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Original Research Paper

Groundwater Quality Assessment of Bhaskar Rao Kunta Watershed, Nalgonda District, Andhra Pradesh, India

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ABSTRACT

Semi-arid region of Bhaskar Rao Kunta watershed was studied to evaluate hydrogeochemical characteristics of the fractured, semi-confined and water-stressed aquifers. Twenty groundwater samples were collected from deeper bore wells during pre and post monsoon seasons in June and December 2009. The samples were analysed for concentration of physico-chemical parameters (pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and F^-). The results were interpreted with Piper, Gibbs and Wilcox diagrams. For interrelationships, the parameters were measured with correlation matrix and *t*-test methods. Bureau of Indian Standards specifications were used and verified for suitability of groundwater quality. The type of the groundwater quality was understood from the interpreted diagrams of Piper (85% magnesium bicarbonate and 15% mixed type of samples), Gibbs (100% evaporation type samples) and Wilcox (85% high salinity and 15% moderate salinity type of samples). The highest correlation was found between EC and TDS with a correlation coefficient of 0.98 and the *t*-test behaviour was not significance, therefore, the geogenic and rock water interaction was negligible with respect to seasonal variation. Due to high concentration of fluoride (<1.5mg/L) and salinity (750 ≤ 2250 µS/cm), the groundwater quality was not suitable for drinking, and special drainage system and crop practices are requisite for irrigation purpose in the study area.

INTRODUCTION

Water quality is required to be determined to know whether water is safe for drinking, irrigation and industrial purposes. A number of studies on groundwater quality with respect to various purposes have been carried out in the different parts of India (Majumdar et al. 2000, Sujatha et al. 2003, Sunitha et al. 2005, Subba Rao 2006, Reddy 2010, Ravi Kumar et al. 2011). The groundwater quality in shallow aquifers is generally suitable for use for different purposes and its quality is generally of calcium bicarbonate (EC<750 µS/cm) and mixed type (EC is 750 ≤ 3000 µS/cm) (CGWB 2010). The quality in deeper aquifers also varies from place to place and was generally found suitable for all uses. In some cases, groundwater has been found unsuitable for specific uses due to various contaminations mainly because of geogenic reasons (Reddy et al. 2009). It is essential to classify the groundwater on the basis of chemical analysis to know the type of water, composition and concentration of various constituents. In the present study, the physico-chemical quality of groundwater has been assessed with reference to its suitability for drinking/agricultural purpose and inferred interrelationship of variables with different statistical methods.

STUDY AREA

The Bhaskar Rao Kunta watershed is located at the Krishna lower basin and covered in Survey of India (SoI) topo sheet No: 56 P/6 & 56 P/10 (1:50000 scale). It is geographically located between northern latitudes from 16°42'25" to 16°37'58" and eastern longitudes from 79°28'15" to 79°32'30" and politically placed in Damaracherla Mandal, Nalgonda district of Andhra Pradesh state, India (Fig. 1).

The watershed area is exposed 40.25 sq.km and slightly undulated terrain with moderate slopes. Altitude varies in the range of 80 to 140m above the mean sea level. Annual normal rainfall remains 737mm and average maximum and minimum temperature varies 40°C and 28°C respectively. Drainage pattern shows dendritic to sub-dendritic, governed by relief, regional slope, and homogenous lithology, exhibited by streams, which could be either due to structural or topographic control. 146 streams contribute the flow of mostly dry except for seasonal run-off.

Geology and soils: The area is geologically consisted of the Kurnool group of Palnadu sub-basin and partially covered by Srisailam succession of Kadapa super group. General sequence of sub-surface strata was encountered with top soil, weathered/semi weathered, and shale/quartzite. Srisailam sub basin rock is exposed with Quartzites. The Quartzites are inter bedded with thin siltstone units and usually thick bedded, dense and fine to medium grained. Palnadu sub-basin rocks were exposed with calcareous (chemical precipitates)

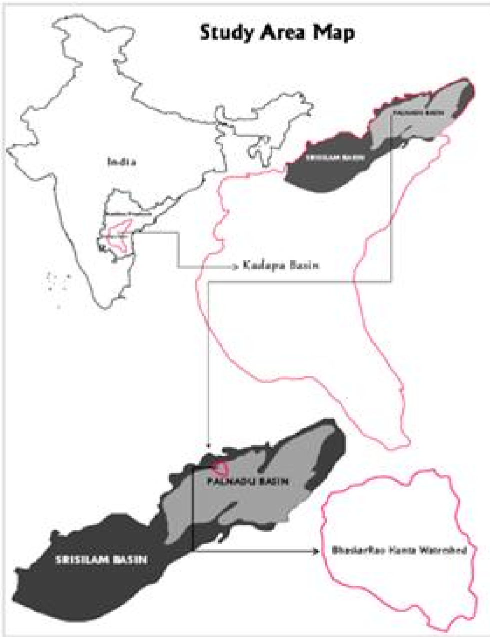

Fig.1: Location map of the study area.

