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 the main agenda of the UN-Sustainable Development Goals by the year 2030. To achieve the goal of water secure future in rapidly urbanizing cities, the sustainable water supplies are necessary. In the western part of India, the city of Surat is continuously growing and rapidly urbanized, which exerting massive pressure on groundwater water supply to meet increasing water demands. The study adopted the investigative approach, in which a total 33 groundwater samples were collected in and around the city from open, bore and dug wells and hand pumps. The selection of sampling sites was based on the land use signature, areas with a different depth of aquifers and different geological formations. 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, $Cl-$, pH, SO_4^{2-}, and NO_3- concentrations. An interpolation technique, known as ordinary kriging, was used to acquire the spatial distribution of parameters of groundwater quality parameters. The result showed that the groundwater quality falls under class I (>25%) and class II (25 to75%) category. The study recommends that the groundwater in the study area is not suitable for potable purposes, especially without any improved onsite water treatment facilities but it is appropriate for the irrigation purposes in City.

Keywords: Water Security, Water for all, Groundwater assessment, Groundwater quality, Water scarcity.

1. Introduction

On the earth, more than 96.5% of water is salt water stored in the form of the oceans and only 2.5% of freshwater is available for the human survival. In which the groundwater makes up 30.1% of the available freshwater, which is approximately 0.61% of the entire world water (Gleick, 2000; Tanvir, 2008). It is estimated that the total available groundwater is equal to the total fresh water available and stored in the form of ice and snow. This shows the importance of groundwater and relevance as

natural storage that can buffer against shortages of surface water (Hassan, 2008). According to the United States geological survey states that there are about 4.2 million cubic kilometers of water within 0.8 kilometers of the planet's surface (Hinrichsen and Tacio, 2002). Every year due to the hydrological cycle, more than 500 thousand cubic kilometres of renewable freshwater shifts from oceans to the land through rain/snow but only 10% of which can be considered accessible for human use (Gleick, 2000). There is a strong linkage between freshwater and population, which is explained in figure 1, the increase in population is directly proportional to the water demand (Vörösmarty et al., 2000). The factors responsible for water quality crisis and water scarcity, are constantly increasing water demands, population explosion, changes in land use, groundwater mining, pollution, deteriorating water quality and pollution from diffuse and local sources (Saraswat et al., 2016). Generally, both surface water and groundwater provide potable water, as long as it is treated sufficiently (Miller, 2006; Bauder et al., 2011). Groundwater is preferred over surface water because of its reliability during droughts or dry season, while surface water sources can deplete quickly. Also, as groundwater is less polluted, it is easier and cheaper to treat it in comparison with surface water. In present most of the people around the are sustaining on groundwater.
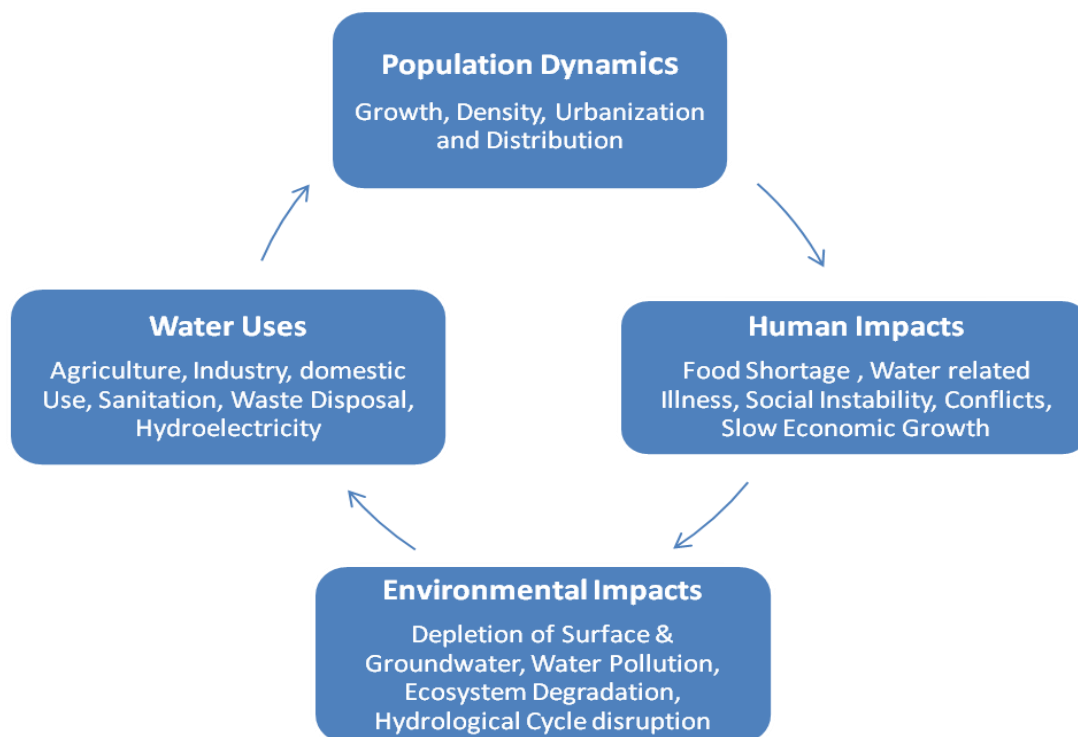

Figure 1: Dynamics of population, human health and freshwater impacts (Adapted from Gleick, 1993)

The groundwater usage is popular in comparison of surface water because of its wide availability and good quality, which can be adequately used for potable water supplies with very less or almost without treatment facilities. In India, around 80% of rural population and more than 50% of the urban population are directly dependent on groundwater for the domestic purpose (Biswas et al.,

2014). The possible uses of water are dependent on the trace elements available or found in groundwater. The hydrogeochemical process, which is taking place in aquifer system is responsible for the concentration of dissolved ions in groundwater (Mukherjee et al., 2015). To demonstrate the mechanism of groundwater evolution in any aquifer system, generally, the ionic ratios are used. Therefore, it is very important to analyze the hydrogeochemical characteristics of the aquifer in different seasons to understand the groundwater quality changes (Uddin et al., 2011). To study the groundwater quality changes various graphical methods and interpreting different indices are used (Srivastava and Ramanathan, 2008). In the composition, the saturation level of various minerals can give a signal of the vulnerability of the aquifers for future enrichment (Das et al., 2015; Das and Kumar, 2015). Although in major parts of India, the groundwater is drinkable and suitable for potable uses but due to contamination, various reports indicated the impact on human well being (Mahanta et al., 2015; Meliker et al., 2008). The extent of groundwater contamination problem is stern in Bangladesh and the eastern part of India, West Bengal, India (Ahmed et al., 2004; McArthur et al., 2004). After detection of groundwater contamination in various parts of India and Bangladesh, it is estimated that areas in eastern side of country and western Bangladesh, specifically region lie on and near Ganga, Meghna, Brahmaputra plains are at severe risk of groundwater contamination (Mukherjee et al., 2015; Singh et al., 2014; Nickson et al. 2007). The region with an area more than 570,000 square kilometer is home to more than 500 million population

