 doi:10.20944/preprints201805.0199.v2

Sustainability Assessment of the Groundwater Quality in the Western India to Achieve Urban Water Security

Chitresh Saraswat[a], Pankaj Kumar[a,b*], Rajarshi DasGupta[b], Prashant Bhalani[c]

[a] United Nations University – Institute for the Advanced Study of Sustainability, 4-53-70, Jingumae, Shibuya, Tokyo 150-8925, Japan,
[b] Natural Resources and Ecosystem Services, Institute for Global Environmental Strategies, Hayama, Kanagawa, Japan;
[c] Institute of Science & Technology for Advanced Studies & Research, Sardar Patel University, Gujarat, India

*Corresponding Author - Pankaj Kumar- kumar@iges.or.jp

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 hydro geochemical characteristics of groundwater and thereby, assess 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, 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, 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. 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 1-24%, 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 outlines the unsustainability of groundwater for direct consumption, especially without any improved onsite water treatment, but it is appropriate for the irrigation purposes.

Keywords: Water Security, Groundwater assessment, Groundwater quality, India

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

1. Introduction

Despite two-thirds of our planet is covered with water, the spectre 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, landuse 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. 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 increasing becoming unsuitable or even dangerous for human consumption (Vörösmarty et al., 2000; Saraswat et al., 2016). 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.

In general, both surface and ground water can be used to meet the demands for potable water, when it is treated sufficiently to meet the prescribed standards (Miller, 2006; Bauder et al., 2011). Nonetheless, traditionally groundwater is preferred over surface water because of its reliability during droughts or dry seasons, 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 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. Goundwater contamination is found in a range of aquifers of unconsolidated sediment to bedrocks (Kumar et al., 2015; Smedley and Kinniburgh 2002). Ground water contamination by trace elements have recently turned-out as a major concern for policy-planners in India and in the sub-continent (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 ground water (Dasgupta & Shaw, 2014; Ahmed et al., 2004; McArthur et al., 2004, Nickson et al. 2007; Mukherjee et al., 2015; Singh et al., 2014). Yet, continued use of hazardous, arsenic bearing groundwater for drinking, cooking and agriculture purposes have led to an unprecedented crisis in the state of West Bengal and Bangladesh, which the World Health

Organization (WHO) described as the *'worst case of mass poisoning in human history'* (Dasgupta & Shaw, 2014). Despite the GBM delta is typically blessed in high-yielding aquifers, the situation underpins the importance of monitoring groindwater quality and integration of water quality in sustainable water supply schemes.

The use of groundwater as a potential and reailale alternative, thus, depends on the concentration of trace elements, which gets dissolved from the aquifer bearing rocks through complex hydro-geochemical 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 hydro-geochemical characteristics of the aquifer in different seasons (Uddin et al., 2011). A variety of methods are presently available to monitor the hydro-geochemincal processes responsible for groundwater contamination. Of which, graphical methods and interpreting different indices have been commonly used (Srivastava and Ramanathan, 2008; Das and Kumar, 2015; Kumar et al., 2016; Coetsiers and Walraevens 2006).

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 classification. 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.

2. 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 commenrical 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^2. The city experiences a tropical climate with a temperature frequently rise above 40°C in summer and falls to about 12-15°C in the winter. On the other hand, the elevation varies between 10 to 18 Mt. With 92% of the world's diamonds are cut and polished here, Surat has contributed more than 40 billion US dollars in the country's GDP and have 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 down-stream industries that support its robust economy (CDP, 2008). With its vibrant economy, the city of Surat expanded unprecedently 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 2020, 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.

3. Methodology

A total of 33 groundwater samples were collected from the bore, dug, open wells and hand pumps in the study area. The sampling sites are selected based on their distinct geological formations, land use charesteristics, and depths of the aquifers. Using a handheld GPS receiver (GPS III, Garmin), precise coordinates of the sample size were recoded, followed by on-site measurements of electrical conductivity (EC), temperature and pH. These parameters were meaured 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 thoroughly rinsed polyethylene bottles, groundwater samples were collected from each location and filtered against 0.2µm Millipore membrane filters. The samples collected for major ions analysis were acidified by 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 transported to the laboratory and stored at below 4^{o}C temperature. The samples were analyzed for anion, cations and trace metals. 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 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; 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 is supported by observed charge balance, which is better than ±5% and generally this imbalance is skewed towards positive charge.

4. Results and discussion

4.1 Groundwater chemistry

The summary of the chemical constituents of groundwater samples are funsihed in Table 1. The results suggested the anionic abundance in the order of Cl^- > HCO_3^- > SO_4^2- > PO_4^{2-} > $NO3^-$, while the high 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 Mg^{2+} > Ca^{2+} > Na^+ > K^+ > Fe^{3+} > Cr^{2+} in which the higher content of Mg^{2+} compared to Ca^{2+} indicates the effect of dolomite and limestone weathering. The result also reveals that relative high concentration of HCO_3^- and Ca^{2+} content which is possibly due of 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
Alkalinity	(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
Fe^{2+}	(mg/L)	0.41	0.32	6.1	0.15
Cr	(µg/L)	137	106	1205	118

*BDL= Below detectable limit

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

Value of pH for all ground water samples were observed between 6.7 to 7.9. Within the samples from different wells, there was no significant variation of pH, which indicates that the samples are from the aquifers of continuous formation. 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 have TDS values beyond the limit, while all the samples showed EC above the prescribed drinking water standards. The concentrations of Cl^- ranges from 62.04 and 1717.85, which reflects its evolution from fresh water to saline water when compared with its desirable limit shown in Table 2. The higher concentrations of 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 highest, 1717.85 mg/L. The chloride is actively circulating at relatively shallow depths of ground water, which is derived from rain or from the saline water intrusion along the coast. In the coastal region, depletion of ground water due to over pumping of groundwater which often leads to the movement of the saline water into the fresh water aquifers, and the results are indicative of such possibilities. Further, it was found that all the samples have the amount of sulfate and nitrate within the prescribed limit. Among cations, permissible limit for Ca and Mg is 200 mg/l and 150 mg/l, respectively according to the WHO standards. The samples showed Ca and Mg concentration in the range of 65-340 mg/l, and 110-495 mg/l respectively, with 40% and 80% samples have 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 were 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.*).