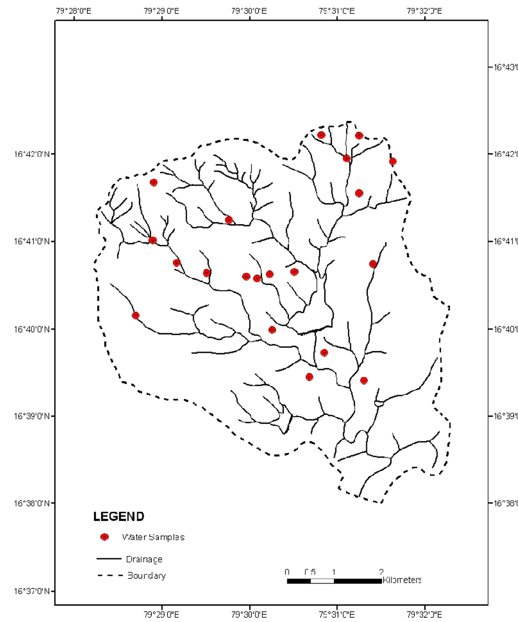

Fig.2: Groundwater samples location map.

sediments like quartzites, shales and flaggy-massive limestones. Soils are consisted with red, red sandy and black soils.

MATERIALS AND METHODS

Twenty groundwater samples were collected from working deeper bore wells (depth 60m) during the pre and post monsoon seasons at identical locations. Locations of sampling points were determined using a Global Positioning System (GPS). The locations of the collected groundwater samples are shown Fig. 2. Collected sample bottles were labelled, sealed and transported to the laboratory under standard preservation methods. The major anion and cation concentrations were determined in the laboratory following standard analytical procedures of American Public Health Association (APHA 1998). The accuracy of the chemical analyses was checked by taking the relationship between the total cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and the total anions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and F^-). Analytical data were interpreted through different plotting/graphical representation such as those of Piper (1994), Wilcox (1995) and Gibbs (1970) diagrams. Interrelationships of variables were measured with correlation matrix and *t*-test using software Windows XP, and SPSS 18.0. Suitability of this water for its utility was verified by comparing the results with Bureau of Indian Standards specification: BIS (1998).

RESULTS AND DISCUSSION

General parameters: pH is the measure of the balance between the concentration of hydrogen (H^+) ions and hydroxyl (OH^-) ions in solution. In the study area, the pH values show minimum and maximum range of 8 to 9 in pre and post monsoon seasons respectively (Table 1), indicating a basic nature. 75% and 100% of the samples showed a pH value within the permissible limit of 6.5 to 8.5 (BIS 1998), except 25% of the samples (sample no. 10, 14, 19 and 20) crossing the permissible limit in pre-monsoon (Table 1).

Electrical conductivity (EC) measures presence of cations and anions in the water; with more ions in the water the water's electrical conductivity (EC) increases making the water saline. It is generally considered problematic for irrigation use with crops of low or medium salt tolerance. In the study area, the electrical conductivity (EC) varies widely in the range of 650 to 1497 µS/cm and 650 to 1526 µS/cm in pre and post-monsoon seasons respectively (Table 1). 100% of the samples showed EC within the permissible limit of 3000 µS/cm (BIS 1998).

The total mass of dissolved constituents is referred to as the total dissolved solids (TDS) concentration. In water, all the dissolved solids are either positively charged ions (cations) or negatively charged ions (anions). The total negative charge of the anions always equals the total positive charge of the cations. A higher TDS means that there are more cations and anions in the water. In the study area, the TDS values varied widely from 321 to 729 mg/L to 325 to 730mg/L in pre and post-monsoon seasons respectively (Table 1), All the samples showed TDS within the permissible limit of 2000 mg/L (BIS 1998).

