

Hydrogeochemical Assessment of Groundwater quality for Drinking purpose in parts of Rupnagar district, Punjab, India.

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Abstract: Groundwater being a vital resource is under a great threat both qualitatively and quantitatively. Its demand increasing exponentially has made the groundwater analysis an important issue today. The study area is a fertile alluvial plain where two blocks are under over-exploited category. Quality of groundwater is altered if over abstraction occurs. A detailed study has been done where all the parameters were within the limits given by BIS (2012), except for TDS, Ca^{2+} and Mg^{2+} . TDS and Mg^{2+} at few sampling sties were above the desirable limits. Hydrogeochemical character of groundwater in both seasons (Pre and Post monsoon) were investigated by calculating the major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^-). Ionic relationship was assessed to get a clear understanding of the groundwater chemistry. Groundwater of the study area is Ca-HCO₃ type and mixed type (Ca-Mg-Cl), i.e. the groundwater has temporary hardness which can be removed by simple boiling. Various geochemical processes and ionic study reveals that groundwater chemistry is mainly affected by carbonate weathering, rock-water interaction, dissolution and anthropogenic activities. An attempt has been made in the present study to assess the groundwater quality and its suitability (by WQI) for drinking purpose.

Key words: Physico-chemical analysis, Drinking purpose, Hydrochemical facies, WQI, Chlor-alkaline indices.

1. Introduction

We rely on groundwater and it relies on us. Water is the key to life on this planet, which makes it a huge importance to the people of the world, but everyone somehow seems to overlook it. In many parts of the world, especially where the availability of surface water is minimal; domestic, agricultural and industrial water needs can only be met by using the water beneath the ground. Groundwater is one of the major sources of drinking water all over the world (Bear, 1979). Approximately one-third of the world's

population depends on groundwater for drinking purpose (UNEP, 1999). Poor quality of water adversely affects the human health and plant growth (WHO, 2004). In past decades increase in population, high crop production and industrialization has increased the dependency on groundwater manifolds. Quality of groundwater is equally important as its quantity owing to the suitability of water for various purposes. Variation of groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Subramani et al., 2005; Singh and Mukherjee, 2010; Krishna Kumar et al., 2011; Magesh and Chandrasekar, 2011). The chemistry of groundwater depends on the minerals present in geological formations and is also controlled by many interrelated processes and thus can be used to understand the hydrogeological processes, the mechanisms controlling of quality of groundwater (Zuane, 1990). The study area is an agricultural zone which makes it prone to over abstraction of groundwater and usage of pesticides and fertilizers to enhance the crop productivity. These anthropogenic activities will eventually degrade the quality of groundwater making it unfit for any human use. The present paper discusses the hydrogeochemical processes and its quality to evaluate its suitability for drinking purpose.

2. Study Area

Rupnagar district, included in the Patiala Division of Punjab falls between North latitude 30°-32' and 31°-24' and East longitude 76°-18' and 76°-55' (Fig. 1). All the towns except Chamkaur Sahib falls on railway line. It has an average elevation of 260 metres (853 ft). The Sutlej river passes close (2 to 5 km) to the towns of Nangal, Rupnagar and Anandpur Sahib. The district is divided into five blocks – Anandpur Sahib, Chamkaur Sahib, Morinda, Nurpur Bedi and Rupnagar. The climate of Rupnagar District is generally dry (except in the south-west monsoon season), a hot summer and a bracing cold winter. The average annual rainfall in district is 775.6mm. Relative humidity is very high, averaging about 70% during monsoon. Most of the area is covered by alluvial plain which makes the area fertile and suitable for high density cropping. Geologically, the study area is constituted by two main units (i) the Siwalik and (ii) The Indo-Gangetic Alluvium. The Siwalik (Mid Miocene to Pleistocene) has been classified into Lower, Middle and Upper Siwalik formation, (Pascoe, 1959; Wadia, 1979 and Chaudhary, 1971). The alluvial flood plain is marked with the confluence of Sutlej and Sirsa rivers with 1% to 3% slope. Most of the area covered by alluvial plain is used for agriculture (Singh et al., 2011). The soils of the District vary in texture generally from loam to silty clay loam except along the Sutlej River and choes where some sandy patches may be found. The main rock types are sandrock, sandstone, clays, siltstones, conglomerates and boulders.

3. Materials & Methods

The samples were collected from tube wells and hand pumps. 60 samples of groundwater were collected in polypropylene bottles during the months of May (Pre monsoon) and October (Post monsoon), 2013 from Ropar, Morinda and Chamkaur Sahib blocks of Rupnagar district. Water samples were collected after pumping the water for 10 minutes from hand pumps in order to have minimum effect of iron pipes through which the water was pumped out. Plastic bottles were filled up to the brim and immediately sealed to prevent any exposure to the air. Electrical conductivity (EC), pH and TDS were measured using portable field kit immediately after sampling. Water samples collected in the field were analysed for chemical constituents, such as sodium, potassium, calcium, magnesium, chloride, bicarbonate, carbonate, sulphate, nitrate and fluoride in the laboratory using the standard methods as suggested by the American Public Health Association (APHA, 2012). Ca^{2+} , Mg^{2+} , HCO_3^- , CO_3^{2-} and Cl^- were analysed by volumetric titrations. Concentrations of Ca^{2+} and Mg^{2+} were estimated using EDTA and H_2SO_4 was used to determine the concentrations of HCO_3^- and CO_3^{2-} . AgNO_3 was used to estimate Cl^- . Na^+ and K^+ concentrations were determined using Flamephotometric method. PO_4^{3-} and NO_3^- are estimated by UV Spectrophotometric method. Whereas, SO_4^{2-} and F^- were determined using turbidity and SPADNS method respectively

4. Results & Discussions

Chemical constituents of the groundwater samples were statistically analyzed and its summary is given in table 1 for both pre and post monsoon seasons.