Table 3, showed 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 samples fall in the 'poor category' while 85% of the samples fall in the 'unacceptable category'. Results further showed that only 15% of samples fall in the category of fresh water, while 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. Also in terms of hardness, 30% of groundwater samples fall in the hard water category and 70% samples fall in the very hard category. However, hardness does not poses 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, presence of calcium and magnesium in drinking water with relatively high hardness ensure the fulfillment of average daily requirements of these related minerals. Nevertheless, when in more quantity, hard water can cause aesthetic problems and other physiological difficulties.

Table 2: Comparison of different sampled water quality parameters with desirable and permissible limit given by different organizations and the resulting health implications

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

Table 3: Suitability of Groundwater for drinking Purposes

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

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 Hydro-geochemical evolution

Different scatter plots used to decipher hydrogeochemical evolution processes responsible for determining the water quality 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 inclining towards Tz^+, which suggest that sodium and potassium are not dominant in groundwater samples. Contrarily, another cationic activity is also present rather than sodium and potassium, which also suggested that there was no considerable agricultural impacts on groundwater. Graphical representation of Tz^+ versus Ca^{2+} +$Mg^{2+,}$ in figure 2 (b), showed 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, magnesium are from carbonate weathering, and the potential source minerals is most likely to be calcite and dolomite. In figure 2 (c), 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, which is probably due to weathering of muscovite, illite, calcium hydroxide (lime) other than limestone. In figure 2 (d), 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 towards Ca^{2+} + Mg^{2+} representing that there is enrichment of Ca^{2+} + Mg^{2+} over HCO_3^- + SO_4^{2-} which implies calcite

 doi:10.20944/preprints201805.0199.v2

dissolution is abundant. The extent of contamination is further examined by the graph in figure 3(a), HCO_3^- 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 influenced by a secondary process such as anthropogenic activities. In figure 3(b), the plot represents that 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 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-}, where most of the samples tends to migrate towards Cl^- + SO_4^{2-} clearly indicating the presence of secondary salinity sources. The main driving factors for this secondary salinity are degradation of organic matter and untreated sewage. From scatter plot between Ca^{2+} and SO_4^{2-} (figure 3 (d)), most of the samples tends to move towards the Ca^{2+}, indicating that Ca^{2+} also originated from different minerals like calcite, dolomite or silicate minerals like feldspar, other than that of gypsum.

 doi:10.20944/preprints201805.0199.v2

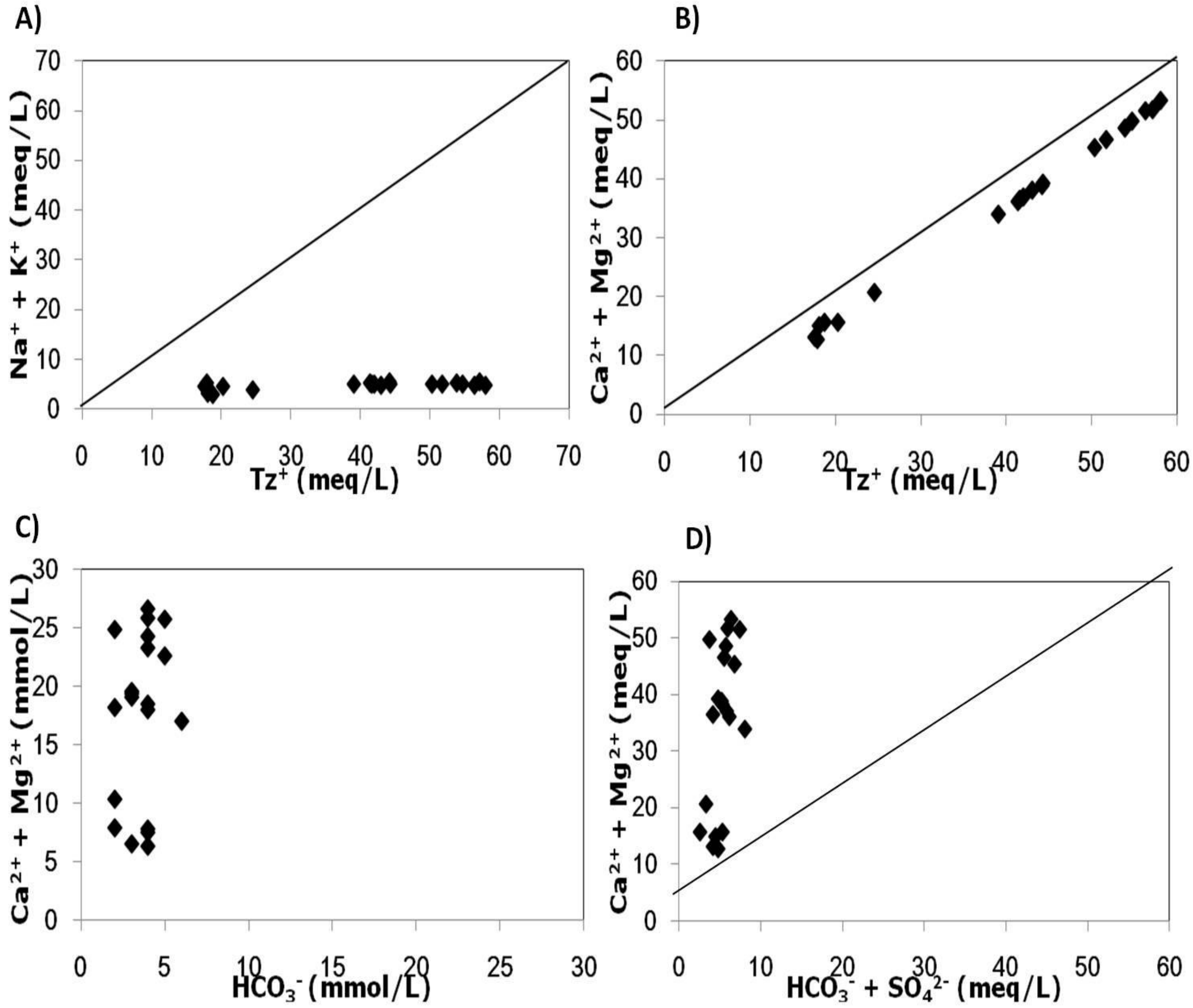

Figure 2: Scatter plot between (A) Tz^+ and $Na^+ + K^+$, (B) Tz^+ and $Ca^{2+} + Mg^{2+}$, (C) HCO_3^- and $Ca^{2+} + Mg^{2+}$, (D) $Ca^{2+} + Mg^{2+}$ and $HCO_3^- + SO_4^{2-}$