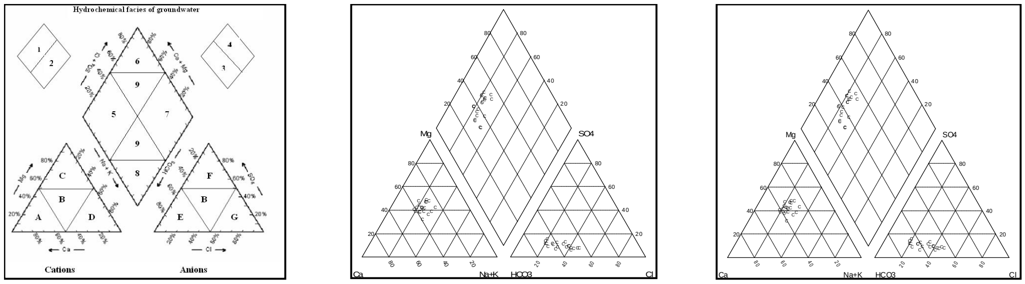

Fig. 3: Classification diagram of Piper (a) hydrochemical facies, (b) Pre-monsoon, (c) Post-monsoon

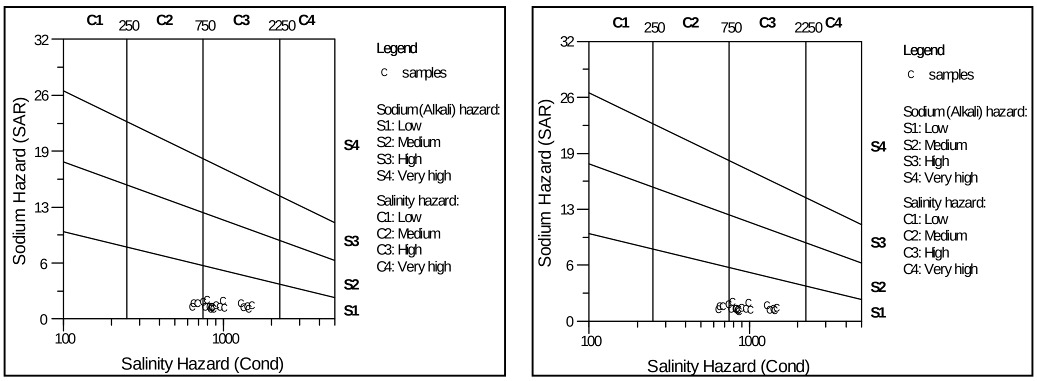

Fig.4: Wilcox diagram (a) Pre-monsoon, (b) Post-monsoon

Cation Chemistry

Ca^{2+} are present in all natural water and contribute to the hardness of water. It sources of Ca^{+2} in sedimentary minerals such as dolomite, calcite, aragonite; gypsum, anhydride, and igneous rocks are weathering of feldspathic and ferro-magnesium such as plagioclase feldspars, amphiboles, pyroxenes and clay minerals. In the study area Ca^{+2} concentrations are varies minimum and maximum range of 73 to 151 and 72 to 152mg/L in pre and post-monsoon seasons respectively. 100% of the samples are within the permissible limits of 200 mg/L (BIS 1998).

Magnesium is present in all natural waters and one of the common elements in the earth crust. Common minerals as source of magnesium are mafic minerals (amphiboles, olivine, pyroxenes), dolomite, chlorite, magnesite and clay minerals. It is an important contributor to water hardness. In the study area, Mg^{2+} concentration varies widely in the range of 53 to 102 mg/L and 53 to 107 mg/L in pre and post-monsoon seasons respectively, with 90% and 95% samples in permissible limits of 100 mg/L (BIS 1998), except 10% (Sample Nos. 12 and 7) and 5% of the samples (Sample No. 7) crossing the permissible limits.

Na^{+} is a common chemical in minerals, commonly found in soils and minerals like feldspars (albite), evaporites, such as halite (NaCl), clay and industrial wastes. In these forms, they readily dissolve in water. It is released slowly upon dissolution of rocks. Consequently, concentration increases as residence time in ground water increases. There are no health-based drinking water standards for sodium, neither has a secondary drinking water standard. Sodium intake may lead to hypertension and be a concern for people with heart conditions. In the study area sodium concentration varies from 63 to 120 mg/L and 66 to 122 mg/L in pre and post-monsoon seasons respectively.

K^{+} is common in many rock sources such as weathering of feldspar minerals (orthoclase, microcline) feldspathoids, micas, and clay. Potassium is gradually released from rocks. Many of these rocks are relatively soluble and potassium concentration in groundwater increases with time. There are no health-based drinking water standards for potassium, neither it has a secondary drinking standard. In the study area potassium concentration varies in the range of 0.6 to 1.5 mg/L and 0.5 to 1.1 mg/L in pre and post-monsoon seasons respectively.

Total hardness (TH) is primarily imparted by cations such as calcium and magnesium, and anions such as carbonate, bicarbonate, chloride and sulphate in water. In the study area, the total hardness varies from 323 to 325 mg/L and 325 to 575 mg/L in pre and post-monsoon seasons respectively. 100% of the samples were within the permissible limit of 600 mg/L (BIS 1998).

