



# Sustainability assessment of the groundwater quality in the Western India to achieve urban water security

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## Abstract

Achieving water security and availability for all is among the principle agenda of the UN Sustainable Development Goals. To achieve the goal of water security, particularly in rapidly expanding cities, identification of safe and sustainable water resources is an absolute necessity. The paper conducts an exploratory investigation in the hydrogeochemical characteristics of groundwater and thereby assesses the suitability of groundwater as an alternative and reliable resource for public water supply in the Indian city of Surat. A total of 33 groundwater samples, selected on the basis of aquifer depth and land use signatures, were collected from open, bore, dug wells and hand pumps. After the hydrogeochemical analysis, the study evaluated the present state of the groundwater quality and determined the spatial distribution of groundwater quality parameters such as hardness, electrical conductivity,  $\text{Cl}^-$ , pH,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations. Based on the permeability index, result showed that 80% of the sampled groundwater quality falls under excellent class, i.e., category I with PI value ranging from 1 to 24%, whereas the rest 20% of the samples has fallen under good class, i.e., category II with PI value ranging from 25 to 75% on the suitability of water for irrigation. The results of this study outline the unsustainability of groundwater for direct consumption, especially without any improved on-site water treatment, but it is appropriate for the irrigation purposes.

**Keywords** Water security · Groundwater assessment · Groundwater quality · India

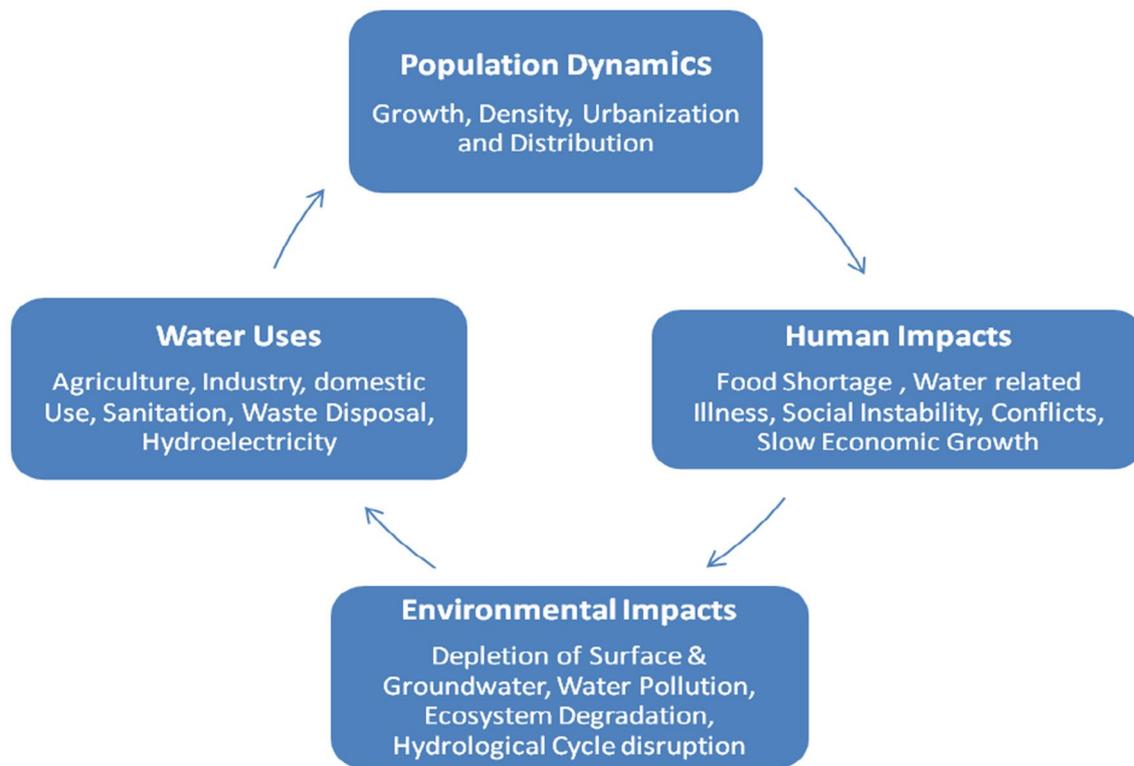
## Introduction

Despite two-thirds of our planet is covered with water, the specter of water insecurity, i.e., lack of reliable source of freshwater with appropriate quality and quantity, is hovering over almost all parts of the world. With unprecedented population growth, rapid urbanization, land use transformation and changes in lifestyle, “providing adequate and

safe water supply to all” is increasingly becoming a challenge and the core agenda for sustainable development and well-being of human societies. Interaction between global changes and dynamics of population growth and their usage pattern is shown in Fig. 1. The Goal 6 of the UN Sustainable Development Goals (SDG), in particular, recognizes the importance of achieving “universal and equitable access to safe and affordable drinking water for all” by the year 2030. As such, the problem of water insecurity is essentially two-faced. First, owing to a rapid expansion of population and industrialization, primary water demands are rising by leaps and bounces, and consequently the existing sources are gradually becoming inadequate and unreliable. Second, due to severe deterioration of water quality, available water resources are increasingly becoming unsuitable or even dangerous for human consumption (Saraswat et al. 2016; Vörösmarty et al. 2000). Therefore, while traditionally water resource planning and designing of public water supply revolved around finding a reliable source, it is increasing becoming evident that it is not only the quantity, but also the quality, which needs to be considered for designing robust and resilient water supply schemes.

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**Fig. 1** Dynamics of population, human health and freshwater impacts Adapted from Gleick (2000)

In general, both surface and groundwater can be used to meet the demands for potable water, when it is treated sufficiently to meet the prescribed standards (Bauder et al. 2011; Miller 2006). Nonetheless, traditionally groundwater is preferred over surface water because of its reliability during extreme weather situation, namely droughts/floods, lesser contamination and relatively lower treatment costs. More specifically, due to the lesser probability of bacterial contaminations, groundwater serves as a popular and reliable source that can be consumed with little or even without any treatment. In India, for instance, around 80% of the rural population and more than 50% of the urban population directly depend on groundwater for the domestic water consumption (Biswas et al. 2014). Yet, recent research indicated a number of adverse impacts of groundwater on human health, owing to the occurrence of undesired trace elements. Groundwater contamination is found in a range of aquifers of unconsolidated sediment to bedrocks (Kumar et al. 2010; Smedley and Kinniburgh 2002). Groundwater contamination by trace elements has recently turned out as a major concern for policy planners in India and in the subcontinent (Mahanta et al. 2015; Meliker et al. 2008). For instance, it is estimated that at least 35 million people in Bangladesh and 6 million people in India are severely affected by arsenic-contaminated groundwater (Ahmed et al. 2004; Dasgupta and Shaw 2014; McArthur

et al. 2004; Mukherjee et al. 2015; Nickson et al. 2007; Singh et al. 2014). Yet, continued use of hazardous, arsenic-bearing groundwater for drinking, cooking and agriculture purposes has led to an unprecedented crisis in the state of West Bengal and Bangladesh, in which the World Health Organization (WHO) is described as the “worst case of mass poisoning in human history” (Dasgupta and Shaw 2014). Despite the GBM delta is typically blessed in high-yielding aquifers, the situation underpins the importance of monitoring groundwater quality and integration of water quality in sustainable water supply schemes.

The use of groundwater as a potential and reliable alternative, thus, depends on the concentration of trace elements, which gets dissolved from the aquifer-bearing rocks through complex hydrogeochemical process (Mukherjee et al. 2015). It is, therefore, imperative to understand these processes considering both current and future possibilities before turning on to groundwater as reliable water resource. To demonstrate the mechanism of groundwater evolution in any aquifer system and to understand how groundwater quality changes over time, it is important to analyze the hydrogeochemical characteristics of the aquifer in different seasons (Uddin et al. 2011). A variety of methods are presently available to monitor the hydrogeochemical processes responsible for groundwater contamination. Of which, graphical methods and interpreting different indices have been commonly

used (Coetsiers and Walraevens 2006; Das and Kumar 2015; Kumar et al. 2016a, b, c; Srivastava and Ramanathan 2008).

In this research, an attempt has been made to understand the complex geochemical evolution of groundwater by evaluating its chemical characteristics and suitability analysis using different classifications. The location of the study is set to the city of Surat in Western India, where groundwater is being developed for meeting the rising water demand.

## Study area

Located at the bank of River Tapi, at about 25 km from the Arabian sea, the city of Surat in the western state of Gujarat is among the major commercial hubs of India, widely known as “diamond capital of the world.” It is the eighth largest city in India and globally ranks 73rd in terms of overall extent of urban area. As per the latest census (2011), the population of Surat is estimated around 5 million, which is expected to grow to 6.4 and 8.5 million by the year 2021 and 2031, respectively. Geographically, the city is located at 21°15' Northern latitude and 72°52' Eastern longitude and covers an area of approximately 335 km<sup>2</sup>. The city experiences a tropical climate with a temperature that frequently increases above 40 °C in summer and decreases to about 12–15 °C in the winter. On the other hand, the elevation varies between 10 and 18 Mt. Tapi is the major River, which traverses through the center of the city and flows toward west direction. Geographically, the study area is located into western coastland of the Deccan Peninsula. It covers hilly areas, piedmont slopes, alluvial plains and coastal plains. Geologically, quaternary alluvium, tertiary limestone, sandstone, and Deccan Trap basalt dominate the area.