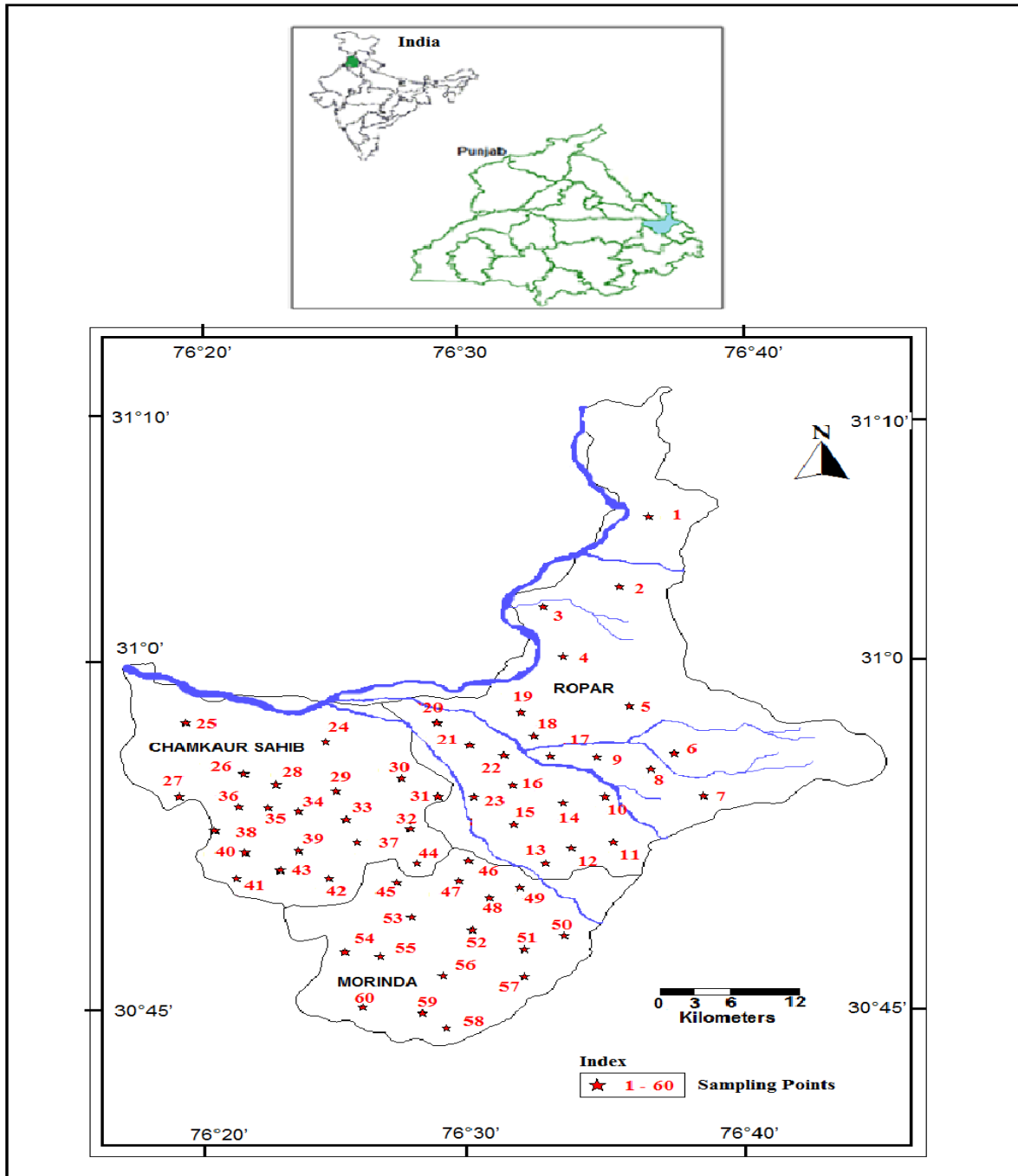


Fig. 1 Location map and sampling points in Rupnagar District, Punjab, India.

4.1 Drinking Water Quality

The pH values of groundwater varied from 7.4 to 8.5 and 7.3 to 8.5 in pre and post monsoon respectively, indicating slightly alkaline nature, and the mean value was 7.85. Desirable limit prescribed by BIS of pH ranges from 6.5 to 8.5, which is safe for drinking (Table 1). EC is used to evaluate the amount of dissolved solids. It increases as the

amount of dissolved mineral (ions) increases. Majority of salts in water are present in their ionic state and they are capable of conducting current and conductivity is a good indicator to assess groundwater quality. In the study area, EC varied from 458 to 1126 $\mu\text{S}/\text{cm}$ in pre monsoon and 478 to 1089 $\mu\text{S}/\text{cm}$ in post monsoon season (Table 1).

Table 1: Descriptive Statistics of Physico-chemical analysis of the groundwater samples during Pre Monsoon and Post Monsoon seasons. All parameters are in mg/l, except pH and EC (expressed in micromohos/cm at 25°C).

Water quality parameters	Minimum		Maximum		Average		Std. deviation	
	Pre Monsoon	Post Monsoon	Pre Monsoon	Post Monsoon	Pre Monsoon	Post Monsoon	Pre Monsoon	Post Monsoon
pH	7.4	7.3	8.5	8.5	7.9	7.8	0.231	0.18
EC	458	478	1126	1089	694	682	109.6	105
TDS	293	323	633	687	462	454	70.6	66
TH as CaCO ₃	64	84	184	162	112.7	112.5	27	19.5
CO ₃ ²⁻	5	5	9	12	7	8	1.8	2.2
HCO ₃ ⁻	126	118	390	423	244.9	274	47.6	45
Ca ²⁺	26.9	35.3	77.4	68.1	47.4	47	11.4	8.5
Mg ²⁺	11.7	15.1	63.4	47.6	36.6	34.7	9.03	7.3
Na ⁺	2.6	3.7	50.4	53	19.8	23.4	8.4	9.2
K ⁺	0.9	1.5	6.3	6.6	3.8	4.3	1.6	1.5
Cl ⁻	13.9	10.8	115.3	133.2	50.6	50	17.9	19
F ⁻	0.12	0.15	0.3	0.42	0.2	0.27	0.07	0.07
SO ₄ ²⁻	2.9	4.18	52.7	57.1	26	29.7	12.3	13.2
NO ₃ ⁻	0.5	0.6	25.5	28	6.8	8.1	4.5	4.9
PO ₄ ³⁻	0.002	0.004	0.2	0.2	0	0.05	0.04	0.04