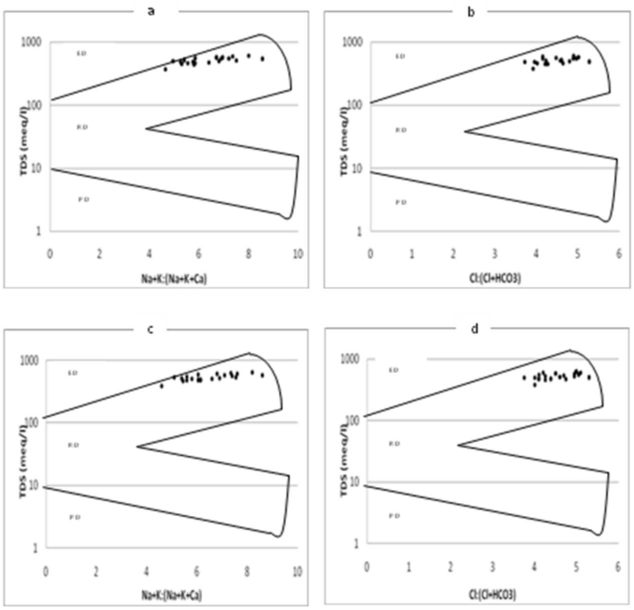

Fig.5: Gibbs diagram of (a&b) Pre-monsoon (c&d) Post-monsoon.

Anion Chemistry

HCO_3 source rocks are limestones and dolomites. The source of bicarbonate is attributed to the dissociation of the carbonic acid. Oxidation of organic matter by microbes generates CO_2 which then combines with water to from carbonic acid. The high carbonate indicates that intense chemical weathering has taken place in the drainage basin due to microbial activity. In the study area, bicarbonate concentration varies from 165 to 260 mg/L and 168 to 262 mg/L in pre and post-monsoon seasons respectively. All the samples were within the permissible limits of 400 mg/L (BIS 1998).

SO_4^{2-} has major sources like oxidation of sulfide ores, gypsum and anhydrides. It occurs in water as the inorganic sulphate salts as well as dissolved gas (H_2S). Sulphate is not a noxious substance although high sulphates in water may have a laxative effect. High concentration of sulphates indicated pollution from application of fertilizers to agricultural lands. In the study area, sulphate concentration varies in the range of 19 to 43 mg/L and 19 to 46mg/L in pre and post-monsoon seasons respectively. All the samples are within the permissible limits of 400 mg/L (BIS 1998).

NO_3^- sources commonly include human activity such as application of fertilizer in farming practices, and human and animal wastes. The concentration of nitrate varies from 17 to 49 mg/L to 18 to 51mg/L in pre and post-monsoon seasons respectively. In the study area, 95% and 100% of the samples are within the permissible limits of 45mg/L (BIS 1998) in the two seasons.

Chloride is present in all natural waters. Chief sources of it are igneous and sedimentary rocks (evaporites), and human sources. High concentration of chloride content imparts a salty taste to the water. In the study area, the concentration of chloride varies from 30 to 150 mg/L and 31 to 120 mg/L in pre and post-monsoon seasons respectively. All the samples have chloride within the permissible limits of 250mg/L (BIS 1998).

Apatite minerals are principal sources of fluoride content in groundwaters. Natural concentration of fluoride commonly varies from about 0.01 to 10 mg/L. Fluoride in excessive concentration may case dental defects, affect bone structure and in acute causes fluorosis. In the study area, fluoride concentration varies from 2 to 4 mg/L in pre and post-monsoon seasons respectively. In all the samples concentration is crossing the permissible limits of 1.5 mg/L (BIS 1998), therefore, the groundwater is not suitable for the drinking purposes.

Piper Trilinear Diagram

The hydrogeochemical nature of groundwater can be understood by plotting the major cations and anions in the Piper trilinear diagram (Piper 1994). This diagram revels similarities and differences among groundwater samples because those with similar qualities will tend to plot together as groups (Todd 2001). This diagram is very useful in bringing out chemical relationships among groundwaters in more definitive terms (Walton 1970). The geochemical evolution can be understood from the Piper plots, which has been divided into four divisions and nine subdivisions (Table 3 and Fig. 3).

An intervening major divisions of diamond shaped field, all the water samples are covered under class of alkaline earth (Ca + Mg) exceed alkalies (Na + K), and 85% and 15% of samples are covered in the weak acids (CO_3 + HCO_3) exceed strong acids (SO_4 + Cl) type, and strong acids exceed weak acids type respectively. In the subdivision of diamond shaped field, 85% and 15% of similar samples are covered in the magnesium bicarbonate type and mixed type in pre and post-monsoon seasons respectively (Table 4 and Fig. 3).

Wilcox Diagram

Wilcox (1995) classified groundwaters for irrigation purposes based on salinity and sodium hazard.

