg/l and from 0.29 to 1.40 mg/l with an average value of 0.05 and 0.61 mg/l, respectively. Table 1 indicates that the chemical composition of water samples shows a

wide range and has high standard deviations especially with EC, TDS, Cl and SO_4. These observations suggest that the water chemistry is heterogeneous and regulated by distinct processes.

Vertical variation

The groundwater samples were collected from wells tapping from either shallow unconfined (first aquifer) or deeper confined (second) aquifer in the study site. In the sampled wells, the depth of the shallow and deep wells ranges from 9.14 to 18.3 and from 39.6 to 53.3 m, respectively (Table 1). The shallow wells tap water in the first aquifer (unconfined aquifer), while the deep wells tap water from the second aquifer (confined aquifer). Table 1 and Fig. 2 illustrate that the water chemistry is not similar in the shallow and deep wells. Figure 2 also shows the vertical variation of EC and pH of both the surveyed and sampled wells. The shallow wells have high EC and pH compared to the deep wells. Similar trend is observed with respect to the other variables such as TDS, Ca, Mg, Cl and SO_4, and the shallow wells have low HCO_3/Cl ratio (Figs. 2, 3). In these wells, Ca dominates over Na ($Mg > Ca > Na > K$). In the shallow wells, pH, EC and TDS vary from 7.2 to 8.3, 680 to 1394 μS/cm and 435 to 892 mg/l with an average value of 7.6, 1044 μS/cm and 668 mg/l, respectively. Likewise, the concentrations of Ca, Mg, Cl and SO_4 range from 22 to 101, 26 to 95, 51 to 207 and 10 to 93 mg/l with an average value of 57, 70, 124 and 51 mg/l, respectively. The standard deviation of these variables is generally high. However, the average concentration of Na, HCO_3, NO_3, PO_4, F and Mn does not significantly vary with depth (Table 1; Fig. 3). The absence of vertical variations in the concentrations of Na and HCO_3 suggests that the variation in the water chemistry with depth is due to not only the mineral dissolution but also that the surface contamination sources affect and modify the water chemistry in the shallow unconfined aquifer. Figure 3 illustrates that the $Ca + Mg/HCO_3$ ratio is close to 0.5 in the deep wells that indicates mineral dissolution (Sami 1992; Rajmohan and Elango 2004). Nevertheless, this ratio is more than 0.5 in the shallow wells. The excess Ca and Mg over HCO_3 in the shallow wells is originated from the reverse ion exchange as discussed in a later section.

In the case of trace metals, the concentration of Mn does not vary with depth; however, the concentration of Fe is slightly high in the shallow wells (Table 1; Fig. 3). In the groundwater, the trace metals generally originate from the reduction of respective hydroxides and carbonates in the anaerobic environment and subsequently increase the pH of water. If Fe, Mn and Zn are solely formed by the reductive dissolution process, these metals should not be
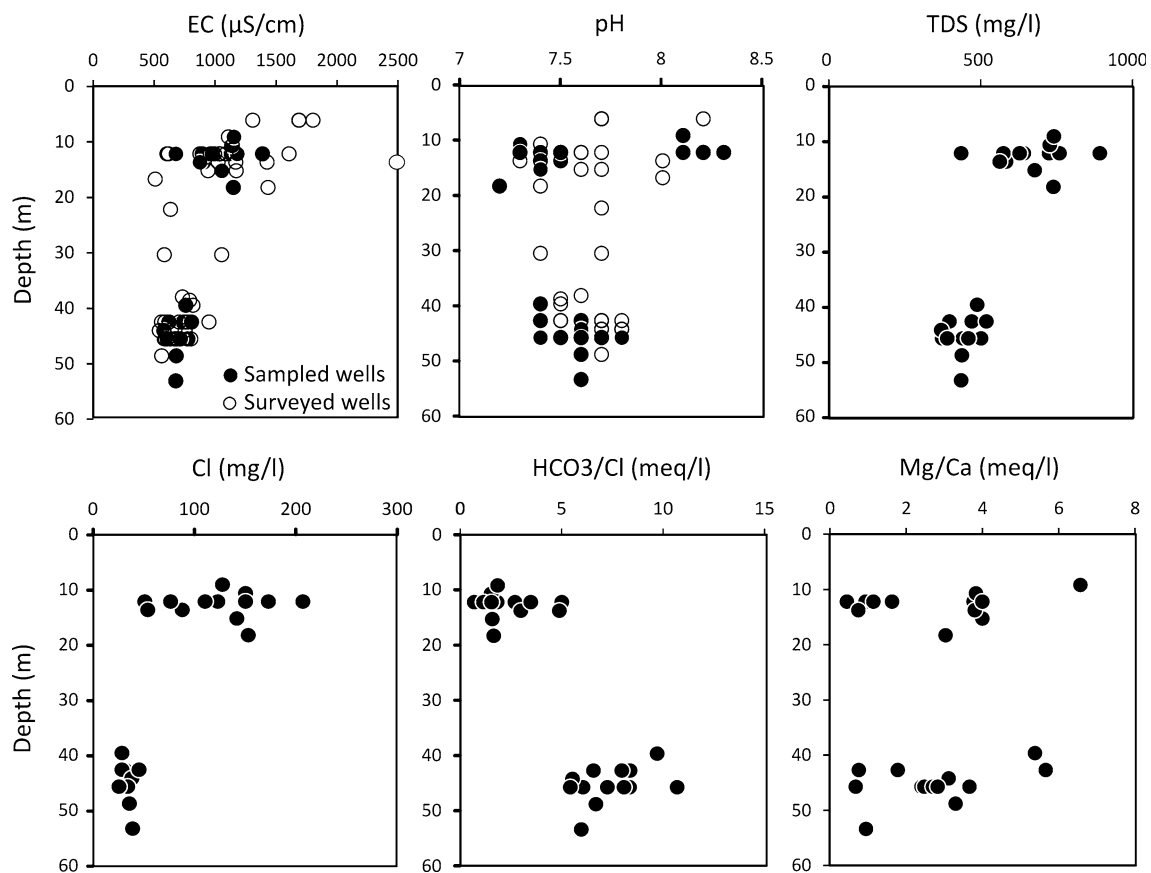
Fig. 2 Vertical distribution of EC, TDS, pH, Cl, HCO₃/Cl and Mg/Ca in the groundwater samples

varied with depth. The high concentrations of Fe and Zn in the shallow unconfined aquifer are likely to be added by the surface contamination sources such as fertilizers (zinc sulphate), irrigation return flows and domestic wastewater (Table 1). Zinc is generally used in the brass, paint and rubber manufacturing industry and products (WHO 2003). Zinc coating protects stainless steel and iron products. In addition, zinc is also used in tyres as zinc oxide and in some cosmetics. In the study site, high concentrations of Fe, Mn and Zn are reported in the top soil layers (Rajmohan et al. 2014).