The contamination in potable water is a major source of different kinds of skin problems ranging from hyper pigmentation (Kazi et al., 2009) and impose big health risk in many countries, especially developing countries. The potential impacts of groundwater contamination on human health and well being are severe from increased cancer risks to increased chronic (long-term) and acute (short-term) noncancer health hazards. The groundwater contamination is found in a range of aquifers of unconsolidated sediment to bedrocks but it is analyzed that it is serious in unconsolidated sedimentary aquifers (Kumar et al., 2015; Smedley and Kinniburgh 2002). It is identified that the common mechanism responsible for groundwater contamination is is desorption from Fe-(hydro) oxides and reductive dissolution (Mukherjee et al., 2015; Kim et al. 2012). The degree of equilibrium between water and respective minerals are evaluated by saturation indexes (SI) (Das and Kumar, 2015) and the changes in saturation state help in distinguishing the different stages of hydrogeochemical analysis. The evolution helps to identify the important geochemical reactions leading to arsenic enrichment (Kumar et al., 2016; Coetsiers and Walraevens 2006). There is wide literature available on groundwater contamination in India, such as in the northeastern part of country, in different timeline various attempts are made to evaluate the interrelationship between groundwater quality parameters to understand the probable mechanism of groundwater contamination (Kumar et al., 2016; Mahanta et al., 2015, Radloff et al., 2011). The impact of groundwater contamination is severe on human well-being, it is explained in study by Goswami et al. (2014), the magnitude of human exposure in intermittent locations of Brahmaputra floodplain

and impact on human well-being. The central Brahmaputra floodplain is a populated region and the health risk assessment is of urgent need but there is a huge gap in the literature on studies of hydrogeochemistry and health risk assessments together in the country. This research paper attempts to narrow this gap by tracing the responsible factors for groundwater geochemical evolution by evaluating the interrelationships between the key water quality parameters using multivariate statistical techniques and mineral saturation (usingPhreeqC) in western part of India

2. Study Area

The Surat city is playing a significant role in the upliftment of Indian economy, as the city is one of the most developed commercial city of Western part Gujarat state.The city has contributed more than 40 billion US dollars in the country's GDP. The city is also famous with the title of textile capital of the country and diamond capital of the world. The diamond business and real estate are new emerging businesses in the study area with 92% of the world's diamonds are cut and polished. The other major industries of the study area are steel production, petrochemical and Jari manufacturing (CDP, 2008). The study area is the 8th largest city in India and the 73rd largest urban area of the world. As per the census 2011, Surat city has a population of around 5 million and is expected to grow to 6.4 in the year 2021 and 8.5 million by the year 2031. The city growing at the decadal growth rate of more than 60% and is located on the bank of river Tapi in the southern zone of Gujarat state, India, an estuarian region and only 25 km away from the Arabian sea. The city experiences a tropical climate with a temperature rising above 40°C in summer and in between 12 to 15°C in winters. The city area is 335 sq km and located at 21°15'N latitudes and 72°52'E longitudes and covered by alluvial aquifer of medium to the coarse sandy soil. The elevation varies between 10 to 18 Mt and the infrastructure includes a computerized water distribution and drainage system. The area of Surat city didn't increase significantly from 1688 to 1910, during 1990 to 2004 there was an increase in the area of city, moderately but after that from 2004 to 2013, Surat city area is expanded drastically because of rapid urbanization and industrialization which also indicate that there is demand on resources largely (CDP, 2008).

The study region can be divided into the coastal and alluvial region. In which, the coastal region represents the muddy shoreline with tidal flat stretch cut off by estuaries. The other one, the alluvial region is formed by river Tapi and distinguishes by flood plain of the river Tapi and Mindhola with a thick alluvial cover. The study area is dependent on river Tapi for meeting the water demands but rapid urbanization and industrialization impacted the water quality of the river, resulting in groundwater as an alternative and the main source of potable water in the region (CDP, 2008). During the many summer seasons, the drought and late onset of southwest monsoon already created the situations of water scarcity in the city. Various studies showed the negative impact on water supply and demand under the rapid economic and population growth in the city. For meeting the water demand of the future population of around 8 million people by the year 2020, it is estimated

that minimum of 1200-1500 MLD water is required to cater to rising water needs of the study area. Including water, for domestic use, additional water will be needed for the industrial purpose (Kapshe et al., 2013). This situation puts grave danger on the limited water resources system allocated to cater irrigation and power generation need of the city. With the business as usual scenario, it is imminent that study area will be water scarce in near future and there is huge need to understand the water allocation to manage the future water demands.

3. Methodology

In total 33 groundwater samples were collected from the bore, dug, open wells and hand pumps in the study area. The sampling sites are selected because of their different geological formations, land use signature, and depths of the aquifers. Using Global Positioning System (GPS III, Garmin), the sample coordinates were recorded and on-site measurements of the electrical conductivity (EC), temperature and pH were recorded 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 kind of on-site measurements. Using the thoroughly rinsed polyethylene bottles the groundwater samples were collected from each location and filtered using 0.2μm Millipore membrane filters. The samples collected for major ions analysis were acidified using 1% HNO_3 to stabilize trace metals (pH~2), while samples collected for nitrate were acidified with H_3BO_3. In an ice chest, all the samples were brought to the laboratory and stored at below 4^oC temperature. The samples were analyzed for anion, cations and trace metals. The analysis of the concentration of HCO_3^- was analyzed by acid titration (using Metrohm Multi-Dosimat) while other anions Cl^-, NO_3^-, SO_4^{2-}, F^- and PO_4^{3-} were analyzed by DIONEX ICS-90 ion chromatograph with an error percentage of less than2 %, using duplicates. The trace elements and major cations are evaluated by inductively coupled plasma-mass spectrometry (ICP-MS) with a precision of less than2%, using duplicates. For major ions, analytical precision was checked by the NICB, normalized inorganic charge balance (Kumar et al., 2010; Kumar et al., 2016). This is defined as [(Tz+ - Tz-)/(Tz+ + Tz-)] and signify the fractional difference between total cations and anions. The quality of the data points are supported by observed charge balance, which is better than ±5% and generally this charge imbalance comes in favor of positive charge. In the study area, to understand the origin of groundwater mineralization the saturation index (SI) was calculated. Mineral saturation states with respect to selected minerals were computed as shown by equation (1), put forwarded by Garrels and Christ, 1965,

$$SI = log_{10}(K_{IAP}/K_{SP})$$ Eqn. (1)

Where, SI → Saturation index,

K_{IAP} → Ion activity product of particular solid phase and

K_{SP} → solubility product of the phase.

Based on the value of the SI, the saturation states were identified as oversaturated (precipitation; SI > 0), saturated (equilibrium; SI = 0) and unsaturated (dissolution; SI < 0).

