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Groundwater Quality and Suitability of PG2 Watershed, Chandrapur District, Maharashtra: An Appraisal of Hydrogeochemical Behavior

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Abstract

Groundwater samples were studied to understand the concentrations of cations and anions, rock-water interaction as well as groundwater suitability from PG2 watershed of Chandrapur district, Maharashtra. The samples were collected from the phreatic aquifers where in, $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ is the dominance sequence with $Ca2^{+}$ as dominant cation. The geogenic processes like dissolution of calcium rich minerals are responsible for increase of Ca^{2+} content in groundwater. HCO_3^- and SO_4^{2-} are the prevailing dominant anions, with the dominance sequence as $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$. The mixed sectional types suggest the geogenic as well as anthropogenic sources of cations and anions; and the combinational water type. The interrelationship of HCO_3^- and Ca^{2+} divulges negative correlation also, the scatter diagram of Na^+ *vs* Cl^- interpret the rock-water interaction, which points out towards the silicate weathering as well as sources of calcium and bicarbonate. The groundwater is marginally suitable for drinking purpose. However, it is not appropriate for the intolerant crops which are vulnerable to anions of Cl^- and SO_4^{2-}.

Keywords: Rock-water Interaction, Phreatic Aquifers, Groundwater Quality, Silicate Weathering, PG2 Watershed, Chandrapur District

Introduction

The geochemical processes, occurring within the aquifer are solely responsible for geogenic changes in groundwater chemistry (Pandit *et al.*, 2009). Similarly, the anthropogenic activities responsible for the groundwater contamination from the dug wells of phreatic aquifers tend to be more polluted than deeper penetrated bore wells (Bhardwaj *et al.*, 2010). The irrigation runoff, high evaporation-climatic conditions, percolation of insecticides and pesticides as well as the situations of scanty rainfall along with other natural processes affect the groundwater quality (Wagh *et al.*, 2018; Panigrahi and Das, 2022).

The groundwater from shallow aquifers of PG2 watershed is solely the prime source for drinking, domestic and irrigation utilization from this area. The efforts have been made here to understand the hydrogeochemical behavior of groundwater, using multi criteria indicative methods/model.

Study Area

PG2 watershed (lat. 19º 38' 32”: 19º 48' 23" N and long. 78º 50' 12": 79º 05' 51" E) lies 250 km in southwest direction of Nagpur city and is bounded by hilly region from southern and southwestern boundary. The overall drainages exhibit dendrtic drainage pattern and drains out in Penganga River.

The study area experiences the semi-arid climatic conditions, where in temperature flares up to 46ºC in summer seasons and drops down up to 8ºC in winter season. The average annual rainfall is 1200 mm in the monsoon season (middle of June to September) and the humidity ranges between 7 to 91% (http://imdnagpur.gov.in).

Geology and Hydrogeology

The oldest Neoprotreozoic Penganaga limestones and limestone-shale units are unconformably overlain by the Lower Gondwana Supergroup of rocks (Lr. Permian to Lr. Cretaceous) (Fig.1). These rocks are covered by Deccan Trap basaltic flow (Upper Cretaceous to Lower Eocene). The sand, silt and clays of local Alluvium are noted from river sections.

The dugwells penetrating the Penganga limestone have an average depth between 7 to 18 meters below ground level (mbgl) and have diameters ranging from 2.5 to 5.5 m. These wells have the groundwater discharge of 50 to 300 m^3/ day (GSDA, 2009). The Deccan basaltic lava-flows exhibit vesicular nature and also disposed with deep weathering as well as well developed joints. The average depth of dugwells in basaltic lava flows ranges from 9 to 21 mbgl and the yield shows variation from 75 to 100 m^3/ day (GSDA, 2009). The details of groundwater assessment from the study area are given in Table 1.

Materials and Methods

30 groundwater samples were collected in pre-monsoon

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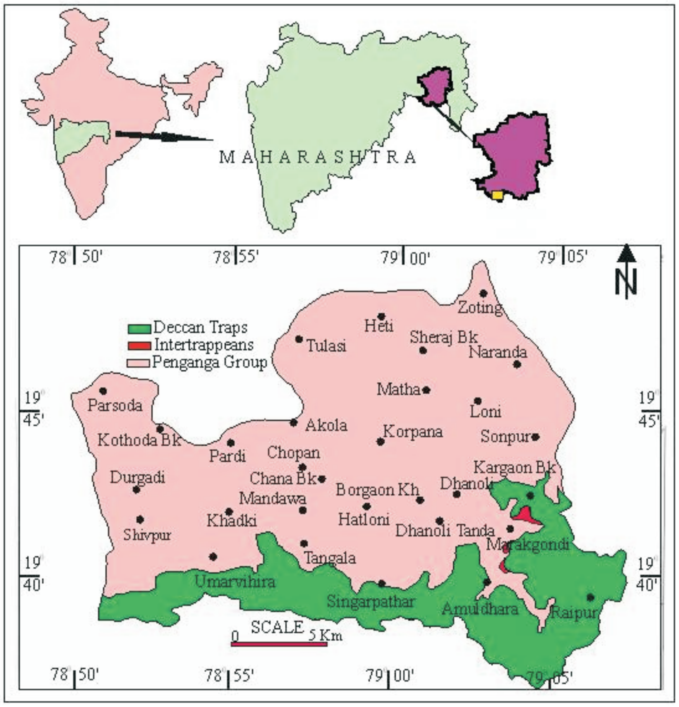

Fig.1. Location and geological map of PG2 Watershed

season (2022) in already cleaned polyethylene bottles of 1000 ml capacity. The guidelines given by BIS (2003) and WHO (2011) were used for the standard analytical procedures (APHA, 2005). The suitability of groundwater from the study area was checked for drinking, domestic use through the various classification schemes. Irrigation utility was ensured through the mathematical expressions using various parameters as given in equations 1 to 8.