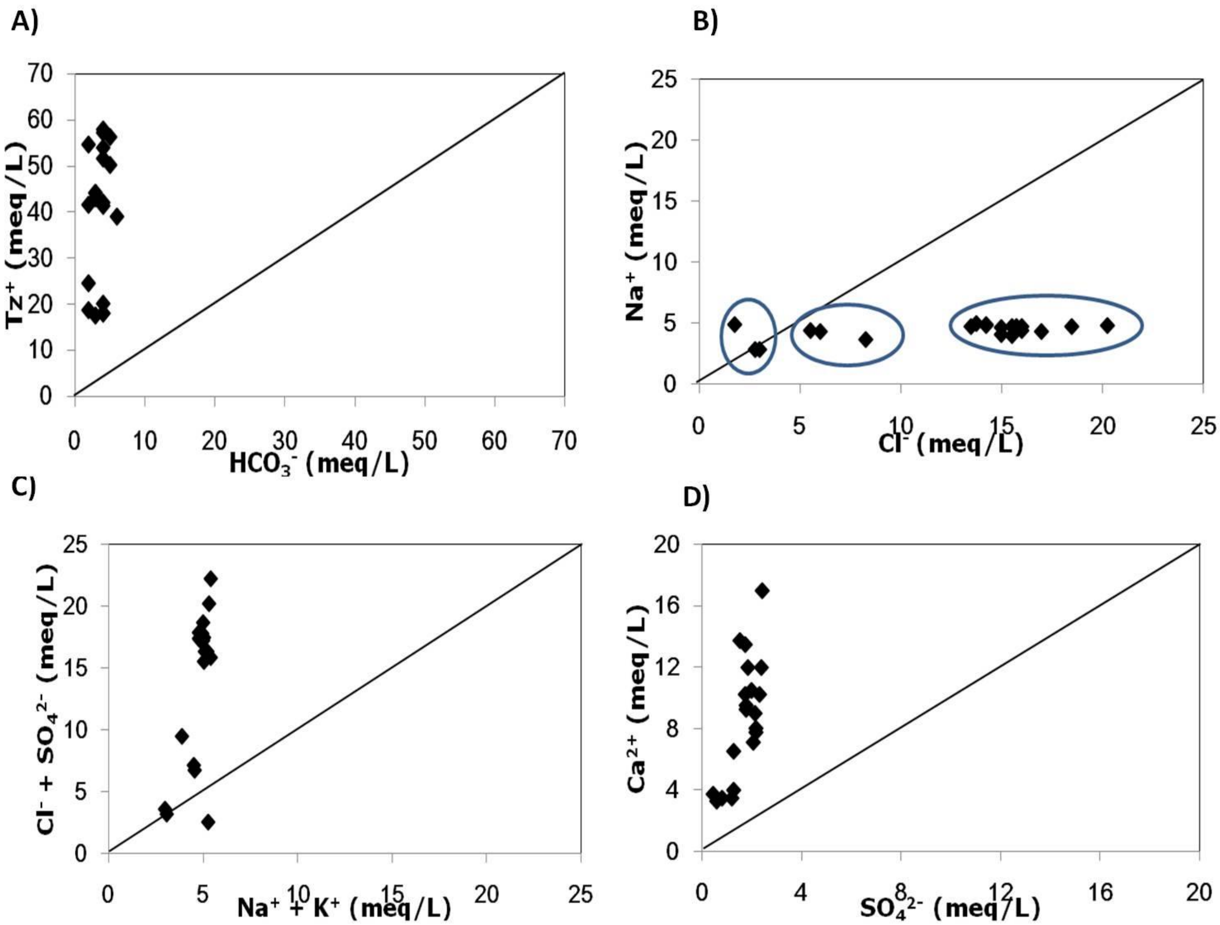

Figure 3: Scatter plot between (A) HCO_3^- and Tz^+, (B) Cl^- and Na^+, (C) $Na^+ + K^+$ and $Cl^- + SO_4^{2-}$, (D) SO_4^{2-} and Ca^{2+}

In figure 4 (a), the plot of Cl^- versus $Ca^{2+} + Mg^{2+}$ (mmol/L) indicates that the concentration of Ca and Mg increased with salinity, which could be an indication of the absence of greater anionic exchange, possibly through naturally inert material like clay. In the figure 4 (b), the plot for Cl^- versus $Na^+ + K^+$, showed that most of the sampling points are below equiline which is indicative that the higher concentration of Cl^- is probably due to 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. Scatter plot in figure 4 (c), showed that the molar ratio of Na/Cl for ground water samples for study area ranging from 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 other geochemical processes operating at local scale which alters the groundwater chemistry.