4. Results and Discussion

4.1 Ground Water Chemistry

The statistical summary of the chemical constituents of groundwater from the study area is shown in Table 1. The Table 1, explained the distribution pattern of average values of major cations and anions (mg/L) in groundwater. The results indicated the anionic abundance is in the order of Cl- > HCO3- > SO42- > PO42- > NO3-, the high Cl- content signifies the impact of the coastal environment or local anthropogenic activities in the region. Another side, the results of cationic abundance found in the order of Mg2+ > Ca2+ > Na+ > K+ > Fe > Cr2+, in which the higher content of Mg2+ is higher than Ca2+, which shows the effect of dolomite and limestone weathering. The result found that the HCO3- and Ca2+ content are because of the carbonate weathering.

Table 1: The Statistical summary of groundwater chemical constituents

Parameter	Unit	Average	Minimum	Maximum	SD
pH		7.11	6.70	7.90	0.27
EC	(µS/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
Alkality	(mg/L)	180.00	100.00	300.00	54.77
TH	(mg/L)	489.50	180.00	755.00	200.70
Ca^{2+}	(mg/L)	174.38	65.00	340.00	77.78
Mg^{2+}	(mg/L)	315.13	110.00	495.00	131.77
K^+	(mg/L)	14.21	6.00	29.25	7.77
Na^+	(mg/L)	100.89	64.90	115.38	14.50
Cl^-	(mg/L)	438.69	62.04	1717.85	199.28
HCO_3^-	(mg/L)	219.60	122.00	366.00	66.82
SO_4^{2-}	(mg/L)	80.01	21.25	115.78	28.03
PO_4^{3-}	(mg/L)	3.51	2.09	9.86	2.24
NO_3^-	(mg/L)	0.23	0.09	0.42	0.11
F^-	(mg/L)	BDL	BDL	BDL	BDL

BDL= Below Detectable Limit

Table 1, indicated the pH values of ground water varied between into 6.7-7.9. In the different wells, there is no variation in pH found, which indicates that the groundwater is tapped from aquifers of

single formations. The results indicated that there are 30% of groundwater samples have TDS beyond the limit and all the groundwater samples have EC beyond the limits (Table 2). Table 3, showed the suitability of groundwater for potable/ drinking purposes, analyzed that the 15% of samples fall in the poor category and 85% of the samples fall in the unacceptable category for drinking. Results showed that there is only 15% of samples falls in the category of fresh water and 85% of samples fall in the brackish water category. Total hardness of all samples ranged between 180-755 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. Table 2, analyzed that 30% of groundwater samples fall into the hard category and 70% samples fall in the very hard category. Hardness doesn't mean that it poses a severe threat to health or well-being, in fact, the calcium and magnesium in drinking water ensure the average daily requirements of such these minerals in the diet. But in more quantity, the hard water can cause aesthetic problems and other difficulties. The Chloride is the most important parameter for determining salinization and the 15% of groundwater samples have the chloride beyond the limit, in the sample (S16), the amount of chloride is highest, around 717.85 mg/L. The chloride is actively circulating at relatively shallow depths of ground water, which is derived from rain or nearer to coastlines. The continuous depletion of ground water along the coastal regions often leads to the movement of the saline sea water into fresh water wells spoiling their water quality. Referring to the recommended limit, it is found that all the samples have the amount of sulfate and nitrate under the required limit. Among cations, the range of permissible limit for Ca and Mg hardness prescribed by WHO is 200 mg/l and 150 mg/l, respectively, but in the collected samples it is estimated as, Ca hardness is in the range of 65-340 mg/l, and Mg hardness is in the range of 110-495 mg/l. The 40% and 80% samples have the hardness beyond the permissible limit. The sources of calcium in groundwater is calcite, aragonite and gypsum and the source of is dolomites and mafic minerals in rocks. The solubility of dolomite in water is dependent on the composition. This concludes that the magnesium source is from the carbonate rock (limestone) deposited in the area which changes to dolomite due to the dissolution of calcium.

Table 2: Values for the drinking water with the percentage of samples beyond permissible limit (PL) and the resulting health implications (WHO, 2004)

Sr. No	Parameter	Unit	WHO Standard (1994, 2004)		IS:10500:1991 Standard		% of Sample beyond Limit	Effects
			Desirable Limit (D.L)	Permissible Limit (P.L)	Desirable Limit (D.L)	Permissible Limit (P.L)		
1	P^H	--	7-8.5	9.2	6.5-8.5	No relaxation	0	Bitter taste, Mucous membrane
2	EC	(μS/cm)	500	1400	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^{2+}	(mg/L)	75	200	75	200	40	Scale formation
6	Mg^{2+}	(mg/L)	50	150	30	100	80	Encrustation in water supply structure
7	K^+	(mg/L)	--	200	--	200	0	Interfere with nerve impulse
8	Na^+	(mg/L)	--	200	--	--	0	Scale formation
9	Fe	(mg/L)	--	0.1	--	0.3	100	Promotes bacterial growth
10	Cl^-	(mg/L)	200	600	250	1000	15	Salty taste
11	SO_4^{2-}	(mg/L)	200	400	200	400	0	Laxative effects
12	NO_3^-	(mg/L)	--	45	45	100	0	Methanoglobinemia

Results for sodium and potassium in the samples, found under recommended limit, except a few. The reason for the higher concentration of potassium in groundwater could be fertilizer used for farming and it is penetrated into groundwater. 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, and promotion in iron bacteria.

Table 3: Suitability of Groundwater for drinking Purposes

Parameter	Water Class	% of Sample
TDS		
<300	Excellent	NIL
300–600	Good	NIL
600–900	Fair	NIL
900–1,200	Poor	15
>1,200	Unacceptable	85
Based on total hardness as CaCO3 (mg/l) after Sawyer and Mc Cartly (1967)		
<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
1001-10000	Brackish	85
10001-100000	Salty	NIL
>100000	Brine	NIL

4.2 Hydrogeochemical Evolutionary Processes

The graphical representation of scatter plots for hydrogeochemical evolutionary process are shown in figures 2, 3 and 4. In figure 2(a), the graph of Tz+ versus Na+ + K+ showed that all the sample points are in favor of Tz+, which suggest that sodium and potassium are not dominant in groundwater samples. Another cationic activity is also present rather than sodium and potassium, which also indicated that there will be no agricultural impact on groundwater. The graphical representation of Tz+ versus Ca2+ +Mg2+, in figure 2 (b), showed that all the samples fall near to (1:1) equiline, it means Tz+ concentration due to dominance of Ca2+ +Mg2+ which implies that source of calcium and magnesium are from carbonate weathering and most potential minerals suggested to be calcite and dolomite. In figure 2 (c), the graphical representation of HCO3- versus Ca2+ +Mg2+ showed that the Ca2+ +Mg2+ > HCO3- relation, suggesting that additional Ca2+ +Mg2+ are coming from muscovite, illite, calcium hydroxide (lime) weathering other than that of limestone. In figure 2 (d), the graphical representation of versus HCO3- + SO42- versus Ca2+ + Mg2+, showed that all the sample points are above equiline representing that there is the enrichment