With 92% of the world's diamonds cut and polished here, Surat has contributed more than 40 billion US dollars in the country's GDP and has attracted workforces from all parts of India. The city is equally well-known for its gigantic textile and ornamental manufacturing industry, together with steel production, petrochemical and other downstream industries that support its robust economy (CDP 2008). With its vibrant economy, the city of Surat expanded unprecedentedly since 2004 due to rapid urbanization and industrialization. In terms of water infrastructure, the city boasts of a computerized water distribution and drainage system commensurate to its rapidly advancing commercial and residential need.

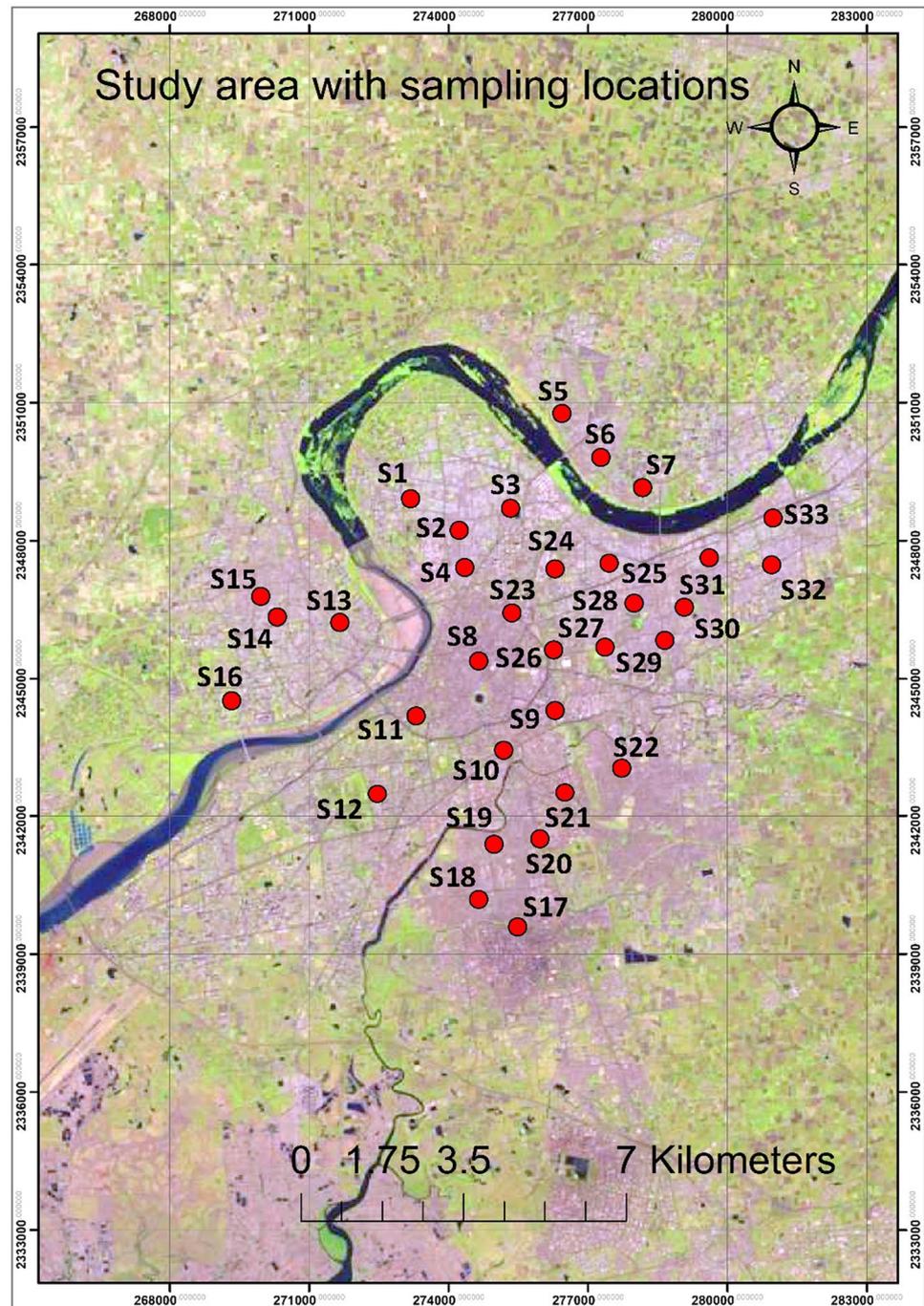
Surat, the study area for the present research, is divided into the coastal and alluvial region. The coastal region represents the muddy shoreline with tidal flat. The alluvial region is formed by River Tapi and is distinguished by flood plain of the River Tapi and Mindhola. In recent past decades, because of fast deterioration of Tapi River water quality due to rapid urbanization and industrialization, groundwater became the sole source for potable water in the region (CDP

2008). For meeting the water demand of 8 million people by the year 2030, it is estimated that minimum 1200–1500 million liter per day of water will be required to cater to rising water needs (Kapshe et al. 2013). So, it is imminent that study area will face severe water scarcity in near future under the business as usual scenario, given the rising water demand from both domestic and industrial sectors, unless alternative sources are harnessed.

## Methodology

Whole study area was divided into grid of 3 × 3 km<sup>2</sup> and after that 33 groundwater samples representing spectral signature of each grid was collected. All groundwater samples were collected from the bore, dug, open wells and hand pumps in the study area. Main attributes used for groundwater sampling were distinct geological formations, land use characteristics, accessibility and permission for taking samples from some households and depths of the aquifers. This is the reason why some of the grids have more than one water samples as shown in Fig. 2. Using a handheld GPS receiver (GPS III, Garmin), precise coordinates of the sample location were recorded, followed by on-site measurements of electrical conductivity (EC), temperature and pH. These parameters were measured using an inline flow cell ensuring the exclusion of atmospheric contamination and minimized fluctuations. The transportable “Orion Thermo water analyzing kit (Model Beverly, MA, 01915)” with a precision of 2% was used for all kinds of on-site measurements. Using thoroughly rinsed polyethylene bottles, three groundwater samples were collected from each location and filtered against 0.2-µm Millipore membrane filters. The samples collected for major cations analysis were acidified by 1% HNO<sub>3</sub> to stabilize trace metals (pH ~ 2), while samples collected for nitrate were acidified with H<sub>3</sub>BO<sub>3</sub>. In an ice chest, all the samples were transported to the laboratory and stored at below 4 °C temperature. The samples were analyzed for anion, cations and trace metals. The concentration of HCO<sub>3</sub><sup>-</sup> was analyzed by acid titration (using Metrohm Multi-Dosimat), while other anions Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> were analyzed by DIONEX ICS-90 ion chromatograph with an error percentage of less than 2%, using duplicates. The trace elements and major cations are evaluated by inductively coupled plasma-mass spectrometry (ICP-MS) with a precision of less than 2%, using duplicates. For major ions, analytical precision was checked by the NICB, normalized inorganic charge balance (Kumar et al. 2010, 2016a, b, c). This is defined as [(Tz+ - Tz-)/(Tz+ + Tz-)] and signifies the fractional difference between total cations and anions. The quality of the data points is supported by observed charge balance, which is better than ± 5% and generally this imbalance is skewed toward positive charge.

**Fig. 2** Study area map with sampling locations



In order to understand the origin of groundwater mineralization in the study area, saturation index (SI) was calculated. Mineral saturation states with respect to selected minerals are computed as shown by Eq. 1, mentioned by Garrels and Christ (1965)

$$SI = \log_{10} (K_{IAP}/K_{SP}) \quad (1)$$

where SI is the saturation index,  $K_{IAP}$  is the ion activity product of particular solid phase and  $K_{SP}$  is the solubility product of the phase. Based on the value of the SI, the saturation states were recognized as saturated (equilibrium;  $SI = 0$ ), unsaturated (dissolution;  $SI < 0$ ) and oversaturated (precipitation;  $SI > 0$ ).

## Results and discussion

### Groundwater chemistry

The summary of the chemical constituents of groundwater samples is furnished in Table 1. The results suggested the anionic abundance in the order of  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{NO}_3^-$ , while the high  $\text{Cl}^-$  content particularly signifies the impact of the coastal environment and/or local anthropogenic activities in the region. Conversely, the results of cationic abundance found in the order of  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Fe}^{2+} > \text{Cr}^{2+}$  in which the higher content of  $\text{Mg}^{2+}$  is compared to  $\text{Ca}^{2+}$  indicate the effect of dolomite and limestone weathering. It also supports the weathering of high Mg rocks as ultramafic rocks, namely serpentine as supported by the geology of the study area. The result also reveals that relative high concentration of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  content is possibly due to weathering of carbonate minerals related to the flushing of  $\text{CO}_2^-$  rich water from unsaturated zone, where it is formed by decomposition of organic matter degradation and silicate weathering.

