



Full Length Research Paper

Hydrogeochemical characterisation of Shallow and Deep aquifers in and around Limestone Mining Area from Gadchandur, Chandrapur District (Maharashtra), India

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ABSTRACT

Evaluation of ground water quality and hydro-geochemistry of shallow and deep aquifer (with respect to guideline values of WHO 2004, geochemical classifications, ion exchange processes and mechanisms controlling ground water chemistry) and evaluation of water quality (with respect to different sodium hazards, Ca^{2+}/Mg^{2+} ratio) for irrigation purpose in mining area were the aims of the present study. Accordingly ground water samples were collected from shallow, deep aquifers of Gadchandur, Chandrapur in pre and post monsoon seasons 2010. Quality of the water samples collected from the deep aquifer found satisfactory in comparison with water samples collected from the shallow aquifer. Geochemical nature of shallow aquifer was earth alkaline with increased portion of alkalis with prevailing bicarbonate, followed by chloroalkaline disequilibrium type of ion exchange process. Chemical weathering of rock forming minerals was the major driving force controlling shallow aquifer water chemistry. Hydro-geochemistry of deep aquifer in pre-monsoon season hydro-geochemistry of the deep aquifer shifted towards alkaline with sulphate and bicarbonate. Ion exchange process in this aquifer showed complete dominance of base exchange reaction in both the seasons. Chemical weathering along with evaporation was the two major driving forces controlling the water chemistry of the shallow and deep aquifer in pre-monsoon and post-monsoon seasons. RSC (residual sodium carbonate), %Na, SAR (sodium adsorption ratio), Ca^{2+}/Mg^{2+} ratio and concentration of Cl, F in irrigation water revealed that some water samples were not good enough for irrigation in pre-monsoon season in comparison to that of post monsoon season.

Keywords: Shallow aquifer, Deep aquifer, Hydro-geochemistry, Irrigation water

INTRODUCTION

The ever-growing utilization of water resources have led to lowering of water table as well as degradation of its quality in the past few decades. Number of studies on groundwater and surface water quality in parts of India

with respect to drinking and irrigation purposes have been carried out extensively by Central Ground Water Board, Geological Survey of India as embodied in various publications. Mining activity threatens the quality and