of Ca2+ + Mg2+ over HCO3- + SO42- which implies that the dissolution of calcite is abundant in the sand. It was found that Mg2+ and Ca2+ are first and second dominant ion in all cation concentration, whereas HCO3- is second dominant ion in the total anion. The extent of contamination is further examined by the graph in figure 3(a), HCO3- versus Tz+ plot. The results showed that all the samples points occupy the area above equiline and closer to the y-axis, which confirms that water chemistry of the area is also influenced by a secondary process such as anthropogenic activity. In figure 3(b), the plot represents that the most of the groundwater samples are in a relation of Cl- > Na+, meaning the existence of salinization. The category-I, the abnormal higher value of Cl- can be attributed to the surface sources through the leaching from domestic wastewaters, septic tanks, and animal waste. Category II shows the migration path of change in water quality and while category III, occupies very few samples clearly demonstrate cumulative effect of salt water up-coming because of the high extraction rate supported by slight mixing of fresh water and salt water. In figure 3 (c), the scatter plot between Na+ + K+ and Cl- + SO_4^{2-} that clearly showed that the presence of secondary salinity source in the aquifer system. The main driving factors are degradation of organic matter and sewage. In figure 3 (d), the comparison of the sulfate and calcium contents showed, it was found that all the samples show the relation of Ca2+>SO42- indicate that calcium source of ground water is from calcite, dolomite or silicate minerals like feldspar rather than gypsum.
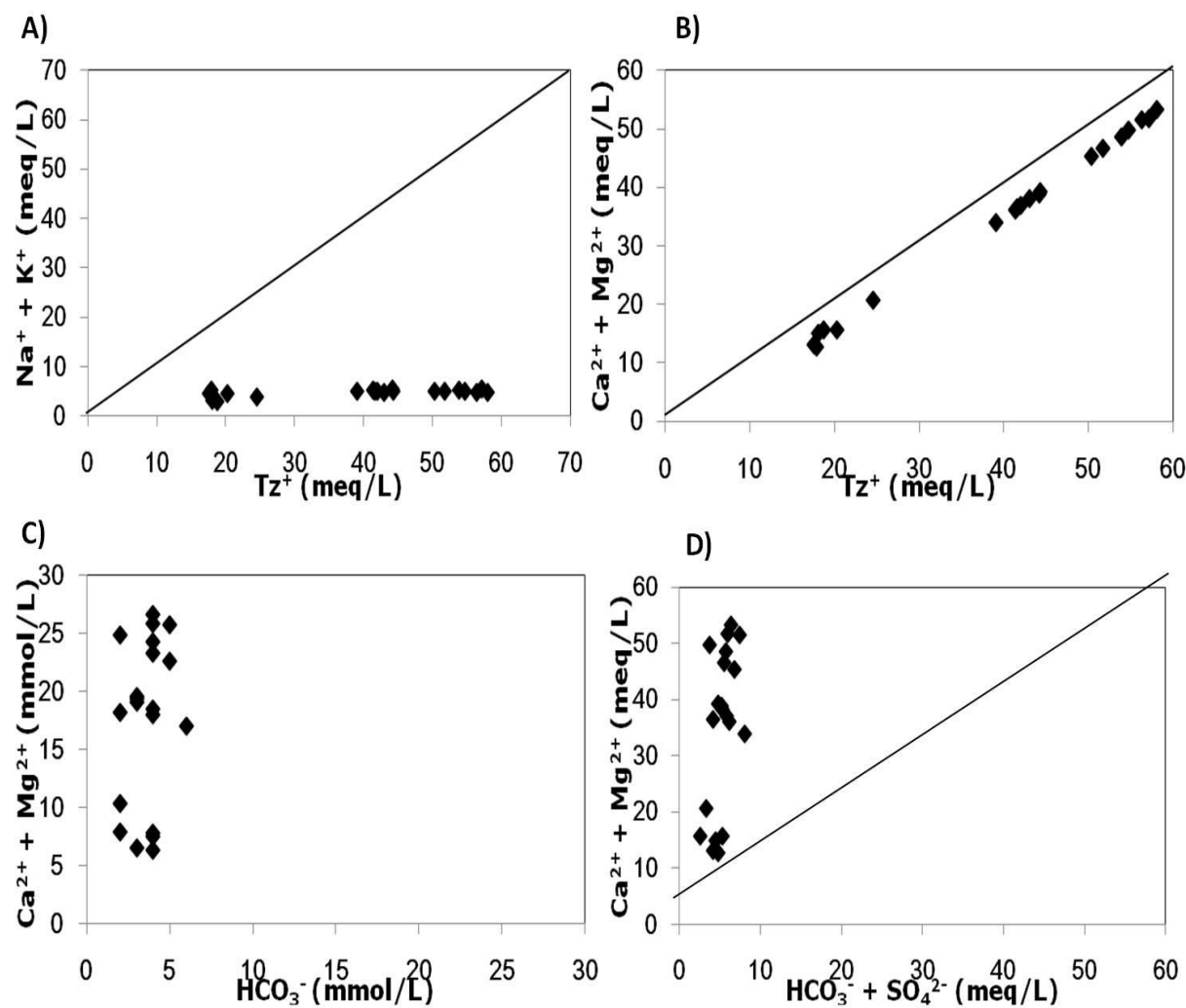
Figure 2: Scatter plot for Hydrogeochemical Evolutionary Process, (A) Scatter plot between Tz^+ and $Na^+ + K^+$, (B) Scatter plot between Tz^+ and $Ca^{2+} + Mg^{2+}$, (C) Scatter plot between HCO_3^- and $Ca^{2+} + Mg^{2+}$, (D) Scatter plot between $Ca^{2+} + Mg^{2+}$ and $HCO_3^- + SO_4^{2-}$
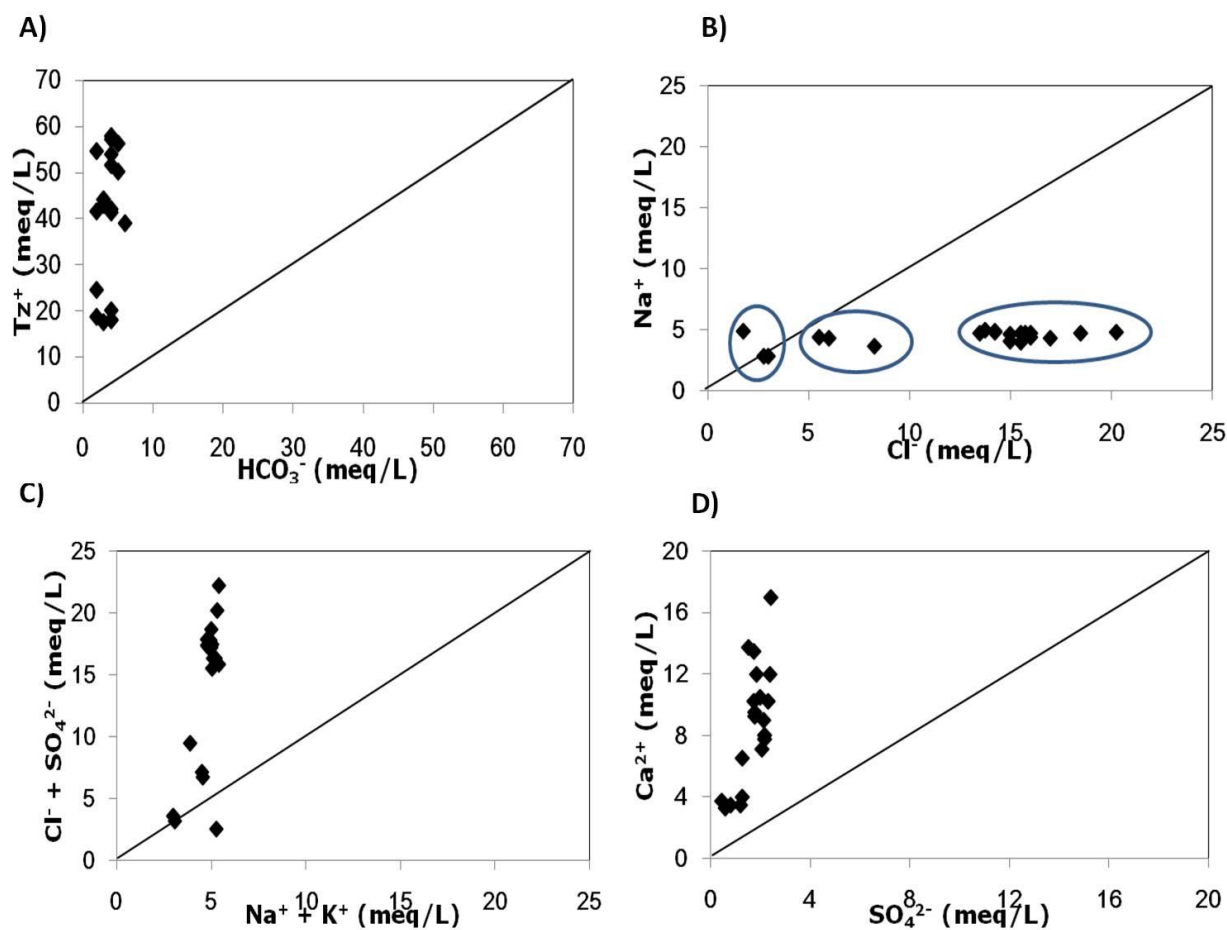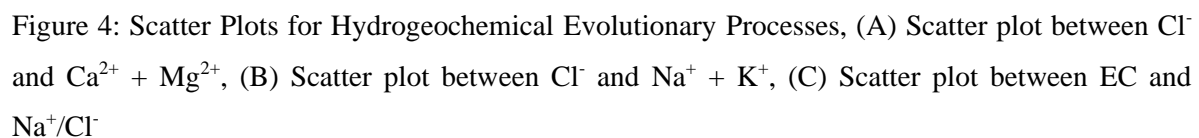
Figure 3: Scatter Plots for Hydrogeochemical Evolutionary Processes, (A) Scatter plot between HCO_3^- and Tz^+, **(B)** Scatter plot between Cl^- and Na^+, **(C)** Scatter plot between $Na^+ + K^+$ and $Cl^- + SO_4^{2-}$, **(D)** Scatter plot between SO_4^{2-} and Ca^{2+}