Value of pH for all groundwater samples was observed between 6.7 and 7.9. Average pH value was 7.11, supporting the idea of groundwater being slightly alkaline because of interaction between soil and rainwater (Subramanian and

Saxena 1983). The higher value of EC suggests high concentration of dissolved solids and, thus, high ionic strength of the groundwater and intensive rock-water interaction compounded by anthropogenic activities in the area. When compared to the prescribed standards (shown in Table 2), the results suggested that there are 30% of the samples having TDS values beyond the limit, while all the samples showed EC above the prescribed drinking water standards. The concentrations of  $\text{Cl}^-$  range from 62.04 to 1717.85, which reflects its evolution from freshwater to saline water when compared with its desirable limit shown in Table 2. The higher concentrations of  $\text{Cl}^-$  can be attributed to the input from sewage effluents in the village areas and salinization to areas in close proximity to the coast. It is found that about 15% of the samples have indicated chloride concentration beyond the limit. In the sample (S16), the amount of chloride was the highest, 1717.85 mg/L. In addition, the other supporting facts leading to high chloride concentration in this sample is the depth of this well, i.e., 51 m. The chloride is actively circulating at relatively shallow depths of groundwater, which is derived from rain or from the saline water intrusion along the coast. In the coastal region, depletion of groundwater due to over-pumping of groundwater often leads to the movement of the saline water into the freshwater aquifers, and the results are indicative of such possibilities. For sample S16, deep well screen facilitates the possibility of migration of sea water–freshwater interface toward inland and touches this screen because of high groundwater withdrawal. Further, it was found that all the samples have the amount of sulfate and nitrate within the prescribed limit. Among cations, permissible limit for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is 200 mg/L and 150 mg/L, respectively, according to the WHO standards. The samples showed  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in the range of 65–340 mg/L and 110–495 mg/L, respectively, with 40% and 80% samples having the hardness beyond the permissible limit. Most common sources of calcium in the groundwater are calcite, aragonite and gypsum, while that for Mg are dolomites and mafic minerals in the bedrocks. Concentration for Na and K in the samples was generally found under recommended limit. Results for iron as trace metal showed that in all the samples the concentration of iron is higher than the desirable limit (0.3 mg/L). This is important because of its adverse effect on domestic uses and water supply structures, together with promotion in iron bacteria growth (*Ferrobacillus* sp.). Because of high iron content in the water, the tube well platform turns red in color. Chromium ( $\text{Cr}^{2+}$ ), another trace metal, was also analyzed in the water samples. The main reason behind selection of this metal was the presence of huge textile and chemical industries, where its usage is very prominent. Result shows that all water samples are having chromium beyond permissible limit. Although this higher concentration of chromium is not so harmful for human consumption

**Table 1** Statistical summaries of chemical constituents of groundwater in Surat city, Gujarat

Parameter	Unit	Average	Minimum	Maximum	SD
Depth	Meter (bgl)	24.00	6.00	72.00	3.00
pH		7.11	6.70	7.90	0.27
EC	( $\mu\text{S}/\text{cm}$ )	2647.53	1156.83	3478.12	781.50
TDS	(mg/L)	1935.13	845.55	2542.22	571.21
Acidity	(mg/L)	243.75	125.00	325.00	54.94
Alkalinity	(mg/L)	180.00	100.00	300.00	54.77
TH	(mg/L)	489.50	180.00	755.00	200.70
$\text{Ca}^{2+}$	(mg/L)	174.38	65.00	340.00	77.78
$\text{Mg}^{2+}$	(mg/L)	315.13	110.00	495.00	131.77
$\text{K}^+$	(mg/L)	14.21	6.00	29.25	7.77
$\text{Na}^+$	(mg/L)	100.89	64.90	115.38	14.50
$\text{Cl}^-$	(mg/L)	438.69	62.04	1717.85	199.28
$\text{HCO}_3^-$	(mg/L)	219.60	122.00	366.00	66.82
$\text{SO}_4^{2-}$	(mg/L)	80.01	21.25	115.78	28.03
$\text{PO}_4^{3-}$	(mg/L)	3.51	2.09	9.86	2.24
$\text{NO}_3^-$	(mg/L)	0.23	0.09	0.42	0.11
$\text{F}^-$	(mg/L)	BDL	BDL	BDL	BDL
$\text{Fe}^{2+}$	(mg/L)	0.41	0.32	6.18	0.15
$\text{Cr}^{2+}$	( $\mu\text{g}/\text{L}$ )	137.03	106.58	1205.22	118.54

BDL below detectable limit, bgl below ground level

**Table 2** Different guideline values for the drinking water with the percentage of samples beyond permissible limit (PL) and the resulting health implications (WHO 2011)

S. no.	Parameter	Unit	WHO standard (2011)		BIS, IS:10500:2012 Standard		% of sample beyond limit	Effects
			Desires limit (DL)	Permissible limit (PL)	Desires limit (DL)	Permissible limit (PL)		
1	pH	–	6.5–8.5	–	6.5–8.5	No relaxation	0	Bitter taste, mucous membrane
2	EC	( $\mu\text{S}/\text{cm}$ )	500	–	500	1000	85	Gastro-intestinal irritation
3	TDS	(mg/L)	–	–	500	2000	–	Undesired taste, gastro-intestinal irritation
4	TH	(mg/L)	100	500	300	600	65	Scale formation
5	Ca <sup>2+</sup>	(mg/L)	75	200	75	200	40	Scale formation
6	Mg <sup>2+</sup>	(mg/L)	50	150	30	100	80	Encrustation in water supply structure
7	K <sup>+</sup>	(mg/L)	–	200	–	200	0	Interfere with nerve impulse
8	Na <sup>+</sup>	(mg/L)	–	200	–	–	0	Scale formation
9	Fe <sup>2+</sup>	(mg/L)	–	0.1	–	0.3	100	Promotes bacterial growth
10	Cl <sup>–</sup>	(mg/L)	200	600	250	1000	15	Salty taste
11	SO <sub>4</sub> <sup>2–</sup>	(mg/L)	250	400	200	400	0	Laxative effects
12	NO <sub>3</sub> <sup>–</sup>	(mg/L)	–	50	45	–	0	Methanoglobinemia
13	Cr (total)	( $\mu\text{g}/\text{L}$ )	50	50	50	150	100	Allergic, skin rashes

except skin rashes and allergy, it may cause serious threat to aquatic ecosystem by affecting respiratory system, birth rate for aquatic animals and fishes.

Table 3 shows the suitability of groundwater sample for potable/drinking purposes based on its TDS and hardness value. Based on the TDS value, it is found that 15% of the samples fall in the “poor category” while 85% of the samples fall in the “unacceptable category.” Results further showed that only 15% of the samples fall in the category of freshwater, while 85% of the samples fall in the brackish water category. Total hardness of all samples ranged between 180

and 755 mg/L, and 65% samples have the hardness beyond the permissible limit. The sample 1 (S1) has the highest hardness, that is 755 mg/L. Also in terms of hardness, 30% of the groundwater samples fall in the hard water category and 70% samples fall in the very hard category. However, hardness does not pose a serious threat to human health and at least primary hardness can be easily removed with common methods like boiling and precipitation. On the other hand, the presence of calcium and magnesium in drinking water with relatively high hardness ensures the fulfillment of average daily requirements of these related minerals.