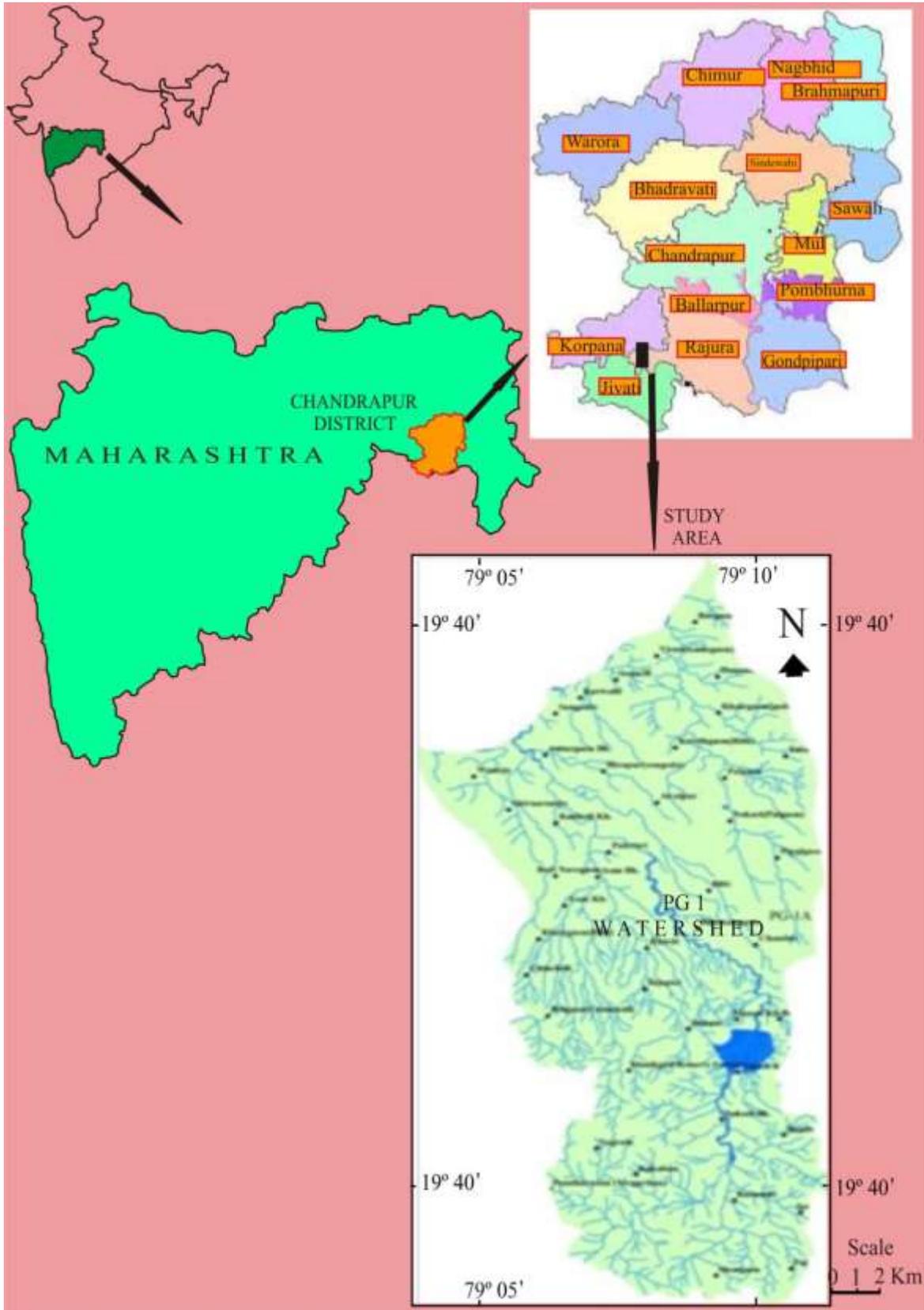


Figure1. The location of study area and water sample points

quantity of surface and ground water resources in many parts of world (Allen et al., 1996; Choubey, 1991; Gupta, 1999; Khan et al. 2005; Singh et al. 2008; Singh 1998; Tiwary 2001; Soni, 2007). Mining activity, thus in many areas can seriously pollute surface and groundwater resources. The various studies on interrelationship between water quality, geology and mining activities have been carried out (Singh et al., 2010). The present study was performed with an objective to evaluate ground water quality and hydro-geochemistry of shallow and deep aquifer water quality for irrigation purpose in and around limestone mining area from Gadchandur, Chandrapur District Maharashtra.

STUDY AREA

The study area is located in south-western part of Chandrapur District (around Gadchandur), Maharashtra state and lies between latitudes 19°38'30" to 19°50'30"N and longitudes 79°04'00" to 79°11'00"E (Figure1). The area under investigation is covered under Survey of India topographic sheet No. 56 M/1, M/2. The study area is around 90 Km away from Chandrapur and it is approachable by Rajura - Korpana Road.

In the study area dendritic (major), trellis and combination of dendritic and (minor) parallel drainage patterns have been observed. The climate is semiarid with minimum temperatures drops up to 10°C in winter (January) and 48°C in summer (May). The study area receives an average annual rainfall 1132.21 mm.

The study area covers Geological formations *viz.* Limestone-shale and Limestone sequences belonging to Penganga Group of Godavari valley, Lower Gondwana sediments i.e. Talchir, Barakar and Kamthi formations, Deccan Trap Basalts, Alluvium, soil and Laterite.

The two mining areas fall in the study area *viz.*, i) Naokari Limestone Mining Area in northern part and ii) Manikgarh limestone mining area in the southern part. Naokari Limestone Mining area occupied by limestone and shale sequences belonging to Penganga Group and the rocks of Gondwana Supergroup in the extreme northern part. Manikgarh limestone mining area in the southern part study area is occupied by Penganga Limestone, along with Deccan Trap basaltic flows with laterite capping. In the study area three types of soil textures are found Clayey Soil 43.08%, Sandy Soil 13.96 % and Gravelly Soil 42.97 %.

The groundwater occurs under phreatic conditions in all the water bearing formations, in weathered fractured zone (limestone), fractured and vesicular basalts (shallow aquifer) and under semi-confined to confined conditions in the deeper aquifers. The thickness of weathered zone varies from 5m to 18m in Penganga rocks and 2 to 12 m in basaltic formations. In Penganga rocks groundwater occurs in fractures and cavities in krastified limestones and joints of sandstone. In Gondwanas, groundwater

occurs in the pore spaces of Barakars and Kamthi sandstones and in deeper aquifers it occurs under semi-confined conditions. In alluvium, groundwater exists in sandy layers under phreatic conditions. Local confined conditions are sometimes simulated by clay lenses. The water bearing zone occurs at a depth of 1.8 to 13.5 m in shallow aquifers in the present area.