Abbreviations: EC electrical conductivity. TDS total dissolved solids. TH total hardness

To apprehend the suitability of groundwater for any purpose, it is necessary to categorize the groundwater depending on the hydrochemical properties based on their TDS values given in table 2. In pre monsoon season, TDS varied from 293 to 622 mg/l and in post monsoon it was from 323 to 687 mg/l. All the samples were within the permissible limit of Indian standards but 26.6% samples in pre monsoon and 18.3% samples in post monsoon were above the desirable limit i.e. 500 mg/l (Table 2). Hard water is unsuitable for domestic use and it is a measure of the Ca²⁺ and Mg²⁺ content expressed in equivalent of calcium carbonate. Temporary hardness is mainly due to the presence of calcium carbonate and gets removed by boiling the water. Permanent hardness is caused by the presence of Ca²⁺ and Mg²⁺ which gets removed by ion exchange processes. In pre monsoon season, hardness (as CaCO₃) varied

from 64 to 184 mg/l and in post monsoon it was from 84 to 162 mg/l. Table 2 shows that in pre monsoon season, 83.4% of samples fall in the moderately hard category and remaining samples were in soft and hard category; in post monsoon 93.3% samples were moderately hard and 6.7 % samples were in hard category.

Among the alkaline earths, calcium was in the range of 26.9 to 77.4 mg/l and 35.3 to 68.1 mg/l in pre monsoon and post monsoon season respectively. Magnesium in pre monsoon was in the range of 11.7 to 63.4 mg/l and in post season it was from 15.1 to 47.6 mg/l. Whereas, among the alkalis, sodium concentration ranged from 2.6 to 50.4 mg/l in pre monsoon season and in post monsoon it varied from 3.7 to 53 mg/l. On the other hand, potassium concentration in pre monsoon ranged from 0.9 to 6.3 mg/l and from 1.5 to 6.6 mg/l in post monsoon (Table 1)

Table 2: Classifications showing the suitability of groundwater for drinking purpose

TDS (mg/l) (Davies and DeWiest, 1966)	Water Class	No. of Samples (% of samples)	
		Pre monsoon	Post monsoon
<500	Desirable for drinking	44(73.4)	49(81.7)
500-1000	Permissible for drinking	16(26.6)	11(18.3)
<3000	Useful for irrigation	-	-
>3000	Unfit for drinking and irrigation	-	-
TH as CaCO ₃ (mg/l) after Sawyer and Mc.Cartly (1967)			
<75	Soft	5(8.3)	-
75-150	Moderately hard	50(83.4)	56(93.3)
150-300	Hard	5(8.3)	4(6.7)
>300	Very Hard	-	-

For Ca²⁺, one sample was above the desirable limit of 75 mg/l in pre monsoon and for Mg²⁺, 75% in pre monsoon and 71.7% samples in post monsoon was above the desirable limit of 30 mg/l (BIS, 2012) (Table 3). At few locations contribution of Mg²⁺ is higher

compared to that of Ca²⁺ which can be due to the effect of ferromagnesium minerals, ion exchange (between Na⁺ and Ca²⁺) and precipitation of CaCO₃ (Hem, 1991; Subba Rao, 2002).

Table 3: Drinking water standard with the number of samples beyond desirable limit (mg/l except for pH)

Water quality Parameter	Indian standards (IS:10500-2012)		No. of samples beyond Desirable limit(% of samples)	
	Desirable	Permissible	Pre	Post
	Limit	Limit	Monsoon	Monsoon
pH	6.5-8.5	No relaxation	-	-
TDS	500	2000	16(26.7)	11(18.3)
TH as CaCO ₃	200	600	-	-
Ca ²⁺	75	200	1(0.01)	-
Mg ²⁺	30	100	45(75)	43(71.6)
Cl ⁻	250	1000	-	-
F ⁻	1	1.5	-	-
SO ₄ ²⁻	200	400	-	-
NO ₃ ⁻	45	NR	-	-

The ratio of Ca²⁺/Mg²⁺ has been used to determine the sources of calcium and magnesium ions into the groundwater environment (Maya and Loucks, 1995). If the ratio of Ca²⁺/Mg²⁺ is equal to 1 that indicates dissolution of dolomite and if greater than 2 it reflects an effect of silicate minerals that contributes calcium and magnesium into the groundwater (Katz et al., 1998). Majority of samples (88.34%) during pre monsoon season fall below 1 ratio line indicating precipitation

of Ca²⁺ as CaCO₃ which results in a decline of Ca²⁺ values or ion exchange process (Fig. 2). About 11.66% of samples were near and above the 1 ratio line indicating ion exchange with Na⁺ resulting in an increase of magnesium ions. During post monsoon 81.67% of samples were above the 1 ratio line and 18.33% of samples are below 1 ratio line. Possibly the presence of 'kankar' carbonates in alluvial sediments in the study area could favor the weathering process.

