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ORIGINAL ARTICLE

Influence of geochemical processes on hydrochemistry and irrigation suitability of groundwater in part of semi-arid Deccan Plateau, India

Duraisamy Vasu[1] · Surendra Kumar Singh[1] · Pramod Tiwary[1] · Nisha Sahu[1] · Sanjay Kumar Ray[2] · Pravin Butte[1] · Veppangadu Perumal Duraisami[3]

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Abstract Major ion geochemistry was used to characterise the chemical composition of groundwater in part of semi-arid Deccan plateau region to understand the geochemical evolution and to evaluate the groundwater quality for irrigation. The study area comprises peninsular gneissic complex of Archean age, younger granites and basaltic alluvium. Forty-nine georeferenced groundwater samples were collected and analysed for major ions. The ionic sequence based on relative proportions was $Na^+ > Mg^{2+} > Ca^{2+} > SO_4^{2-} > HCO_3^- > Cl^- > CO_3^{2-} > BO_3^{3-} > K^+$. High Na^+, Mg^{2+} and Ca^{2+} were generally associated with basaltic alluvial formation, whereas pH, electrical conductivity (EC) and total dissolved salts (TDS) were found to be higher in granitic formations. High standard deviation for EC, TDS, Na^+, Ca^{2+} and Mg^{2+} indicated the dispersion of ionic concentration throughout the study area. Four major hydrochemical facies identified were Na-Mg-HCO_3 type; Mg-Na-HCO_3 type; Na-Mg-Ca-SO_4 and Mg-Na-Ca-SO_4 type. The graphical plots indicated that the groundwater chemistry was influenced by rock–water interaction, silicate weathering and reverse ion exchange. Sodium-dominated waters might have impeded the hydraulic properties of soils as a result of long-term irrigation.

Keywords Hydrogeochemistry · Groundwater quality · Deccan plateau · Silicate weathering · Rock–water interaction

Introduction

Agriculture sector consumes about 70% of available groundwater in India and out of total irrigated area of 64.05 m ha, 66% (42.5 m ha) is irrigated by groundwater. The depth of groundwater table decreased over the past few decades due to poor recharge of the groundwater aquifers caused by gradual decrease in annual rainfall (Singh et al. 2006). The rate of decline in groundwater depth is so alarming that 34% of the wells studied showed more than 4 m decrease in depth of water level (CGWB 2015). The Deccan plateau region covers most of the central and southern parts of the country with an area of 0.42 million km^2 (Vasu et al. 2016). It is characterised by semi-arid climate coupled with high mean annual evapotranspiration of 1800 mm (Perrin et al. 2012) than precipitation (700–900 mm). The reduction (7–20%) in seasonal monsoon (IMD 2015) along with depleting groundwater in the past two decades has made agriculture a challenging task. Thus, vagaries of climate change have pronounced impacts on agriculture, livelihood and economy in this region. Groundwater is the major source for irrigation in Deccan plateau and its quality depends on its chemical composition. The hydrochemistry of groundwater is influenced by aquifer characteristics and the strata over which they flow (Rengaraj 1996). The factors that control the dissolved minerals in groundwater are types of minerals that make up the aquifer, length of time that the water is in contact with the minerals and the chemical state of the groundwater.

✉ Duraisamy Vasu
d.plantdoctor@gmail.com

[1] ICAR-National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur 440033, Maharashtra, India

[2] Regional Centre, ICAR-National Bureau of Soil Survey and Land Use Planning, Jorhat 785 004, Assam, India

[3] Directorate of Natural Resource Management, Tamil Nadu Agricultural University, Coimbatore 641003, Tamil Nadu, India

Different rocks (e.g. sandstone, limestone and basalt) with varying composition in contact with groundwater will result in groundwater varying in ionic compositions. Hydrogeochemical study of groundwater helps to determine the origin of chemical constituents (Zaporozec 1972) and to identify the factors governing it, contribution made by each factor and type of the geochemical reactions that are taking place within an aquifer system. Identification of geochemical processes helps to understand the quality of water and assist in planning irrigation management.

Many researchers around the world (Moller et al. 2007; Belkhiri et al. 2010; Glover et al. 2012) and in India (Srinivas et al. 2013; Selvakumar et al. 2014; Nageswara Rao et al. 2015) showed the role of hydrogeochemistry in groundwater quality. Earlier investigations indicated that hydrochemistry of groundwater is controlled by geochemical processes in semi-arid regions of India (Subramani et al. 2010). Processes such as evaporation, oxidation/reduction, ion exchange, minerals weathering, precipitation of secondary minerals and mixing of waters control the chemical composition of groundwater and temporal changes in it (Kumar et al. 2009). Telangana is by far the state in the Deccan plateau region receiving very less average annual rainfall (450–700 mm) which is unevenly distributed and the agriculture sector registered a mixed growth rate varying from 25.2 to −10.0% during the past decade due to frequent droughts. Hence, there is sharp rise in area under irrigation through tube wells and out of 3 million ha irrigated area, about 3/4th area is irrigated by groundwater. This has led to over-exploitation of groundwater from deep bore-wells (Chandra et al. 2012). Studies on groundwater quality for domestic and irrigation purposes in this region (Pophare and Dewalkar 2007; Satyanarayanan et al. 2007) and in similar kind of geological formations around the world (Belkhiri et al. 2010; Aghazadeh and Mogaddam 2011) indicated the influence of geochemical processes on ionic composition of groundwater.

Recently, several graphical methods and different indices were used for evaluating groundwater quality (Elango et al. 2003; Subbarao 2006). Reddy and Kumar (2010) found that groundwater in Anantapur region is Ca^{2+}-Mg^{2+}-Cl^--HCO_3^- type and their composition was influenced by ion exchange and dissolution processes. Rajesh et al. (2012) found that the cationic and anionic concentrations were in the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > CO_3^{2-}$, respectively, in groundwater of Nalgonda district and concluded that ion exchange process controls the concentration of calcium, magnesium and sodium. Studies in the watersheds of Mahabubnagar district showed that waters are sodium bicarbonate, sodium chloride, mixed cationic–mixed anionic, mixed cationic Na-dominating bicarbonate and are medium salinity low-sodium (C2S1), high salinity low-sodium (C3S1) and high salinity medium-sodium (C3S2) for irrigation (Raju and Goud 1990; Reddy 2013). Moreover, the groundwater of Peninsular gneissic complex aquifers in the Deccan plateau region are suspected to have high salt content and to be poor in quality (Suresh and Kottureshwara 2009; Kumar et al. 2009; Reddy and Patode 2013; Yadagiri et al. 2015). Thus, groundwater quality has become the topic of debate among researchers and groundwater authorities and its allocation to different sectors viz., agriculture, industry and drinking water use has become a challenging task for the policy makers. Since agriculture is the mainstay of rural people of Telangana, an attempt has been made in the present study to assess the groundwater quality in Thimmajipet mandal, Mahabubnagar district in Telangana, India, with the following objectives: (i) to determine the major ion chemistry of groundwater, (ii) to identify the hydrogeochemical processes responsible for the groundwater quality and (iii) to assess the groundwater suitability for irrigation purpose.