In figure 4 (a), the plot of Cl- versus Ca2+ + Mg2+ (mmol/L) indicates the Ca and Mg increased with salinity, which could be indication of absence of greater anionic exchange through natural inert resin like clay and weathered rock and in figure 4 (b), the graphical representation of Cl- versus Na+ + K+, showed that most of the sampling point falls below equiline which indicated that Cl may derive from the human activities, use of fertilizer, road salt, animal wastes and some of the samples falls near to equiline which indicate that coastal environmental effect and few sample fall in intermediate category which indicate that water will be salinized near future. In figure 4 (c), showed, that the molar ratio of Na/Cl for ground water samples for study area generally range in 0.2 to 2.7. As most of the samples have Na/Cl ratio below one which implies it's not solely because of ground water salinization rather than geochemical processes operating at local scale.

Figure 4: Scatter Plots for Hydrogeochemical Evolutionary Processes, (A) Scatter plot between Cl^- and $Ca^{2+} + Mg^{2+}$, (B) Scatter plot between Cl^- and $Na^+ + K^+$, (C) Scatter plot between EC and Na^+/Cl^-

4.3 Assessment Of Groundwater Quality for Irrigation Use

Groundwater is confined to coastal alluvium and its suitability for irrigation is assessed by considering salinity, chlorinity and sodicity apart from other parameters (Mills, 2003; Nishanthiny et al., 2011). In table 4, the water salinity measured with respect to EC, 60% of samples falls in slight to moderate (700-3,000 µS/cm) and 40% samples are in a severe category (>3,000 µS/cm) and The water salinity measured with respect to TDS, 30% of samples fall into slight to moderate (450-2000 mg/L) and 70% samples are in the severe category (>2,000 mg/L).

Table 4: Evaluation of the Suitability of groundwater samples for irrigation (Guidelines adapted from Pettygrove and Asano, 1985; Ayers and Westcot, 1985; 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(μS/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) Na^+						
Surface Irrigation	SAR < 3	3-9	>9	NIL	85	15
Sprinkler irrigation (mg/l)	<70	>70	--	10	90	--
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						
HCO_3^-(mg/l)	<90	90-500	>500	NIL	100	NIL

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

The soil permeability reduces due to the excessive sodium content relative to the calcium and magnesium and thus restrain the supply of water needed for the crops. All the water samples fall in the excellent category, which is good for irrigation on every kind of soils. Based on SAR, the degree of restriction on the use of water for irrigation with respect to EC is shown in Table 4.

 The results showed (Table 6), that no single sample of groundwater is in the permissible, doubtful or unsuitable category. Interestingly, all samples fall in safe water class (classifications by Eaton (1950) and Wilcox (1955)). The classification is helpful in understanding the criteria for quality of different types of irrigation water. The Na % indicates, that the groundwater is excellent to good for irrigation. The higher concentration of sodium in irrigation water displace the Mg2+ and Ca2+ ions and tends to be absorbed by clay particles. This exchange process of Na+ in water for Ca2+ and Mg2+ in the soil decrease the permeability and results in soil with poor internal drainage.