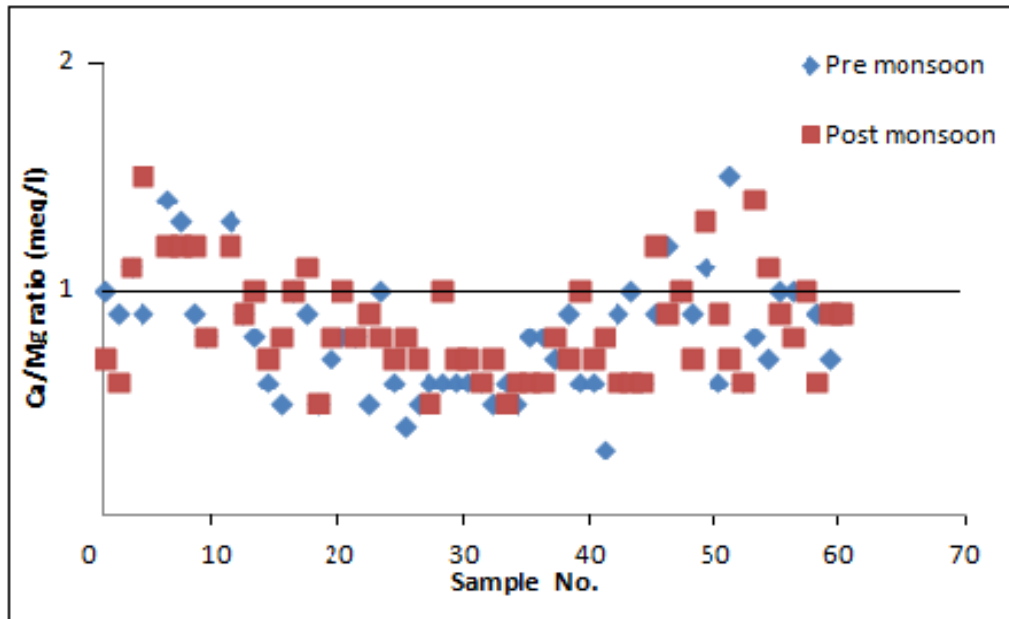


Fig. 2 Scatter plot showing Ca/Mg ratio

Na^+ versus Cl^- plot (Fig.3) shows that 85% of samples in pre monsoon and 80% in post monsoon season lie below the equiline, indicating that evaporation can be the cause of addition of Cl^- causing more salt dissolution from the soil. Chloride ions are present in the groundwater as sodium chloride. Chloride content exceeding sodium may be due to the Base Exchange phenomena or due to pollution by anthropogenic activities (Jones et al., 1999). Agricultural return flow water is characterized by higher ratios of $\text{SO}_4^{2-}/\text{Cl}^-$ (1995).

$\text{Ca}^{2+} + \text{Mg}^{2+}$ Vs $\text{SO}_4^{2-} + \text{HCO}_3^-$ plot shows that majority of samples (85%) in pre monsoon and 62% in post monsoon fall above the equiline pointing towards the abundance of $\text{Ca} + \text{Mg}$ in groundwater which can be attributed to mainly carbonate weathering (Fig.3). Predominantly the samples fall to the right of

(>0.05) attributing to the application of gypsum fertilizers (Vengosh et al., 2002) and in both the seasons except for one sample (no.6) the ratios of sulphate to chloride were greater than 0.05.

The plot for $\text{Ca}^{2+} + \text{Mg}^{2+}$ Vs HCO_3^- (Fig.3) shows, majority of data plot during pre monsoon and post monsoon fall above the equiline (1:1) suggesting an excess of alkaline earth elements ($\text{Ca}^{2+} + \text{Mg}^{2+}$) over HCO_3^- reflecting extra sources of Ca^{2+} and Mg^{2+} ions balanced by Cl^- and SO_4^{2-} (Zhang et al., 1:1 equiline indicating ion exchange process dominance. During infiltration or along the flow, groundwater may dissolve the CaCO_3 , and $\text{CaMg}(\text{CO}_3)_2$ present in the rocks by increasing calcium and magnesium ions in groundwater. The samples approaching the 1:1 equiline suggest ions from weathering of silicates (Datta and Tyagi, 1996).