Correlation analysis

Inter-elemental correlation analysis provides the information about the origin and source of variables and their evaluation pathway. The individual correlation analysis was carried out for both the shallow and deep wells. Table 2 shows Pearson's correlation coefficient of the selected variables analysed in the water samples. Variables such as K, NO₃, F and Zn in the shallow wells and NO₃ and Mn in the deep wells do not correlate with the other variables. In the shallow wells, Cl shows a significant positive correlation with EC ($r^2 > 0.7$, $p < 0.01$) and TDS

($r^2 > 0.7$, $p < 0.01$) and a negative correlation with HCO₃ ($r^2 > -0.6$, $p < 0.05$) and PO₄ ($r^2 > -0.6$, $p < 0.05$). This observation indicates that the surface contamination sources have affected the water chemistry in the shallow unconfined aquifer. Likewise, Mg has a negative correlation with Ca ($r^2 > -0.8$, $p < 0.01$) and pH ($r^2 > -0.6$, $p \leq 0.05$). Similarly, SO₄ has a positive correlation with Mn ($r^2 > 0.6$, $p < 0.05$) and a negative correlation with pH ($r^2 > -0.6$, $p \leq 0.05$). Sodium has a significant positive correlation with Fe ($r^2 > 0.6$, $p < 0.05$).

In the deep wells, HCO₃ exhibits a strong positive correlation with EC ($r^2 > 0.8$, $p < 0.01$) and TDS ($r^2 > 0.8$, $p < 0.01$) and a negative correlation with pH ($r^2 > -0.9$, $p < 0.01$). The positive correlations between Na and K ($r^2 > 0.6$, $p < 0.05$); K and Fe ($r^2 > 0.6$, $p < 0.05$); Ca and PO₄ ($r^2 > 0.8$, $p < 0.01$); Mg and SO₄ ($r^2 > 0.6$, $p < 0.05$); and HCO₃ ($r^2 > 0.7$, $p \leq 0.01$) are observed (Table 2). Likewise, the negative correlations between pH and EC ($r^2 > -0.9$, $p < 0.01$); TDS ($r^2 > -0.9$, $p < 0.01$); Ca and Mg ($r^2 > -0.6$, $p < 0.05$); Zn and Cl ($r^2 > -0.6$, $p < 0.05$); and F ($r^2 > -0.6$, $p < 0.05$) are noticed. The correlation analysis indicates that the mineral dissolution has contributed much to the water chemistry in the deeper confined aquifer.

Table 1 Statistical summary of physio-chemical parameters analysed

	Depth	EC	TDS	PH	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	NO$_3$	PO$_4$	F	Fe	Mn	Zn
Shallow wells (n = 13)																	
Minimum	9.14	680	435	7.2	33	1.4	22	26	51	10	246	1.2	0.03	0.24	0.32	0.02	0.34
Maximum	18.3	1394	892	8.3	53	2.7	101	95	207	93	513	3.4	0.33	1.49	1.01	0.09	1.40
Mean	12.8	1044	668	7.6	41	1.89	57	70	124	51	408	2.1	0.10	0.67	0.58	0.05	0.67
STD	2.2	180	115	0.4	5.4	0.4	27	22	46	25	72	0.6	0.09	0.33	0.20	0.02	0.30
Skewness	1.2	−0.1	−0.1	0.8	0.6	0.8	0.5	−0.7	−0.1	−0.5	−1.1	0.6	2.2	1.3	0.6	0.5	1.3
Kurtosis	2.8	0.7	0.7	−1.1	0.6	1.3	−1.3	−0.9	−0.5	−0.3	1.3	0.0	4.2	2.5	−0.2	−1.1	1.9
Deep wells (n = 13)																	
Minimum	39.6	578	370	7.4	33	1.7	21	22	26	9	295	1.2	0.03	0.12	0.14	0.03	0.29
Maximum	53.3	810	518	7.8	48	3.4	87	83	45	49	512	3.7	0.43	1.21	2.11	0.08	0.88
Mean	45.3	687	440	7.6	42	2.4	39	53	32	25	406	2.20	0.11	0.66	0.48	0.05	0.56
STD	3.3	75	48	0.1	5.0	0.5	18	16	6	13	66	0.83	0.11	0.32	0.51	0.02	0.19
Skewness	0.9	0.0	0.0	0.1	−0.9	0.8	1.7	−0.2	0.8	0.9	−0.1	0.6	2.6	−0.2	3.1	0.6	0.2
Kurtosis	2.4	−0.9	−0.9	−0.9	−0.4	0.2	3.1	0.0	0.1	0.0	−1.0	−1.1	6.9	−0.7	10.1	−1.2	−1.2
Total (n = 26)																	
Minimum	9.14	578	370	7.2	33	1.4	21	22	26	9	246	1.20	0.03	0.12	0.14	0.02	0.29
Maximum	53.3	1394	892	8.3	53	3.4	101	95	207	93	513	3.70	0.43	1.49	2.11	0.09	1.40
Mean	29	866	554	7.6	42	2.13	48	62	78	38	407	2.16	0.10	0.66	0.53	0.05	0.61
STD	16.8	227	145	0.3	5.1	0.49	24	21	57	24	67	0.72	0.10	0.32	0.39	0.02	0.25
Skewness	0.04	0.61	0.61	1.22	−0.1	0.88	1.02	−0.05	0.81	0.51	−0.60	0.63	2.36	0.56	2.89	0.50	1.29
Kurtosis	−2.03	−0.64	−0.64	0.73	−0.3	0.75	−0.2	−0.98	−0.75	−0.75	0.00	−0.64	5.24	0.54	11.0	−1.1	2.43