**Table 3** Suitability of groundwater for drinking based on many classifications

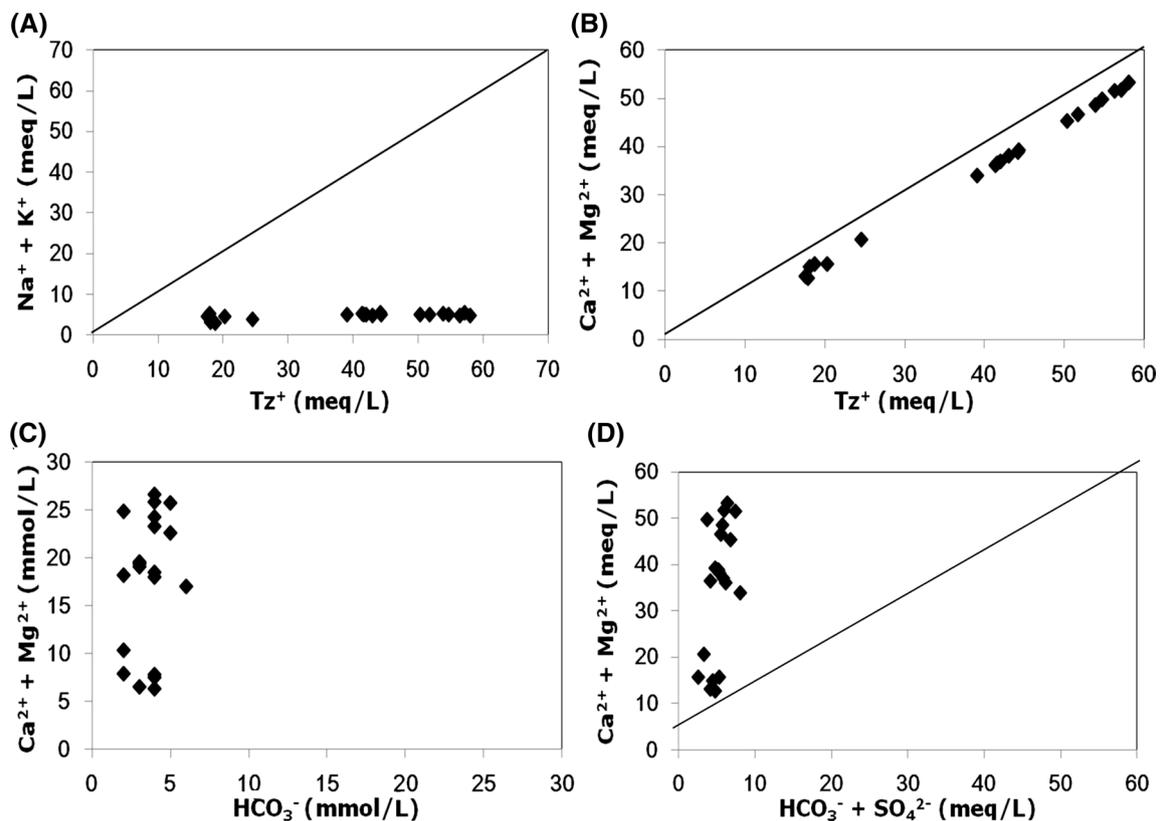
Parameter	Water class	% of sample
TDS		
< 300	Excellent	NIL
300–600	Good	NIL
600–900	Fair	NIL
900–1200	Poor	15
> 1200	Unacceptable	85
Based on total hardness as CaCO <sub>3</sub> (mg/L) after Sawyer and McCarty (1978)		
< 75	Soft	NIL
75–150	Moderately hard	NIL
150–300	Hard	30
> 300	Very hard	70
Nature of groundwater based on TDS (mg/L) values		
0–1000	Fresh	15
1001–10,000	Brackish	85
10,001–100,000	Salty	NIL
> 100,000	Brine	NIL

Nevertheless, when in more quantity, hard water can cause aesthetic problems and other physiological difficulties.

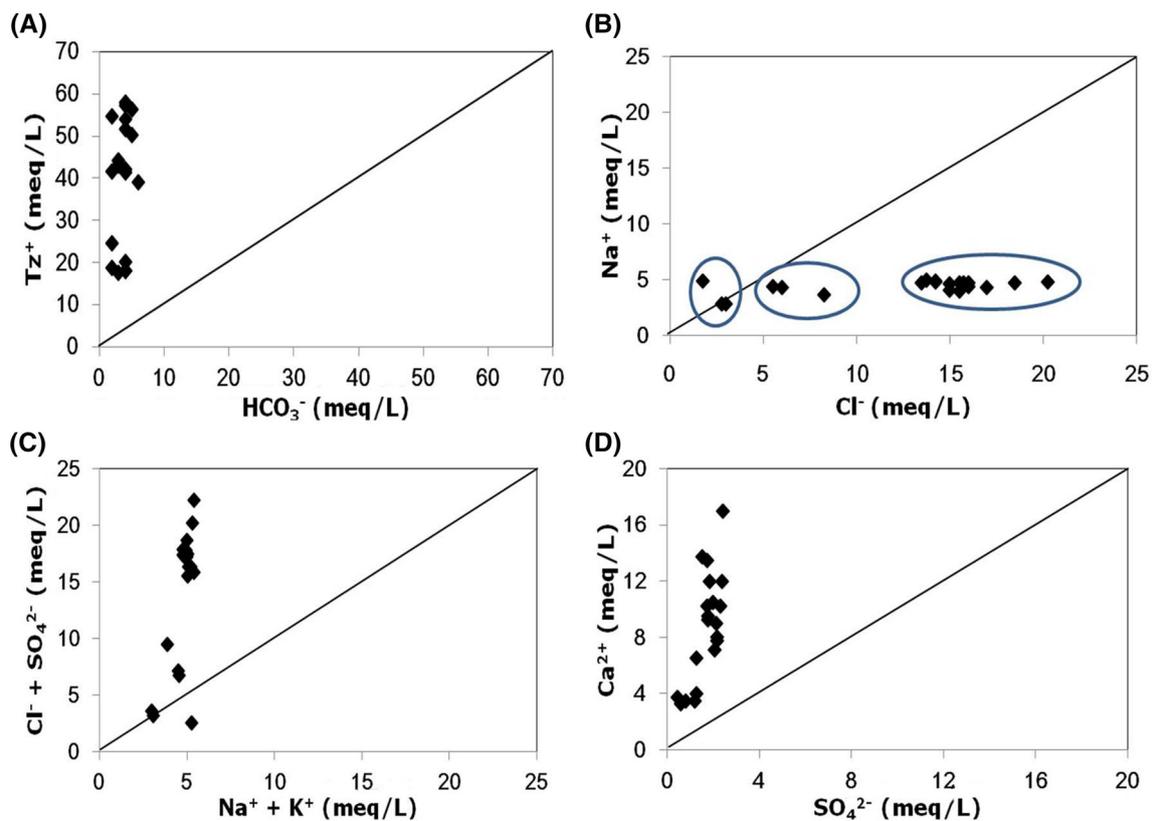
### Hydrogeochemical evolution

Different scatter plots are used to decipher hydrogeochemical evolution processes responsible for determining the water quality shown in Figs. 3, 4 and 5. In Fig. 3a, the graph of  $Tz^+$  versus  $Na^+ + K^+$  showed that all the sample points are inclining toward  $Tz^+$ , which suggests that sodium and potassium are not dominant in groundwater samples. Contrarily, another cationic activity like silicate weathering precipitation of Ca as calcium carbonate coupled with enrichment of Mg concentration in the groundwater. Along with that, agriculture activity, which is also one of the prominent sources of K, is not dominant in the study area. Graphical representation of  $Tz^+$  versus  $Ca^{2+} + Mg^{2+}$  in Fig. 3b shows that all the samples fall near to (1:1) equiline, which depicts  $Tz^+$  is dominated by  $Ca^{2+} + Mg^{2+}$ . This implies that source of calcium and magnesium is from carbonate weathering, and the potential source minerals are the most likely to be calcite and dolomite. In Fig. 3c, the graphical representation of  $HCO_3^-$  versus  $Ca^{2+} + Mg^{2+}$  showed that

groundwater samples lying near the  $Ca^{2+} + Mg^{2+}$  axis, suggesting that the additional  $Ca^{2+} + Mg^{2+}$  are coming from a different source, is probably due to weathering of muscovite, illite and calcium hydroxide (lime) other than limestone. In Fig. 3d, the graphical representation of  $HCO_3^- + SO_4^{2-}$  versus  $Ca^{2+} + Mg^{2+}$  showed that all the water samples are placed above equiline and toward  $Ca^{2+} + Mg^{2+}$  representing that there is enrichment of  $Ca^{2+} + Mg^{2+}$  over  $HCO_3^- + SO_4^{2-}$  which implies calcite dissolution is abundant. The extent of contamination is further examined by the graphs shown in Fig. 4. Figure 4a shows plot of  $HCO_3^-$  versus  $Tz^+$ , where all the sample points occupy the area above equiline and closer to the y-axis, which confirms that water chemistry of the area is influenced by secondary process such as anthropogenic activities. In Fig. 4b, the plot represents the most of the groundwater samples occupying the places near the  $Cl^-$  axis, indicating salinization. The category I, i.e., the abnormal higher value of  $Cl^-$ , can be attributed to the surface sources through leaching from domestic wastewaters, septic tanks and animal waste. Category II shows the migration path of change in water quality, i.e., changing from inland aquifer system to coastal environment, while category III occupies very few samples that clearly



**Fig. 3** Scatter plot for hydrogeochemical evolutionary process, **a** scatter plot between  $Tz^+$  and  $Na^+ + K^+$ , **b** scatter plot between  $Tz^+$  and  $Ca^{2+} + Mg^{2+}$ , **c** scatter plot between  $HCO_3^-$  and  $Ca^{2+} + Mg^{2+}$  and **d** scatter plot between  $Ca^{2+} + Mg^{2+}$  and  $HCO_3^- + SO_4^{2-}$