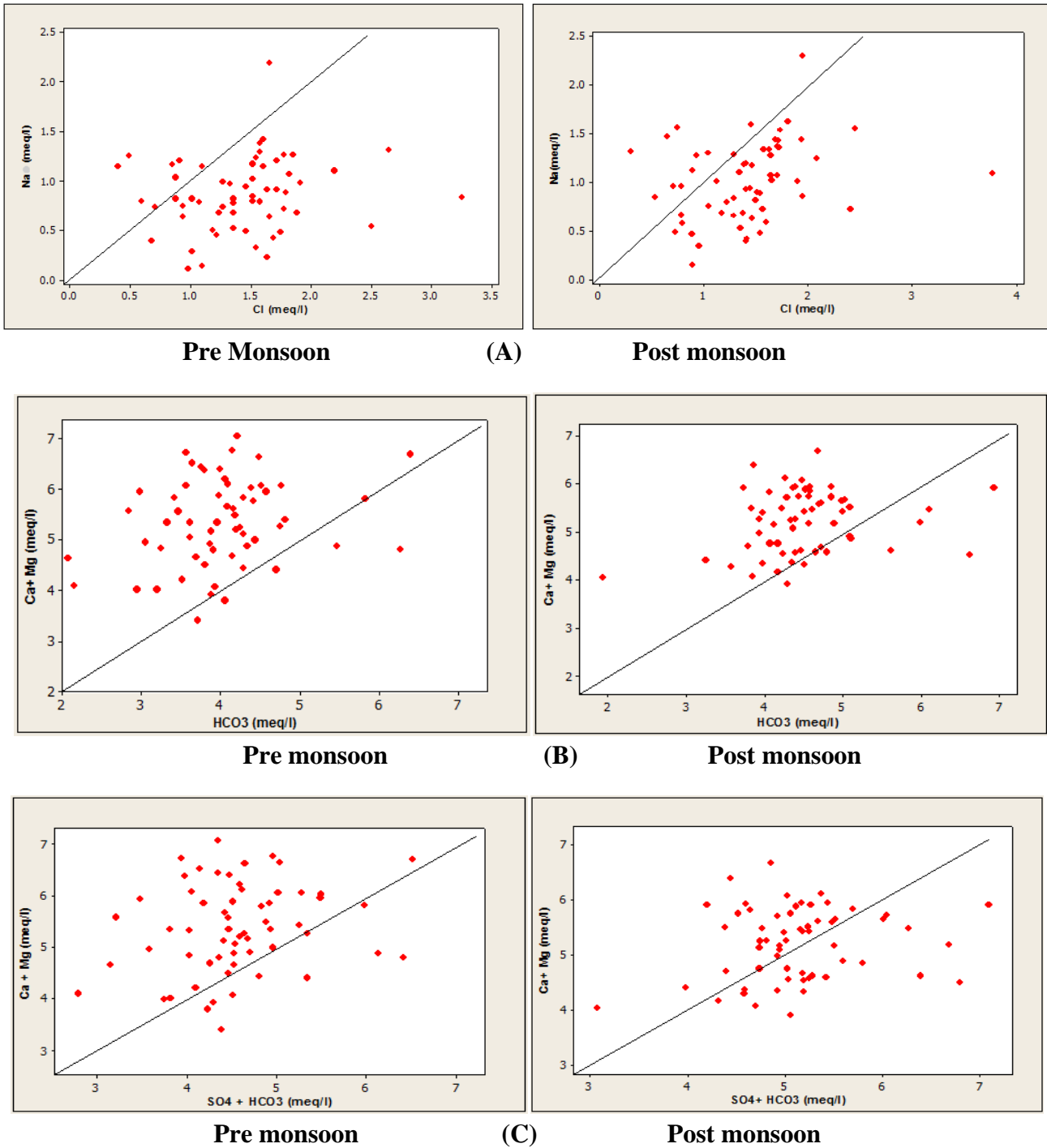


Fig. 3 Ionic relationship on scatter plots
 [(A) Na Vs Cl, (B) Ca+Mg Vs HCO₃, (C) Ca+Mg Vs SO₄+HCO₃

4.2 Water Quality Index

WQI is an important parameter for demarcating groundwater quality and its suitability for drinking purposes (Tiwari and

Mishra, 1985; Singh, 1992; Subba Rao, 1997). The standards for drinking purposes as recommended by WHO (2008) and BIS 10500

(2012) have been considered for the calculation of WQI. For computing WQI three steps are followed. In the first step, each of the 12 parameters (TDS, HCO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , F^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+) has been assigned a weight (w_i) according to its relative importance in the overall quality of water for drinking purposes. The maximum weight of 5 has been assigned to the parameters like nitrate, total dissolved solids, chloride, fluoride, and sulfate due to their major importance in water quality assessment (Srinivasamoorthy et al., 2008). Bicarbonate and phosphate is given the minimum weight of 1 as it plays an insignificant role in the water quality assessment. Other parameters like calcium, magnesium, sodium, and potassium were assigned weight between 1 and 5 depending on their importance in water quality determination. In the second step, the relative weight (W_i) is computed from the following equation:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

where

W_i is the relative weight

w_i is the weight of each parameter

n is the number of parameters

Calculated relative weight (W_i) values of each parameter are given in Table 3. In the third step, a quality rating scale (q_i) for each parameter is assigned by dividing its concentration in each water sample by its respective standard according to the guidelines

laid down in the BIS (2012) and the result is multiplied by 100:

$$q_i = \left(\frac{C_i}{S_i} \right) * 100 \quad (2)$$

where

q_i is the quality rating

C_i is the concentration of each chemical parameter in each water sample in milligrams per liter

S_i is the Indian drinking water standard for each chemical parameter in milligrams per liter according to the guidelines of the BIS (2012).

For computing the WQI, the SI is first determined for each chemical parameter, which is then used to determine the WQI as per the following equation:

$$SI_i = W_i * q_i \quad (3)$$

$$WQI = \sum SI_i \quad (4)$$

where

SI_i is the sub-index of i th parameter

q_i is the rating based on concentration of i th parameter

n is the number of parameters

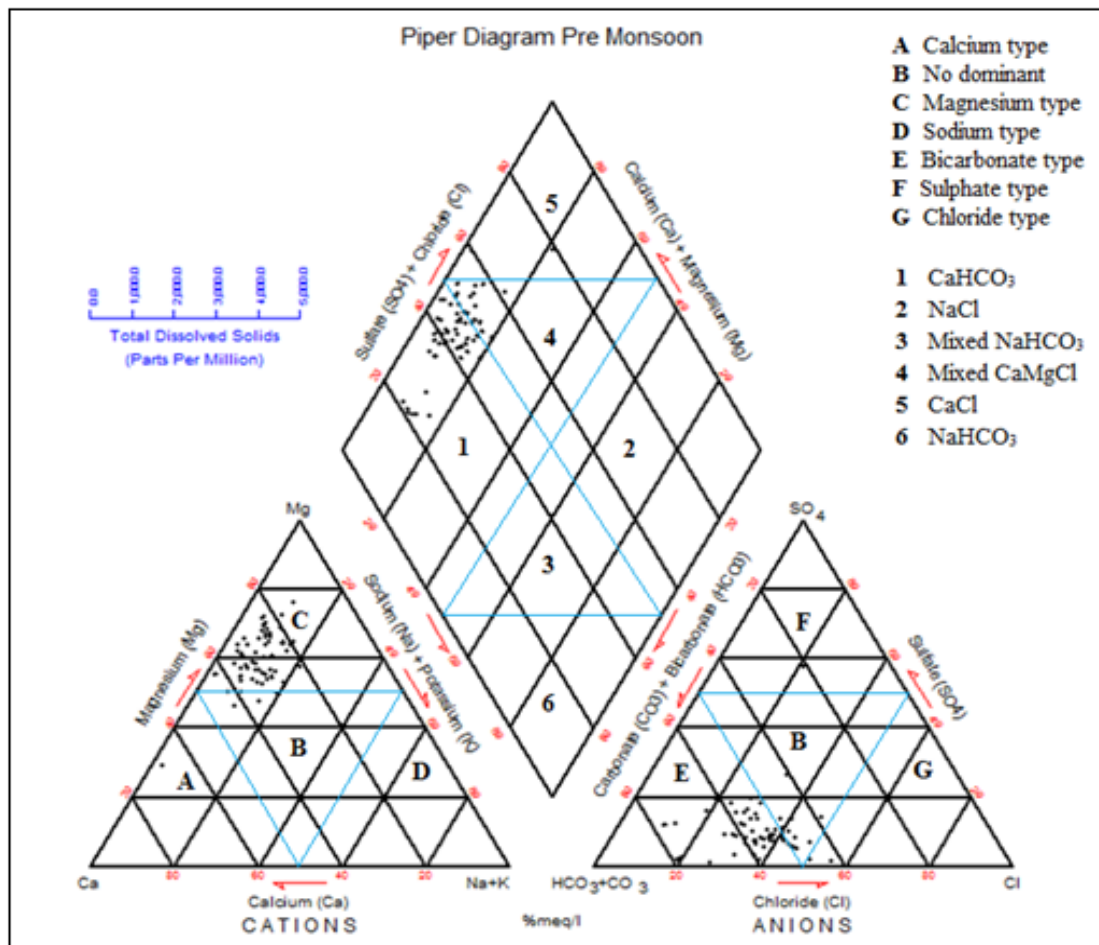
Water quality types, were determined on the basis of WQI (Table 3). The computed WQI values ranged from 29.7 to 45.9 and 31.5 to 47.6 for pre monsoon and post monsoon respectively. In post monsoon, the quality of groundwater deteriorated marginally which has to be regularly examined in future to check the further degradation. But the values were well within the range mentioned, i.e. the samples from both the seasons are excellent for drinking in the study area.