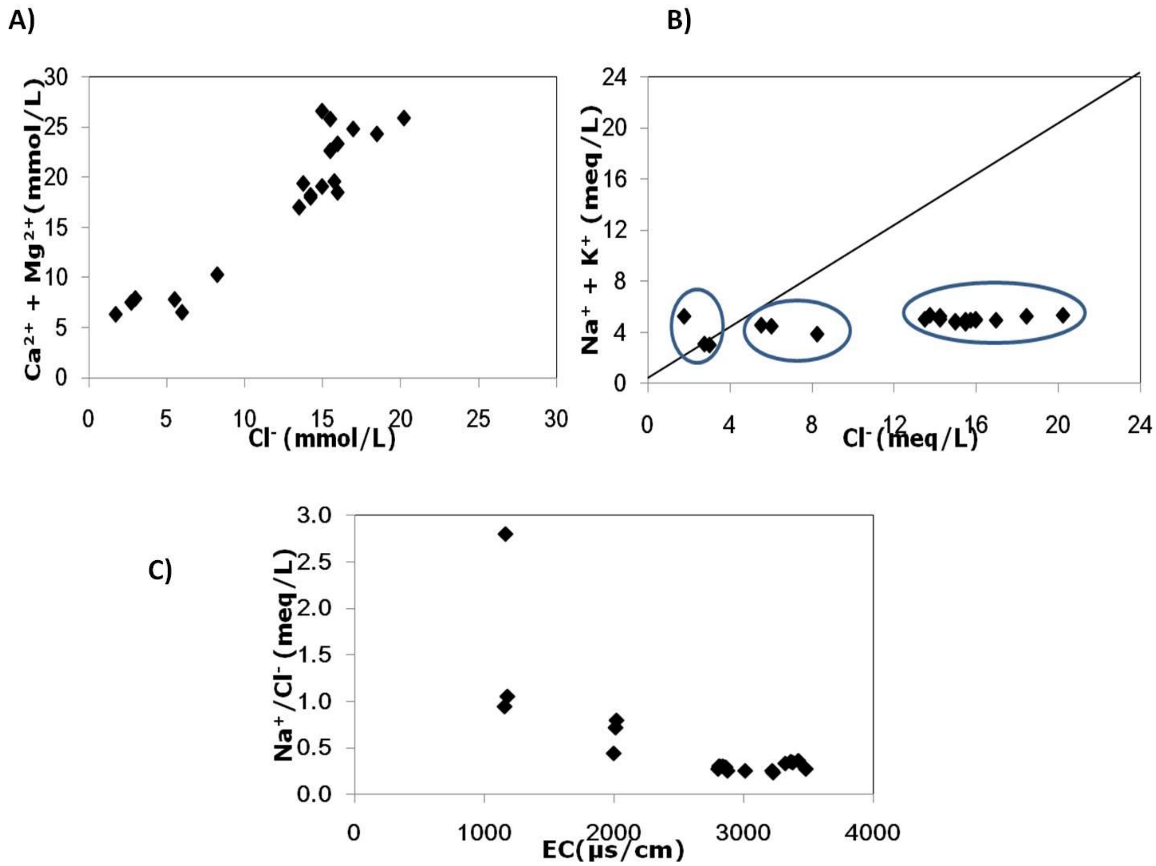

Figure 4: Scatter plot between (A) Cl^- and Ca^{2+} + Mg^{2+}, (B) Cl^- and Na^+ + K^+, (C) EC and Na^+/Cl^-

4.3 Assessment of groundwater quality for irrigation use

The suitability of ground water for irrigation is assessed by considering salinity, chlorinity and sodicity in addition to other parameters (Mills, 2003; Nishanthiny et al., 2011) and result is shown in Table 4. When salinity of groundwater was measured against EC, it is found that, 60% of samples falls in slightly to moderate saline category (700-3,000 µS/cm) whereas rest of 40% samples falls in severely saline category (>3,000 µS/cm). On the other hand, when salinity is measured with respect to TDS, 30% of samples fall into slightly to moderate saline (450-2000 mg/L) and 70% samples are in the severely saline 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

Sodium adsorption ratio is one of the criteria to evaluate suitability of water for irrigation purposes and is calculated using equation 1. 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 to moderate category, which is good for irrigation especially sprinkler irrigation on every kind of soils (Table 4). On the contrary, if the suitability of groundwater will be assessed on the basis of EC value only, it is found that all the groundwater samples falls under doubtful or unsuitable category (Table 5), while looking in to the other classifications (Richard (1995); Wilcox (1955); Eaton (1950)), interestingly all samples fall in safe water class. The classification is helpful in

 doi:10.20944/preprints201805.0199.v2

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

$$SAR = \frac{Na^{+}}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$ Eqn (1)

$$\%Na = \frac{(Na^{+} + K^{+})\ X\ 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})}$$ Eqn (2)

Table 5: Suitability analysis 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

Groundwater chemistry and its effect on soil permeability can be well reflected by permeability index calculated by equation 3. In general, the soil permeability is affected by long-term irrigation from water chemistry dominated 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 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 to 24%) and 20% of the sample falls under class II category (PI ranged in 25 to 75%).

$$PI = \frac{\left(Na^{+} + \sqrt{HCO_3}\right) X\ 100}{\left(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}\right)} \quad \text{Eqn (3)}$$

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 equation 4 and 5) denoted by Chloro alkaline index 1 (CAI 1) and Chloro alkaline index 2 (CAI 2) are recommended by Schoeller (1977), which specifies that the ion exchange between the groundwater and the aquifer minerals/rock environment. The ion exchange of Na^{+} and K^{+} from water with Ca^{2+} and Mg^{2+} in the aquifer matrix meaning that the exchange is direct and the indices are positive, and otherwise the exchange is indirect and indices are negative if it happens in reverse order. It has been observed that 90% of samples show positive ratios and only 10% of samples show negative ratios. Magnesium ratio is another way to estimate groundwater suitability for irrigation. 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).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

$$Chloro\ alkaline\ index\ 1 = (Cl\ - (Na + K))/Cl$$ Eqn (4)

$$Chloro\ alkaline\ index\ 2 = \frac{(Cl\ - (Na + K))}{(SO_4 + HCO_3 + CO_3 + NO_3)}$$ Eqn (5)

Table 6: Statistical summaries of chemical properties of groundwater samples

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

4.4 Groundwater hydrochemical facies

Plotting the concentrations of major cations and anions in trilinear diagram, suggested by Piper (1994), is helpful in analyzing the geochemical evolution of groundwater. Here Piper diagram was made using Aquachem software, and shown in Figure 5. 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_3 i.e. fresh water or water originated from environment with minimum anthropogenic interferences. Whereas rest 10 % of water samples showing the migration from fresh water system to saline water indicating high pressure from different drivers to deteriorate the water quality.