**Fig. 4** Scatter plots for hydrogeochemical evolutionary processes, **a** scatter plot between  $\text{HCO}_3^-$  and  $\text{Tz}^+$ , **b** scatter plot between  $\text{Cl}^-$  and  $\text{Na}^+$ , **c** scatter plot between  $\text{Na}^+ + \text{K}^+$  and  $\text{Cl}^- + \text{SO}_4^{2-}$  and **d** scatter plot between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$

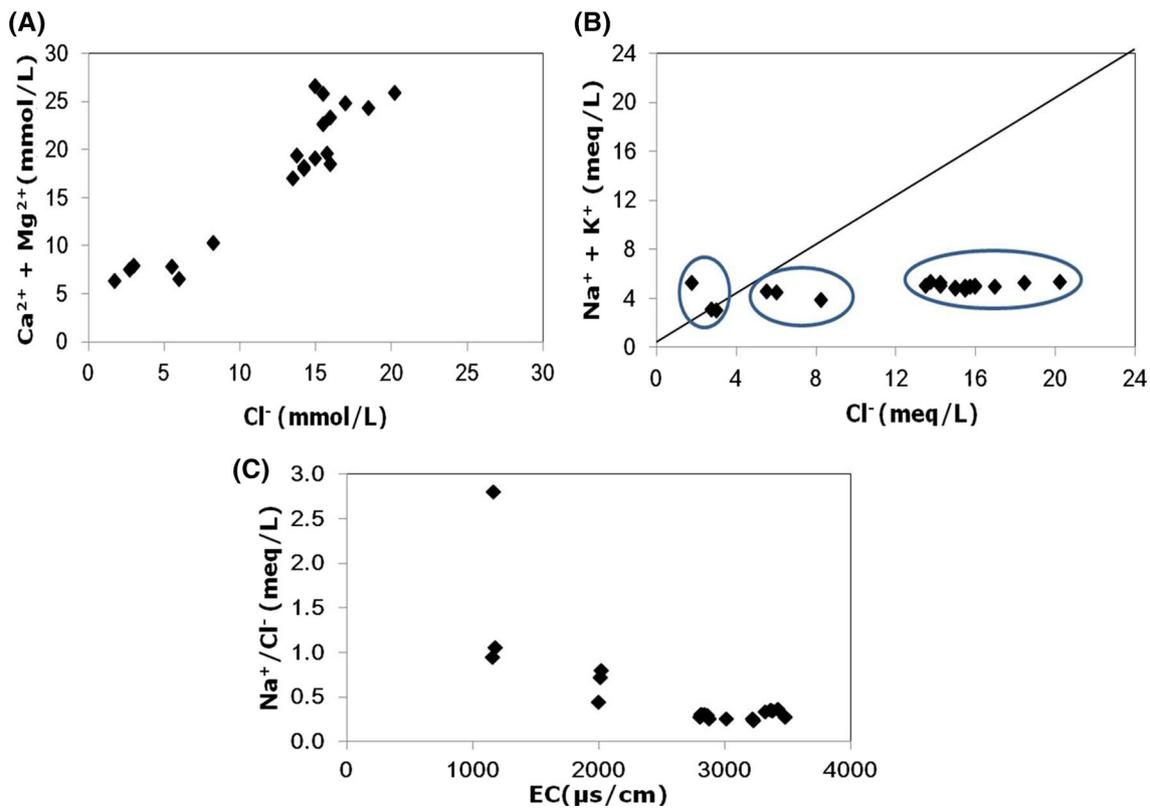
demonstrate cumulative effect of upcoming salt water because of the high extraction rate supported by slight mixing of freshwater and salt water. In Fig. 4c, the scatter plot between  $\text{Na}^+ + \text{K}^+$  and  $\text{Cl}^- + \text{SO}_4^{2-}$ , where most of the samples tend to migrate toward  $\text{Cl}^- + \text{SO}_4^{2-}$ , clearly indicates the presence of secondary salinity sources. The main driving factors for this secondary salinity are degradation of organic matter and agricultural runoff carrying unutilized  $\text{SO}_4^{2-}$  along with infiltration of untreated sewage effluent (Anderson 1979). From scatter plot between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (Fig. 4d), most of the samples tend to move toward the  $\text{Ca}^{2+}$ , indicating that  $\text{Ca}^{2+}$  also originated from different possible minerals like calcite, dolomite or silicate minerals like feldspar, other than that of single mineral gypsum which is the common source for both  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ .

In Fig. 5a, the plot of  $\text{Cl}^-$  versus  $\text{Ca}^{2+} + \text{Mg}^{2+}$  (mmol/L) indicates that the concentration of Ca and Mg increased with salinity, which could be an indication of the simple ion exchange between Na of seawater and Ca/Mg from freshwater possibly through naturally inert material like clay. In Fig. 5b, the plot for  $\text{Cl}^-$  versus  $\text{Na}^+ + \text{K}^+$  showed that most of the sampling points are below equiline which is indicative that the higher concentration of  $\text{Cl}^-$  is

probably due to contribution from human activities such as use of fertilizer, animal wastes etc. On the other hand, the samples near to equiline indicate the coastal environmental effect while samples falling in the intermediate category indicate that water will be salinized in near future if similar trend of anthropogenic pressure (groundwater withdrawal, encroachment of coastal aquifer system) will continue. Scatter plot in Fig. 5c shows the molar ratio of Na/Cl for groundwater samples for study area ranging from 0.2 to 2.7. Most of the samples have Na/Cl ratio below one, which implies that it is not solely because of groundwater salinization rather than other geochemical processes operating at local scale which alters the groundwater chemistry.

#### Assessment of groundwater quality for irrigation use

The suitability of groundwater for irrigation is assessed by considering salinity, chlorinity and sodicity in addition to other parameters (Mills 2003; Nishanthiny et al. 2010), and result is shown in Table 4. Along with that of a brief statistical summary for different chemical indices (SAR, %Na, PI, Mg/Ca, Mg ratio, CAI-1 and CAI-2), the groundwater is



**Fig. 5** Scatter plots for hydrogeochemical evolutionary processes, **a** scatter plot between  $\text{Cl}^-$  and  $\text{Ca}^{2+} + \text{Mg}^{2+}$ , **b** scatter plot between  $\text{Cl}^-$  and  $\text{Na}^+ + \text{K}^+$  and **c** scatter plot between EC and  $\text{Na}^+/\text{Cl}^-$

shown in Table 5. When salinity of groundwater was measured against EC, it is found that 60% of the samples fall in slight-to-moderate saline category (700–3000  $\mu\text{S}/\text{cm}$ ), whereas rest of 40% samples fall in severely saline category (> 3000  $\mu\text{S}/\text{cm}$ ). On the other hand, when salinity is measured with respect to TDS, 30% of the samples fall into slight-to-moderate saline (450–2000 mg/L) and 70% samples are in the severely saline category (> 2000 mg/L).

Sodium adsorption ratio is one of the criteria to evaluate suitability of water for irrigation purposes and is calculated using Eq. 2. The soil permeability reduces due to the excessive sodium content relative to the calcium and magnesium and thus restrains the supply of water needed for the crops. All the water samples fall in the excellent-to-moderate category, which is good for irrigation especially sprinkler irrigation on every kind of soils. On the other hand, this table also shows interesting facts about selecting different indices for determining suitability of groundwater for irrigation, where we will get contrasting result for different indices (Richard 1995; Wilcox 1955; Eaton 1950) (Table 6). Therefore, it is decision makers or scientific community who should advocate the indices local farmers should consider for the suitability analysis calculation for their groundwater samples, actually depending on the quality and quantity of alternate resources available. The

classification is helpful in understanding the criteria for quality of different types of irrigation water. From Na % indicates calculated as shown by Eq. 3, all the groundwater falls in good-to-excellent category for irrigation. The higher concentration of sodium in irrigation water displaces the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions and tends to be absorbed by clay particles. This exchange process of  $\text{Na}^+$  in water for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the soil decreases the permeability and results in soil with poor internal drainage.