Materials and methods

Study area

Thimmajipet mandal is situated at a distance of 100 km from Hyderabad, India, and lies between 16°35′ to 16°44′N latitude and 78°07′ to 78°18′E longitude with total geographical area of 200.90 km^2 (Fig. 1). The topography of the area comprises an undulating terrain with a maximum elevation of 662 m on south-western side and minimum elevation of 434 m on the northern side. In general, the ground surface slopes towards north-eastern direction with intermittent hillocks. The study area falls under southern Telangana agro-climatic zone and is characterised by ustic soil moisture and hyperthermic soil temperature regimes (Soil Survey Staff 2003). The average annual rainfall is 450–550 mm which occurs mostly during southwest monsoon (July–September). Major crops grown are cotton (*Gossypium hirsutum*), maize (*Zea mays*), pigeon pea (*Cajanus cajan*), rice (*Oryza sativa*) and sorghum (*Sorghum bicolor*).

Geology and hydrogeology

In the arid and semi-arid regions of southern India, Peninsular Gneissic Complex (PGC) type aquifers are dominant (CGWB 2012). They are formed on the base of migmatites, granite gneiss and granites ranging in composition from granodiorite to tonalite and intruded younger dolerites. These abundant granitoid rocks are of calc-

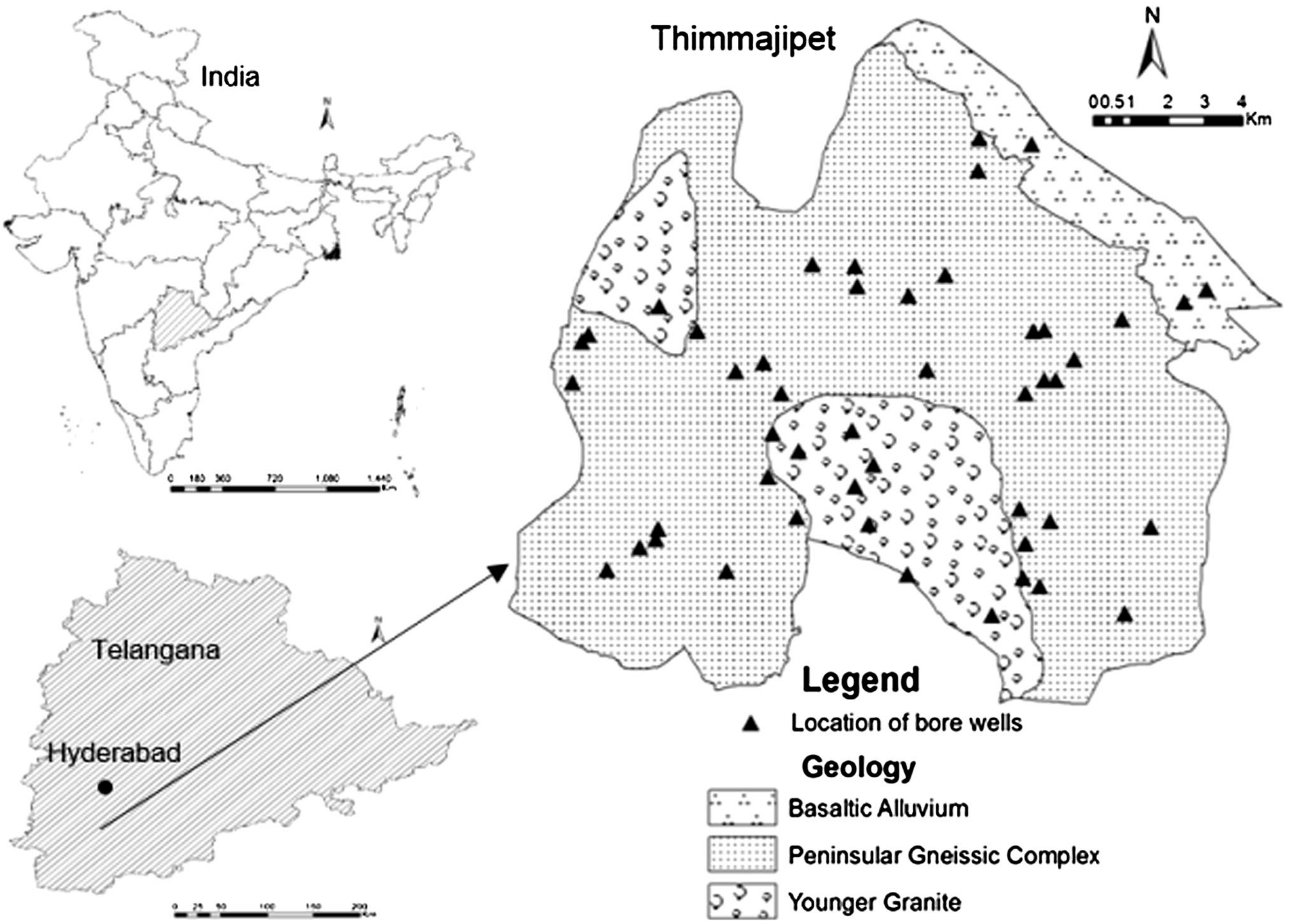

Fig. 1 Location of the study area and sampling locations in different geological formations

alkaline nature (Balakrishnan et al. 1990; 1999; Krogstad et al. 1991). Sanukitioids, a high Mg, high Ni granitoids are also present and monoclinic series of amphiboles tremolite, actinolite comprising Ca, Mg and halogens (F, Cl) occur as intrusive with the PGCs. Being of Archean age, the south Indian Peninsula has long been exposed to weathering agents and the rocks have undergone different degrees of secondary decomposition resulting in layers of weathered, semi-weathered zones, as well as massive fractured rocks and fissures, cracks and joints. The fracture zones are hydraulically connected with the overlying weathered and saturated residuum (CGWB 2009) and upon weathering they result in salts rich in calcium, magnesium, sodium, fluoride and chlorides. Hydrogeologically, the subsurface of this region can be characterised by three distinct layer systems viz., soil zone, weathered zone and massive rock layers zone. Thickness of the soil zone varied from 0.16 to 3 m and is comparatively thicker in the northern, north-western and north-eastern boundaries of the study area due to basaltic alluvial depositions. The granite-gneiss lacks primary porosity and occurrence of groundwater is limited to secondary porosity developed by weathering and fracturing (CGWB 1975). The diameter of waterwells is 15–20 cm and their depth varied from 40 to 160 m. The thickness of weathered zone ranged from 3 to 15 m with granular fractured zones occuring at 20–60m below ground level. The yield of water wells ranged from 0.11 to 0.18 m^3 per minute.