Unit—mg/l except EC (µS/cm), pH and depth (m)
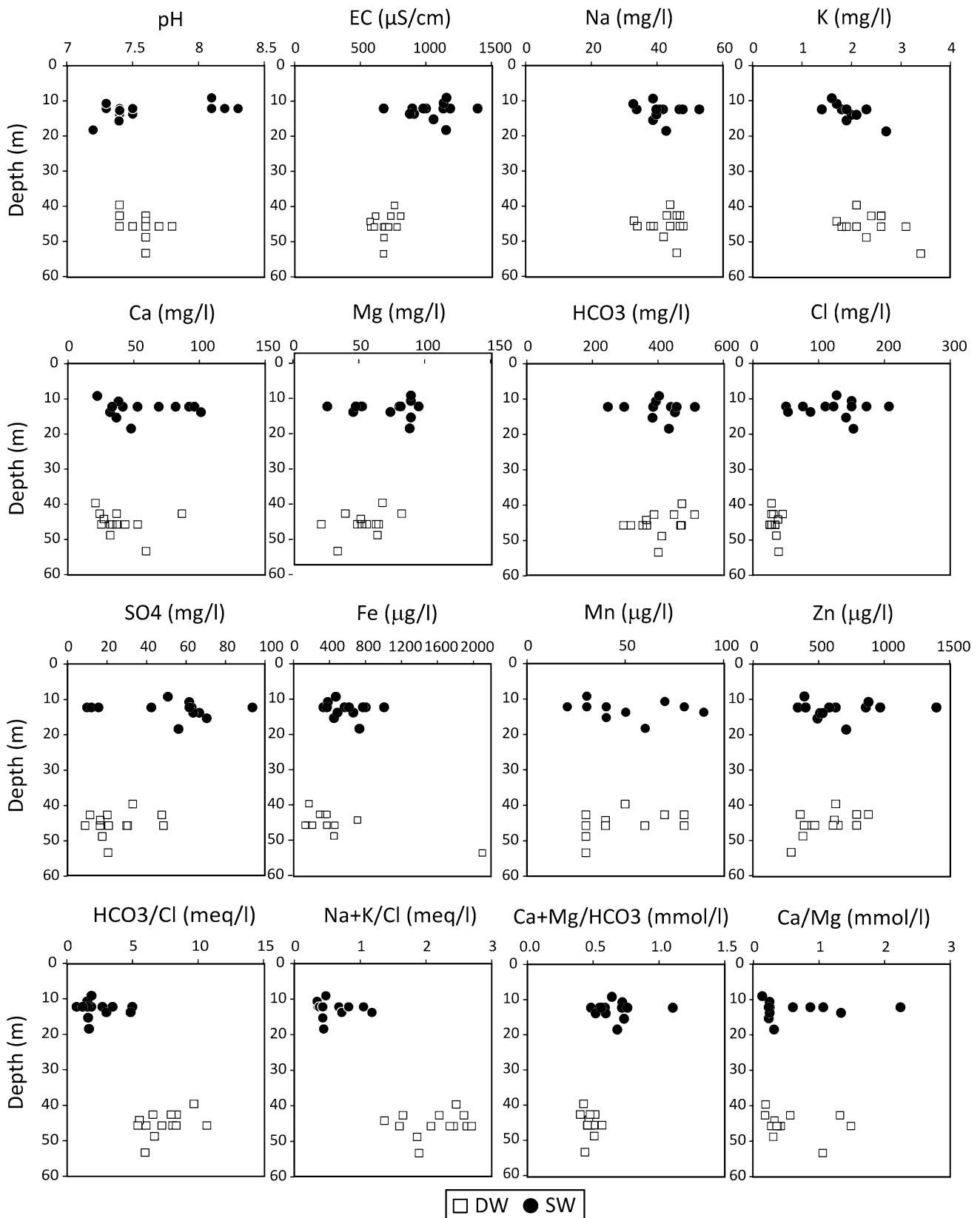
Fig. 3 Vertical distribution of the selected variables and their ratio in the groundwater samples

Table 2 Inter-elemental correlation analysis matrix of the selected variables in the groundwater samples

	EC	TDS	PH	Na	Ca	Mg	Cl	SO$_4$	HCO$_3$	PO$_4$	Fe	Mn
Shallow wells												
EC	1.0	**1.0**	−0.3	0.4	0.2	0.3	**0.7**	0.3	−0.1	−0.4	0.0	0.0
TDS	**1.0**	1.0	−0.3	0.4	0.2	0.3	**0.7**	0.3	−0.1	−0.4	0.0	0.0
PH	−0.3	−0.3	1.0	0.1	0.1	**−0.6**	−0.2	**−0.6**	−0.3	−0.1	−0.2	−0.3
Na	0.4	0.4	0.1	1.0	0.5	−0.4	0.3	−0.1	−0.2	−0.2	**0.6**	0.0
Ca	0.2	0.2	0.1	0.5	1.0	**−0.8**	0.3	0.1	−0.3	−0.5	0.1	0.4
Mg	0.3	0.3	−0.6	−0.4	−0.8	1.0	0.1	0.2	0.4	0.2	0.1	−0.2
Cl	**0.7**	**0.7**	−0.2	0.3	0.3	0.1	1.0	0.4	**−0.6**	**−0.6**	0.1	0.4
SO4	0.3	0.3	−0.6	−0.1	0.1	0.2	0.4	1.0	−0.4	0.1	0.0	**0.6**
HCO3	−0.1	−0.1	−0.3	−0.2	−0.3	0.4	−0.6	−0.4	1.0	0.3	0.0	−0.5
PO4	−0.4	−0.4	−0.1	−0.2	−0.5	0.2	−0.6	0.1	0.3	1.0	0.0	−0.2
Fe	0.0	0.0	−0.2	**0.6**	0.1	0.1	0.1	0.0	0.0	0.0	1.0	0.3
Mn	0.0	0.0	−0.3	0.0	0.4	−0.2	0.4	**0.6**	−0.5	−0.2	0.3	1.0
n	13	13	13	13	13	13	13	13	13	13	13	13