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}} \tag{2}$$

$$\% \text{Na} = \frac{(\text{Na}^+ + \text{K}^+) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \tag{3}$$

Groundwater chemistry and its effect on soil permeability can be well reflected by permeability index calculated by Eq. 4. In general, the soil permeability is affected by long-term irrigation from water chemistry dominated by  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  contents and permeability index (PI) values indicate the suitability of groundwater for irrigation purposes. The PI ranged from 10.46 to 38.44% with the

**Table 4** Evaluation of the suitability of groundwater samples for irrigation based on the guidelines. Guidelines adapted from Ayers and Westcott (1985), Pettygrove and Asano (1985) and Metcalf and Eddy (2003)

Potential irrigation problem	Degree of restriction on use			% of sample		
	None (N)	Slight to moderate (S–M)	Severe (S)	N	S–M	S
Salinity (affects crop water availability)						
EC ( $\mu\text{S}/\text{cm}$ )	< 700	700–3000	> 3000	NIL	60	40
TDS (mg/L)	< 450	450–2000	> 2000	NIL	30	70
Permeability (affects infiltration rate of water into the soil)						
SAR = 0–3	EC > 700	700–200	< 200	NIL	NIL	NIL
3–6	1200	1200–300	< 300	25	NIL	NIL
6–12	1900	1900–500	< 500	60	15	NIL
12–20	2900	2900–1300	< 1300	NIL	NIL	NIL
Specific ion toxicity (affects sensitive crop)						
(Sodium) $\text{Na}^+$						
Surface irrigation	SAR < 3	3–9	> 9	NIL	85	15
Sprinkler irrigation (mg/L)	< 70	> 70	–	10	90	–
$\text{Cl}^-$ (mg/L)						
Surface irrigation	< 140	140–350	> 350	15	15	70
Sprinkler irrigation	< 100	> 100	–	NIL	100	–
Miscellaneous effects (affect susceptible crops)						
Overhead sprinkling only						
$\text{HCO}_3^-$ (mg/L)	< 90	90–500	> 500	NIL	100	NIL

Figures are in percentage of samples in the particular categories of degree of problem and evaluated using EC and SAR of the groundwater

average value of 18.41% (Table 6). Based on WHO criterion for assessing the suitability of water for irrigation based on the permeability index (WHO 2004), the permeability index values for 80% of the groundwater samples fall under class I (PI in range of 1–24%) and 20% of the samples fall under class II category (PI ranged in 25–75%).

$$\text{PI} = \frac{(\text{Na}^+ + \sqrt{\text{HCO}_3^-}) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \quad (4)$$

It is significant to understand the groundwater chemical composition changes with its movement in aquifer environment. The chloro-alkaline indices also known as index of

base exchange (calculate by Eqs. 5 and 6) and denoted by chloro-alkaline index 1 (CAI 1) and chloro-alkaline index 2 (CAI 2) Schoeller (1977) signify the ion exchange between the groundwater and the aquifer minerals/rock environment. The ion exchange of  $\text{Na}^+$  and  $\text{K}^+$  from water with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the aquifer matrix means that the exchange is direct and the indices are positive, and the exchange is indirect and indices are negative if it happens in reverse order. It has been observed that 90% of the samples show positive ratios and only 10% of the samples show negative ratios. Magnesium ratio is another way to estimate groundwater suitability for irrigation. In most of the groundwater samples, the calcium and magnesium maintain a state of equilibrium with aquatic environment. The more amount of  $\text{Mg}^{2+}$  in the water adversely affects the soil quality and results in decreased crop yields. The results found that all samples have magnesium ratio more than 50%. The magnesium deteriorates soil structure, particularly when waters are sodium dominated and highly saline. The Mg/Ca ratio can classify suitability of water for irrigation purposes, and analysis results evaluated that 20% of the groundwater samples fall in the safe category and 80% fall in the moderate category. This indicates the high suitability of groundwater for irrigation purposes (Table 6).

$$\text{Chloro alkaline index 1} = (\text{Cl} - (\text{Na} + \text{K}))/\text{Cl} \quad (5)$$

**Table 5** Statistical summaries of chemical data of groundwater samples, Surat

Parameter	Unit	Average	Minimum	Maximum	SD
SAR		6.90	4.75	11.86	1.78
% Na	%	13.76	8.25	29.33	5.83
PI	%	18.42	10.47	38.45	8.27
Mg/Ca		1.85	1.22	2.36	0.39
Mg ratio		64.28	54.97	70.21	5.04
CAI-1		0.60	–1.04	0.81	0.42
CAI-2		1.07	–0.23	2.33	0.64

**Table 6** Suitability of groundwater for irrigation based on several classifications

Parameter	Water class	% of sample
EC ( $\mu\text{S}/\text{cm}$ )		
< 250	Excellent	NIL
250–750	Good	NIL
750–2000	Permissible	NIL
2000–3000	Doubtful	20
> 3000	Unsuitable	80
Based on alkalinity hazard (SAR) after Richards (1954)		
< 10	Excellent	100
10–18	Good	NIL
18–26	Doubtful	NIL
> 26	Unsuitable	NIL
Based on percent sodium after Wilcox (1955)		
< 20	Excellent	85
20–40	Good	15
40–60	Permissible	NIL
60–80	Doubtful	NIL
> 80	Unsafe	NIL
% Na (Eaton 1950)		
> 60	Safe	100
< 60	Unsafe	NIL
Based on residual Mg/Ca ratio		
< 1.5	Safe	20
1.5–3	Moderate	80
> 3	Unsafe	NIL

$$\text{Chloro alkaline index } 2 = \frac{(\text{Cl} - (\text{Na} + \text{K}))}{(\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3)} \quad (6)$$

### Groundwater hydrochemical facies

Plotting the concentrations of major cations and anions in trilinear diagram, suggested by Piper (1944), is helpful in analyzing the geochemical evolution of groundwater. Here Piper diagram was made using Aquachem software and is shown in Fig. 6. It is found that 80% of the groundwater samples are in the category of Mg–Cl type of water, which indicates the water affected by carbonate hardness and salinity and 10% of the samples fall in Mg–HCO<sub>3</sub>, i.e., freshwater or water originated from environment with minimum anthropogenic interferences. Whereas rest 10% of the water samples show the migration from freshwater system to saline water indicating high pressure from different drivers to deteriorate the water quality.

In Fig. 7, the major ion plotted in showed that the lateral distribution of select ions and the milliequivalent concentration of ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) range between 0.5 and 30 meq/L. Generally, water with high

Mg content also has high Cl content. The high Mg is of two types, one with Cl in the range 1.8–21 meq/L, known as Mg–Cl, and another with HCO<sub>3</sub> in the range of 2–7 meq/L, known as Mg–HCO<sub>3</sub>. The results evaluated that in the study region the salinization and mineralization phenomena are active (Fig. 8). Durov plot is analyzed that all samples have a high TDS with Mg as dominant cation and Cl as a dominant anion in groundwater of the study area.

### Origin of groundwater mineralization

Table 7 shows the degree of dependency and relationship between two variables using correlation coefficient. In the study, Spearman rank coefficient is used to understand the relationship between various elements, based on the ranking of the data and not absolute values. The correlation matrix prepared for the analyzed ions of the samples shows the absolute correlation between EC and TDS. Strong correlation also exists ( $r=0.91$ – $0.99$ ) among TDS, EC, TH, Cl<sup>-</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> which indicate that TDS and EC are mainly due to the presence of TH, Cl<sup>-</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. The results found that Cl<sup>-</sup> is significantly correlated with Ca<sup>2+</sup> and Mg<sup>2+</sup>, indicating the presence of chloride salts of Ca<sup>2+</sup> and Mg<sup>2+</sup>. On the other hand, SO<sub>4</sub><sup>2-</sup> is moderately correlated ( $r=0.61$ ) with Na, indicating the presence of Na–SO<sub>4</sub><sup>2-</sup> salt. TH showed a high degree of positive correlation with Mg<sup>2+</sup> ( $r=0.98$ ). Cl<sup>-</sup> was moderately correlated ( $r=0.57$  and  $0.55$ ) with Na<sup>+</sup> and K<sup>+</sup>, respectively, indicating the occurrence of Na–Cl and K–Cl, possibility due to salt intrusion. The cursory examination of the data reveals that the majority of the samples are dominated by Mg<sup>2+</sup> hardness in comparison with Ca<sup>2+</sup> hardness, and the strong correlation ( $r=0.93$ ) between Cl<sup>-</sup> and Mg<sup>2+</sup> showed salinity intrusion, anthropogenic activities and mineral dissolution.

To better be under groundwater geochemical evolution, saturation index (SI) of six potential minerals, namely CO<sub>2</sub> (g), halite, dolomite, calcite, siderite and anhydrite, is calculated using Eq. 1. The calculated result is shown in Fig. 9, where it is found that most of the water samples are showing positive value of SI with respect to calcite, dolomite and anhydrite while negative values for the minerals CO<sub>2</sub> (g), siderite and halite. Getting an in-depth sight in these values, it can be suggested that majority of the water samples suggest their oversaturation with respect to this mineral which mainly has a geological origin derived from the abundant carbonate weathering in the plain area. Here, saturation with calcite along with undersaturation with respect to CO<sub>2</sub> (g) suggests the origin of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> for these water samples, well described by Appelo and Postma (2005) as shown in Eqs. 7 and 8. Although SI value for the siderite mineral is negative for all the samples, the value is approaching zero which indicates the high concentration of iron in water samples.