Sodium Absorption Ratio (SAR);

$$SAR = Na^{+}/\sqrt{[(Ca^{2+}+Mg^{2+})/2]} \quad (1)$$

Percent Sodium (%Na);

$$\%\,Na = Na^{+} + K^{+}/\,(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) \times 100 \quad (2)$$

Residual Sodium Carbonate (RSC);

$$RSC = (HCO_3^{-} + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (3)$$

Residual Sodium Bicarbonate (RSBC);

$$RSBC = HCO_3^{-} - Ca^{2+} \quad (4)$$

Soluble Sodium Percentage (SSP);

$$SSP = [(Na^{+}+K^{+})/\,(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+})] \times 100 \quad (5)$$

Mg Ratio (MR);

$$MR = (Mg^{2+} \times 100)/\,(Ca^{2+} + Mg^{2+}) \quad (6)$$

Corrosivity Ratio (CR);

$$CR = [(Cl^{-}/35.5) + 2(SO_4^{2-}/96)]\,/\,2(HCO_3^{-} + CO_3^{2-}/100) \quad (7)$$

Kelley's Ratio (KR);

$$KR = Na^{+}/\,(Ca^{2+}+Mg^{2+}) \quad (8)$$

Hydrogeochemical Characteristics

Physical Parameters

The temperature of each sample, after the abstraction of groundwater from dug wells was measured, which was found to range from 24 to 28ºC. The water samples have pH values ranging from 7.7 to 8.8, indicating dominantly alkaline nature (Table 2). It is observed that the pH of groundwater from the study area is within the permissible limit (BIS, 2003). The values of EC found to grade between 912.3 and 2237.7µS/cm. All the groundwater samples have TDS value (583.9 to 1432.1 mg/l) greater than the 500mg/l, the desirable limit of recommended by WHO (1997). US Geological Survey (2000) provided a classification for groundwater based on the TDS concentration. This classification brings out that 74% of groundwater samples from the study area are fresh (TDS ≤ 1000 mg/l) while 26% water represents slightly saline nature (TDS between 1000 to 3000 mg/l).

Table 1: Details of PG2 watershed (*after* GSDA, 2015)

S. No.	Parameters	Particulars
1	Starting Latitude	19º 38' 32"
2	Ending Latitude	19º 48' 24"
3	Starting Longitude	78º 50' 12"
4	Ending Longitude	79º 05' 51"
5	Index to Toposheet (India)	56 I/13,14 and 56 M/1,2
6	Watershed Area	339.98 Sq. km.
7	Number of Taluka	02
8	Number of Villages	30 villages
9	Total annual groundwater recharge	1363 Ham
10	Natural discharge	68.15 Ham
11	Net groundwater availability	1294.85 Ham
12	Pre-monsoon water table trend	Rising
13	Post-monsoon water table trend	Rising
14	Category of watershed	Safe

Ham – Hectare meter (1crore liters)

The range of concentration from 174.9 to 781.5 mg/l of TH as $CaCO_3$ exhibits that 77% all the samples have TH value less the desirable limit of 500 mg/l, as suggested by WHO (1997). Total alkali (TA) values grade from 137 to 662 mg/l, and almost 52% of groundwater samples show TH values exceeding

Cation Hydrogeochemistry

Amongst the cations, Ca^{2+} is the dominant constituent and $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ is the dominance sequence of cations. Ca^{2+} and Mg^{2+} vary between 32.9 to 156.3 mg/l and 22.6 to 98.5 mg/l respectively and are well within the safe limit (WHO, 1997; BIS, 2003). Generally, Ca^{2+} values are more than the Mg^{2+} values, however, 17% of the samples (5 samples) are having Mg^{2+} content exceeding the Ca^{2+} values. Generally, the geogenic processes like dissolution of calcium rich minerals are responsible for increase of Ca^{2+} content in groundwater (Karanth, 1987). In some of the samples Mg^{2+} content exceeds the Ca^{2+} values as reported above; indicate excess use of fertilizers and pesticides along with Mg rich carbonate rock (dolomite) (Roy *et al.*, 2018). The concentration of Na^{+} in the study area that grades from 13.6 to 69.5 mg/l with an average of 39.01 mg/l; points out that Na^{+} content is within the permissible limit as prescribed by WHO (1997) and BIS (2003). The concentration of K^{+} in the study area grades from 0.40 to 6.40 mg/l with an average of 2.52 mg/l.

Anion Hydrogeochemistry

In the groundwater samples HCO_3^{-} and SO_4^{2-} are the prevailing dominant anions while Cl^{-} and NO_3^{-} are the other minor contributing anions with the dominance sequence $HCO_3^{-} > SO_4^{2-} > NO_3^{-} > Cl^{-}$. The HCO_3^{-} content ranges between 158.3 to 671.4 mg/l,

Table 2: Analytical data of cations and anions with physical and computed parameters from PG2 watershed