	EC	TDS	PH	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	PO$_4$	F	Fe	Zn
Deep wells														
EC	1.0	**1.0**	**−0.9**	0.2	0.1	0.1	0.5	0.3	0.5	**0.8**	0.1	0.5	−0.1	−0.2
TDS	**1.0**	1.0	**−0.9**	0.2	0.1	0.1	0.5	0.3	0.5	**0.8**	0.1	0.5	−0.1	−0.2
PH	**−0.9**	**−0.9**	1.0	0.1	0.0	−0.1	−0.5	−0.3	−0.4	**−0.9**	−0.2	−0.1	0.1	0.0
Na	0.2	0.2	0.1	1.0	**0.6**	0.1	−0.2	0.0	0.3	−0.2	0.0	0.3	0.2	0.0
K	0.1	0.1	0.0	**0.6**	1.0	0.3	−0.2	0.4	0.4	−0.1	0.3	0.2	**0.6**	−0.5
Ca	0.1	0.1	−0.1	0.1	0.3	1.0	**−0.6**	−0.1	−0.3	0.0	**0.8**	−0.2	0.3	0.4
Mg	0.5	0.5	−0.5	−0.2	−0.2	−0.6	1.0	0.3	**0.6**	**0.7**	−0.2	0.3	−0.4	−0.5
Cl	0.3	0.3	−0.3	0.0	0.4	−0.1	0.3	1.0	0.5	0.3	0.0	0.4	0.5	**−0.6**
SO4	0.5	0.5	−0.4	0.3	0.4	−0.3	0.6	0.5	1.0	0.3	−0.2	0.5	−0.1	−0.5
HCO3	**0.8**	**0.8**	**−0.9**	−0.2	−0.1	0.0	**0.7**	0.3	0.3	1.0	0.1	0.1	−0.1	−0.2
PO4	0.1	0.1	−0.2	0.0	0.3	**0.8**	−0.2	0.0	−0.2	0.1	1.0	−0.3	0.0	0.4
F	0.5	0.5	−0.1	0.3	0.2	−0.2	0.3	0.4	0.5	0.1	−0.3	1.0	0.1	**−0.6**
Fe	−0.1	−0.1	0.1	0.2	**0.6**	0.3	−0.4	0.5	−0.1	−0.1	0.0	0.1	1.0	−0.4
Zn	−0.2	−0.2	0.0	0.0	−0.5	0.4	−0.5	**−0.6**	−0.5	−0.2	0.4	**−0.6**	−0.4	1.0
n	13	13	13	13	13	13	13	13	13	13	12	13	13	13

Bold—significant correlation ($p < 0.01$ or $p < 0.05$; $r^2 > 0.5$)

Mineral equilibrium and geochemical stability

The mineral equilibrium calculations are generally employed to predict the occurrence of the reactive minerals in the groundwater systems and to estimate the mineral reactivity (Deutsch 1997). According to Deutsch (1997), it is possible to predict the reactive mineralogy of the subsurface from the groundwater data using the saturation index approach, without collecting the samples of the solid phase to analyse the mineralogy.