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

The soil permeability is affected by long-term irrigation influenced by Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- contents and permeability index (PI) values indicates the suitability of groundwater for irrigation purposes. The PI ranged from 10.46 to 38.44% with the average value of 18.41% (Table 5). Based on WHO criterion for assessing the suitability of water for irrigation based on the permeability index (WHO, 1993; WHO 2004), the permeability index values for 80% of the groundwater samples fall under class I (PI in range of1 to 24%) and 20% of the sample falls under class II category (PI ranged in 25 to 75%).

Table 6: Suitability of Groundwater for Irrigation

Parameter	Water Class	% of Sample
EC(μS/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

It is significant to understand the groundwater chemical composition changes during the sub-surface travel. The Chloro-alkaline indices CAI 1 and CAI 2 are recommended by Schoeller, 1977), which specifies that the ion exchange between the groundwater and the host environment. The ion exchange of Na^+ and K^+ from water with magnesium and calcium in the rock meaning that the exchange is direct and the indices are positive and otherwise, the exchange is indirect and indices are negative.It has been observed that 80% of samples show positive ratios and only 10% of samples show negative ratios, there is no strong indirect exchange was present. In most of the waters, the calcium and magnesium maintain a state of equilibrium. The more amount of Mg^{2+} in the water adversely affect 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 groundwater samples fall in the safe category and 80% falls in the moderate category. This indicates the high suitability of groundwater for irrigation purposes (Table 6).

4.4 Groundwater Hydrochemical Facies

Plotting the concentrations of major cations and anions in tri linear diagram, suggested by Piper, 1994, the is helpful in analyzing the geochemical evolution of groundwater. Using the "Aquachem software", Piper diagram plotted and Figure 5 showed that the 90% 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 other 10% of the samples fall in Mg-HCO$_3$.
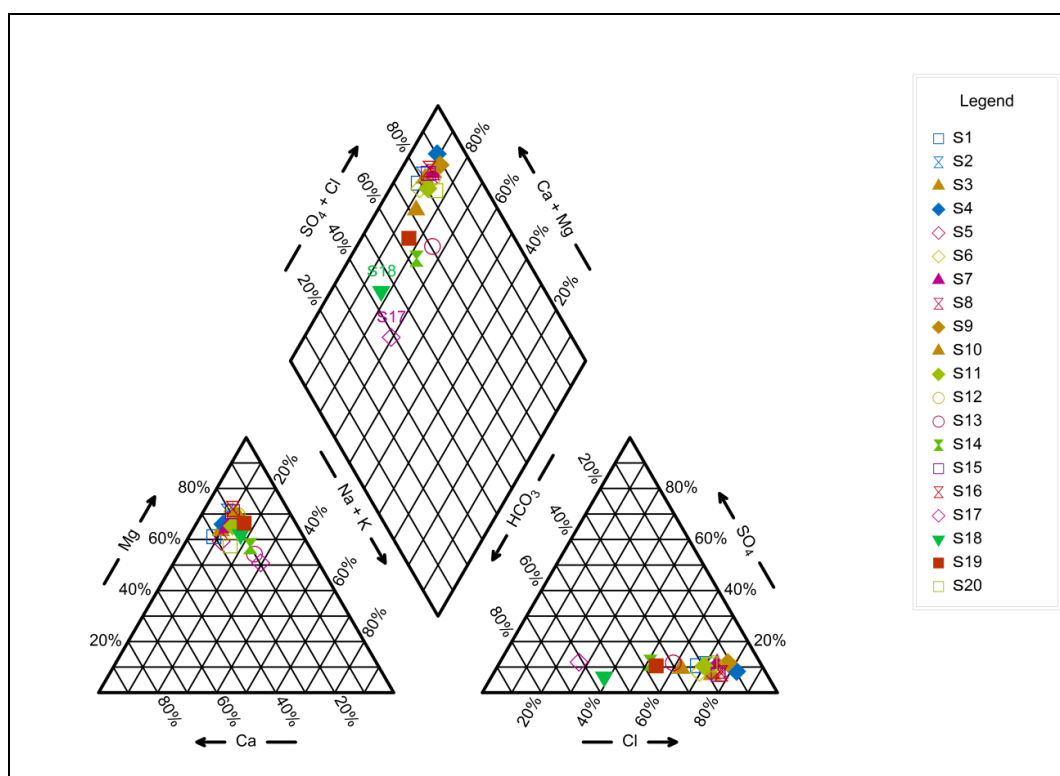
Figure 5: Piper diagram showing ground water quality for the Study Area