Sr. No .	Village	Sample No.	pH	EC	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_{3-}	Cl -	SO_4^{2-}	NO_3^{-}	CA-I	CA-II	Gibbs Cations	Gibbs Anions
1	Parsoda	PG2 1	7.7	1311.5	839.3	212	249.7	42.8	34.8	13.6	6.3	412.8	267.8	344.8	168.5	0.97	0.28	0.32	0.39
2	Khatoda Bk	PG2 2	7.9	1632.8	1045.0	236	473.0	45.7	87.5	34.7	2.4	345.6	157.8	278.5	156.8	0.80	0.16	0.45	0.31
3	Durgadi	PG2 3	8.2	2216.7	1418.7	365	174.9	32.9	22.6	18.4	1.6	642.5	276.3	158.5	97.4	0.94	0.29	0.38	0.30
4	Shivpur	PG2 4	7.6	1856.9	1188.4	654	435.5	56.6	71.7	25.7	5.6	458.2	137.6	234.7	123.7	0.85	0.14	0.36	0.23
5	Pardi	PG2 5	7.8	1578.7	1010.3	145	321.4	51.8	46.8	43.7	2.9	513.9	156.8	179.5	46.7	0.74	0.16	0.47	0.23
6	Khadki	PG2 6	8.1	912.3	583.9	487	400.3	67.8	56.3	48.3	0.7	629.5	211.4	279.4	68.6	0.77	0.17	0.42	0.25
7	Umarvihira	PG2 7	7.9	1852.7	1185.7	623	270.5	45.7	38.1	29.7	1.4	369.4	197.5	158.3	156.3	0.86	0.25	0.40	0.35
8	Akola	PG2 8	7.9	1634.8	1046.3	148	323.8	56.2	44.7	37.4	0.5	258.3	134.8	239.7	68.4	0.73	0.17	0.40	0.34
9	Chopan	PG2 9	8.2	1145.8	733.3	389	397.4	51.7	65.4	39.6	1.6	188.5	247.2	614.8	78.2	0.85	0.24	0.44	0.57
10	Chana Bk	PG2 10	8.1	956.1	611.9	462	339.6	46.8	54.3	42.6	3.7	412.8	158.7	587.4	159.5	0.75	0.10	0.50	0.28
11	Mandawa	PG2 11	7.7	1134.9	726.3	583	322.0	52.2	46.7	38.3	0.8	659.3	168.3	467.3	37.7	0.78	0.11	0.43	0.20
12	Tanagala	PG2 12	7.9	2237.7	1432.1	137	747.9	137.6	98.5	57.4	3.4	515.7	132.7	312.7	117.6	0.59	0.08	0.31	0.20
13	Sigarpathar	PG2 13	8.1	1423.7	911.1	662	448.9	87.4	56.2	44.2	1.8	478.3	268.5	427.8	145.8	0.84	0.21	0.34	0.36
14	Hatloni	PG2 14	7.9	967.2	619.0	193	542.7	89.5	77.8	47.6	3.2	389.6	97.2	176.8	89.6	0.54	0.08	0.36	0.20
15	Korpana	PG2 15	8.3	934.1	597.8	458	418.1	74.4	56.6	37.3	1.8	497.5	112.4	199.3	64.3	0.68	0.10	0.34	0.18
16	Tulsi	PG2 16	8.2	1435.6	918.8	457	463.5	96.5	54.2	69.5	6.4	512.6	164.2	212.7	73.7	0.62	0.13	0.44	0.24
17	Heti	PG2 17	8.3	987.5	632.0	651	655.7	133.7	78.4	54.2	5.7	671.4	84.8	653.2	146.8	0.43	0.02	0.31	0.11
18	Sheraj Bk	PG2 18	8.2	1667.7	1067.3	478	521.9	97.4	67.9	44.7	3.8	348.3	137.5	374.8	58.4	0.70	0.12	0.33	0.28
19	Matha	PG2 19	7.9	932.9	597.0	493	649.9	114.8	88.5	67.2	1.7	479.2	288.3	146.8	45.2	0.77	0.33	0.38	0.38
20	Borgaon Kh	PG2 20	8.5	1187.6	760.0	369	781.5	156.3	95.3	27.7	2.9	158.3	269.5	233.4	173.8	0.91	0.43	0.16	0.63
21	Dhanoli Tanda	PG2 21	8.8	1029.7	659.0	651	581.2	87.5	88.4	43.8	4.2	267.4	78.3	413.6	87.5	0.49	0.05	0.35	0.23
22	Dhanoli	PG2 22	8.6	1266.8	810.8	542	276.2	45.7	39.5	34.5	2.7	564.2	256.8	333.7	136.7	0.88	0.22	0.45	0.31
23	Amuldhara	PG2 23	8.4	1187.5	760.0	567	325.0	55.7	45.3	27.4	1.6	542.7	82.5	417.5	71.8	0.69	0.05	0.34	0.13
24	Raipur	PG2 24	8.4	1459.6	934.2	439	326.9	51.4	48.4	24.8	1.2	269.4	173.7	125.3	64.4	0.86	0.33	0.34	0.39
25	Marakgondi	PG2 25	7.9	1763.2	1128.5	358	517.3	86.2	73.6	39.5	3.6	314.7	96.4	178.7	156.3	0.63	0.09	0.33	0.23
26	Loni	PG2 26	8.8	1649.4	1055.6	379	403.0	67.9	56.9	43.7	1.2	278.5	75.8	278.5	94.7	0.44	0.05	0.40	0.21
27	Kargaon Bk	PG2 27	7.9	1278.6	818.3	247	338.7	54.8	49.2	32.6	0.7	257.7	69.3	123.7	68.3	0.54	0.08	0.38	0.21
28	Sonpur	PG2 28	7.8	1367.8	875.4	612	476.3	78.5	68.3	41.9	0.4	355.3	47.8	368.4	89.5	0.13	0.01	0.35	0.12
29	Naranda	PG2 29	8.6	1564.9	1001.5	358	456.3	88.4	57.4	26.8	0.6	179.4	139.7	159.5	47.5	0.81	0.29	0.24	0.44
30	Zoting	PG2 30	8.4	1444.6	924.5	431	386.4	67.3	53.2	33.6	1.2	368.2	63.7	379.2	127.4	0.49	0.04	0.34	0.15
		Min	7.6	912.3	583.9	137	174.9	32.90	22.60	13.60	0.40	158.30	47.80	123.70	37.70	0.13	0.01	0.16	0.11
		Max	8.8	2237.7	1432.1	662	781.5	156.30	98.50	69.50	6.40	671.40	288.30	653.20	173.80	0.97	0.43	0.50	0.63
		Average	8.1	1400.6	896.4	426	434.2	74.04	60.75	39.01	2.52	411.31	158.44	301.95	100.70	0.70	0.16	0.37	0.28
		STDEV	0.3	364.6	233.3	164	144.5	30.68	18.92	12.68	1.76	146.10	73.15	145.98	42.59	0.18	0.11	0.07	0.12
		Covariance	4.0	26.0	26.0	39	33.3	41.44	31.14	32.51	69.95	35.52	46.17	48.35	42.29	26.30	66.32	18.64	42.74

Gibbs Cations: (Na+K)/ (Na+K+Ca), Gibbs Anions: (Cl/(Cl+HCO_3)), cation and anion values are presented in mg/l.

with average of 411.3 mg/l. The occurrence of SO_4^{2-} in groundwater divulges anthropogenic contamination. In the present study the concentration of SO_4^{2-} has been found in the grade between 123.7 to 653.2 mg/l. The NO_3^- concentration shows its variation from 37.7 to 173.8 mg/l with an average value of 301.9 mg/l. About 62% of the groundwater samples from the study area have NO_3^- concentration more than the prescribed limit set BIS (2003). The desire limit for Cl^- in potable groundwater is 200 mg/l (WHO, 1997), which can further be relaxed up to 1000 mg/l (permissible limit) for Indian conditions (BIS, 1991). The Cl^- content from the groundwater samples range from 47.8 to 288.3 mg/l. 26% of the groundwater samples from the study area exceeds the limit of desirable value of Cl^- as prescribed by WHO (1997).

Hydrogeochemical Classification and Interrelationship

The data sets on the concentrations of the cations and the anions were subjected to Aquachem-4 software and Piper trillinear diagram (Piper, 1953) was generated for the groundwater samples of the study area (Fig.2). In the study area, in general, alkaline earths (Ca + Mg) exceed the alkalis (Na + K); however, in 28% samples alkalis (Na + K) exceed alkaline earths (Ca + Mg). The 35% of the groundwater samples show weak acid (CO_3 + HCO_3) exceeding the strong acids (SO_4+Cl).