The saturation indices (SI) of the selected phases are plotted as a function of the depth (Fig. 4). The dissolved CO_2 gas pressure in the water samples varies from −2.84 to −1.61 with an average value of −2.0, which is greater than the atmospheric CO_2 (−3.5). The decay of organic matter and root respiration cause higher CO_2 in the soil zone that is consumed by the infiltrating water (Appelo and Postma 2005). The calculated saturation indices indicate that the water samples are saturated and oversaturated with respect to carbonate mineral phases (Fig. 4). The SI values of calcite, aragonite and dolomite vary from −0.1 to 1.3, −0.2 to 1.1 and 0.6 to 2.5 with a mean value of 0.4, 0.2 and 1.2, respectively. In contrast, sulphate minerals are undersaturated (gypsum and anhydrite, SI < −1.5) in the water samples. Likewise, fluorite is also undersaturated in the water samples (SI < −1). In the case of metals, carbonate phases are near to saturation, whereas hydroxide phases are either oversaturated or undersaturated (Fig. 4). The SI value Fe(OH)$_3$(a) and goethite ranges from 1.6 to 2.8 and 7.7 to 8.9 with an average 2.1 and 8.2, respectively. However, the SI value of siderite varies from −2.3 to 0.1 with a mean value of 0.9. Similarly, the SI value of rhodochrosite and smithsonite is between −0.7 and 0.2 and −1.1 and −0.3, respectively. The hydroxide phases (manganite and Zn(OH)$_2$) are
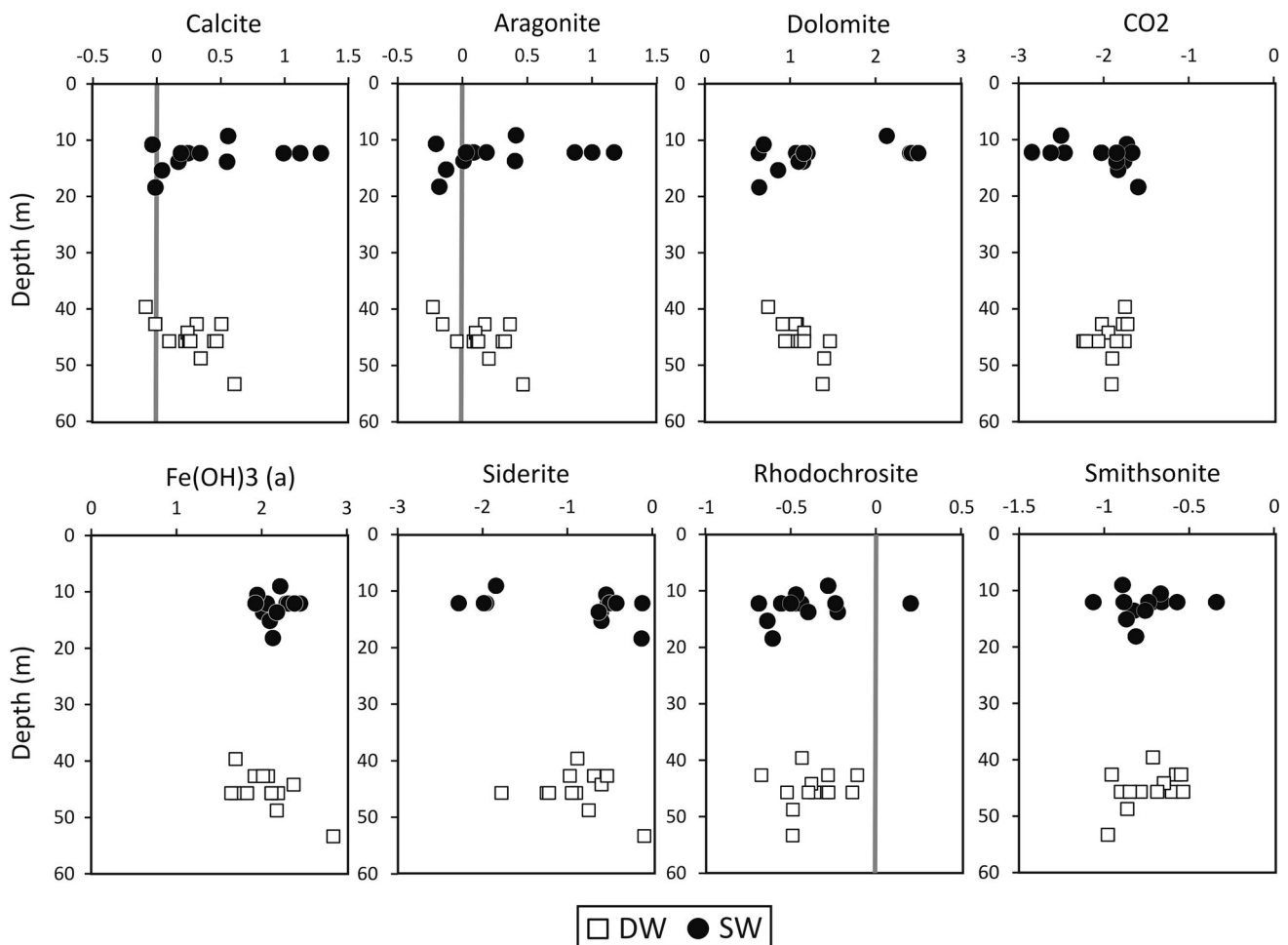
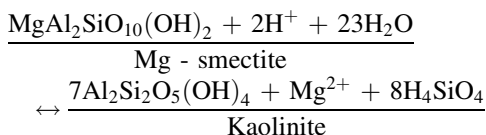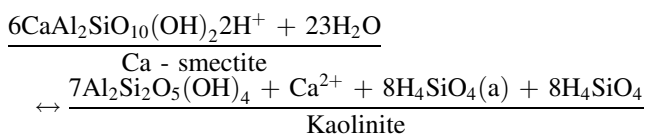**Fig. 4** Saturation indices of selected mineral phases in groundwater versus well depth

undersaturated (SI < −3; SI < −2). The dissolution and precipitation of carbonate minerals play a major role in the water chemistry of the study area. In the case of metals, hydroxide phases may also influence the water chemistry, especially in the case of iron, along with carbonate phases.

The mathematical and graphical approaches are commonly employed for the mineral equilibrium calculations. The mathematical methods are often used for the calculation of saturation indices, whereas the graphical approach explains the mineral stability fields of the mineral equilibrium in the groundwater using ion activity ratios (Njitchoua et al. 1997; Helgeson et al. 1969; Fritz 1975; Rajmohan and Elango 2004). As mentioned earlier, Quaternary alluvial deposits consisting of alternate layers of sand, silt, clay and gravel form prolific unconfined and confined aquifer systems in the study area. Hence, the clay–water interaction is a common process in this aquifer. Water samples were plotted in the stability diagram of the partial system MgO–Na_2O–Al_2O_3–SiO_2–H_2O to identify and understand this process (Fig. 5). Figure 5 shows that most of the samples were plotted on kaolinite stability field and a few samples

on Mg-smectite field (Nesbitt and Young 1984; Rogers 1989; Helgeson et al. 1969; Rajmohan and Elango 2004). The following reactions explain the equilibrium relation between kaolinite and smectite group clays:
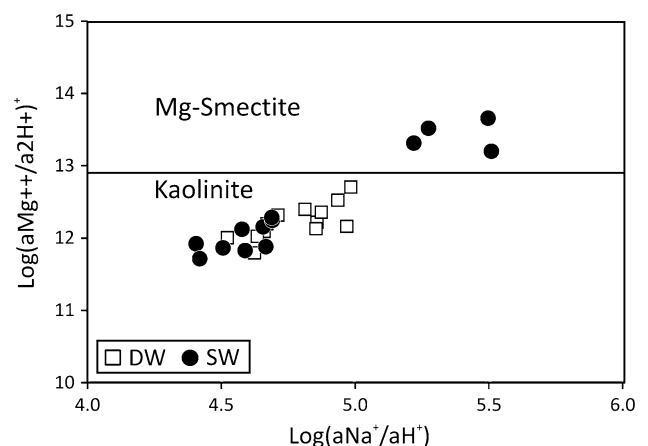
Fig. 5 Stability field diagram of partial system MgO–Na_2O–Al_2O_3–SiO_2–H_2O with sample points

$$\underset{\text{Ca - smectite}}{6CaAl_2SiO_{10}(OH)_2 2H^+ + 23H_2O}$$
$$\leftrightarrow \underset{\text{Kaolinite}}{7Al_2Si_2O_5(OH)_4 + Ca^{2+} + 8H_4SiO_4(a) + 8H_4SiO_4}$$

$$\underset{\text{Mg - smectite}}{MgAl_2SiO_{10}(OH)_2 + 2H^+ + 23H_2O}$$
$$\leftrightarrow \underset{\text{Kaolinite}}{7Al_2Si_2O_5(OH)_4 + Mg^{2+} + 8H_4SiO_4}$$

Hence, the water chemistry in the study area is largely controlled by kaolinite and to some extent by smectite group clays. Shah (2014) carried out the XRD analysis of clayey sand collected from the Newer Alluvium sediments in the Ganges basin near Varanasi, India, and reported that the presence of quartz, muscovite, chlorite, montmorillonite, kaolinite, feldspar and goethite implies the occurrence of kaolinite and montmorillonite in this study region.