In Figure 6, the major ion plotted in showed that the lateral distribution of select ions and the milliequivalent concentration of ions (Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, Na^+, K^+, and HCO_3^-) ranges between 0.5 and 30 meq/L. Generally, water with high Mg content with 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_3 is in the range of 2-7 meq/L, known as Mg- HCO_3. The results evaluated that in the study region the salinization and mineralization phenomena are active and from the (Figure 7) Durov plot it is analyzed that all samples have a high TDS with Mg as dominant cation and Cl as a dominant anion in ground water of the study area.
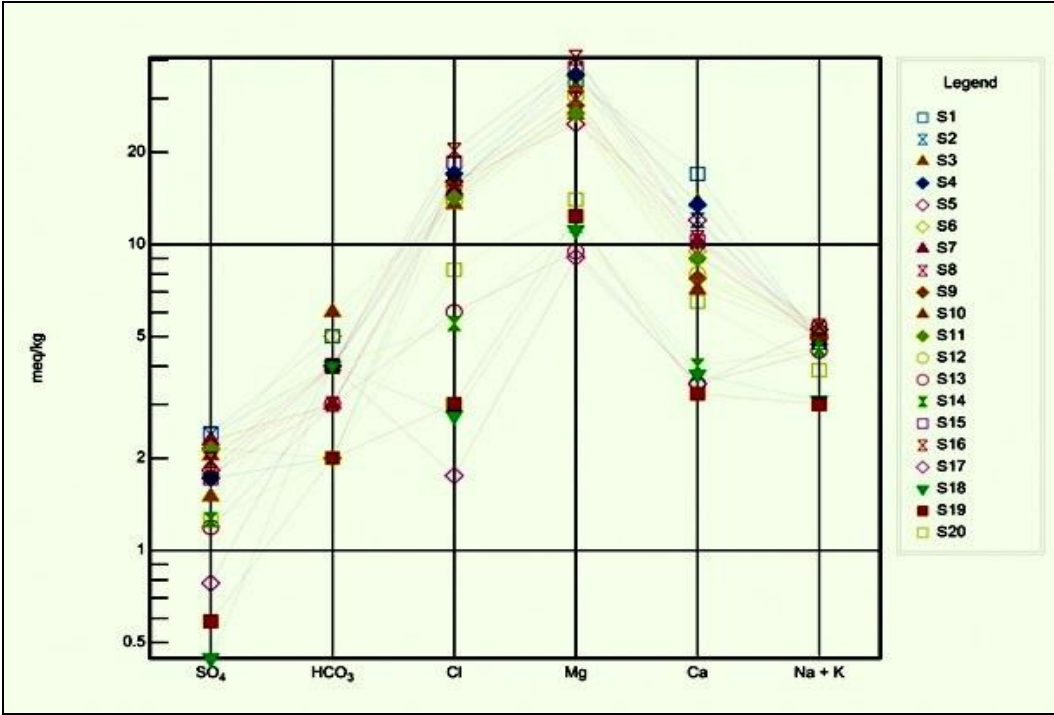
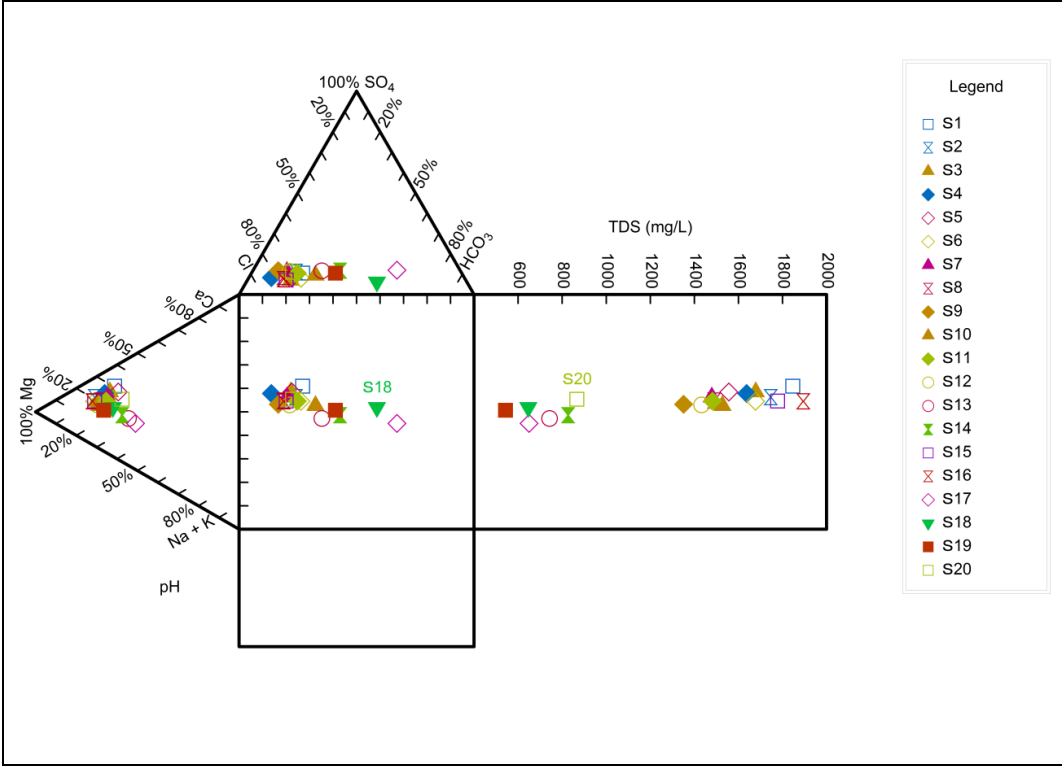Figure 6: Schoeller Diagram of Groundwater Chemistry of the Study Area

Figure 7: Durov Plot for Groundwater Parameters of the Study Area

Table 7, showed 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 show the absolute correlation among EC and TDS. A

good correlation (r = 0.91-0.99) among TDS, EC, TH, Cl, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- which indicate that TDS and EC mainly due to the presence of TH, Cl, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^-. The results found that Cl is significantly correlated with Ca^{2+} and Mg^{2+}, indicating the presence of chloride salts of Ca^{2+} and Mg^{2+} and SO_4^{2-} is moderately correlated (r = 0.61) with Na, evaluating the presence of Na–SO_4^{2-} salt. TH showed a high degree of positive correlation with Mg^{2+} (r = 0.98). Cl was moderately correlated (r = 0.57 and 55) with Na and K respectively, indicating salt of Na-Cl and K-Cl is present due to coastal environmental effect. The cursory examination of the data reveals that the majority of the samples are dominated by Mg^{2+} hardness in comparison of Ca^{2+} hardness and the strong correlation (r = 0.93) between Cl and Mg showed coastal saline water inflow along with anthropogenic activities and mineral dissolution in the study area.

1. **Table 7: Correlation matrix of chemical constituents of ground water (Spearman rank coefficient)**

	pH	EC	TDS	Acidity	Alkality	TH	Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	PO$_4^{3-}$	Fe
EC	-0.54															
TDS	-0.54	**0.98**														
Acidity	0.06	-0.11	-0.12													
Alkalinity	-0.09	0.22	0.23	-0.68												
TH	-0.67	**0.82**	**0.85**	-0.21	0.23											
Ca^{2+}	-0.71	**0.68**	**0.65**	-0.28	0.22	**0.93**										
Mg^{2+}	-0.60	**0.85**	**0.87**	-0.16	0.23	**0.98**	**0.82**									
K$^+$	-0.24	0.46	0.47	-0.22	0.21	**0.76**	**0.77**	**0.70**								
Na$^+$	-0.15	0.65	0.63	0.12	0.26	0.40	0.28	0.44	0.12							
HCO$_3^-$	-0.09	0.22	0.24	-0.68	**0.98**	0.23	0.22	0.23	0.21	0.26						
Cl$^-$	-0.70	**0.90**	**0.92**	-0.07	0.18	**0.93**	**0.83**	**0.93**	**0.55**	**0.57**	0.18					
SO$_4^{2-}$	-0.55	**0.92**	**0.89**	-0.14	0.23	**0.79**	**0.72**	**0.78**	0.45	**0.61**	0.23	**0.82**				
NO$_3^-$	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			
PO$_4^{3-}$	-0.37	0.23	0.25	-0.32	0.25	**0.57**	**0.76**	0.43	**0.77**	-0.14	0.25	0.33	0.35	-0.34		
Fe	-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	
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

4.5 Temporal variation assessment of groundwater

In the study area, the temporal variation assessment of groundwater quality is performed to analyze the groundwater quality from 2004 to 2013 and evaluated the concentration behavior of EC, TDS, TH, and Chloride (Table 8)., is represented by scattering with line graph in figure 8.