The Ca-HCO_3 (34%) is the most prominent water type found in the present investigation, which is an indicator of geogenic mixing of groundwater. The two mixed sectional, Ca - Mg - Cl (19%) and Ca - Na - HCO_3 (17%) water types suggest the geogenic as well as anthropogenic sources of cations and anions; however the contribution of geogenic source is revealed through Ca - Mg - HCO_3 - Cl (65%) than the Ca - Na - HCO_3 - Cl (35%) combinational water type (Murkute, 2022).

Rock-Water Interaction and Source Recognition

The distinct processes which are responsible for the generation of various ions are discussed here.

Silicate Weathering

The interrelationship of HCO_3^- and Ca^{2+} divulges negative correlation in present investigation (Fig.3a). The scatter diagram of Na^+ *vs* Cl^- has been used to interpret the rock-water interaction (Fig.3b), which points out towards the silicate weathering as well as sources of calcium and bicarbonate (Lakshmanan *et al.*, 2003). The scatter points falling below the equiline reveal high Na/Cl ratio, which is due to water-rock interaction, most likely by feldspar weathering (Zhu *et al.*, 2008). The Na^+/ Cl^- molar ratios in most of the groundwater samples are more than 1, which suggests that the silicate weathering reactions are probably the sources for Na^+ in the study area (Meybeck, 1987). In the same scatter plots, the points which lie above the equiline indicate excess of Cl-, which is probably due to interface on human interventions *i.e.* domestic waste, animal waste, septic tanks, *etc* (Murkute, 2014). The feldspars, pyroxenes and amphiboles are the primary sources of Ca^{2+} in groundwater samples from Deccan Trap while the feldspars, calcite and clay minerals are the probable sources of Ca^{2+} from the sedimentary rock (Todd, 1995; Murkute, 2014).

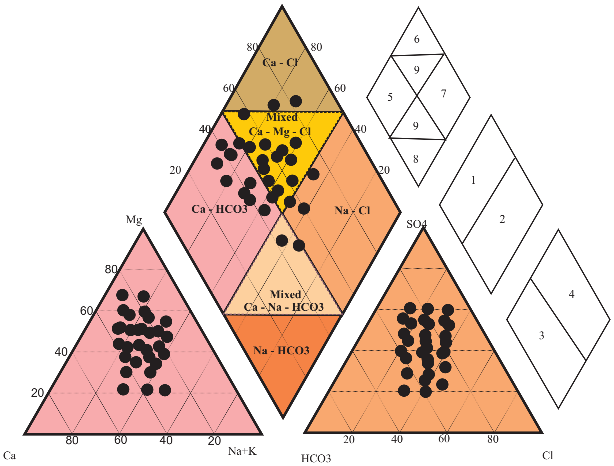

Fig.2. Piper's trillinear diagram for study area

The interrelationship diagram of Ca^{2+}+ Mg^{2+} *and* SO_4^{2-}+ HCO_3^- (Fig.3c), is a prime tool for interpreting the rock-water interaction that reveals the two parts above and below the equiline. The points below the equiline represent the silicate weathering (Lakshmanan *et al.*, 2003) and also suggest excess of SO_4^{2-} + HCO_3^- values, moreover is indicative of excess of alkalinity (HCO_3^-) in the groundwater (Bhardwaj *et al.*, 2010). Thus, the silicate weathering suggested by the dominance of SO_4^{2-} + HCO_3^- reveals dissolution of silicate minerals, thereby, falling trend calcium content in groundwater (Ramesh and Elango, 2011).

Carbonate and Gypsum Dissolution

The interrelationship of alkaline earth metals with the bicarbonate and sulphate also divulges the carbonate dissolution above the equiline (Fig. 3c; Ramesh and Elango, 2011). The change in the concentration of Ca^{2+} and SO_4^{2-} at rock-water interface is responsible for dissolution of calcite and gypsum. Nearly 4.6% of the points above the equiline are indicative of strong dissolution of calcite and dissolution of dolomite when Mg^{2+} concentration is more (Yang *et al.*, 2016; Murkute, 2014). Moreover, the dispersion of SO_4^{2-} on the pertinent sites is the source of gypsum formation. Many times, the presence of clayey rock material in the aquifer facilitates the reverse cation exchange by liberating Ca^{2+} and Mg^{2+} ions. The interrelationship diagram of Ca^{2+} + Mg^{2+} and SO_4^{2-} + HCO_3^- (Fig.3c), also focuses on the reverse ion exchange in the groundwater (Wagh *et al.*, 2018). The points lying above the equiline are indicative of carbonate dissolution. The scatter plot of Ca^{2+} and SO_4^{2-} (Fig. 3d) reveals the scattering of sampling points which expresses that gypsum dissolution is highly masked by the other factors also for instance recharge water chemistry, precipitation, evaporation and anthropogenic sources (Wu and Sun, 2016). Moreover, some groundwater samples lie towards the 1:1 line of the Ca^{2+} + Mg^{2+} than the HCO_3^- diagram (Fig.3e), demonstrating dissolution of carbonates (Wu and Sun, 2016).

Evaporite Dissolution

Bivariate plot of Na^+ and Cl^-, some groundwater sampling points which cluster along the 1:1 line, suggest the dissolution of halite in minor percentage (Hussin *et al.*, 2016). If the groundwater samples have Na^+/Cl^- ratio > 1, then it corresponds to the release of Na^+ from weathering of feldspars such as plagioclase instead of halite dissolution (Hussin *et al.,* 2016). In about 52% of the total groundwater samples, the value of Na^+/Cl- ratio is more than one,