Role of mineral dissolution and reverse ion exchange on water chemistry

The groundwater chemistry is highly affected by the soil–water interaction in the study site, especially in the confined aquifer. Figure 6 illustrates the relation between Ca + Mg and HCO_3 + SO_4 in the groundwater of the study site. If Ca, Mg, HCO_3 and SO_4 solely originated from the dissolution of carbonate (calcite, aragonite and dolomite) and sulphate minerals (gypsum, anhydrite), the groundwater samples will plot on or close to 1:1 line (Fig. 6). Likewise, if Ca and Mg originate from silicate weathering, HCO_3 alone will balance it because the water samples of the study area do not possess CO_3. In the silicate terrain, the groundwater chemistry is largely controlled by silicate weathering and total cation ($\sum$ cation = Na + K+Ca + Mg in meq/l) in the groundwater would be balanced by alkalinity (HCO_3 + CO_3) alone (Kim et al. 2004; Rajmohan and Elango 2006). The deep wells are plotted close to or slightly above the 1:1 line which ensures the slight excess of HCO_3 + SO_4 over Ca + Mg (Fig. 6). In contrast, the shallow wells are plotted below 1:1 line and show excess Ca + Mg over HCO_3 + SO_4. The excess HCO_3 over Ca and Mg may be due to silicate weathering or the depletion of Ca and Mg by cation exchange reactions in the deeper confined aquifer (Cerling et al. 1989; Fisher and Mulican 1997; Rajmohan and Elango 2004). Nevertheless, the excess Ca and Mg over HCO_3 and SO_4 indicates that these are likely to be derived from reverse ion exchange process, other than the mineral dissolution. The ratio of mCa/Mg is employed to differentiate the role of carbonate and silicate weathering on Ca and Mg concentrations in the water chemistry. If Ca and Mg are derived from the dissolution of dolomite

minerals, mCa/Mg ratio = 1, whereas higher ratios suggest the role of silicate weathering process (Mayo and Loucks 1995; Rajmohan and Elango 2004). The mCa/Mg ratio varies from 0.15 to 1.5 except for one well (Fig. 3). In the study site, a few samples have the ratio equal to one and most of them are below one, which suggests that the concentration of Ca and Mg in the water is predominantly controlled by carbonate minerals dissolution.

The ratio of Na + K/Cl indicates that the deep wells have a higher ratio (Na + K > Cl) compared with the shallow wells (Fig. 3). In the shallow and deep wells, the ratio varies from 0.35 to 1.18 and from 1.37 to 2.69 with an average of 2.1 ± 0.43 and 0.62 ± 0.27, respectively. The ratio of Na + K/Cl = 1 explains the input of chloride salts from the surface contamination sources since halite is highly undersaturated (SI < −7) in this aquifer. The ratio is greater than one in the deep wells, which indicates that silicate weathering and excess Na + K over Cl are balanced by HCO_3. In contrast, the lower value (Na + K/Cl < 1) encountered in the shallow wells suggests the depletion of Na and K due to ion exchange reactions.

The ion exchange reactions are very common in the aquifer especially when the kaolinite and smectite group clays are present in the system. In the cation exchange reactions (Na-Clay + Ca^{2+}(Mg^{2+}) = $2Na^+$ + Ca(Mg)-Clay), Na is released to water and Ca(Mg) can be retained in the aquifer material. In the reverse process, called reverse ion exchange, aquifer material adsorbs Na and releases Ca(Mg) to water (Cerling et al. 1989; Fisher and Mulican 1997; Rajmohan and Elango 2004; Rajmohan et al. 2009). Figure 6 depicts the ratio of m(Ca + Mg)/HCO_3 plotted against chloride. In the shallow wells, Ca and Mg are added in water when the salinity increases and are identified with strong positive correlation between m(Ca + Mg)/HCO_3 and Cl. This is not observed in the deep wells. According to Sami (1992), the dissolution of carbonate minerals and weathering of pyroxene and amphibole minerals can maintain the (Ca + Mg)/HCO_3 molar ratio equal to 0.5. Figure 6 indicates that the deep wells have m(Ca + Mg)/HCO_3 ratio equal to 0.5 or slightly less. In contrast, the shallow wells have higher values and increase with salinity. The low ratio may be due to the depletion of Ca + Mg by cation exchange or enhancement of HCO_3 by silicate weathering. However, a higher ratio is not due to the depletion of HCO_3 through carbonic acid (H_2CO_3) formation because the water samples are neutral to alkaline in nature. Hence, excess Ca + Mg over HCO_3 is mainly derived by the reverse ion exchange process. In addition, the plot of Na + K − Cl versus Ca + Mg–HCO_3–SO_4 illustrates that the shallow wells show strong correlations (R^2 = 0.92) with a negative slope of −1.06. These observations strongly imply that the