Salinity hazard: Low salinity water (C-1) can be used for irrigation of most crops on most soils; medium salinity water (C-2) can be used if a moderate amount of leaching occurs; high salinity water (C-3) can not be used on soils with restricted drainage, and very high salinity water (C-4) is not suitable for irrigation.

Table 1: Results of hydrochemical parameter concentrations in pre and post-monsoon seasons.

Longitude	Latiitude	Pre-monsoon													Post-monsoon												
		pH	EC	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	TDS	F^-	pH	EC	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	TDS	F^-
79.48184	16.69462	8	859	407	96	72	72	0.8	199	57	23	25	425	3	8	862	418	103	78	75	0.8	206	61	27	29	431	3
79.52091	16.69261	8	795	446	79	83	120	1.0	231	37	39	26	395	3	8	798	450	82	89	122	1.0	241	39	41	28	399	3
79.51853	16.69924	8	840	495	88	87	80	1.0	219	95	33	25	425	4	8	855	500	92	89	81	0.9	226	97	34	29	427	4
79.50391	16.67703	8	1300	423	127	88	110	1.0	192	115	28	26	650	4	8	1304	425	132	89	109	0.9	195	120	29	26	652	4
79.50153	16.67625	8	751	422	97	65	103	0.8	184	50	31	23	377	2	8	758	425	101	68	106	0.7	189	51	32	24	379	2
79.49611	16.68746	8	1349	523	140	94	81	1.0	237	110	23	40	670	3	7	1355	525	144	97	86	1.1	244	113	25	41	677	3
79.49947	16.67665	8	873	396	116	100	70	0.8	217	60	19	29	435	3	8	876	400	118	103	74	0.8	220	61	19	30	438	3
79.49188	16.67732	8	965	446	118	72	81	0.8	241	95	31	30	480	3	8	967	450	122	73	82	0.7	247	96	32	32	483	4
79.52731	16.69863	8	689	323	108	53	89	0.7	165	93	23	29	348	2	8	698	325	112	53	91	0.6	168	96	26	31	349	2
79.51375	16.70373	9	781	397	86	91	81	0.6	196	47	27	21	390	2	8	782	400	89	92	82	0.5	198	48	29	22	391	2
79.52091	16.70356	8	829	370	91	67	75	1.0	221	38	43	35	414	3	8	830	375	92	69	74	1.0	229	39	46	39	415	3
79.47841	16.66934	8	661	573	95	102	102	0.9	179	30	25	40	328	4	8	662	575	96	107	106	0.9	183	31	26	41	331	4
79.48162	16.68361	8	650	349	73	56	63	0.7	177	35	19	38	321	3	8	650	350	72	58	66	0.7	183	36	19	39	325	3
79.48616	16.67927	9	852	447	130	76	71	0.8	196	73	39	24	420	4	8	849	450	131	76	72	0.7	198	76	41	26	425	4
79.52356	16.67901	8	1001	347	85	69	106	1.0	260	46	36	17	500	2	8	1008	350	88	71	110	0.9	262	47	38	18	504	2
79.51143	16.65753	8	1421	396	114	70	80	1.0	244	102	37	49	711	2	8	1428	400	116	73	83	0.9	250	109	39	51	714	2
79.51427	16.66217	9	1453	520	151	91	77	1.0	236	54	35	20	729	3	8	1460	525	152	93	78	1.1	241	59	37	21	730	4
79.50864	16.67751	8	1027	542	124	95	80	0.9	192	97	24	31	573	3	8	1031	550	128	96	81	0.7	189	99	25	32	576	3
79.50442	16.66661	9	901	497	97	97	91	1.0	212	98	27	41	452	3	8	910	500	101	98	93	1.0	214	106	29	43	455	3
79.52186	16.65682	9	1497	536	119	88	91	1.5	237	83	38	34	651	3	8	1526	550	127	94	97	1.0	243	87	42	39.7	663	3

All units are expressed in mg/L except pH, EC (μS/cm)

Table 2: Summary statistics of hydrochemical parameter concentrations.