The study area forms a part of the stable Dharwar Craton of south Indian shield. It consists of exposed rocks of Peninsular Gneissic Complex (Archaean to Paleoproterozoic age), Dharwar Supergroup, Cuddapah Supergroup, Kurnool and Bhima Groups and also alluvium of basaltic Deccan Traps (CGWB 2013). Three geological formations comprise the study area: (1) Peninsular Gneissic Complex, (2) Basaltic Alluvium and (3) Younger Granite. The Peninsular gneissic complex (PGC), which covers most of the area, comprises granites, gneisses and migmatites with undigested patches of older metamorphic rocks. The rocks of PGC and Dharwar Supergroup are intruded by younger granitoids of tonalite–trondhjermite–grandodiortite composition (Sharma 2009). These rocks are generally medium- to coarse-grained and are foliated due to the alternate arrangements of minerals and the dimensional orientation

Table 1 Summarised results of water chemistry analysis and their indices

Geology	Basic statistics	pH	EC (µs cm^{-1})	TDS (mg L^{-1})	Cations				Anions					Indices				
					K^+ (meq L^{-1})	Na^+ (meq L^{-1})	Ca^{2+} (meq L^{-1})	Mg^{2+} (meq L^{-1})	Cl^- (meq L^{-1})	CO_3^{2-} (meq L^{-1})	HCO_3^- (meq L^{-1})	SO_4^{2-} (meq L^{-1})	BO_3^{3-} (meq L^{-1})	Ca/Mg	$Na/(Ca)^{1/2}$	$Na/(Ca + Mg)^{1/2}$	RSC	Na %
Basaltic Alluvium	mean	7.25	1068	1619	0.49	74	35.8	55.5	9.3	0	12.7	15.5	0.24	0.76	12.5	7.9	−32.9	36.10
	min	6.96	770	582	0.18	39	25	36	5	0	8.5	1	0.15	0.32	6.8	4.6	−71	29.30
	max	7.48	1550	3283	1.10	117	44	129	18	0	15	28	0.54	1.05	18.3	10.5	−16	43.59
	SD	0.169	295	1161.7	0.320	28.80	6.99	36.20	4.58	0	2.77	12.94	0.14	0.234	4.4	2.3	19.79	5.980
Younger Granite	mean	8.00	2852	1723	0.33	72.6	34.6	39.6	10.3	1.5	9.51	14.7	0.57	0.98	14.5	9.0	−26.1	40.65
	min	7.21	910	836	0.20	46	15	17	6	0	1	0	0.31	0.35	6.6	5.0	−84.5	23.09
	max	8.91	4900	3136	0.51	114	114	84	15	10	16	48	1.25	2.24	25.8	13.1	−11.5	50.39
	SD	0.583	1563.112	901.6	0.097	23.39	30.59	21.82	2.73	3.43	5.42	14.63	0.30	0.579	6.6	2.7	23.35	9.19
Peninsular Gneissic Complex	mean	7.87	1750	1007	0.391	67.8	31.3	40.9	8.2	0.5	11.3	9	0.56	0.84	12.6	8.4	−24.2	40.12
	min	6.91	500	320	0.13	36	11	14	5	0	4.5	1	0.15	0.31	5.5	3.3	−89	17.30
	max	8.8	5130	2758	1.97	106	68	126	15	8	17.5	63	1.1	2.79	25.0	16.4	−5	59.35
	SD	0.360	996	551.1	0.305	21.11	10.53	19.44	1.95	1.89	3.53	11.03	0.22	0.393	4.4	3.1	15.48	10.17

of light minerals such as quartz and feldspar (Balakrishnan et al. 1990).

Sample collection and analysis

Forty-nine georeferenced (GPS location with latitude and longitude) groundwater samples, i.e., 34, 10 and 5 from PGC, younger granite and basaltic alluvium, respectively, were collected during February (2015) from water wells in pre-cleaned 500 ml plastic bottles after pumping water for 10–15 min to minimise errors due to oxidising and carbonating agents. All the sampling bottles were rinsed thoroughly two times using the well water before sampling. The collected samples were tightly packed to protect from atmospheric CO_2 and transported to laboratory and stored in a refrigerator at 4°C before analysis. The extra-pure analytical-grade reagents and chemical standards (Merck Grade) were used for the groundwater quality analysis by adopting standard procedures suggested by American Public Health Association (APHA 2005). The samples were analysed for pH and electrical conductivity (EC) using digital pH and EC meter (ELICO make). Ca^{2+} and Mg^{2+} were measured in ICP-AES. Na^+ and K^+ were determined by flame photometer. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were measured using acid titration method. Chloride (Cl^-) was measured by $AgNO_3$ titration method. Sulphate (SO_4^{2-}) was measured by $BaCl_2$ method using UV spectrophotometer (Shimadzu UV-2600, A116652). Total dissolved solids (TDS) were computed by the method of Hem (1991). Blank, standards and triplicate samples were run during the analysis of samples to check the accuracy and reliability of analysis methods. The ion charge balance was less than ±5% for all the samples.

Statistical analysis

The Statistical package for social sciences (SPSS) version 20 was used to carry out all the statistical analysis. In the factor analysis, 'principal components' was selected as the solution method, whereas the varimax rotation was used to maximise the differences among selected factors to facilitate interpretation of analysis results. Important indicators of water quality for irrigation were derived using the guidelines given by United States Salinity Laboratory (USSL 1954) and FAO (Ayers and Westcot 1985). Parameters such as pH, electrical conductivity, soluble sodium percentage (Todd 1995), residual sodium carbonate (Gupta and Gupta 1987), potential salinity (Hammet 1992), magnesium hazard (Raghunath 1987), Kelly's ratio (Kelly 1963) and permeability index (Doneen 1964) were used to assess the suitability of water for irrigation.

Results and discussion

Major ion chemistry and spatial distribution

The variation in the concentration levels of different hydrogeochemical constituents dissolved in water determines its usefulness for domestic, industrial and agricultural purposes (Obiefuna and Sheriff 2011). The results showed that pH varied from 6.91 to 8.91, the mean pH value (8.0) indicating marginal alkalinity of the groundwater (Table 1). Electrical conductivity varied from 500 to 5130 μS cm^{-1} and total dissolved salts (TDS) varied from 320 to 3283 mg L^{-1}. Electrical conductivity was found be higher in the southern and central part of the study area and it decreased towards north and north eastern direction (Fig. 2). Among the cations Ca^{2+} varied from 11 to 114 meq L^{-1}; Mg^{2+} from 14 to 129 meq L^{-1}; K^+ from 0.13 to 1.97 meq L^{-1} and Na^+ from 35.65 to 117 meq L^{-1}. Among the anions Cl^- varied from 5 to 18 meq L^{-1}; CO_3^{2-} from 0 and 10 meq L^{-1} and 88% of the samples were found to be without CO_3^{2-} content. HCO_3^- varied from 0.3 to 17.5 meq L^{-1}; SO_4^{2-} from 0 to 63 meq L^{-1} and BO_3^{3-} from 0.2 to 1.25 mg L^{-1}.