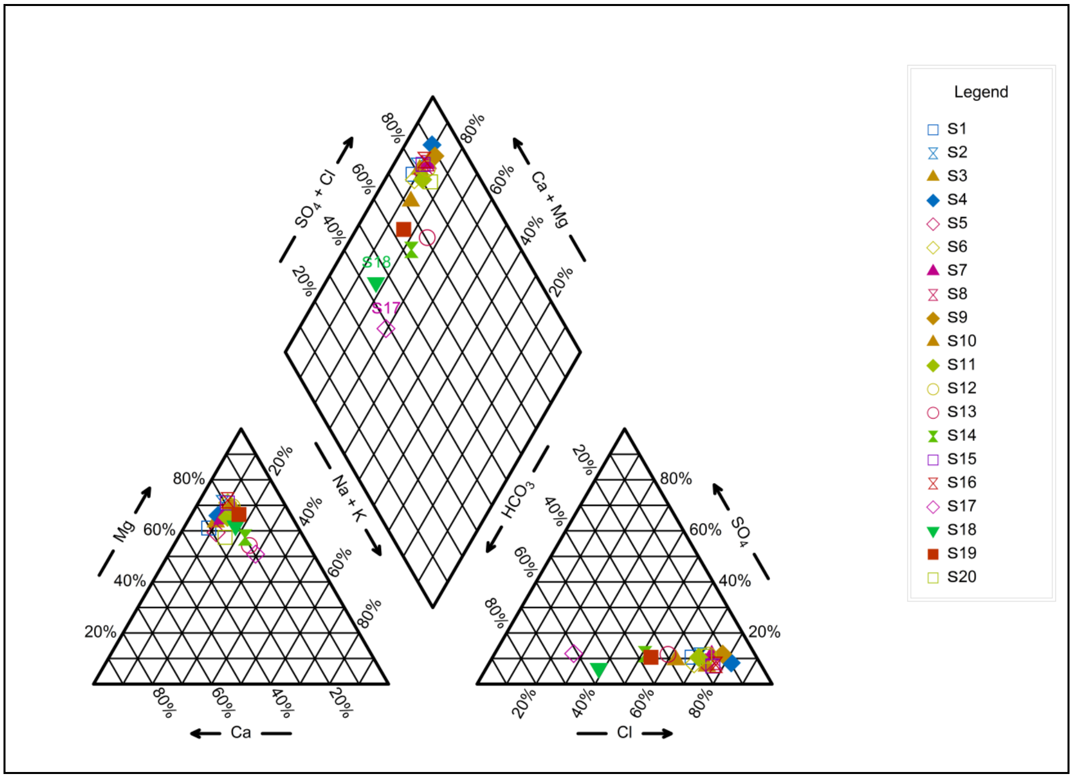

Figure 5: Piper diagram showing ground water quality for the Study Area

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.