Param-eters	Pre-monsoon									Post-monsoon								
	Min	Max	Mean	SD	SE	SV	CV	Kur-tosis	Skew ness	Min	Max	Mean	SD	SE	SV	CV	Kur-tosis	Skew ness
pH	8	9	8	0.35	0.08	0.13	4.29	-0.59	0.36	7	8	8	0.24	0.05	0.06	2.97	1.53	-0.73
EC	650	1497	981	281	65	79167	28.69	-0.80	0.78	650	1526	987	285	65	81094	28.86	-0.75	0.80
TH	323	573	445	74	17	5469	16.63	-1.09	0.09	325	575	449	75	17	5658	16.76	-1.11	0.10
Ca	73	151	107	22	5	470	20.22	-0.74	0.29	72	152	110	22	5	492	20.13	-0.87	0.15
Mg	53	102	81	15	3	222	18.33	-0.96	-0.44	53	107	84	15	4	239	18.51	-0.82	-0.44
N a	63	120	87	15	3	229	17.40	-0.23	0.66	66	122	89	15	4	236	17.25	-0.53	0.60
K	0.57	1.53	0.92	0.20	0.04	0.04	21.38	5.01	1.38	0.46	1.12	0.84	0.18	0.04	0.03	20.79	-0.50	-0.41
HCO3	165	260	212	27	6	732	12.73	-1.13	-0.07	168	262	217	28	6	794	13.00	-1.35	-0.09
Cl	30	115	71	29	7	826	40.22	-1.65	-0.01	31	120	74	30	7	903	40.49	-1.64	0.00
SO4	19	43	30	7	2	52	23.75	-1.12	0.02	19	46	32	8	2	61	24.47	-0.89	0.02
NO3	17	49	30	8	2	71	27.71	-0.33	0.47	18	51	32	9	2	77	27.18	-0.52	0.34
TDS	321	729	488	134	30.73	17945	27.46	-1.01	0.64	325	730	491	135	31	18171	27.44	-1.05	0.63
F	2	4	3	0.70	0.16	0.50	24.02	-1.13	-0.17	2	4	3	0.74	0.17	0.54	23.88	-1.34	-0.30

All units are in mg/L, EC in μS/cm; SD = Standard Deviation; SE = Standard Error; SV = Sample Variance; CV = Coefficient of Variation

Sodium hazard: Low sodium water (S-1) can be used for irrigation on almost all soils; medium sodium waters (S-2) will present an appreciable sodium hazard in fine textured soils; high sodium water (S-3) may produce harmful levels of exchangeable sodium in most soils; and very high sodium water (S-4) is generally unsatisfactory for irrigation purposes.

In the study area, the groundwater quality of 85% and 15% of similar samples were falling under the category C_3-S_1 and C2-S1 class in pre and post-monsoons seasons respectively (Table 5 and Figs. 4a & 4b). A high salt concentration present in the water will negatively affect the crop yields. Its results are required for soil and water management practices for salinity control like salt tolerance of the type of crop. For low sodium irrigation water may use all soils with all crops.

Gibbs Diagram

Lastly, to know the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, Gibbs (1970) has suggested a diagram in which ratio of dominant anions and cations are plotted against the value of TDS. Gibbs diagrams, representing the ratio 1 for cations [(Na+K)/(Na+K+Ca)] and

Table 3: Hydrochemical results in Piper trilinear diagram.

Subdivision of the diamond	Class	Samples Falling in Dissimilar Seasons Pre-monsoon No. of samples	%	Post-monsoon No. of samples	%
1	Alkaline earth (Ca + Mg) exceed alkalies (Na + K)	100	All samples	100	All samples
2	Alkalies exceeds alkaline earths	00	Nil	00	Nil
3	Weak acids (CO_3 + HCO_3) exceed strong acids(SO_4 + Cl)	85	(17) expect 4,9,18	85	(17) expect 4,9,18
4	Strong acids exceeds weak acids	15	(3) 4,9,18	15	(3) 4,9,18
5	Magnesium bicarbonates	85	(17) expect 4,9,18	85	(17) expect 4,9,18
6	Calcium-chloride type	00	Nil	00	Nil
7	Sodium-chloride type	00	Nil	00	Nil
8	Sodium-bicarbonate type	00	Nil	00	Nil
9	Mixed type (no cation-anion exceed 50%)	00	(3) 4,9,18.	00	(3) 4,9,18.

Table 4: Results of hydrogeochemical facies.

	Hydrogeochemical facies of the different seasons: Pre-monsoon		Post-monsoon		
Facies	No. of samples & S.No	Percent	Facies	No. of samples & S.No	Percent
Mg-Ca-Na-HCO_3	(8) 1,2,3,4,5,13,16,18	40	Mg-Ca-Na-HCO_3	(9)1, 2, 3,4,5,9,13,16,18	45
Mg-Ca-Na-HCO_3-Cl	(6) 8,10,11,14,17,19	30	Mg-Ca-Na-HCO_3-Cl	(5)8, 10,11,14,17	25
Mg-Na-Ca-HCO_3	(2) 7,12	10	Mg-Na-Ca-HCO_3	(2)7,12	10
Ca-Mg-Na-HCO_3	(2) 9,6	10	Ca-Mg-Na-HCO_3-Cl	(2)19,20	10
Mg-Ca-Na-Cl-HCO_3	(1) 15	5	Mg-Ca-Na-Cl-HCO_3	(1)15	5
Ca-Mg-Na-HCO_3-Cl	(1)20	5	Ca-Mg-Na-HCO_3	(1)6	5

Table 5: Wilcox classification of groundwater.