The mean values of each of pH, EC and TDS were found to be higher in granitic formations whereas the mean of Na^{2+}, Ca^{2+} and Mg^{2+} was higher in basaltic alluvial formation. The mean anionic concentration was similar in three geological formations, except for SO_4^{2-} which was lower in gneissic terrains. The standard deviation (SD) was high for EC, TDS, Na^+, Ca^{2+} and Mg^{2+} indicating dispersion of ionic concentration from the mean (Table 1). SD was low for pH, K^+, Cl^-, HCO_3^- and BO_3^{3-} indicating their limited variability. Na^+ constituted 29–43.5% of the ionic composition in groundwater of basaltic alluvium origin, 23–50% in granitic terrain and 17–59% in peninsular gneissic complex origin aquifers (Table 1). The variation in ionic content of water within the samples of geological region, as established by high SD, may be due to the differences in mineral makeup in aquifer material (Randall et al. 1996; Reddy and Kumar 2010). The ionic

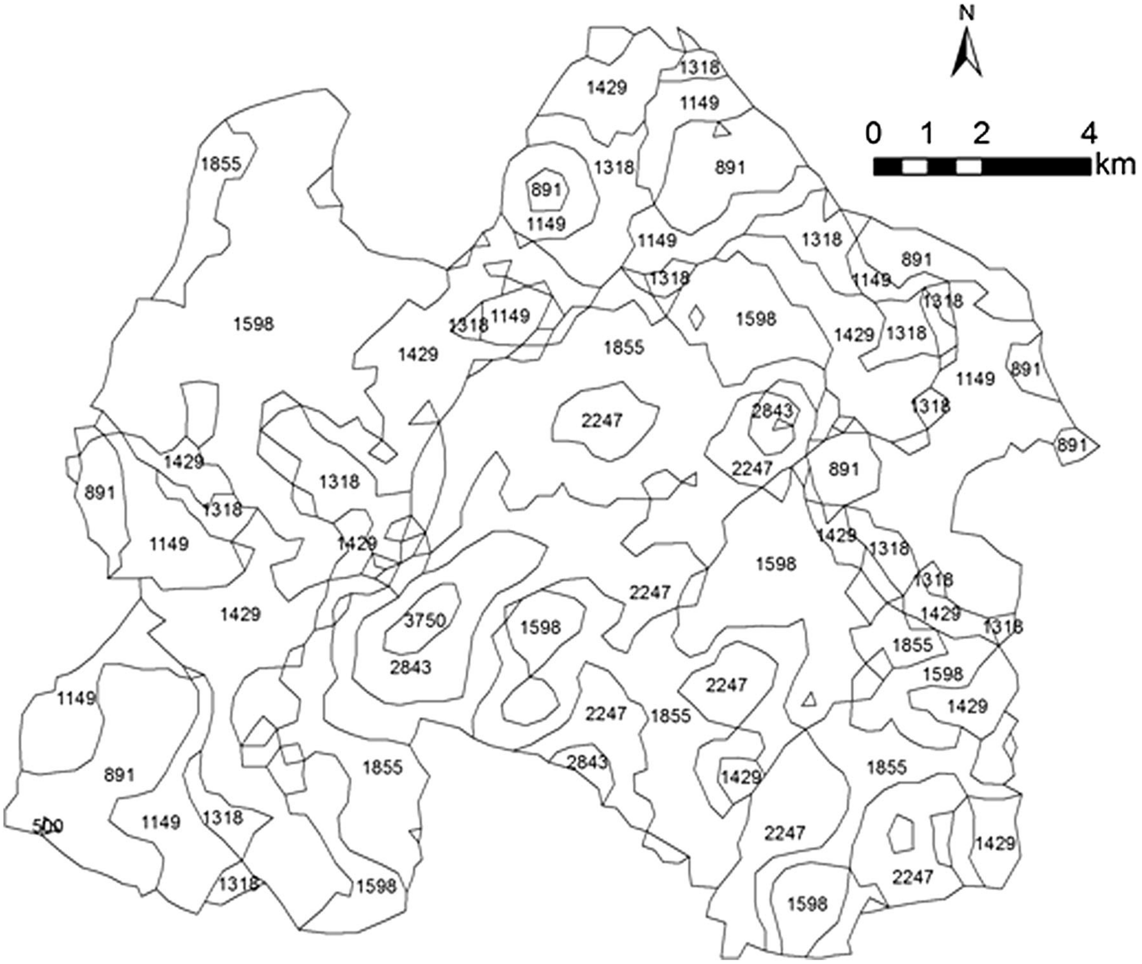

Fig. 2 Spatial distribution of EC (μs cm^{-1}) in the study area

sequence based on relative proportions was $Na^+ > Mg^{2+} > Ca^{2+} > SO_4^{2-} > HCO_3^- > Cl^- > CO_3^{2-} > BO_3^{3-} > K^+$. Higher content of Ca^{2+} and Mg^{2+} over K^+ in the groundwater may be due to their mineralogical origin in the soils. During monsoon season, water percolates down to aquifer through soil and the weathered mantle gains Ca^{2+} and Mg^{2+}. High Na^+ content may be attributed to weathering of silicate rocks containing sodium (e.g. feldspars) which was further enhanced by decreasing soil:water ratio due to high evaporative demand.

Classification of groundwater

The water type classification for the study area was done based on Piper diagram for dominant hydrochemical facies plotted on the cation, anion triangles and diamond matrix (Fig. 3). The samples were classified as Na-Mg-HCO_3 type (50%); Ca-Mg-HCO_3 type (14%); Na-Mg-Ca-SO_4 and Mg-Na-Ca- SO_4 type (10% each). The Na-dominated water was the result of interaction of recharging waters with the sodium feldspars ($NaAlSi_3O_8$). The Na^+ ions in water were added by the weathering of rocks (Keesari et al. 2013). It can be inferred from Piper plots that the groundwater is of mixed type with multiple processes involved in its evolution which further strengthens the fact that the mineralogy of aquifer material played an important role in determining the water chemistry. The plots also suggest that among cations Na^+, Ca^{2+} and Mg^{2+} and among anions SO_4^{2-} and Cl^- dominate the ionic composition of the groundwater.

Hydrogeochemical processes

Silicate weathering

The weathering processes occurring in the aquifer environment were studied by scatter diagrams of ions and ionic combinations. Ca^{2+} and Mg^{2+} were the dominant cations after Na^+ in groundwater of the study area. The study of Ca^{2+}/Mg^{2+} ratio indicated that silicate weathering was one of the process involved in determining ionic chemistry of groundwater. The Ca^{2+}/Mg^{2+} ratio of 1 indicated dissolution of dolomite and of more than 2 silicate mineral weathering (Reddy and Kumar 2010). The majority of the samples in different geological terrains in the study area had Ca^{2+}/Mg^{2+} ratio less than 1 and between 1 and 2, indicating that dolomite and calcite dissolution contributed towards high Ca^{2+} and Mg^{2+} followed by silicate mineral dissolution. The scatter diagram of (Ca^{2+}+ Mg^{2+}) vs