Fig. 6 Plots explain reverse ion exchange process
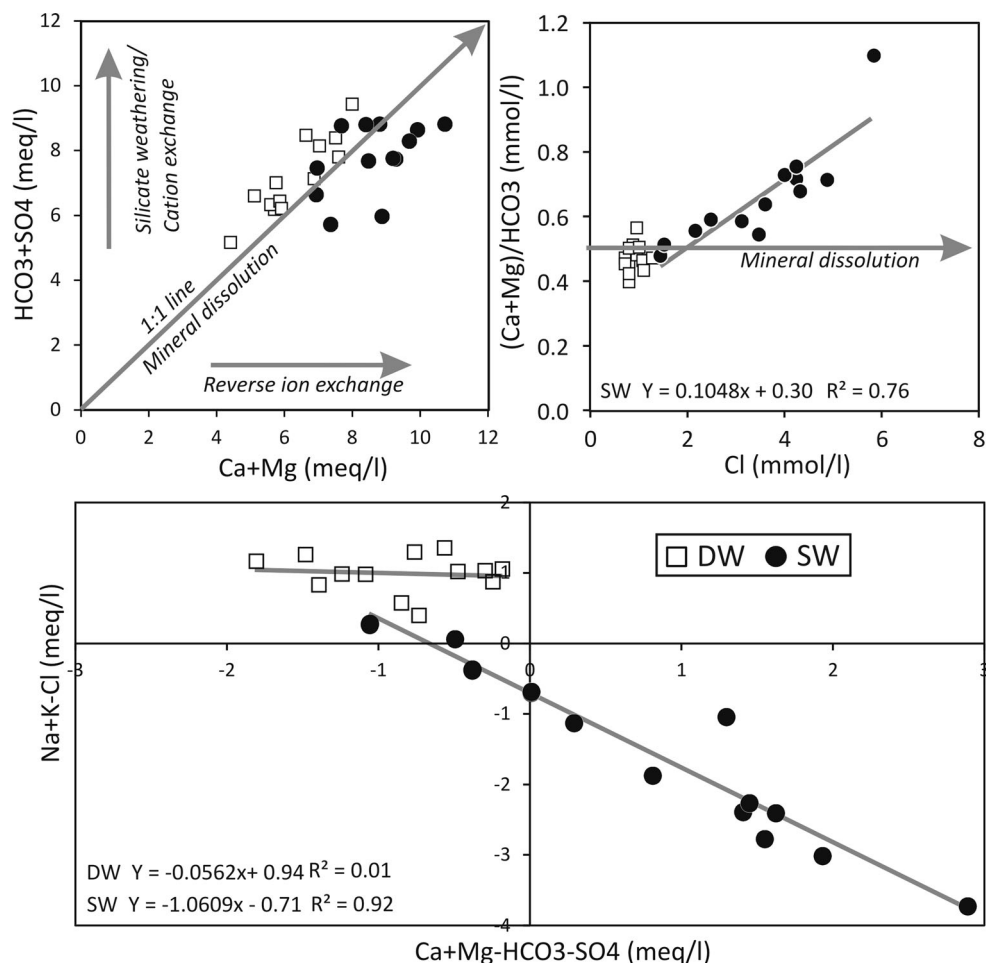
concentration of Ca, Mg and Na in the shallow wells is regulated by the reverse ion exchange reactions along with the mineral dissolutions. In addition, infiltrating wastewater enhances the reverse ion exchange (Ca and Mg release to water) at the expense of Na and K in the wastewater of the study site because Na and HCO_3 do not significantly vary with depth. The deep wells do not show any such relation and the dissolution of carbonate and silicate minerals control the water chemistry in these wells.

Impact of land use on water chemistry

The groundwater chemistry in the study site is largely influenced by the surface contamination sources, especially in the shallow aquifer (Table 1) and is well supported by the concentrations of chloride and sulphate. The saturation indices indicate that the groundwater of the study site is undersaturated with respect to sulphate and halite minerals and there is no known geological source for Cl and SO_4 in the study site. Further, Cl has a significant positive correlation with EC ($R^2 > 0.7$, $p < 0.01$) in the shallow wells.

The average sulphate concentration in the shallow and deep wells is 51 and 25 mg/l, respectively. Similarly, the average chloride concentration in the shallow and deep wells is 124 and 32 mg/l, respectively. In the shallow unconfined aquifer, the sulphate and chloride concentrations are twofold and threefold to fourfold than the confined aquifer, respectively. Both the agricultural land and the residential plots cover the study area. The discharge of domestic wastewater, sewage lines, septic tank effluents, farm manures, fertilizers and irrigation return flow is major surface contamination sources in the study site. The fertilizers such as potash, NPK (nitrogen–phosphorous–potassium), ammonium sulphate, urea and zinc sulphate are generally used during cultivation in the study site. Hence, these are the major sources of chloride, sulphate and nitrate in the shallow unconfined aquifer. However, the concentration of nitrate does not show any variation with respect to depth (Table 1) and it is not correlated with other variables. Nitrate generally originates from the oxidation of ammonium (nitrification, $NH_4^+ + 2O_2 \Rightarrow NO_3^- + 2H^+ + H_2O$) and aerobic decomposition of organic matter

$(C_{106}H_{263}O_{110}N_{16}P + 138O_2 \Rightarrow 106CO_2 + 16NO_3 + HPO_4^{2-} + 122H_2O + 18H^+)$. The acidic proton formed during these processes will reduce the pH, and hence, nitrate expresses negative relation with alkalinity and pH if the nitrification is significant in the groundwater. The groundwater nitrate in the study site does not express such a relation, and the concentration is less than 4 mg/l. In the shallow and deep wells, the concentration of nitrates varies from 1.2 to 3.4 and from 1.2 to 3.7 mg/l with an average value of 2.1 and 2.2 mg/l, respectively. Although the percentage of groundwater nitrate is low in the study site, Cl and SO_4 concentrations strongly imply that the groundwater is affected by the recharge of the contaminated water from various sources. Hence, the low concentration of nitrate in the groundwater seems to be due to the denitrification process. The occurrence of abundant fine-textured materials and clay deposits in the unsaturated zone that have higher organic matter and moisture may facilitate the denitrification process (Hamilton and Helsel 1995). Canter (1997) studied the nitrogen content of the septic tank wastewater and reported that the concentration of ammonia and nitrate is 20–55 and <1 mg/l, respectively, in the total nitrogen (25–60 mg/l). Further, the denitrification process is very common in anaerobic conditions ($5CH_2$-$O + 4NO_3^- + 4H^+ \Rightarrow 5CO_2 + 2N_2 + 7H_2O$), which increases pH in the groundwater. In this study, the shallow wells have high pH compared to the deeper wells (Table 1). In the study site, Rajmohan et al. (2014) reported that the organic carbon in the soil increases with depth based on the analysis of the soil core samples. Hence, this observation supports that the denitrification processes are significant in the study site, especially in the unconfined shallow aquifer. In the deeper confined aquifer, the concentrations of chloride, sulphate and nitrate are regulated by the regional flow since the confined aquifer is isolated from the unconfined aquifer by the thick silty clay layers.