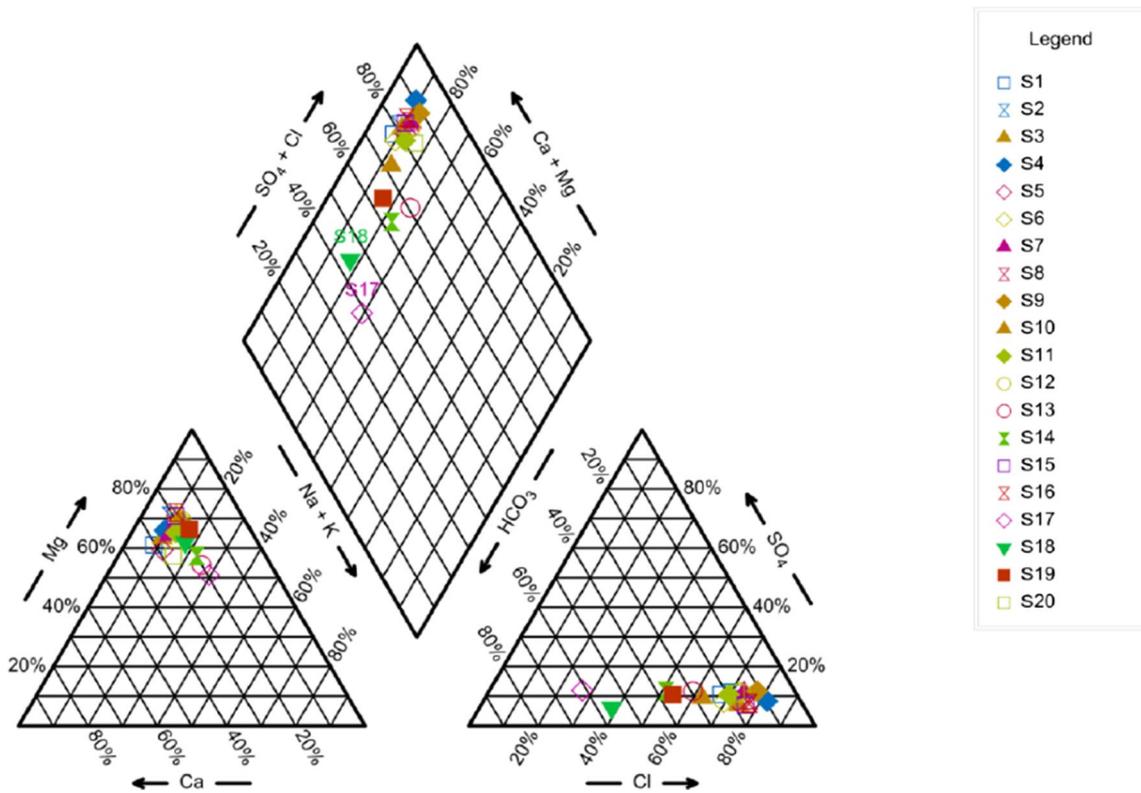
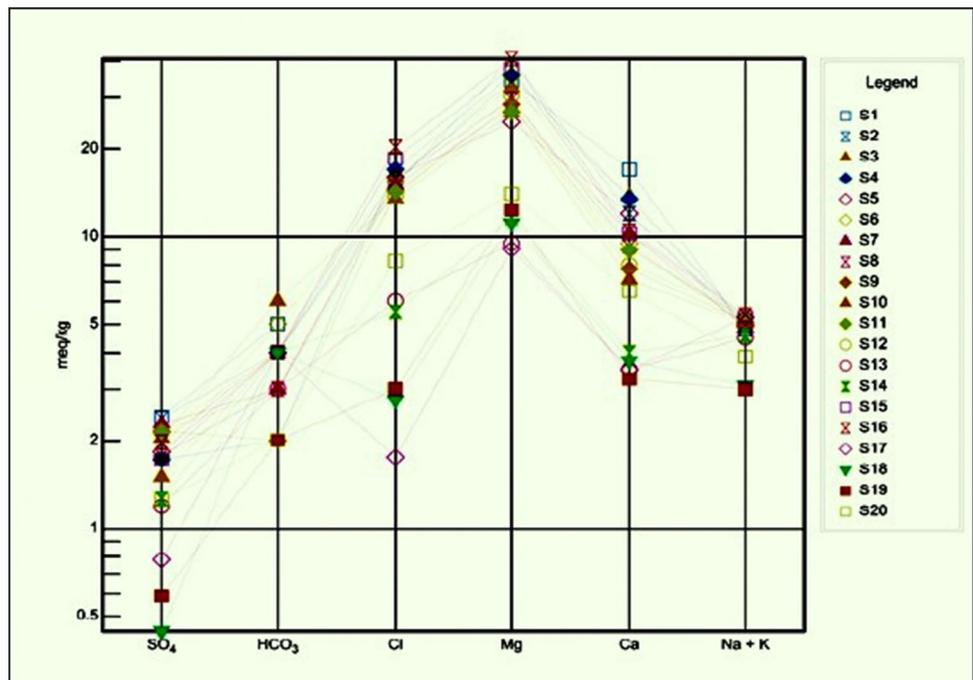


Fig. 6 Piper diagram showing groundwater quality for the study area

Fig. 7 Schoeller diagram of groundwater chemistry of the study area



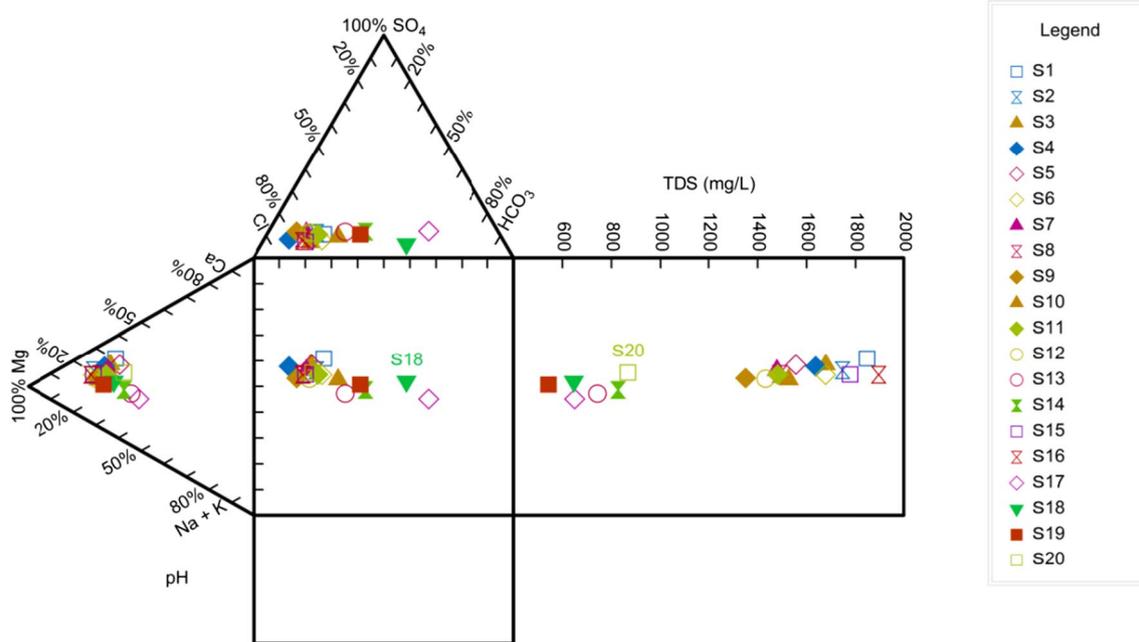
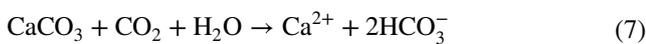


Fig. 8 Durov plot for groundwater parameters of the study area



### Assessment of temporal variation of groundwater quality

Assessment of temporal variation of groundwater quality is performed to analyze the changes in groundwater quality from 2004 to 2013, against the average concentration of EC, TDS, TH and chloride (Fig. 10). Figure 10 represents chorological tendency and indicated that the concentration of chemical constituents in groundwater is continuously increasing due to anthropogenic activities as well as mineral dissolution. On the other hand, subtraction of groundwater in an unprecedented rate over the past few years may have also affected these changes.