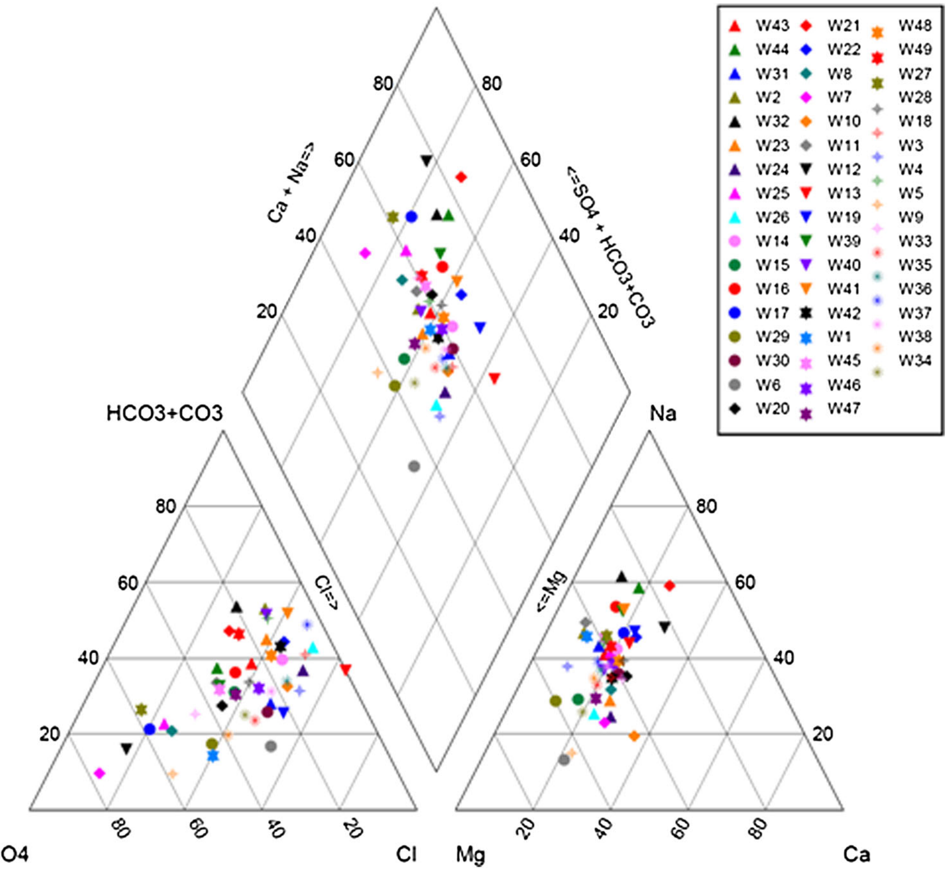

Fig. 3 Piper trilinear diagram showing the major ionic composition of groundwater from the study area

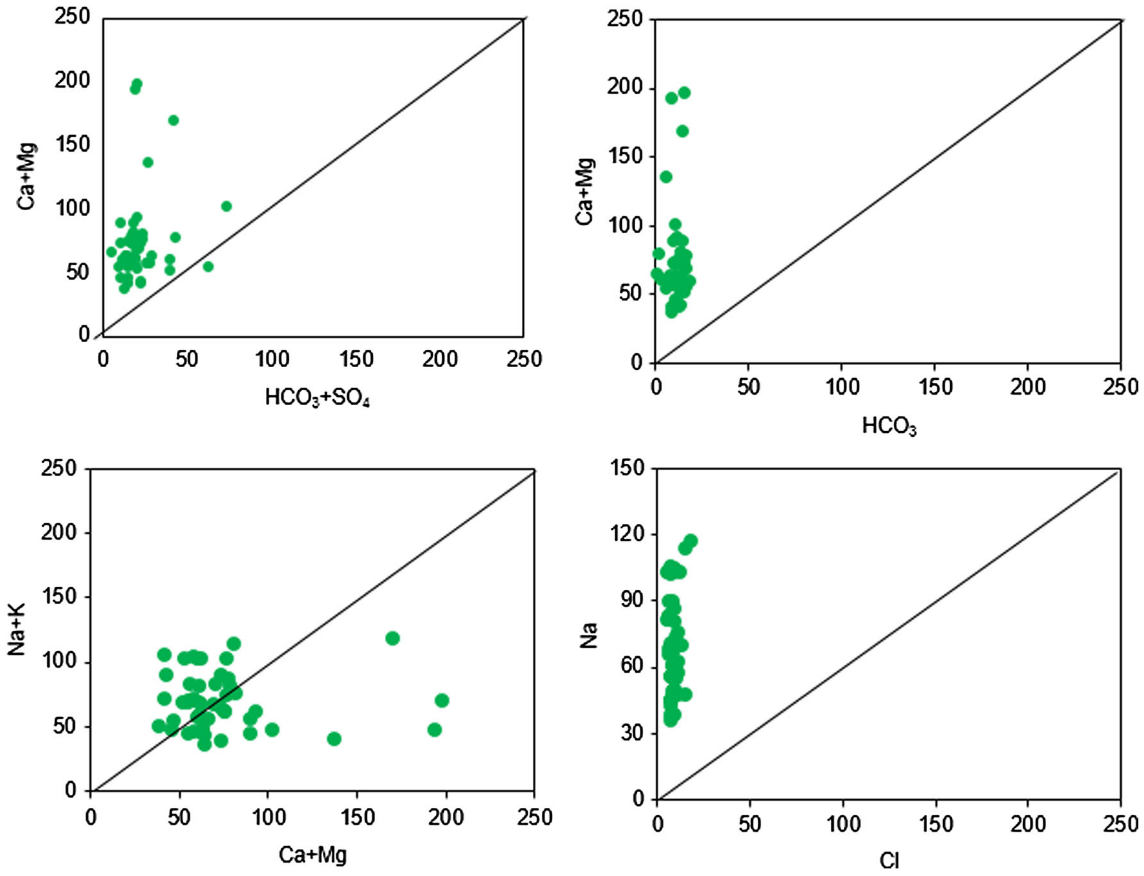

Fig. 4 **a** scatter plot of $Ca^{2+} + Mg^{2+}$ vs $HCO_3^- + SO_4^{2-}$; **b** scatter plot of $Ca^{2+} + Mg^{2+}$ vs HCO_3^-; **c** scatter plot of $Ca^{2+} + Mg^{2+}$ vs $Na^+ + K^+$; **d** scatter *plot* of Na^+ vs Cl^-

($HCO_3^- + SO_4^{2-}$) (Fig. 4a) showed that all samples fall above the equiline, indicating that dolomite dissolution was the primary process determining the chemistry of groundwater. In peninsular gneissic complex and granitic terrains, Mg^{2+} concentration was higher than Ca^{2+} which indicates the weathering of ferro-magnesian minerals (Datta and Tyagi 1996).