4.3 Hydrochemical Facies

4.3.1 Piper Trilinear Diagram

The hydrochemical facies of a particular place are influenced by geology of the area and distribution of facies by the hydro-geological controls (Lata, et. al., 2014). A graphical display of major ions composition of groundwater using Piper trilinear figure (Fig. 4) indicated that in pre monsoon, Ca^{2+} and Mg^{2+} ions dominated the groundwater composition with 37.20% and 47.60% respectively, making it Ca-Mg type water; i.e. alkaline earths exceeding the alkalis (Na+K). In case of anions, it was HCO_3^- and Cl^- with 66.9% and 23.78% respectively that

dominated the groundwater. Similar trend was observed in post monsoon season, where Ca^{2+} with 32.24% and Mg^{2+} with 39% dominated the chemical composition of water and as for anions HCO_3^- and Cl^- dominated with 68.4% and 21.45% respectively. The dominance of HCO_3^- classifies the area as a recharge zone (Subba Rao, 2007). Minor variations in the concentration of ions, points out the influence of monsoon on the chemical constituents of groundwater. It is clear from the diagram that groundwater of the study area is Ca- HCO_3 type and mixed type (Ca-Mg-Cl), which as a whole imparts temporary hardness to the water.



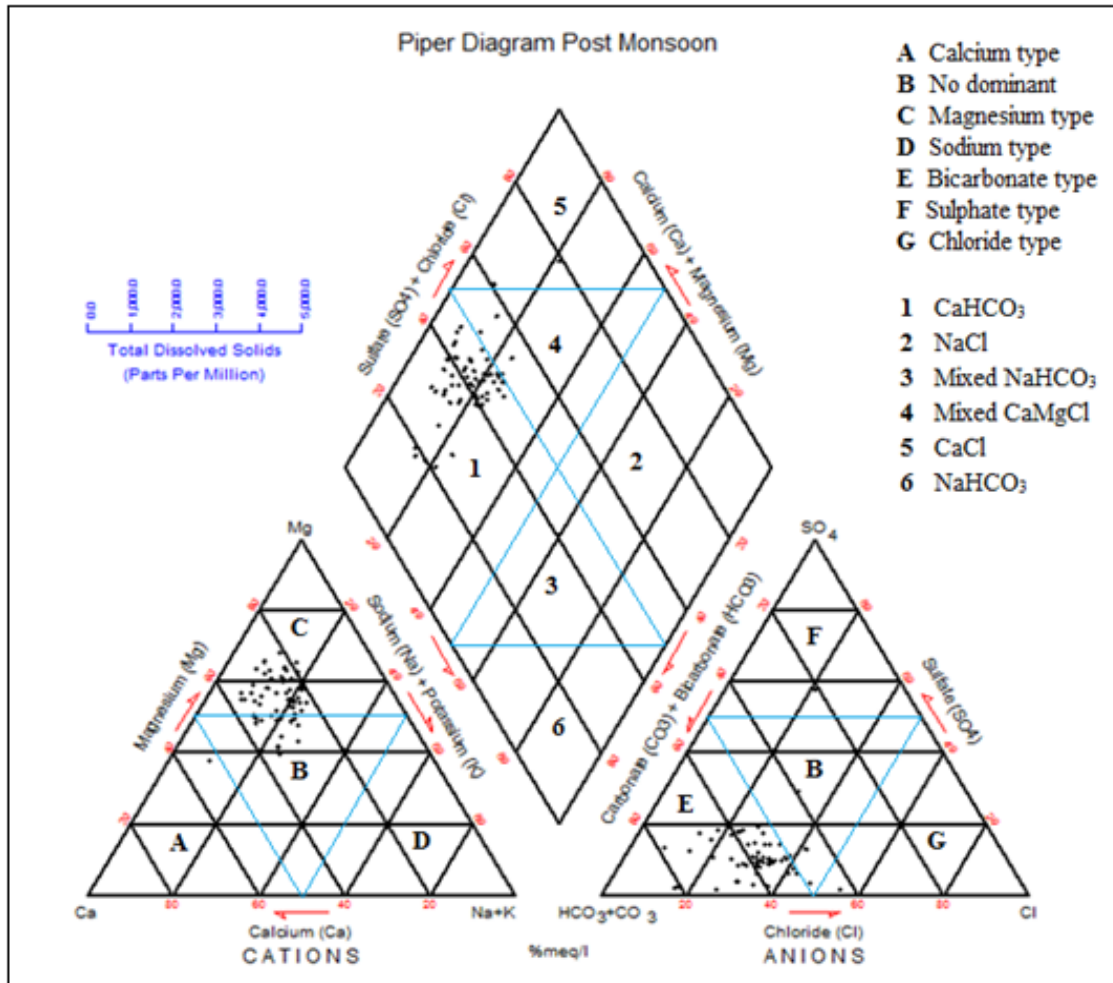


Fig. 4 Geochemical classification of groundwater (Piper, 1944)