### Conclusion and recommendation

The study presented the geochemical analysis of the groundwater using statistical approach and estimated the potential quality of the groundwater resources in the Western Indian city of Surat. In order to classify the suitability of groundwater usages, the water quality data were validated with the existing trends and the evaluated through best-fitted models. The results are substantial to conclude that

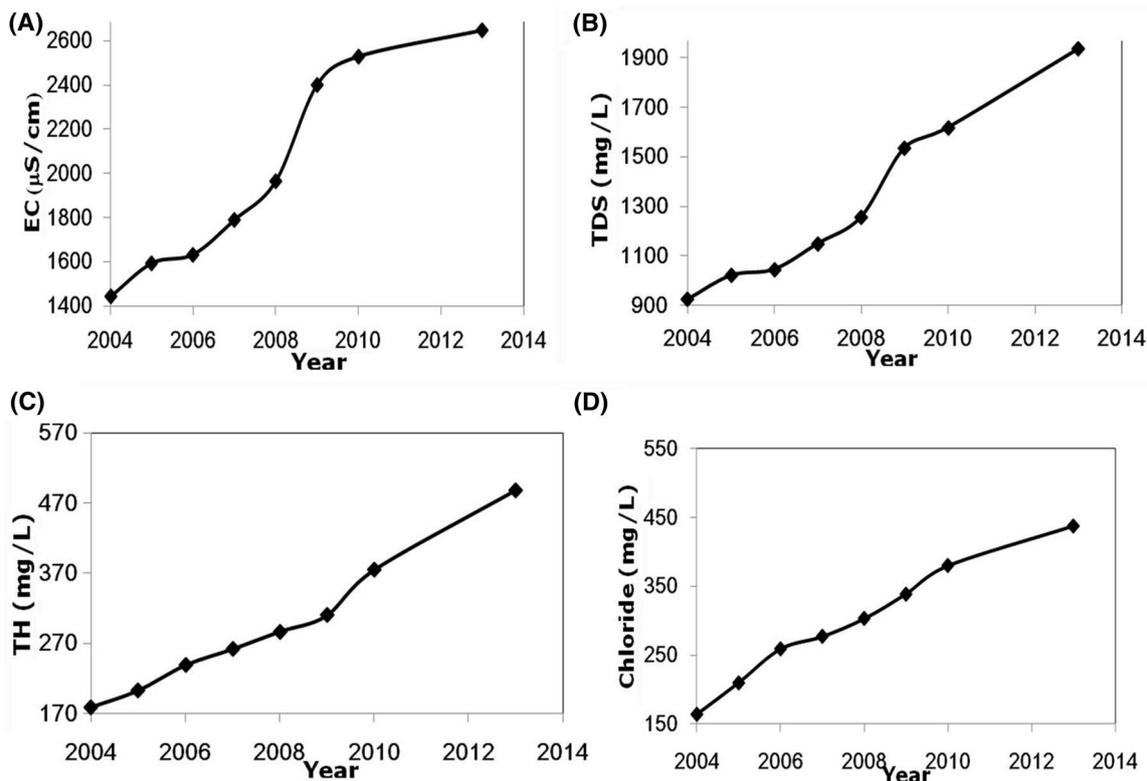
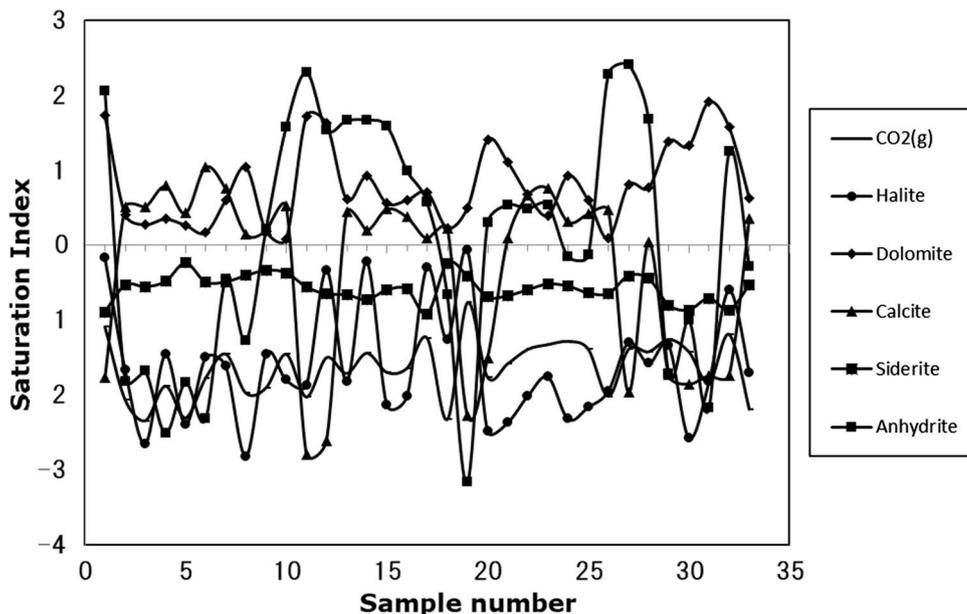
the groundwater in the city is not of drinkable/potable quality, and it is not recommended to consume it without proper treatment. However, the water quality fits well within categories of irrigation usages. The results found that the sequence of the abundance of the major anions and cations is in the order of  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{2-} > \text{NO}_3^-$  and  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Fe}^{2+} > \text{Cr}^{2+}$ . Among these anions, the high  $\text{Cl}^-$  content indicates the possible saline water instruction as well as pollution from anthropogenic sources. The higher  $\text{Mg}^{2+}$  content in comparison with  $\text{Ca}^{2+}$  suggested that the carbonate weathering also affects the groundwater in the study area. To perform the geochemical evaluation of groundwater quality, samples are divided into different water types and result from Piper diagram showed that the water could be classified into two distinct facies, viz.  $\text{Mg}-\text{Cl}$  and  $\text{Mg}-\text{HCO}_3$ . The results obtained from the correlation analysis further revealed that the majority of the groundwater samples are dominated by  $\text{Mg}^{2+}$  hardness in comparison with  $\text{Ca}^{2+}$  hardness and exhibited strong correlation ( $r=0.93$ ) between  $\text{Cl}$  and  $\text{Mg}$  showed the coastal saline water inflow and ion exchange. The results also outlined high concentration of total hardness (TH), chloride and TDS, and consumption of groundwater with proper treatment may cause severe health hazard in near future. Thus, there is an urgent need for water treatment if groundwater is continued as the primary source of drinking water. Thus, to achieve water security in the existing institutional framework, treatment facilities such as reverse osmosis, water softening, ion exchange and distillation need to be constructed. Nonetheless, SAR-based classification of irrigation water indicated

**Table 7** Correlation matrix of chemical constituents of groundwater (Spearman rank coefficient)

	pH	EC	TDS	Acidity	Alkalinity	TH	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Fe <sup>2+</sup>	Cr	
pH	1																	
EC	-0.54	1																
TDS	-0.54	<b>0.98</b>	1															
Acidity	0.06	-0.11	-0.12	1														
Alkalinity	-0.09	0.22	0.23	-0.68	1													
TH	-0.67	<b>0.82</b>	<b>0.85</b>	-0.21	0.23	1												
Ca <sup>2+</sup>	-0.71	<b>0.68</b>	<b>0.65</b>	-0.28	0.22	<b>0.93</b>	1											
Mg <sup>2+</sup>	-0.60	<b>0.85</b>	<b>0.87</b>	-0.16	0.23	<b>0.98</b>	<b>0.82</b>	1										
K <sup>+</sup>	-0.24	0.46	0.47	-0.22	0.21	<b>0.76</b>	<b>0.77</b>	<b>0.70</b>	1									
Na <sup>+</sup>	-0.15	0.65	0.63	0.12	0.26	0.40	0.28	0.44	0.12	1								
HCO <sub>3</sub> <sup>-</sup>	-0.09	0.22	0.24	-0.68	<b>0.98</b>	0.23	0.22	0.23	0.21	0.26	1							
Cl <sup>-</sup>	-0.70	<b>0.90</b>	<b>0.92</b>	-0.07	0.18	<b>0.93</b>	<b>0.83</b>	<b>0.93</b>	<b>0.55</b>	<b>0.57</b>	0.18	1						
SO <sub>4</sub> <sup>2-</sup>	-0.55	<b>0.92</b>	<b>0.89</b>	-0.14	0.23	<b>0.79</b>	<b>0.72</b>	<b>0.78</b>	0.45	<b>0.61</b>	0.23	<b>0.82</b>	1					
NO <sub>3</sub> <sup>-</sup>	0.40	-0.65	-0.67	0.37	-0.27	-0.71	-0.61	-0.72	-0.44	-0.28	-0.27	-0.67	-0.60	1				
PO <sub>4</sub> <sup>3-</sup>	-0.37	0.23	0.25	-0.32	0.25	<b>0.57</b>	<b>0.76</b>	0.43	<b>0.77</b>	-0.14	0.25	0.33	0.35	-0.34	1			
Fe <sup>2+</sup>	-0.13	0.22	0.22	0.22	-0.11	0.23	0.30	0.18	0.40	-0.03	-0.11	0.11	0.28	-0.10	0.48	1		
Cr	-0.13	0.04	0.07	-0.03	0.27	0.14	0.09	0.16	0.11	0.10	0.27	0.12	0.21	-0.03	-0.06	-0.01	1	

Bold number shows statistically significant correlation

**Fig. 9** Summary for saturation indexes for six selected minerals for the water samples



**Fig. 10** Temporal variation graphs between average groundwater data parameters and time **a** temporal variation of year and EC, **b** temporal variation of year and TDS, **c** temporal variation of year and TH and **d** temporal variation of year and chloride

that all groundwater samples belong to excellent category and the results were confirmed with the Wilcox diagram. Sodium percentage and total concentration also showed that the samples fall in excellent category for irrigation usage. In addition, based on the PI values, the groundwater quality

of Surat city is designated to class I (> 25%) and class II (25–75%), which reaffirms the sustainability of groundwater for irrigation purposes. In sum, this study will definitely help the local decision makers to take appropriate actions in timely manner for its sustainable management in Surat city.

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