The high ratio of $Ca^{2+} + Mg^{2+}/HCO_3^-$ indicated that Ca^{2+} and Mg^{2+} were added to the groundwater at a greater rate than HCO_3^- (Glover et al. 2012). In the scattered diagram ($Ca^{2+} + Mg^{2+}$) vs (HCO_3^-), all samples fall above the 1:1 equiline with excess Ca^{2+} and Mg^{2+} indicating the dominance of silicate weathering over carbonate weathering (Fig. 4b). The dominance of silicate weathering was also indicated by the scatter plot between ($Ca^{2+} + Mg^{2+}$) vs ($Na^+ + K^+$) as 55% samples plotted above the equiline (Fig. 4c). It is known that a ratio of $Mg^{2+}/(Mg^{2+}+Ca^{2+})$ greater than 0.5 indicates silicate weathering (Drever 1997), and 80% of the samples in this study area have $Mg^{2+}/(Mg^{2+} + Ca^{2+})$ ratio of >0.5 which suggested that dissolution of silicate minerals significantly contributed towards high concentration of Ca^{2+} and Mg^{2+} to the groundwater in this area. Na^+/Cl^- ratio is indicative of whether halite dissolution or mineral weathering dominated in the aquifer system. The Na^+/Cl^- ratio of 1 indicates halite dissolution and >1 indicates silicate (plagioclase feldspar minerals) weathering process (Meybeck 1987). The Na^+/Cl^- molar ratio in the study area was >1 which indicated that Na^+ was released from silicate weathering which was evident from the scatter plot of Na vs Cl (Fig. 4d). The scatter plots of ($Na^+ + K^+$) vs total cations (Fig. 5a) and ($Ca^{2+}+Mg^{2+}$) vs total cations (Fig. 5b) and Na^+ vs HCO_3^- plot (Fig. 5c) showed that there is circumstantial evidence in favour of the dominance of silicate weathering (Rajmohan and Elango 2004). Gibbs plot (Gibbs 1970) for cations (Fig. 6) indicated that most of the samples were plotted in the rock dominance field and weathering of rocks was the major geochemical process influencing ionic chemistry as weathering of plagioclase feldspars (albite), pyroxenes and hornblende contributed to the high concentration of Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- in groundwater (Senthilkumar and Elango 2013).

Evaporation

In arid and semi-arid regions evaporation may contribute as one of the processes influencing groundwater

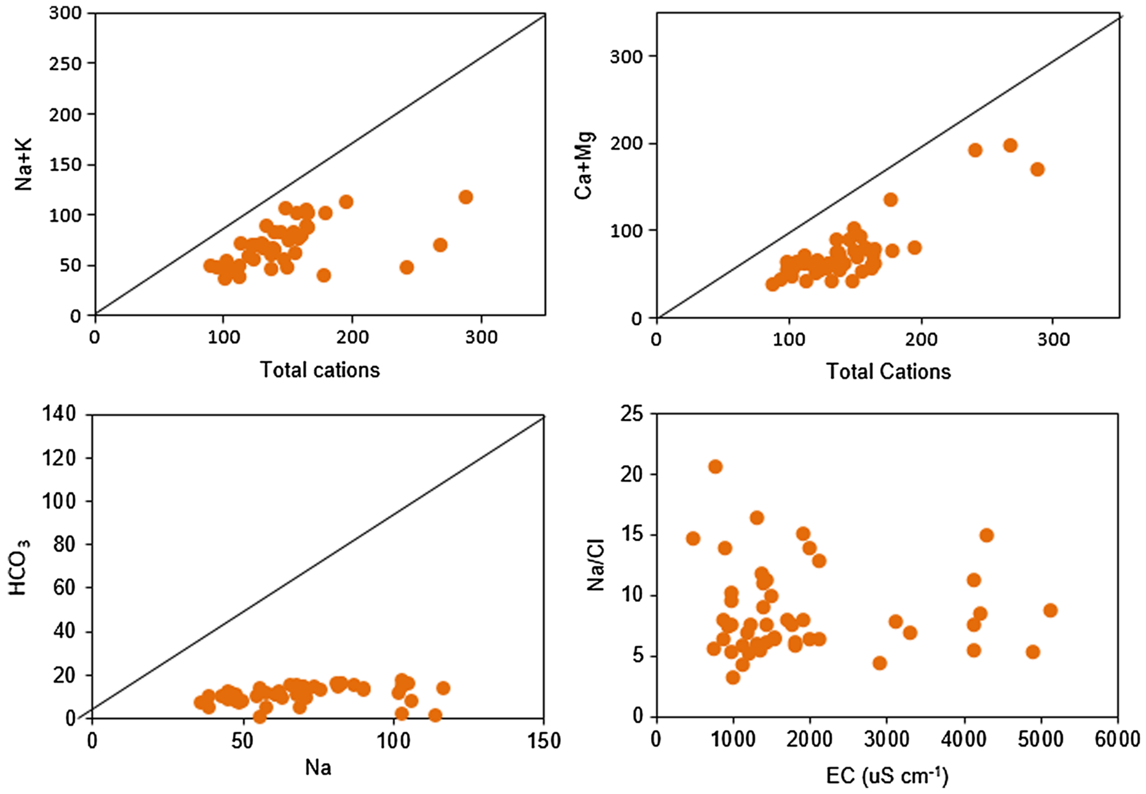

Fig. 5 **a** Scatter plot of $Na^+ + K^+$ vs Total cations; **b** scatter *plot* of $Ca^{2+} + Mg^{2+}$ vs Total cations; **c** scatter *plot* of Na^+ vs HCO_3^-; **d** scatter plot of EC vs Na^+/Cl^-