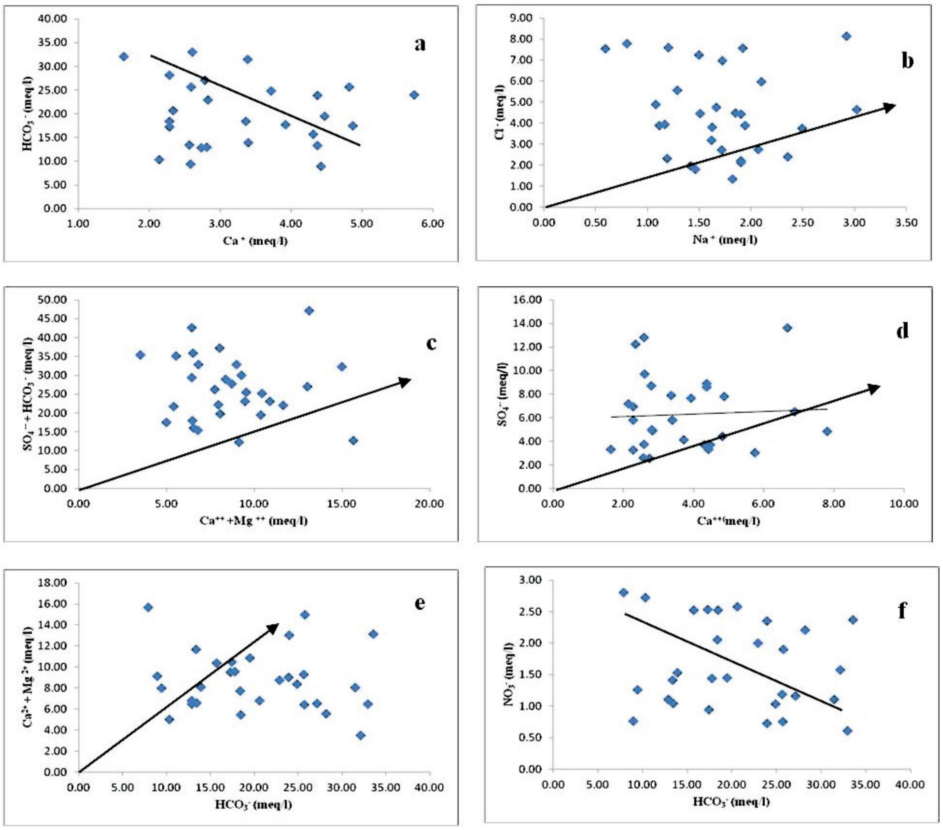

Fig.3. Inter-ionic relationship between ions. a) interrelationship of HCO_3^- and Ca^{2+}, b) scatter diagram of Na^+ *vs* Cl^- and c) interrelationship diagram of $Ca^{2+} + Mg^{2+}$ *and* $SO_4^{2-} + HCO_3^-$, d) scatter diagram of SO_4^{2-} *vs* Ca^{2+}, e) interrelationship diagram of $Ca^{2+} + Mg^{2+}$ *and* HCO_3^-, and f) scatter diagram of NO_3^- *vs* HCO_3^-.

indicating high contribution of Na^+ in the groundwater by the hydrolysis of silicates (Subba Rao and Surya Rao, 2010).

Anthropogenic Interventions

In the groundwater system of the agricultural rural expanse, the irrigation return flow is the prime source of Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^- and SO_4^{2-} (Karanth, 1987). The negative correlation between NO_3^- and HCO_3^- (Fig.3f) indicates the different sources for both the ions, where in $NO3^-$ is mainly consequential of anthropogenic interventions while HCO_3^- is derivative of lithological inputs. The bivariate plot between NO_3^- and HCO_3^- for the groundwater samples of the study area clearly demonstrates the negative correlation exhibiting anthropogenic interventions in the study area.

Ion Exchange Aspects

The interrelationship diagram of $Ca^{2+} + Mg^{2+}$ *and* $SO_4^{2-} + HCO_3^-$ (Fig.3c) suggests the control of anions over the cations. To confirm the existence of ion exchange processes chloro-alkaline indices CAI-1 and CAI-2 were computed and are presented (Schoeller, 1977; Table 2). The negative CAI index values reveal the softening process in which Ca^{2+} and Mg^{2+} exchange with Na^+ and K^+ in the groundwater from the aquifer. Contrary, the positive values exhibit hardening process in which Na^+ and K^+ ions are adsorbed on the aquifer material with instantaneous release of Ca^{2+} and Mg^{2+} pointing reverse ion exchange process (Hussin *et al.*, 2016). Except some negative values, the positive values of CAI-1 (0.03 to 1.05) and CAI-2 (0.02to 0.59) depicts the active reverse ion exchange process, may be due to anthropogenic interventions.

Hydrogeochemistry Controlling Mechanism

The Gibbs plots are depicted by plotting ratio against the TDS by dominant cations [(Na+K) / (Na+K+Ca)] (Fig.4a), and dominant anions [(Cl/Cl+HCO3)] (Fig.4b), to assess the controlling sources of dissolved hydrogeochemical organization. The points for the groundwater samples from the study are spread out in Gibbs Diagram enumerate that chemical weathering of rock forming mineral suites is the key contributing feature in the evolution of

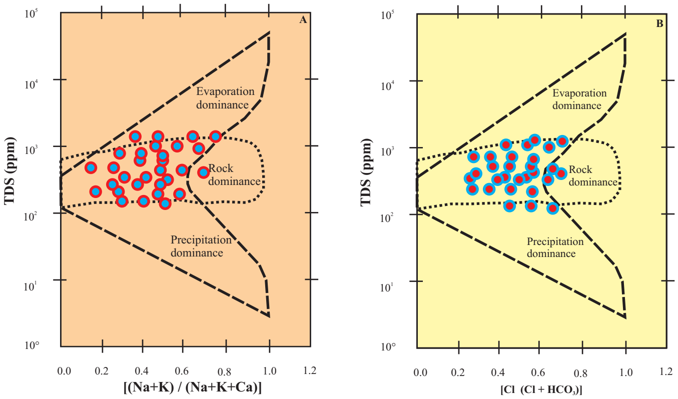

Fig.4. Gibbs diagram. a) TDS with [(Na+K) / (Na+K+Ca)], b) TDS with [(Cl/Cl+HCO_3)]

Table 3: Correlation matrix of hydrochemical parameters from study area

	pH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NO_3^-	HCO_3^-	SO_4^{2-}	Cl^-
pH	1.00											
EC	-0.28	1.00										
TDS	-0.35	1.00	1.00									
TH	-0.22	0.71	0.68	1.00								
Ca^{2+}	-0.38	0.69	0.78	0.95	1.00							
Mg^{2+}	-0.29	0.42	0.43	0.91	0.67	1.00						
Na^+	-0.12	0.71	0.72	-0.26	0.40	0.18	1.00					
K^+	-0.31	0.49	0.71	-0.37	0.37	0.31	0.48	1.00				
NO_3^-	0.44	0.66	0.80	-0.24	0.63	0.49	0.51	0.17	1.00			
HCO_3^-	0.62	0.27	0.29	-0.33	0.17	-0.23	0.42	0.41	-0.22	1.00		
SO_4^{2-}	-0.24	0.68	0.73	0.81	0.79	0.55	0.75	0.35	0.31	0.71	1.00	
Cl^-	-0.41	0.81	0.78	0.21	0.71	0.31	0.81	0.56	0.72	0.28	0.42	1.00

chemical composition of groundwater occurring in all the lithological domains of study area, which is secondarily influenced by the anthropogenic activities (Gibbs, 1970).