S.No	Class	Samples falling in dissimilar seasons: Pre-monsoon %	No. of samples and Range	Post-monsoon %	No. of samples and Range
1	C2-S1	15	(3) 9, 12, 13	15	(3) 9, 12, 13
2	C3-S1	85	(17) Except 9, 12, 13	85	(17) Except 9, 12, 13

ratio 2 for anions [Cl/(Cl+ HCO_3)] as a function of TDS, are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation dominance (PD), rock dominance (RD), and evaporation dominance (ED) (Gibbs 1970).

The chemical data of groundwater samples were plotted in the Gibbs diagram (Fig. 5). All samples were representing evaporation dominance. No significance of precipitation and rock dominance was found in the study area. Evaporation increases salinity by increasing Na^+ and Cl^- in relation to increase of TDS. Anthropogenic activities (agricultural fertilizers and irrigation return flows) also influence the evaporation by increasing Na^+ and Cl^- and thus TDS.

Correlation Matrix

A commonly used method to find the relationship between two variables is the correlation coefficient, which is simply a measure to show how well one variable predicts another (Krumbein et al. 1965). In general, three different sets of strong relationships exist between major cations and anions in an aqueous system (Douglas et al. 1977). Samples showing $r > 0.7$ are considered to be strongly correlated whereas r between 0.5 and 0.7, and $r < 0.5$ show moderate correlation and low correlation at a significance level of $p < 0.05$, respectively (Table 6).

Three different sets of strong relationships existing between major cations and anions are:

1. The highly competitive relationship between ions having same charge but a different valance number, e.g., Ca^{2+} and Na^+.
2. The affinity between ions having different charges but the same valance number, e.g., Na^+ and Cl^-.
3. The non-competitive relationship between ions having the same charge and same valence number, e.g., Ca^{2+} and Mg^{2+}.

Highly competitive ion relationship: Cations such as Ca^{2+}

Table 6(a): Correlation matrix of pre-monsoon season.

Parameters	Pre-monsoon												
	pH	EC	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	TDS	F^-
pH	1												
EC	0.01	1											
TH	0.18	0.36	1										
Ca^{2+}	-0.13	0.71	0.43	1									
Mg^{2+}	0.09	0.28	0.76	0.34	1								
Na^{+}	-0.03	0.02	0.12	-0.19	0.12	1							
K^{+}	0.28	0.65	0.48	0.22	0.29	0.30	1						
HCO_3^-	0.12	0.60	0.12	0.20	0.15	0.08	0.55	1					
Cl^-	-0.30	0.52	0.22	0.56	0.16	-0.04	0.18	0.13	1				
SO_4^{2-}	0.34	0.29	0.03	0.02	-0.15	0.26	0.48	0.54	-0.11	1			
NO_3^-	-0.26	0.16	0.20	0.03	0.08	-0.19	0.22	0.01	0.28	-0.15	1		
TDS	-0.07	0.98	0.36	0.74	0.30	0.00	0.55	0.58	0.56	0.24	0.15	1	
F^-	-0.02	0.11	0.56	0.31	0.43	0.04	0.23	-0.02	0.20	0.21	0.04	0.11	1

Table 6(b): Correlation matrix of post-monsoon season.

Parameters	Post-monsoon												
	pH	EC	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	TDS	F^-
pH	1												
EC	-0.46	1											
TH	-0.21	0.37	1										
Ca^{2+}	-0.71	0.72	0.44	1									
Mg^{2+}	-0.21	0.29	0.77	0.31	1								
Na^{+}	0.21	0.05	0.13	-0.16	0.17	1							
K^{+}	-0.19	0.56	0.41	0.28	0.37	0.24	1						
HCO_3^-	0.06	0.58	0.12	0.17	0.15	0.11	0.62	1					
Cl^-	-0.52	0.54	0.23	0.60	0.11	-0.05	0.16	0.11	1				
SO_4^{2-}	0.29	0.31	0.04	0.03	-0.15	0.22	0.39	0.55	-0.08	1			
NO_3^-	-0.21	0.18	0.21	-0.01	0.08	-0.18	0.30	0.06	0.29	-0.06	1		
TDS	-0.51	0.98	0.37	0.75	0.30	0.01	0.55	0.55	0.58	0.25	0.15	1	
F^-	-0.25	0.21	0.60	0.38	0.45	-0.06	0.42	0.11	0.15	0.21	-0.02	0.21	1

Table 7: Summary statistics of different hydrochemical concentrations between pre-monsoon and post-monsoon seasons.