4.4 Mechanisms Controlling Groundwater Chemistry

Gibbs diagram is used to gain better insight into hydrochemical processes such as precipitation, rock–water interaction, and evaporation on groundwater chemistry. Gibbs (1970) demonstrated that if total dissolved solid is plotted against $\text{Na}+\text{K}/(\text{Na}+\text{Ca}+\text{K})$, it would provide information on the mechanism controlling chemistry of groundwater. There are three major mechanisms that regulate the

chemistry of groundwater: i) Evaporation Dominance, ii) Precipitation Dominance and iii) Rock Dominance. Groundwater samples from both pre and post monsoon season falls in the rock dominance zone which indicates that there is an interaction between the host environment and groundwater (Fig. 5) which suggests that groundwater chemistry in the study region is influenced by carbonate weathering process.

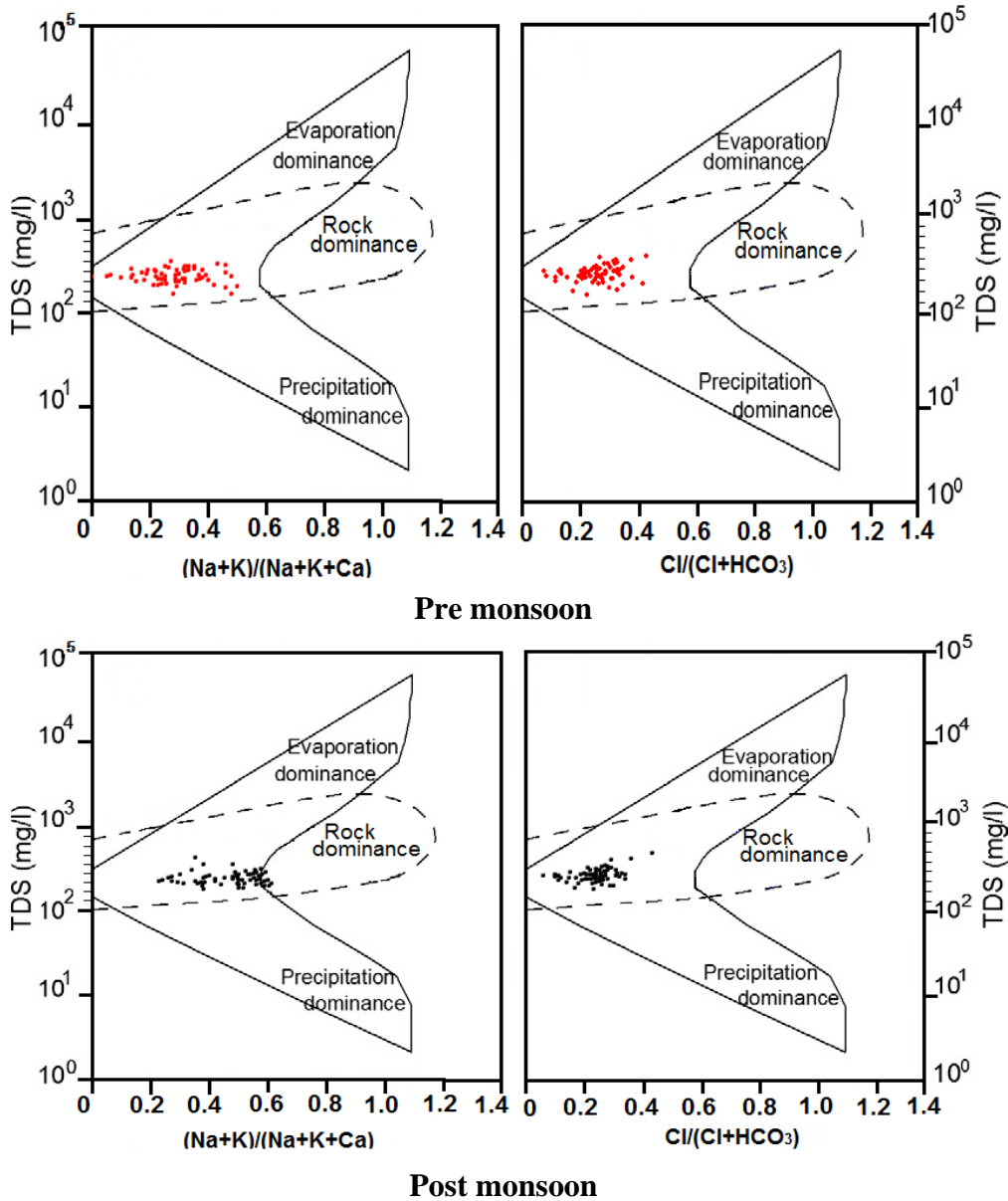


Fig. 5 Mechanism controlling groundwater chemistry (Gibbs, 1970)

4.5 Ion Exchange Index

It is essential to know the various changes in chemical composition of groundwater during its course in the sub-surface (Sastri, 1994). The Chloro-alkaline indices CAI 1 and CAI 2 given by Schoeller (1977), indicates ion

exchange between the groundwater and its host environment. The ion exchange during travel or residence can be better understood by studying the Chloro-alkaline indices using the formulae:

$$\text{Chloro Alkaline Index 1} = \frac{[Cl^- - (Na^+ + K^+)]}{(Cl^-)} \quad (5)$$