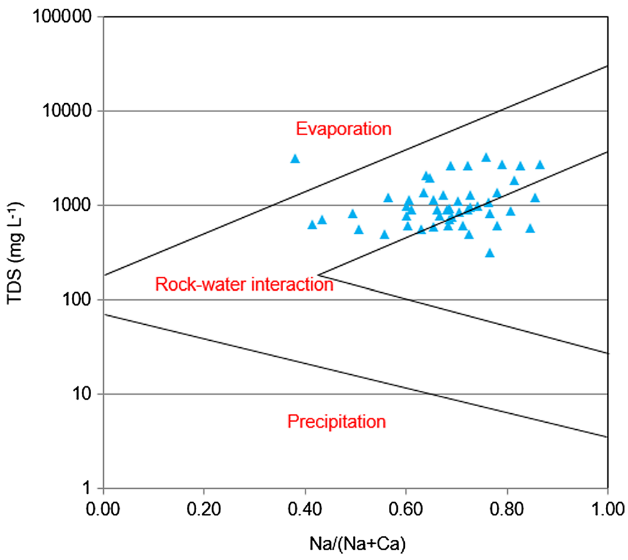

Fig. 6 Gibbs *plot* for cations

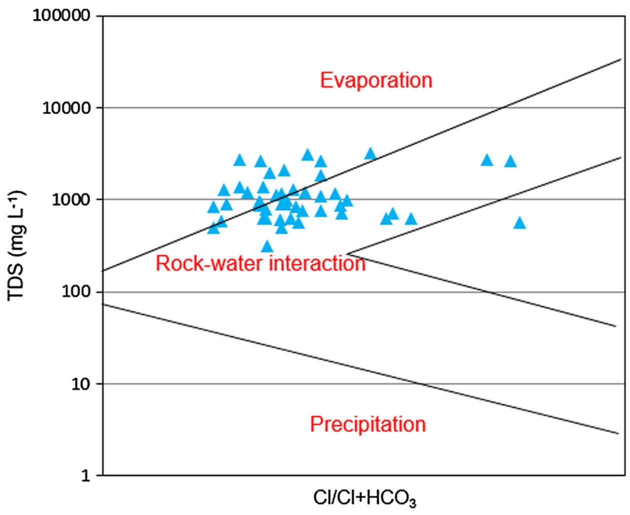

Fig. 7 Gibbs *plot* for anions

chemistry. The Gibbs plots were used to study the effect of precipitation, rock–water interaction and evaporation on chemistry of water. Gibbs plot for anions ($Cl^-/Cl^-+HCO_3^-$) indicated that 28% of the samples were plotted in the evaporation dominance region (Fig. 7). The study area with semi-arid climate experiences high evaporation losses than precipitation (Pal et al. 2000). The influence of evaporation on groundwater is also supported by the scatter plot of EC vs Na^+/Cl^-. If evaporation is dominant process, Na^+/Cl^- ratio should be constant when EC increases (Jankowski and Acworth 1997). The EC vs Na^+/Cl^- scatter plot (Fig. 5d) showed that the Na^+/Cl^- ratio was not static and decreased with

Table 2 Spearman Correlation for the variables in the study area

	pH	EC ($\mu s\ cm^{-1}$)	K^+ ($meq\ L^{-1}$)	Na^+ ($meq\ L^{-1}$)	Ca^{2+} ($meq\ L^{-1}$)	Mg^{2+} ($meq\ L^{-1}$)	Cl^- ($meq\ L^{-1}$)	CO_3^{2-} ($meq\ L^{-1}$)	HCO_3^- ($meq\ L^{-1}$)	SO_4^{2-} ($meq\ L^{-1}$)	BO_3^{3-} ($meq\ L^{-1}$)
pH	1.000										
EC ($\mu s\ cm^{-1}$)	0.783	1.000									
K^+ ($meq\ L^{-1}$)	−0.194	−0.172	1.000								
Na^+ ($meq\ L^{-1}$)	0.152	0.170	−0.065	1.000							
Ca^{2+} ($meq\ L^{-1}$)	0.061	0.056	0.263	−0.090	1.000						
Mg^{2+} ($meq\ L^{-1}$)	−0.036	−0.079	0.557	0.035	0.568	1.000					
Cl^- ($meq\ L^{-1}$)	0.200	0.194	0.267	0.220	0.326	0.681	1.000				
CO_3^{2-} ($meq\ L^{-1}$)	0.436	0.430	−0.081	0.330	−0.256	−0.067	0.177	1.000			
HCO_3^- ($meq\ L^{-1}$)	−0.198	−0.240	−0.206	0.282	0.173	−0.108	−0.244	−0.577	1.000		
SO_4^{2-} ($meq\ L^{-1}$)	−0.140	−0.002	0.231	0.052	0.136	0.176	0.165	−0.020	−0.097	1.000	
BO_3^{3-} ($meq\ L^{-1}$)	0.291	0.218	−0.242	−0.005	0.354	0.093	0.167	−0.074	0.039	−0.338	1.000

Table 3 Rotated component matrix of groundwater properties in the study area

Variable	Component				
	1	2	3	4	5
pH	0.021	0.100	0.870	−0.172	−0.146
EC	−0.003	0.095	0.901	−0.166	0.024
K	0.596	−0.105	−0.334	−0.207	0.302
Na	0.092	0.979	0.084	0.051	0.033
Ca	0.699	−0.219	0.220	0.479	−0.032
Mg	0.944	−0.039	−0.099	−0.020	0.024
Cl	0.770	0.187	0.169	−0.216	−0.032
CO_3^{2-}	−0.033	0.356	0.376	−0.742	0.037
HCO_3^-	−0.142	0.301	−0.174	0.863	−0.053
SO_4^{2-}	0.194	0.000	0.087	0.081	0.882
BO_3^{3-}	0.210	−0.047	0.375	0.240	−0.700
RSC	−0.951	0.234	−0.027	−0.099	−0.009

increase in EC because the transference number (related to velocity or conductance of ions in solution) of all ions increases with increase in EC compared to that of Na^+ which is overshadowed by increase in transference number of all other ions (Glasstone 1968). Gibbs plot suggests that the rate of removal of groundwater being higher compared to its recharge, the concentration of certain ions was higher compared to others depending on their solubility product. Thus the effect of excessive use of groundwater coupled with semi-arid conditions may have an indelible effect on the degradation of water resources in this region.

Ion exchange

Ion exchange was one of the important processes responsible for concentration of ions in the groundwater. In the present study, reverse ion exchange was responsible for increased sodium concentration in gneissic complex terrain (Guo and Wang 2004) and the excess Na^+ over Cl^- was a good indicator of reverse ion exchange process. This can be confirmed by chloro-alkaline index proposed by Schoeller (1977). Positive values (61% samples) suggested that reverse ion exchange occurred in the groundwater. Ca^{2+} and Mg^{2+} exchange Na^+ from exchangeable sites on the aquifer minerals which increases the Na^+ concentration. The remaining 39% samples with negative chloro-alkaline index indicated exchange between Ca^{2+} and/or Mg^{2+} in groundwater with Na^+ and/or K^+ in the aquifer mineral. The molar ratios of sodium to that of divalent cations Ca^{2+} and Mg^{2+} are indicative of the dominance of particular cation. The high ratio of $Na/(Ca)^{1/2}$ and $Na/(Ca+Mg)^{1/2}$ also indicated (Table 1) that Na^+ concentration was higher than Ca^{2+} and Mg^{2+} in the groundwater.

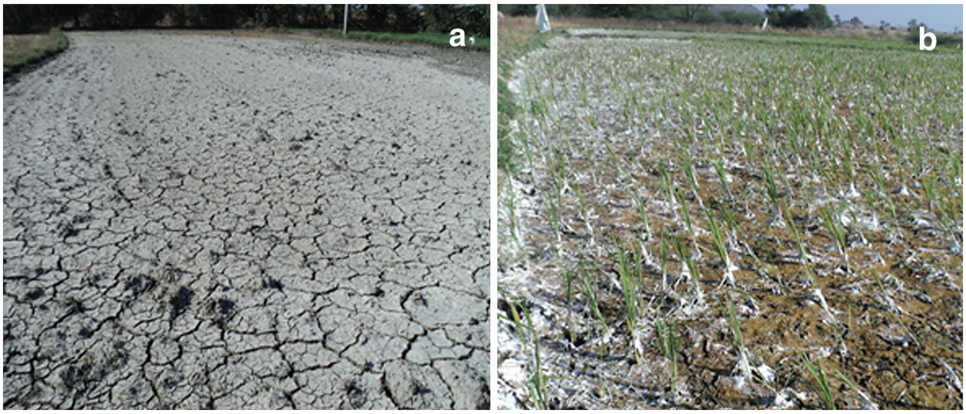

Fig. 8 **a** Surface salt encrustation; **b** wilted rice seedlings after irrigation with groundwater with high salt content