Hydrogeochemical Correlation

The significant positive correlation between TDS (Table 3) with TH (r = 0.68), Ca^{2+} (r = 0.78) and Na^+ (r = 0.71) suggests the hydrochemical processes responsible at rock-water interaction (Tay *et al.*, 2017). The non-lithological source for NO_3^- as well as low correlation between K^+ with NO_3^- (r = 0.17) and SO_4^{2-} (r = 0.35) is attributed to the agricultural fertilizers and domestic wastewaters. Therefore, sporadically the chemical data of the groundwater of sampling points extends in the field of evaporation dominance zone from the field of rock dominance. The samples showing affinity towards the evaporation zone also have high concentration of NO_3^- and Cl- indicating anthropogenic influence. This is also supported by significant positive correlation between TDS with Na^+ (r = 0.71) and Cl^- (r = 0.78). Thus, the anthropogenic influence other than the water-rock interaction is as well the key reason that is considered as the major source of pollution. Na^+ exhibits strong positive correlation with Cl^- (r = 0.81) as well as with SO_4^{2-} (r = 0.75). Such a well-built association in hydrogeochemistry is indicative of high pollution intensity in groundwater (Barzegar *et al.,* 2017). The HCO_3^- which is showing negative correlation with NO_3^- (r = - 0.22) suggests various types of anion sources and also points out non-geogenic source for NO_3^- content (Wu and Sun, 2016).

Groundwater Suitability

Drinking Use

The electrical conductivity (EC) has permissible limit of 1500 mg/l (WHO, 1997) represents the measure of salinity hazard. The 72 % groundwater samples from the study area have EC values less than the prescribed permissible limit indicating their suitability for drinking purpose (Table 4). Considering TA and TH content, all the groundwater samples are suitable for drinking purpose except eight sample for TA and six samples for TH, correspondingly. In addition, as regards to the prescribed limits set by WHO (2011) and BIS (2003), 32% of the groundwater samples from the study area have NO_3^- concentration more than this limit.

Domestic Use

Water with TH content exceeding the 80 mg/l cannot be used for domestic purposes, since it coagulates soap lather. 66.7% of the groundwater samples from the study have SO_4^{2-} concentration less the value of permissible limit of 400 mg/l (BIS, 1991) and hence, may be used for drinking and domestic purposes.

Irrigation Use

Various irrigation quality indicators (Table 5) have been applied to evaluate the suitability of groundwater samples from the study area.

Sodium Adsorption Ratio (SAR)

It measures the soil permeability in respect to Na^+, Ca^{2+} and Mg^{2+} cations. The SAR values of the groundwater samples range from 0.4 to 1.4 meq/l and infer excellent quality for irrigation purpose. The SAR values in terms of sodium hazard are compared with the salinity hazard (Fig.5) in the US Salinity Laboratory's diagram (US Salinity Laboratory Staff, 1954). The main cluster of plots of the groundwater samples spreads in C_3-S_1 type specifying

Table 4: Range of cations and anions with desirable and permissible limits

Parameter	Range			WHO (1997)				BIS (2003) IS: 10500				STDEV	Covariance
	Min	Average	Max	Desirable Limit (DL)	Permissible Limit (PL)	% of Samples above DL	% of Samples above PL	Desirable (DL)	Permissible (PL)	% of Samples above DL	% of Samples above PL		
pH	7.6	8.1	8.8	7.0-8.5	6.5-9.2	10.0	0.0	6.5-8.5	8.5-9.2	10.0	0.0	0.3	4.0
EC	912.3	1400.6	2237.7	750	1500	36.7	23.3	-	-	-	-	364.6	26.0
TDS	583.9	896.4	1432.1	500	1500	100.0	0.0	500	2000	100.0	0.0	233.3	26.0
TA	137.0	426.2	662.0	100	500	100.0	30.0	200	600	83.3	16.7	164.3	38.5
TH	174.9	434.2	781.5	100	500	100.0	26.7	300	600	86.7	13.3	144.5	33.3
Ca^{++}	32.9	74.0	156.3	75	200	40.0	0.0	75	200	40.0	0.0	30.7	41.4
Mg^{++}	22.6	60.8	98.5	30	150	96.7	0.0	30	100	96.7	0.0	18.9	31.1
Na^+	13.6	39.0	69.5	50	200	13.3	0.0	-	-	-	-	12.7	32.5
K^+	0.4	2.5	6.4	100	200	0.0	0.0	-	-	-	-	1.8	69.9
HCO_3^-	158.3	411.3	671.4	200	600	90.0	0.0	200	600	90.0	0.0	146.1	35.5
Cl^-	47.8	158.4	288.3	250	600	20.0	0.0	250	1000	20.0	0.0	73.2	46.2
SO_4^{--}	123.7	302.0	653.2	200	600	66.7	6.7	200	400	66.7	23.3	146.0	48.3
NO_3^-	37.7	100.7	173.8	-	50	-	86.7	45	100	100.0	40.0	42.6	42.3

Cation and anion values are presented in mg/l.