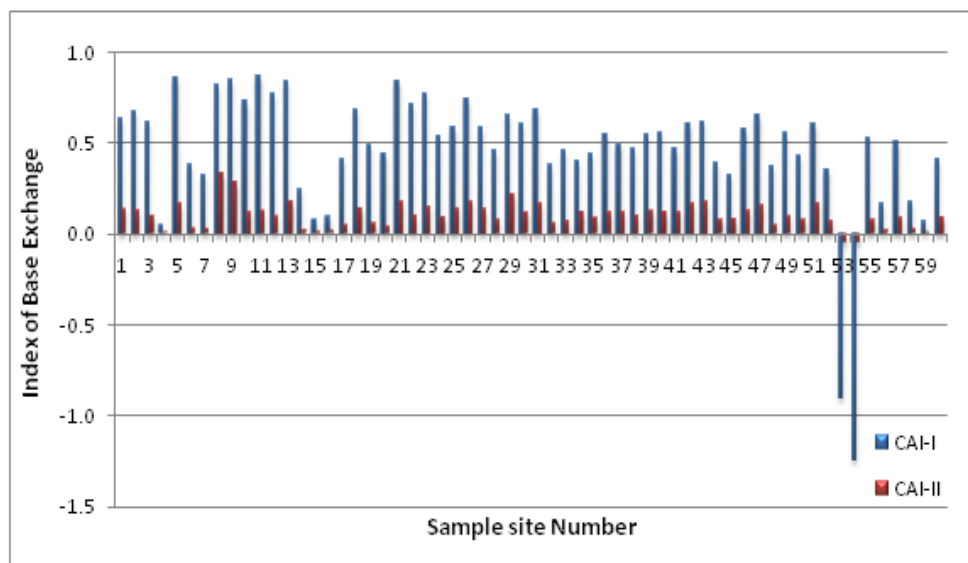
$$\text{Chloro Alkaline Index 2} = \frac{[Cl^- - (Na^+ + K^+)]}{(SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-)} \quad (6)$$

Groundwater with a base exchange reaction in which the alkaline earths have been exchanged

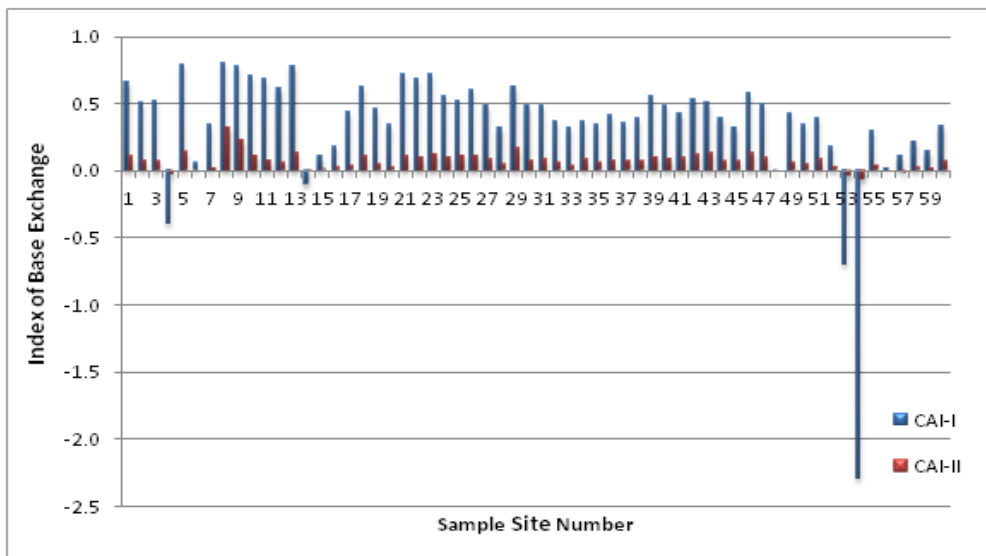
for Na^+ ions ($HCO_3^- > Ca^{2+} + Mg^{2+}$) may be referred to as base exchange-softened water,

and those in which the Na^+ ions have been exchanged for the alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+} > \text{HCO}_3^-$) may be referred to as base exchange-hardened water (Handa, 1969). The indices are positive if there is an ion exchange of Na^+ and K^+ from groundwater with Mg^{2+} and Ca^{2+} in the rocks and the exchange is known as direct base exchange. If the process is in reverse order and the indices are negative then the Ca^{2+} and Mg^{2+} from the groundwater is exchanged with Na^+ and K^+ of rocks and the

exchange is said to be indirect indicating chloro-alkaline imbalance. Figure 6 shows the computed CAI-1 and CAI-2 for groundwater of the study area. 96.7% samples in pre monsoon and 91.7% in post monsoon season had a direct base exchange reaction (chloro-alkaline equilibrium). The index thus shows that groundwater of the study area has higher HCO_3^- concentration than alkaline earths indicating base exchange-softened water.



Pre monsoon



Post monsoon

Fig. 6 Index of Ion Exchange (Schoeller, 1977)

5. Conclusion

The analytical results of physical and chemical parameters of groundwater were compared with the guideline values recommended by the Bureau of Indian Standard (BIS, 2012) for drinking purpose. The results show that the present status of groundwater in the study area is suitable for human consumption. Variations and standard deviations in few parameters suggest that hydrogeochemistry of the area is not consistent. All the parameters for drinking water were well within the permissible limits. The overall geochemistry of groundwater in the study area is controlled by natural geochemical processes like rock water interaction, dissolution, weathering of carbonate minerals including kankar, ion exchange and anthropogenic induced activities like over-exploitation of aquifers, agricultural return flow and use of fertilizers. On the basis of WQI, all the samples from both the seasons were excellent for drinking purpose. The ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ and $\text{Ca}^{2+}+\text{Mg}^{2+}$ Vs $\text{SO}_4^{2-}+\text{HCO}_3^-$ scatter plot suggested the abundance of Ca^{2+} and Mg^{2+} ions in groundwater which can be attributed to mainly carbonate weathering. $\text{SO}_4^{2-}/\text{Cl}^-$ ratio (>0.05) and Na^+ Vs Cl^- plot indicated ion exchange process affecting the hydrochemistry of the area. According to Piper diagram, groundwater of the study area is of Ca- HCO_3 type and (Ca-Mg-Cl) type, which gives temporary hardness to the water and can be removed by boiling. It is suggested that periodic monitoring of groundwater should be conducted in the study area. Awareness and knowledge about the sustainable use of groundwater and maintaining its quality is necessary for the farmers and local residents so as to avoid further exploitation or contamination of the resource.

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