Conceptual model

The groundwater chemistry in the shallow unconfined (first) and deeper confined (second) aquifers in the study site is regulated by various processes as summarized in Fig. 7. In the deeper confined aquifer, silicate and carbonate minerals weathering and regional flow control the water chemistry. In the shallow unconfined aquifer, wastewater infiltration from the surface contamination sources, denitrification, reverse ion exchange and mineral weathering govern the water chemistry. The recharge of wastewater enhances the reverse ion exchange process at the expenses of Na and K in the wastewater. The stability field diagrams indicate that the water samples are plotted mostly in the kaolinite field and few of them in smectite field, which are common weathering products in silicate
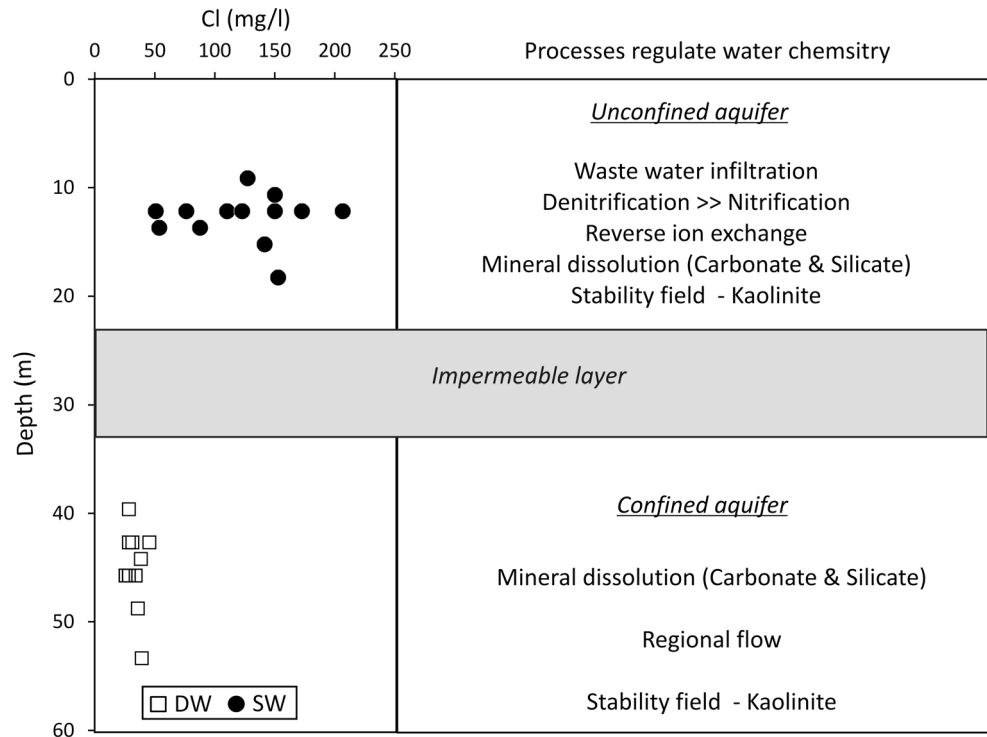
terrain and affect the water chemistry of the study area. The concentrations of chloride, nitrate, phosphate and sulphate are generally low in the deeper confined aquifer, which is likely to be derived by the regional flow since it is protected by the impermeable clay layer in the study site.

Conclusions

The present study was carried out to evaluate the groundwater chemistry and to identify the geochemical processes regulating the water chemistry using geochemical methods in the shallow unconfined and deeper confined aquifers in this basin. The depth of the well varies from 9.14 to 53.3 m with an average value of 29 m in the sampled wells. The groundwater is neutral to alkaline in nature and is classified as freshwater (TDS < 1000 mg/l). The concentration of iron varies from 0.14 to 2.11 mg/l with an average of 0.53 mg/l. The concentrations of Mn and Zn vary from 0.02 to 0.09 and from 0.29 to 1.40 mg/l with an average value of 0.05 and 0.61 mg/l, respectively. The concentrations of As, Cu and Pb are below detection limit (BDL). The shallow wells have high pH, EC, TDS, calcium, magnesium, chloride and sulphate, and low HCO_3/Cl ratio compared to the deep wells. The average concentrations of Na, HCO_3, NO_3, PO_4, F and Mn do not vary significantly with depth and imply that the variation in the water chemistry between the unconfined and confined aquifers is due to not only the mineral dissolution but the surface contamination sources also could have affected the water chemistry in the shallow unconfined aquifer.

The parameters such as EC, TDS, Ca, Mg, Cl and SO_4 significantly vary between the shallow and deep wells and the concentrations of these variables increase from the deep to shallow wells. The mineral equilibrium calculations indicate that the dissolution and precipitation of carbonate minerals drive the water chemistry in the study region. Overall, the water chemistry in the confined aquifer (deep wells) is regulated by silicate and carbonate minerals weathering and regional flow. In the unconfined aquifer (shallow wells), wastewater infiltration from the surface contamination sources, denitrification, reverse ion exchange and mineral weathering govern the water chemistry. The recharge of wastewater enhances the reverse ion exchange processes at the expenses of Na and K in the wastewater. The stability field diagrams indicate that kaolinite and smectite, which are common weathering products in silicate terrain, regulate the water chemistry in the study site. The concentrations of chloride, nitrate, phosphate and sulphate are generally low in the confined aquifer, which are likely to be derived by the regional flow

Fig. 7 Conceptual model explains the processes that regulate the water chemistry in the shallow unconfined (first) and deeper confined (second) aquifers in the study site. Plot of chloride vs depth shows the variation in the water chemistry of the study site

since it is protected by an impermeable clay layer in the study site.

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