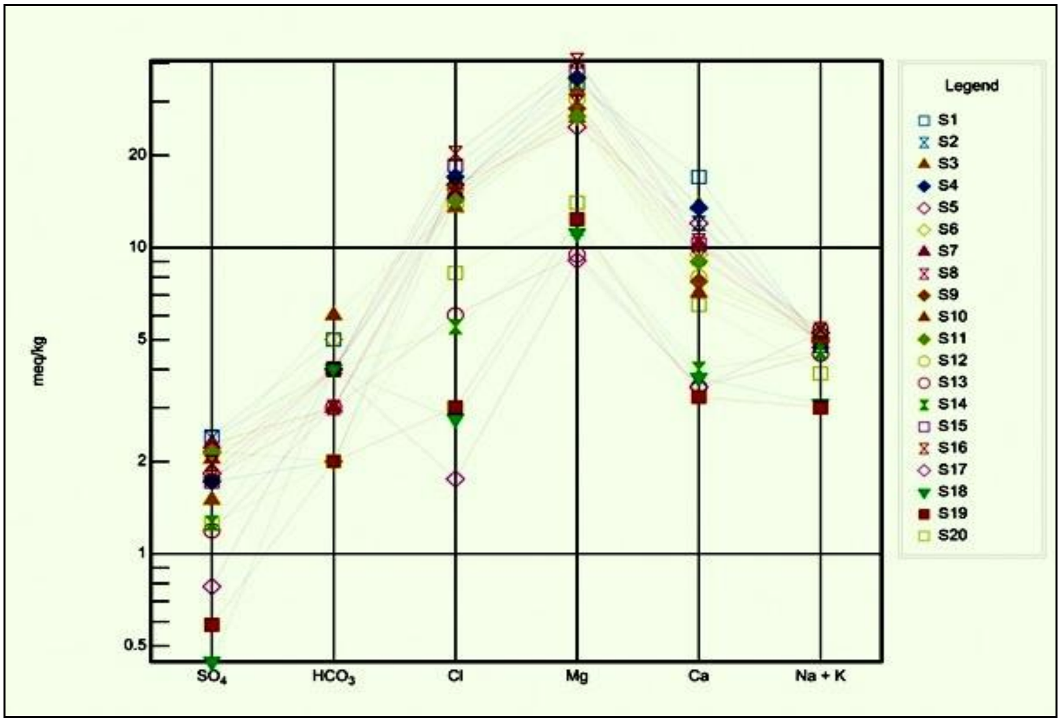

Figure 6: Schoeller Diagram of Groundwater Chemistry of the Study Area

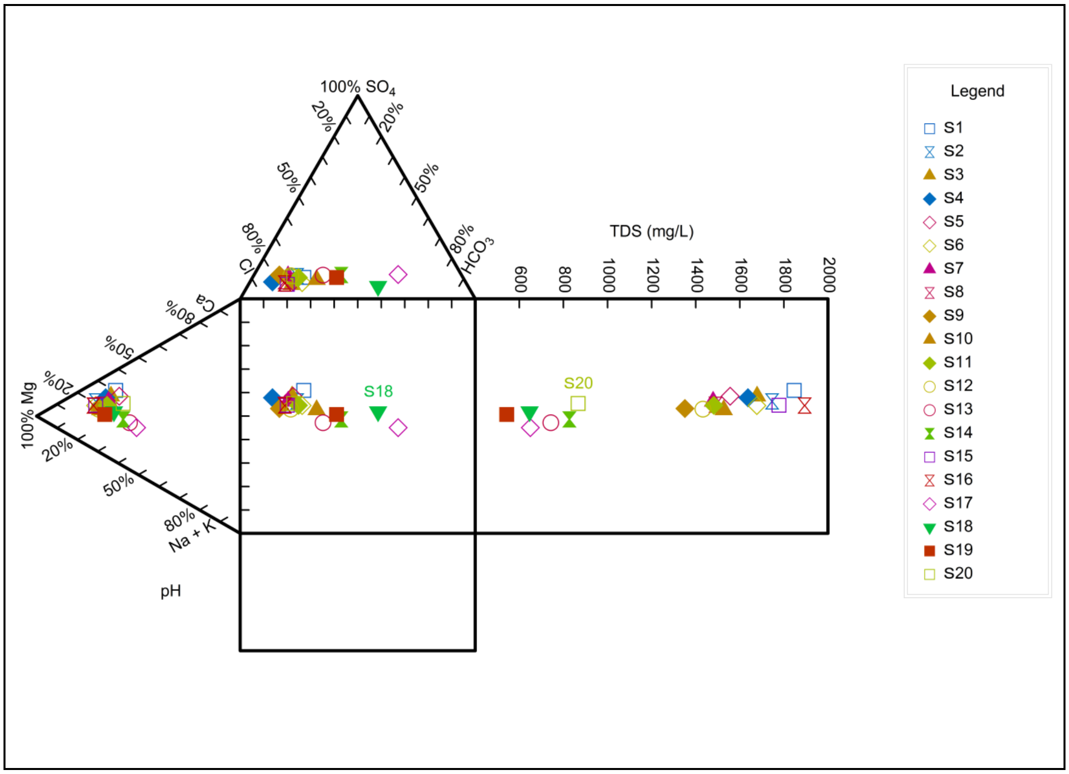

Figure 7: Durov Plot for Groundwater Parameters of the Study Area

 doi:10.20944/preprints201805.0199.v2

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 between EC and TDS. Strong correlation also exist (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+}. On the other hand, SO_4^{2-} is moderately correlated (r = 0.61) with Na, indicating 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 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^{2+} hardness in comparison of Ca^{2+} hardness, and the strong correlation (r = 0.93) between Cl^- and Mg^{2+} showed salinity intrusion , anthropogenic activities and mineral dissolution.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

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

	pH	**EC**	**TDS**	**Acidity**	**Alkalinity**	**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

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

4.5 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 (Table 8). The figure 8 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 ground water in an unprecedented rate over the past few year may have also affected these changes.

Table 8: Average value of different parameters 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

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 May 2018 doi:10.20944/preprints201805.0199.v2

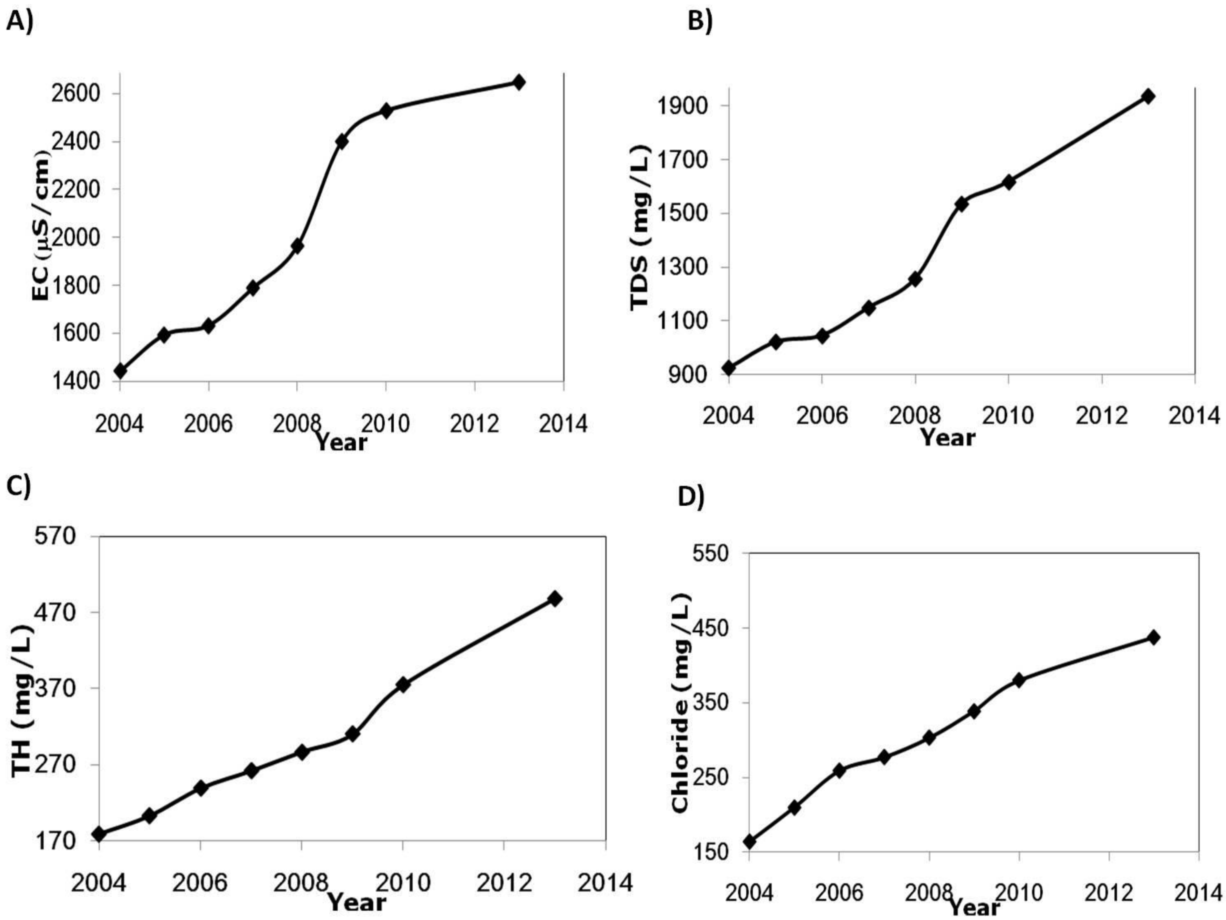

Figure 8: Temporal Variation Graphs between Average Groundwater Data Parameters and time (A) Temporal variation of Year and EC, (B) Temporal variation of Year and TDS, (C) Temporal variation of Year and TH, (D) Temporal variation of Year and Chloride