Table 5: Irrigation suitability indices for groundwater of study area

Sample No	SAR	W_Q	% Na	W_Q	RSC	W_Q	RSBC	W_Q	SSP	W_Q	MR	W_Q	CR	W_Q	KR	W_Q	PS	W_Q	K	W_Q
PG2 1	0.4	E_{XL}	20.2	E_{XL}	0.7	G_D	1.8	S_{TF}	13.4	G_D	57.2	H_{RM}	0.9	G_D	0.1	G_D	11.1	I_{TU}	17.9	E_{XL}
PG2 2	0.7	E_{XL}	16.4	E_{XL}	1.0	G_D	8.1	M_{RG}	14.3	G_D	75.9	H_{RM}	0.5	G_D	0.2	G_D	7.4	I_{TU}	12.1	E_{XL}
PG2 3	0.6	E_{XL}	7.6	E_{XL}	3.6	U_{NS}	25.5	U_{SF}	19.4	G_D	53.1	H_{RM}	0.3	G_D	0.2	G_D	9.4	I_{TU}	18.8	E_{XL}
PG2 4	0.5	E_{XL}	22.5	G_D	1.8	D_{BT}	11.6	U_{SF}	12.8	G_D	67.6	H_{RM}	0.3	G_D	0.1	G_D	6.3	I_{TU}	17.8	E_{XL}
PG2 5	1.1	E_{XL}	15.1	E_{XL}	2.4	D_{BT}	15.3	U_{SF}	23.6	G_D	59.8	H_{RM}	0.3	G_D	0.3	G_D	6.3	I_{TU}	7.6	E_{XL}
PG2 6	1.0	E_{XL}	10.6	E_{XL}	2.9	U_{NS}	17.9	U_{SF}	20.9	G_D	57.7	H_{RM}	0.4	G_D	0.3	G_D	8.9	I_{TU}	4.5	E_{XL}
PG2 7	0.8	E_{XL}	9.3	E_{XL}	1.6	D_{BT}	9.3	M_{RG}	19.7	G_D	57.8	H_{RM}	0.3	G_D	0.2	G_D	7.2	I_{TU}	12.1	E_{XL}
PG2 8	0.9	E_{XL}	8.2	E_{XL}	0.8	G_D	1.7	S_{TF}	20.1	G_D	56.7	H_{RM}	0.5	G_D	0.3	G_D	6.3	I_{TU}	9.3	E_{XL}
PG2 9	0.9	E_{XL}	12.9	E_{XL}	0.2	G_D	-0.9	S_{TF}	18.2	G_D	67.5	H_{RM}	1.6	C_{RS}	0.2	G_D	13.4	I_{TU}	6.8	E_{XL}
PG2 10	1.0	E_{XL}	17.7	E_{XL}	1.7	D_{BT}	11.3	U_{SF}	22.4	G_D	65.6	H_{RM}	0.7	G_D	0.3	G_D	10.6	I_{TU}	4.9	E_{XL}
PG2 11	0.9	E_{XL}	9.2	E_{XL}	3.3	U_{NS}	22.5	U_{SF}	20.7	G_D	59.5	H_{RM}	0.4	G_D	0.3	G_D	9.6	I_{TU}	6.3	E_{XL}
PG2 12	0.9	E_{XL}	21.8	G_D	1.3	G_D	-1.7	S_{TF}	14.8	G_D	54.1	H_{RM}	0.4	G_D	0.2	G_D	7.0	I_{TU}	12.6	E_{XL}
PG2 13	0.9	E_{XL}	13.1	E_{XL}	1.9	D_{BT}	6.4	M_{RG}	18.0	G_D	51.4	H_{RM}	0.6	G_D	0.2	G_D	12.0	I_{TU}	8.0	E_{XL}
PG2 14	0.9	E_{XL}	18.7	E_{XL}	1.1	G_D	1.6	S_{TF}	16.6	G_D	58.9	H_{RM}	0.3	G_D	0.2	G_D	4.6	I_{TU}	5.6	E_{XL}
PG2 15	0.8	E_{XL}	12.5	G_D	2.1	D_{BT}	10.0	U_{SF}	16.6	G_D	55.6	H_{RM}	0.3	G_D	0.2	G_D	5.2	I_{TU}	6.0	E_{XL}
PG2 16	1.4	E_{XL}	26.9	G_D	2.0	D_{BT}	6.3	M_{RG}	25.8	G_D	48.0	H_{RM}	0.3	G_D	0.3	G_D	6.8	I_{TU}	5.2	E_{XL}
PG2 17	0.9	E_{XL}	25.8	G_D	2.6	U_{NS}	6.8	M_{RG}	16.1	G_D	49.1	H_{RM}	0.5	G_D	0.2	G_D	9.2	I_{TU}	5.5	E_{XL}
PG2 18	0.9	E_{XL}	19.2	E_{XL}	0.9	G_D	-2.1	S_{TF}	16.4	G_D	53.4	H_{RM}	0.6	G_D	0.2	G_D	7.8	I_{TU}	10.0	E_{XL}
PG2 19	1.1	E_{XL}	17.5	E_{XL}	1.4	G_D	1.0	S_{TF}	18.6	G_D	55.9	H_{RM}	0.4	G_D	0.2	G_D	9.7	I_{TU}	4.2	E_{XL}
PG2 20	0.4	E_{XL}	17.7	E_{XL}	-1.0	G_D	-23.3	S_{TF}	7.6	G_D	50.1	H_{RM}	0.9	G_D	0.1	G_D	10.0	I_{TU}	14.1	E_{XL}
PG2 21	0.8	E_{XL}	21.8	E_{XL}	0.2	G_D	-4.1	S_{TF}	14.8	G_D	62.4	H_{RM}	0.7	G_D	0.2	G_D	6.5	I_{TU}	6.7	E_{XL}
PG2 22	0.9	E_{XL}	13.2	E_{XL}	2.8	U_{NS}	19.1	U_{SF}	22.2	G_D	58.7	H_{RM}	0.5	G_D	0.3	G_D	10.7	I_{TU}	7.2	E_{XL}
PG2 23	0.7	E_{XL}	10.2	E_{XL}	2.6	U_{NS}	16.0	U_{SF}	16.0	G_D	57.2	H_{RM}	0.4	G_D	0.2	G_D	6.7	I_{TU}	9.2	E_{XL}
PG2 24	0.6	E_{XL}	9.2	E_{XL}	0.9	G_D	3.2	S_{TF}	14.5	G_D	60.8	H_{RM}	0.3	G_D	0.2	G_D	6.2	I_{TU}	12.5	E_{XL}
PG2 25	0.8	E_{XL}	18.7	E_{XL}	0.7	G_D	-1.5	S_{TF}	15.0	G_D	58.4	H_{RM}	0.3	G_D	0.2	G_D	4.6	I_{TU}	12.0	E_{XL}
PG2 26	0.9	E_{XL}	11.6	E_{XL}	0.7	G_D	0.3	S_{TF}	19.3	G_D	58.0	H_{RM}	0.5	G_D	0.2	G_D	5.0	I_{TU}	8.9	E_{XL}
PG2 27	0.8	E_{XL}	8.7	E_{XL}	0.8	G_D	1.9	S_{TF}	17.4	G_D	59.6	H_{RM}	0.3	G_D	0.2	G_D	3.2	I_{TU}	8.5	E_{XL}
PG2 28	0.8	E_{XL}	10.3	E_{XL}	1.0	G_D	2.1	S_{TF}	16.1	G_D	58.9	H_{RM}	0.5	G_D	0.2	G_D	5.2	I_{TU}	8.4	E_{XL}
PG2 29	0.5	E_{XL}	8.6	E_{XL}	0.0	G_D	-8.7	S_{TF}	11.4	G_D	51.7	H_{RM}	0.5	G_D	0.1	G_D	5.6	I_{TU}	14.7	E_{XL}
PG2 30	0.7	E_{XL}	10.4	E_{XL}	1.3	G_D	4.9	S_{TF}	16.2	G_D	56.5	H_{RM}	0.5	G_D	0.2	G_D	5.7	I_{TU}	10.0	E_{XL}