Correlation matrix and factor analysis

The spearman correlation matrix for 13 variables is shown in Table 2. The resultant matrix showed strong correlation between pH and EC. Likewise, strong negative correlation between Ca^{2+}, Mg^{2+} and residual sodium carbonate (RSC) was evident. It also showed weak correlation of pH with other variables. The factor analysis resulted in five factors in a rotated component matrix accounting for 83.76% of the total variation in the hydrogeochemistry of the study area. The extracted factor results were applied to calculate the primary associated factors. Five factor variables (Table 3) with variable factor loadings explain variation in the groundwater chemistry. Mg^{2+}, Ca^{2+}, Cl^{-} and K^{+} have high positive factor loading in factor 1 which accounts for 26.48% of variance. Na^{+}, CO_3^{2-}, HCO_3^{-} and RSC have high positive factor loadings in factor 2 (16.89% variance). pH, EC, HCO_3^{-} and BO_3^{3-} have high positive factor loadings in factor 3 (16.25% variance). HCO_3^{-}, Ca^{2+} and BO_3^{3-} have high positive factor loadings in factor 4 (13.46% variance) and SO_4^{2-} and K^{+} have high positive factor loadings in factor 5 (10.68% variance). Na^{+}, CO_3^{2-} and HCO_3^{-} have high positive factor loadings (factor 2) in rotated component matrix indicating that these ions were a combined result of silicate weathering and other processes in vogue. The high positive loadings for every variable in at least one of the component factors also indicates that rock–water interaction, ion exchange, silicate weathering and to a limited extent, evaporation, determine the groundwater chemistry in the study area.

Irrigation suitability

The safe pH range for irrigation water is 6.5–8.4 (USSL 1954). However, in the study area 12% samples showed pH of more than 8.5 which may harm plant growth by inducing soil alkalinity and specific ion toxicity. Besides, most of the water samples were high in Na^{+} and may develop secondary alkalinity on entry into the exchange complex of soils (more readily with low EC) when used for irrigation (Ray et al. 2000). This is more probable as the solubility of Ca^{2+} encounters a change of phase from a $pH \geq 8.2$. According to USSL (1954) standards, the EC of the water samples varied from low to high and 14% have EC more than the threshold value (4000 $\mu S\ cm^{-1}$) which caused salt injury to the plants due to secondary salinization which was evident from Fig. 8a, b. The results showed that 20% of the groundwater samples have TDS more than 1500 mg L^{-1} and were classified as unsuitable for irrigation. The usual range of Ca^{2+} and Mg^{2+} in irrigation water is 0–20 and 0–5 meq L^{-1}, respectively (Ayers and Westcot 1985). In this study, 92% of water samples have Ca^{2+} more than 20 meq L^{-1} and all the samples have Mg^{2+} above the maximum threshold value. According to Ayers and Westcot (1985), 92% groundwater samples show moderate to high boron toxicity.

The results indicated that 94% of water samples have high sodium content, more than the usual range of 0–40 meq L^{-1} (Ayers and Westcot 1985). High percentage sodium in groundwater which is used for irrigation may stunt the plant growth and reduce soil permeability (Joshi et al. 2009). The soluble sodium percentage of groundwater varied from 19.74 to 71.54% and 17% of water samples are unsuitable for irrigation with SSP > 60%. This may lead to high sodium adsorption ratio in irrigated soils and reduce the hydraulic conductivity of soil. Moreover, the groundwater containing high proportions of sodium will enhance the exchange reaction between water and soil for alkaline earth metals, affecting the soil permeability and the texture which makes the soil hard to plough and unsuitable for seedling emergence (Keesari et al. 2013).

The magnesium hazard in the groundwater samples ranged between 26.42 to 76.09 and 80% of water samples were above the acceptable limit of 50% (Ayers and Westcot 1985). Generally, calcium and magnesium maintain a state of equilibrium in most waters. High level of magnesium deteriorates soil structure, particularly when waters are sodium dominated, and enhances the hazardous effect of Na in irrigated soils and induces hardness in soils. The soils of the study area are red and black soil associations dominated by smectitic clays which swell and shrink during wet and dry seasons, respectively. There are reports of impairment of hydraulic properties due to high exchangeable Na^+ and Mg^{2+} in the exchange complex of the clays (Balpande et al. 1996; Chandran et al. 2014) and precipitation of Ca^{2+} as $CaCO_3$ in the dry season due to high evaporation demand. It leads to decrease in partial pressure of carbon dioxide which induces sodicity in the soils and this gets aggravated if irrigation water with high sodium is used for irrigation. As per USSL (1954) guidelines, 70% groundwater samples were classified as C3S3 (high salinity hazard) and C3S2 (medium to high sodium hazard), 16% as C4S3 and C3S4 (high salinity and sodium hazard) and 10% as C4S4 (high salinity and sodium hazard) which could be attributed to the presence of Na-dominant minerals in the groundwater aquifer material. Padekar et al. (2014) also reported high salinity and alkalinity hazard in irrigation water from semi-arid part of eastern Maharashtra.

Since the calcium and magnesium content was proportionately too high, the effect of carbonate and bicarbonate in terms of RSC index was low (−89 to −5) because of the neutralising effect of other acid anions (Cl^-, SO_4^{2-}) rendering the pH relatively lower (Tables 1 and 2). Potential salinity is an indicator of ability of water to cause salinity in soils and the suitability of water for safe use in different textured soils. Potential salinity ranged between 7 and 40 meq L^{-1} and groundwater was unsuitable for irrigation in fine-textured soils ($PS > 3$). The Kelly's ratio varied from 0.25 to 2.53 in the study area. Kelly's ratio more than 1 is not suitable for irrigation and 49% of water samples were not suitable for irrigation. The chemical or ionic composition of groundwater influences the soil permeability based on the soil type. The results of the present study showed that the permeability index varied from 23 to 77 and suggest that all the water samples fall in the category of class V (>20) and were not safe for irrigation since it will affect the soil permeability upon long-term use.

Conclusions

The groundwater of the study area was slightly alkaline and dominated by Na^+, Ca^{2+} and Mg^{2+}. The groundwater chemistry was influenced by silicate weathering, reverse ion exchange and rock–water interaction. It can be inferred from various geochemical and statistical results that the groundwater is of mixed type with multiple processes involved in its evolution. Mineralogy of the aquifer material played an important role in determining the water chemistry with high values of Na^+ to divalent cation ratios which may pose threat to the cultivated crops by inducing specific ion toxicity and osmotic stress. Since the majority of the water samples were classified as highly saline, use of groundwater blended with freshwater or surface water for irrigation should be an option to minimise the potential of soil salinity and salt injury to the plants. In-spite of the fact that the pH of the groundwater was not exceedingly high, the dominance of Na in the groundwater may have indelible effect on the soils and crops if used for irrigation for a longer time by impeding the hydraulic properties of soils. Hence, the study of hydrogeological processes and water chemistry will be highly beneficial for using these water for irrigation and for the sake of posterity.

Compliance with ethical standards

Conflict of interest None.

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