4. 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 ground water 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 the sequence of the abundance of the major anions and cations are in the order of $Cl^- > HCO_3^- > SO_4^{2-} > PO_4^{2-} > NO_3^-$ and $Mg^{2+} > Ca^{2+} > Na^+ > K^+ > Fe > Cr^{2+}$. Among these anions, the high Cl^- content indicates the possible saline water instruction as well as pollution from anthropogenic sources. The higher Mg^2+ content in comparison of Ca^{2+} suggested that the carbonate weathering also affecting 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 could be classified into two distinct facies viz. Mg-Cl and Mg-HCO_3. The results obtained from the correlation analysis further revealed that the majority of the groundwater samples are dominated by Mg^{2+} hardness in comparison of Ca^{2+} hardness and exhibited strong correlation (r = 0.93) between Cl and Mg showed the coastal saline water inflow and ion exchange. The results also outlined high concentration of TH (Total Hardness), 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 needs to be constructed. Nonetheless, SAR based classification of irrigation water indicated that all groundwater samples belong to excellent category and the results were confirmed with the Wilcox diagram. Sodium percentage and total concentration also showed 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%), that reaffirm the sustainability of ground water for irrigation purposes. In sum, the this study will definitely help the local decision-makers to take appropriate actions in timely manner for its sustainable management in Surat city.

References

Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M., Bhuyian, M.H., Imam, M.B., Khan, A.A. and Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Applied Geochemistry, 19(2), pp.181-200.

Ayers, R.S. and Westcott, D.W., 1985. Water Quality for agriculture, Food and Agricultural Organisation of the United Nations, FAO Irrigation and Drainage, Paper 29, Rome, Italy.

Biswas, A., Bhattacharya, P., Mukherjee, A., Nath, B., Alexanderson, H., Kundu, A.K., Chatterjee, D. and Jacks, G., 2014. Shallow hydrostratigraphy in an arsenic affected region of Bengal Basin: Implication for targeting safe aquifers for drinking water supply. *Science of the Total Environment*, *485*, pp.12-22.

Bauder, T.A., Waskom, R.M., Davis, J.G. and Sutherland, P.L., 2011. Irrigation water quality criteria. Fort Collins, CO: Colorado State University Extension.

CDP. 2008. Revised City Development Plan 2008–2013. Surat Municipal Corporation (2008) http://www.suratmunicipal.org/content/downloads/citydevelopmentplan/Surat_CDP.zip (accessed 21.08.11.)

Coetsiers, M. and Walraevens, K., 2006. Chemical characterization of the neogene aquifer, Belgium. *Hydrogeology Journal*, *14*(8), pp.1556-1568.

Das, A. and Kumar, M., 2015. Arsenic Enrichment in the Groundwater of Diphu, Northeast India: Coupled Application of Major Ion Chemistry, Speciation Modeling, and Multivariate Statistical Techniques. *CLEAN–Soil, Air, Water*, *43*(11), pp.1501-1513.

Das, N., Patel, A.K., Deka, G., Das, A., Sarma, K.P. and Kumar, M., 2015. Geochemical controls and future perspective of arsenic mobilization for sustainable groundwater management: A study from Northeast India. *Groundwater for Sustainable Development*, *1*(1), pp.92-104.

Eaton, F.M., 1950. Significance of carbonate in irrigation water. Soil Science, 69 (2), 123–133.

Garrels R.M., Christ C.L., 1965, Solutions, Minerals, and Equilibria, Freeman, Cooper and Co.

Goswami, R., Rahman, M.M., Murrill, M., Sarma, K.P., Thakur, R. and Chakraborti, D., 2014. Arsenic in the groundwater of Majuli–the largest river island of the Brahmaputra: magnitude of occurrence and human exposure. *Journal of Hydrology*, *518*, pp.354-362.

Gleick, P.H., 1993. Water in crisis: a guide to the worlds fresh water resources.

Gleick, P.H., 2000. A look at twenty-first century water resources development. *Water International*, *25*(1), pp.127-138.

Hinrichsen, D. and Tacio, H., 2002. The coming freshwater crisis is already here. The linkages between population and water. Washington, DC: Woodrow Wilson International Center for Scholars, pp.1-26.

Kapshe, M., Kuriakose, P.N., Srivastava, G. and Surjan, A., 2013. Analysing the co-benefits: case of municipal sewage management at Surat, India. *Journal of Cleaner Production*, *58*, pp.51-60.

Kazi, T.G., Arain, M.B., Baig, J.A., Jamali, M.K., Afridi, H.I., Jalbani, N., Sarfraz, R.A., Shah, A.Q. and Niaz, A., 2009. The correlation of arsenic levels in drinking water with the biological samples of skin disorders. *Science of the Total Environment*, *407*(3), pp.1019-1026.

Kim, S.H., Kim, K., Ko, K.S., Kim, Y. and Lee, K.S., 2012. Co-contamination of arsenic and fluoride in the groundwater of unconsolidated aquifers under reducing environments. *Chemosphere*, *87*(8), pp.851-856.

Kumar, P., Kumar, A., Singh, C.K., Saraswat, C., Avtar, R., Ramanathan, A.L. and Herath, S., 2016a. Hydrogeochemical Evolution and Appraisal of Groundwater Quality in Panna District, Central India. Exposure and Health, 8(1), pp.19-30.

Kumar, P., Saraswat, C., Mishra, B.K., Avtar, R., Patel, H., Patel, A., Sharma, T. and Patel, R., 2016b. Batch technique to evaluate the efficiency of different natural adsorbents for defluoridation from groundwater. Applied Water Science, pp.1-10.