Parameters	Paired Differences Between Pre - Post-monsoon Seasons samples							Correlation	Sig.	*t*
	Mean	SD	SE	SV	CV	Kurtosis	Skewness			
pH	-0.3	0.26	0.06	0.07	1.32	-2.12	1.09	0.67	0.001	-5.23
EC	5.75	6.78	1.52	-1926.72	-0.17	-0.06	-0.02	1.00	0.000	3.79
TH	4.4	3.2	0.72	-189.09	-0.13	0.01	-0.01	1.00	0.000	6.15
Ca^{2+}	3.2	2.12	0.47	-22.22	0.09	0.13	0.14	1.00	0.000	6.76
Mg^{2+}	2.5	1.91	0.43	-17.61	-0.19	-0.13	0.00	0.99	0.000	5.87
Na^{+}	2.25	1.83	0.41	-7.56	0.15	0.29	0.06	0.99	0.000	5.49
K^{+}	-0.07	0.14	0.03	00.01	0.59	5.5	1.79	0.72	0.000	-2.39
HCO_3^-	4.49	2.74	0.61	-62.00	-0.26	0.22	0.03	1.00	0.000	7.31
Cl^-	2.8	2.12	0.47	-76.36	-0.27	-0.02	-0.01	1.00	0.000	5.91
SO_4^{2-}	1.8	1.11	0.25	-9.47	-0.72	-0.23	0.00	0.99	0.000	7.28
NO_3^-	1.94	1.43	0.32	-5.81	0.52	0.19	0.13	0.99	0.000	6.07
TDS	0.17	0.2	0.04	-225.15	0.02	0.03	0.01	0.96	0.000	3.86
F^-	3.5	2.59	0.58	-0.05	0.14	0.21	0.13	1.00	0.000	6.05

All units are in mg/L, EC in µS/cm; SD = Standard Deviation; SE = Standard Error; SV = Sample Variance; CV = Coeffient of Variation with Na^+ negative and with K^+ positive correlation; Mg^{2+} with Na^+ and K^+ positive correlation; anions such as SO_4^{2-} with HCO_3^- and F^- have positive correlation and with Cl^- and NO_3^- has negative correlation.

Affinity ion relationship: Monovalent ions such as Na^+ with Cl^- and NO_3^- have negative and with HCO_3^- positive correlation; K^+ with Cl^-, F^-, HCO_3^- and NO_3^- has positive correlation. Bivalent ions are such as Ca^{2+} with SO_4^{2-} have positive, and Mg^{2+} with SO_4^{2-} has negative correlation.

Non-competitive ion relationship: Bivalent ions are such as between Ca^{2+} with Mg^{2+} correlations are significant. Cl^- with HCO_3^-, F^- and NO_3^- has positive correlations, and HCO_3^- with NO_3^- has positive correlation.

Table 6 (a&b) shows good correlation between EC and TDS with a correlation coefficient of 0.98. It indicates that EC is a measure of dissolved solids in the groundwater. Total dissolved solids have been taken into account as a dependent variable. TDS is mainly dependent on the concentration of major ions such as Ca^{2+}, K^+, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-. TDS shows significant correlation with Cl^-, Mg^{2+}, Ca^{2+}, SO_4^{2-} and NO_3^-. The fluoride concentration has significant correlation with TH, magnesium and potassium.

***t*-Test:** The *t*-test model behaviour was indicated within the same variables (between pre and post monsoon seasons) significance (probability levels: $p<0.05$) and strength (coefficient of determination = R^2) of relationships. The results show that larger the coefficient of determination (R^2), stronger the relationship between pre and post monsoon seasons samples (Table 2). Therefore, hydrogeochemial (geogenic and rock water interaction) reactions were negligible with respect to seasons.

CONCLUSIONS

Semi-arid region of Bhaskar Rao Kunta watershed groundwater quality was evaluated and it was revealed that the chemical parameter concentrations of the groundwater were not suitable for drinking purpose due to high concentrations of fluoride (< 1.5mg/L). Wilcox diagram show that 85% and 15% of similar samples were falling under the category of C_3-S_1 and C_2-S_1 in both the seasons. It indicates that high salt concentrations were present in the groundwater which may cause negative effect of crop yields. Therefore, drainage and crop management practices are required. Low sodium irrigation water may be used for any type of crop practices. Piper trilinear diagram shows 85% and 15% of similar samples falling under the category of magnesium bicarbonate and mixed type water in both the seasons. Gibbs diagram indicates evaporation dominance type, no significance of precipitation and rock dominance type. Correlation matrix table gives interrelationship of the variables. EC and TDS have highest correlation (r = 0.98). The *t*-test behaviour has no significance and strong correlation between pre and post monsoon seasonal variables was found; therefore, the geogenic and rock water interaction was negligible.

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