W_Q – Water Quality, E_{XL} – Excellent, G_D- Good, U_{NS} – Unsuitable, D_{BT} –Doubtful, S_{TF} – Satisfactory, M_{RG} – Marginal, U_{SF} – Unsatisfactory, H_{RM} – Harmful, C_{RS} – Corrosive, I_{TU} – Injurious to Unsatisfactory

the water of medium to high salinity-medium sodium type. The groundwater points corresponding to the C_3-S_2 type (20%) represents the medium salinity - medium sodium type. Such a groundwater for the above two categories may be utilized for irrigation with slight threat of exchangeable sodium. The other very minor clusters of points are in C_2-S_1 (10%) and C_4-S_1 (5%). Such a groundwater for the above two categories may be utilized for salt tolerant or semi tolerant crops under the favourable drainage conditions. Surplus salinity decreases the osmotic activity of plants, moreover impedes the absorption of water and nutrients from the soil (Saleh *et al.*, 1999) as well as affects the chemical as well as physical setup of agricultural soil and consequently directly or indirectly affect the soil structure, permeability and aeration (Subba Rao, 2006).

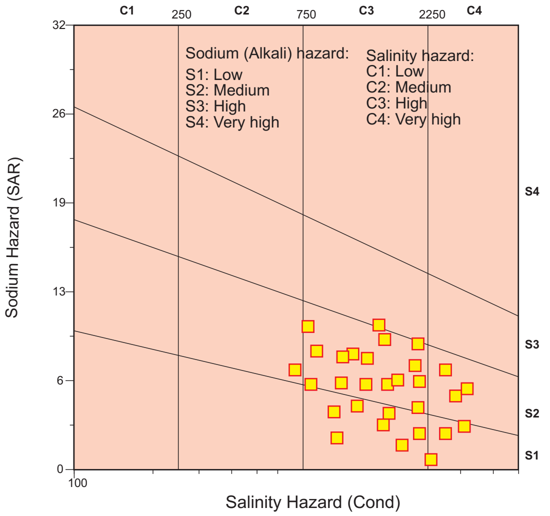

Fig.5. US Salinity diagram for groundwater samples from PG2 watershed

Percent Sodium (%Na)

The groundwater having higher EC as well as high sodium percentage (% Na), due to altered soil structures eventually kill the plant (Atikul Islam *et al.*, 2017). The %Na^+ values for the present investigation exhibit good to excellent water quality.

Residual Sodium Carbonate (RSC)

The RSC involves the combination of HCO_3^-, Ca^{2+} and Mg^{2+}. The higher RSC values (RSC > 2.5 meq/l) are indicative of harmful nature to the growth of plants. In the present investigation the RSC values depicts the good to doubtful category of groundwater with five unsuitable groundwater samples.

Residual Sodium Bicarbonate (RSBC)

The RSBC value represents the mathematical difference between the HCO_3^- anion and Ca^{2+} cation. The 60 % of the groundwater samples from study area shows satisfactory range of water quality. 28% shows unsatisfactory results and 22%

of groundwater samples can be of marginal utilization for irrigation use.

Soluble Sodium Percentage (SSP)

The higher soluble sodium percentage has undeserved consequences in irrigation water due to the process of Base Exchange, which replaces the calcium cation primarily by the sodium cation in the soil, which in turns lowers the soil permeability. The groundwater samples of the study area have good-water quality and hence found to be suitable for irrigation purpose.

Mg Ratio (MR)

The alkaline earth metals (Ca^{2+} and Mg^{2+}) are naturally the sole contributors to chemistry of groundwater at rock-water interface. The MR values of the samples indicate that the groundwater from the study area is harmful to those crops which need the total aeration and which do not have nitrogen fixing capacity (Murkute, 2022).

Corrosivity Ratio (CR)

The CR is crucial parameter, which involves the anthropogenically generated anions (Cl^- and SO_4^{2-}). All the groundwater samples (except sample no 9) from the study area are non-corrosive and hence water can be transported to longer distances for irrigation purpose.

Kelley's Ratio (KR)

The KR involves the mathematical relationship of divalent cations (Ca^{2+} and Mg^{2+}) and univalent cation (Na^+). The KR value for all the groundwater samples from the study area are found to be of good-water quality and therefore suitable for irrigation purpose.

Conclusions

The water samples from the study area are dominantly alkaline nature. 23.3% of groundwater samples having EC value more than the prescribed limit given by WHO exhibit slightly saline nature. The $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ is the dominance sequence with $Ca2^+$ as dominant cation. The geogenic processes like dissolution of calcium rich minerals are responsible for increase of Ca^{2+} content in groundwater. In the groundwater samples HCO_3^- and SO_4^{2-} are the prevailing dominant anions, with the dominance sequence as $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$. Occurrences of SO_4^{2-} anion in groundwater divulges anthropogenic contamination, such as fertilizers and moreover from oxidation of sulphide minerals added in fertilizers. In the study area, in general, alkaline earths (Ca + Mg) exceed the alkalis (Na + K); however in 28% samples alkalis (Na + K) exceed alkaline earths (Ca + Mg). 37% of the groundwater samples show weak acid ($CO_3 + HCO_3$) exceeding the strong acids (SO_4+Cl). 65% samples from study area have strong acids (SO_4 + Cl) exceeding weak acid ($CO_3 + HCO_3$). However, the mixed sectional types suggest the geogenic as well as anthropogenic sources of cations and anions; and the combinational water type. The interrelationship of HCO_3^- and Ca^{2+} divulges negative correlation also, the scatter diagram of Na^+ *vs* Cl^- interpret the rock-water interaction, which points out towards the silicate weathering as well as sources of calcium and bicarbonate. The high Na/Cl ratio corroborates the intense water-rock interaction, most likely by feldspar weathering. The groundwater from the PG2 watershed is marginally suitable for drinking purpose and apt for domestic and irrigation purposes. However, it is not appropriate for the intolerant crops which are vulnerable to anions of Cl^- and SO_4^{2-}.

Conflict of Interest

Author declares no conflict of interest.

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