Kumar, P., Tsujimura, M., Saraswat, C., Srivastava, P.K., Kumar, M. and Avtar, R., 2016c, Quantitative Analysis of Transient Intertidal Submarine Groundwater Discharge in Coastal Aquifer of Western Japan. *Proceedings of the National Academy of Sciences, India Section A: Physical Sciences*, pp.1-10.

Kumar, P., Kumar, M., Ramanathan, A.L. and Tsujimura, M., 2010. Tracing the factors responsible for arsenic enrichment in groundwater of the middle Gangetic Plain, India: a source identification perspective. *Environmental Geochemistry and Health*, *32*(2), pp.129-146.

Mahanta, C., Enmark, G., Nordborg, D., Sracek, O., Nath, B., Nickson, R.T., Herbert, R., Jacks, G., Mukherjee, A., Ramanathan, A.L. and Choudhury, R., 2015. Hydrogeochemical controls on mobilization of arsenic in groundwater of a part of Brahmaputra river floodplain, India. *Journal of Hydrology: Regional Studies*, *4*, pp.154-171.

McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T. and Lowry, D., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. Applied Geochemistry, 19(8), pp.1255-1293.

Mills B., 2003. Interpreting Water Analysis for Crop and Pasture. File No. FS0334, DPI's Ageny for Food and Fiber Sciences, Toowoomba.

Meliker, J.R., AvRuskin, G.A., Slotnick, M.J., Goovaerts, P., Schottenfeld, D., Jacquez, G.M. and Nriagu, J.O., 2008. Validity of spatial models of arsenic concentrations in private well water. Environmental research, 106(1), pp.42-50.

Metcalf and Eddy., 2003. Wastewater Engineering, Treatment and Reuse, 4th Edition, McGraw-Hill, New York.

Miller, G.W., 2006. Integrated concepts in water reuse: managing global water needs. Desalination, 187(1-3), pp.65-75.

Mukherjee, A., Saha, D., Harvey, C.F., Taylor, R.G., Ahmed, K.M. and Bhanja, S.N., 2015. Groundwater systems of the Indian sub-continent. Journal of Hydrology: Regional Studies, 4, pp.1-14.

Nickson, R., Sengupta, C., Mitra, P., Dave, S.N., Banerjee, A.K., Bhattacharya, A., Basu, S., Kakoti, N., Moorthy, N.S., Wasuja, M. and Kumar, M., 2007. Current knowledge on the distribution of arsenic in groundwater in five states of India. Journal of Environmental Science and Health Part A, 42(12), pp.1707-1718.

Nishanthiny, S.C., Thushyanthy, M., Barathithasan, T. and Saravanan, S., 2010. Irrigation water quality based on hydro chemical analysis, Jaffna, Sri Lanka. American-Eurasian J. Agric. & Environ. Sci, 7(1), pp.100-102.

Pettygrove, G.S. and T. Asano., 1985. Irrigation with reclaimed municipal wastewater - a guidance manual. Lewis Publishers, Inc., Chelsea, MI, USA.

Radloff, K.A., Zheng, Y., Michael, H.A., Stute, M., Bostick, B.C., Mihajlov, I., Bounds, M., Huq, M.R., Choudhury, I., Rahman, M.W. and Schlosser, P., 2011. Arsenic migration to deep groundwater in Bangladesh influenced by adsorption and water demand. *Nature geoscience*, *4*(11), pp.793-798.

Rupal, M., Tanushree, B. and Sukalyan, C., 2012. Quality characterization of groundwater using water quality index in Surat city, Gujarat, India. *Int Res J Environ Sci*, *1*(4), pp.14-23.

Saraswat, C., Kumar, P. and Mishra, B.K., 2016. Assessment of stormwater runoff management practices and governance under climate change and urbanization: An analysis of Bangkok, Hanoi and Tokyo. *Environmental Science & Policy*, *64*, pp.101-117.

Saleh A., Al-Ruwaih F., and Shehata M., 1999. Hydrogeochemical processes operating within the main aquifers of Kuwait. J. Arid Environ. 42, 195–209.
Schoeller H., 1977. Geochemistry of groundwater, Chap. 15. In Groundwater Studies: An International Guide for Research and Practice . pp.1–18. UNESCO, Paris.

Singh, S.K., Ghosh, A.K., Kumar, A., Kislay, K., Kumar, C., Tiwari, R.R., Parwez, R., Kumar, N. and Imam, M.D., 2014. Groundwater arsenic contamination and associated health risks in Bihar, India. *International Journal of Environmental Research*, *8*(1), pp.49-60.

Smedley, P.L. and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied geochemistry*, *17*(5), pp.517-568.

Srivastava, S.K. and Ramanathan, A.L., 2008. Geochemical assessment of groundwater quality in vicinity of Bhalswa landfill, Delhi, India, using graphical and multivariate statistical methods. *Environmental Geology*, *53*(7), pp.1509-1528.

Sawyer CN, McCarty PL. 1978., Chemistry for environmental engineering. Mc-Graw Hill, New York, p 532

Tanvir Hassan, S.M. 2008. Assessment of groundwater evaporation through groundwater model with spatio - temporally variable fluxes: case study of Pisoes catchment, Portugal. Enschede, ITC.

Manjusree, T.M., Joseph, S. and Thomas, J., 2009. Hydrogeochemistry and groundwater quality in the coastal sandy clay aquifers of Alappuzha district, Kerala. Journal of the Geological Society of India, 74(4), pp.459-468.

Uddin, M.K., Juraimi, A.S., Ismail, M.R., Othman, R. and Rahim, A.A., 2011. Relative salinity tolerance of warm season turfgrass species. *Journal of Environmental Biology*, *32*(3), p.309.

Vörösmarty, C.J., Green, P., Salisbury, J. and Lammers, R.B., 2000. Global water resources: vulnerability from climate change and population growth. science, 289(5477), pp.284-288.

Wilcox, L.V., 1955. Classification and use of irrigation waters, Agric. Circ. 969, USDA, Washington D.C., pp. 19.

World Health Organization, WHO, 2004. Guidelines for drinking-water quality (Vol. 1). World Health Organization.