Table 8: Average Groundwater Data in the Study Area

Average ground water data of Amroli area, Surat (SMC)				
Year	TDS	EC	TH	Chloride
2004	923	1442	179	164
2005	1020	1593	203	210
2006	1045	1632	239	259
2007	1149	1789	262	277
2008	1257	1964	287	303
2009	1536	2404	310	339
2010	1618	2528	375	380
2013	1935	2647	489	438

The evaluation pointed out the concentration of chemical constituents in groundwater is continuously increasing due to anthropogenic activities as well as mineral dissolution. It is important to take appropriate preventive measures to put a check on the drastic decreasing trend of groundwater abstraction rate.
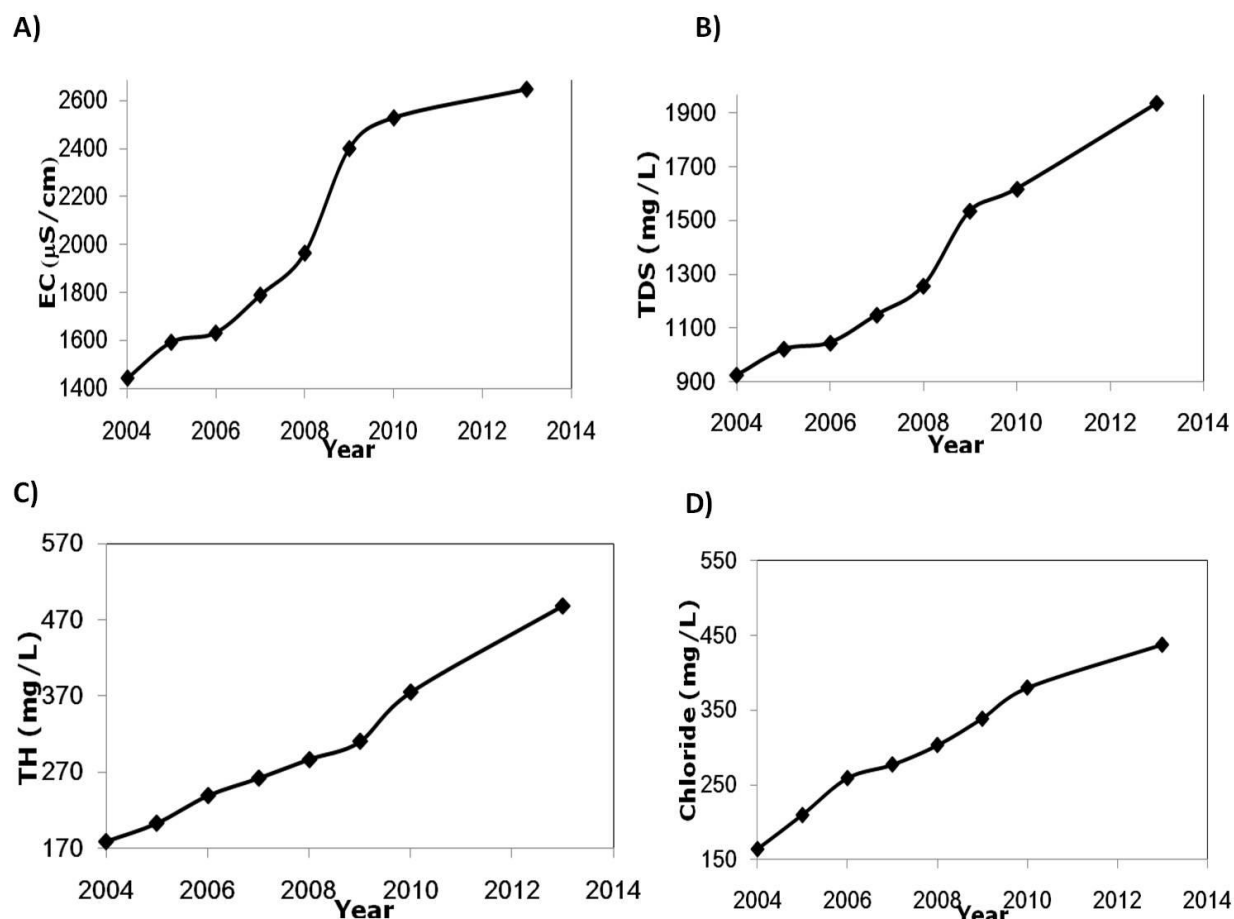
Figure 8: Temporal Variation Graphs between Average Groundwater Data Parameters and time (A) Temporal variation of Year and EC, (B) Temporal variation of Year and TDS, (C) Temporal variation of Year and TH, (D) Temporal variation of Year and Chloride

5. Conclusion and Recommendation

The study presented the geochemical analysis of the groundwater using the statistical approach estimating the potential quality of the groundwater resources in the Western India, Surat city. The water quality data were validated with the existing trends and the evaluation performed based on best-fitted models to classify the suitability of the ground water usages. The results clearly evaluated that the groundwater in the city is not of drinkable/potable quality, without proper treatment but fits well within categories of irrigation usages. The results found the sequence of the abundance of the major ions are in the order of $Cl- > HCO3- > SO42- > PO42- > NO3-$ and $Mg2+ > Ca2+ > Na+ > K+ > Fe > Cr2+$ and among these the high $Cl-$ content indicates the the impact of coastal environment as well as anthropogenic activities on groundwater quality. The higher $Mg2+$ content in comparison of $Ca2+$ suggested that the carbonate weathering also impacting the groundwater in the study area. To perform the geochemical evaluation of ground water quality, samples divided into different water type and result from Piper diagram showed that the water can be classified into two distinct facies viz. Mg-Cl and Mg-HCO3. The results obtained from a statistical analysis, correlation coefficient, revealed that the majority of the groundwater samples are

dominated by Mg2+ hardness in comparison of Ca2+ hardness and strong correlation (r = 0.93) between Cl and Mg showed the coastal saline water inflow and the presence of anthropogenic activities and mineral dissolution impacting the groundwater. The results assess the study region with high concentration of TH (Total Hardness), Chloride, and TDS, and these factors may cause severe health hazard in near future in case of using groundwater for drinking purpose without proper treatment. The study concluded that using groundwater for drinking purposed can cause many health adverse effects such as chronic physiological, so preventive measure such as water treatment should step up the study also presented the evaluation and analysis of the suitability of groundwater for potable and irrigation purposes and found the current groundwater quality is most suitable for the irrigation. SAR based classification of irrigation water indicated that all groundwater samples belong to the excellent category (Manjusree et al., 2009) and the results are confirmed with the Wilcox diagram, for sodium percentage and total concentration also showed the samples fall in excellent category for irrigation usage. Analysis based on the sodium value present in samples highlighted that the water samples belong to the safe category. Also, based on the PI values, the groundwater quality of Surat city is designated to class I (>25%) and class II (25–75%), that reconfirm the analysis of suitability for irrigation. The calculations of chloroalkaline Indices 1 and 2 showed that the 10% of the groundwater sample found negative and 90% found in positive ratios, which analyzed the absence of base-exchange reaction in groundwater.

The study evaluated that the groundwater in Surat city, Western India is not suitable for the potable purposes and cannot be consumed without proper treatment. Based on analysis of major water quality parameters and standards of irrigation waters the research recommends the suitability of groundwater for irrigation purposes in or around the city. Using groundwater for potable purposed will need treatment such as reverse osmosis, water softening, ion exchange and distillation to achieve water security. In the present situation, the suitable use for the groundwater is for agriculture and related sectors. The local planner can plan the right use of groundwater based on current quality parameters to attain sustainable development of Surat City. Also, the presented numerical simulation using hydrochemical data would be very helpful in predicting future mobilization of contamination (especially chloride plume) in the aquifer system.

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