MATERIALS AND METHOD

Sixty two (31×2) water samples (17 shallow aquifer water samples, 14 deep aquifer water samples) were collected from the study area in pre monsoon 2010 and post monsoon 2010. The sampling stations are shown in Figure1.

All the analytical methodologies including sample collection, had been carried out as per Standard Methods for the Examination of Water published by APHA (1998). Physical parameters like pH by pH meter and electrical conductivity (EC) were determined by portable conductivity meter. Total dissolved solids (TDS) were determined by gravimetric method. Chemical parameters like sulphate (SO₄) was determined by UV spectrophotometric model UV- 1201A, whereas, total hardness (TH), TA measured by the titration of the sample with standard N/50 H₂SO₄. Ca hardness (CaH), calcium (Ca²⁺) and magnesium (Mg²⁺) were determined by standard EDTA titrimetric method. Carbonate (CO₃²⁻) and bicarbonate (HCO₃) were estimated by determined by titration of the sample with standard N/50 H₂SO₄, using mixed indicator consisting of methyl red and bromocresol green (1:1). Chloride (Cl) was determined by argentometric titration method. Sodium (Na⁺) and potassium (K⁺) had their measurement by the techniques of emission Flame Photometry. Fluoride (F⁻) was measured by spectrophotometrically by using Simadzu make UV spectrophotometer (model UV-1201A) with automatic sampler (model ASC-5). Rest of the chemical parameters like total iron (Fe), nitrate (NO₃) were measured by using Simadzu make UV spectrophotometric model UV-1201A.

RESULTS AND DISCUSSION

Water quality of shallow and deep aquifer samples

Statistical summary of analytical data of the water samples collected from shallow and deep aquifer are described in Table 1 and Table 2.

Table 3 describes that, 100% of the water samples collected from shallow aquifer were found within safe limit as per with the provisional guideline values of WHO 2004 with respect to pH and SO₄ point of view. pH, Na and SO₄ of all the water samples collected from deep aquifer in

Table 1. Descriptive statistical summary of the analytical data (Shallow aquifers)

Parameters	Range (Pre-monsoon 2010)	Average (Pre-monsoon 2010)	SD	Range (Post monsoon 2010)	Average (Post-monsoon 2010)	SD
pH	7.6-8.3	7.9	0.19	6.9-8.5	7.52	0.52
EC	463-3410	1229.82	955.31	664-2800	1436.57	963.39
TDS	296-2114	785.47	599.54	425-1792	924.5	619.42
TH	232-760	414.88	170.85	304-1136	569.21	311.34
Ca	35-163	69.70	28.30	43-291	120.14	83.46
Mg	19-119	54.23	23.77	35-155	69	35.34
Na	15-216	58.94	65.40	16-255	76.92	50.14
K	1-101	10.29	26.28	1-129	20.21	42.73
Cl	28-438	140.17	145.25	28-316	152.71	209.09
NO ₃	1-57	16.23	18.68	31-421	167.92	121.91
CO ₃	0-0	0	0	0-64	10.28	21.30
HCO ₃	160-548	309.41	86.83	160-560	330.57	80.09
SO ₄	1-172	45.23	44.601	15-204	56.14	38.79

All unites have their measurement in mg/l except, 'T' is expressed in °C, 'EC' is expressed in µS/cm, 'TH and CaH' are expressed in mg/l as CaCO₃, SD=standard deviation, BDL =below detection level

Table 2. Descriptive statistical summary of the analytical data (Deep aquifers)

Parameter	Range (Pre-monsoon 2010)	Average (Pre-monsoon 2010)	SD	Range (Post -monsoon 2010)	Average (Post -monsoon 2010)	SD
pH	7.6-8.5	8.00	0.25	7.1-8.6	0.52	0.46
EC	348-2230	967	440.87	544-4280	963.39	622.84
TDS	296-2114	597	190.38	348-2739	619.42	399.96
TH	312-995	362	136.83	184-1536	311.34	232.08
Ca	184-689	63	31.46	11-336	83.46	64.18
Mg	11-130	47.78	19.14	22-167	35.34	36.46
Na	19-175	72.07	50.23	15-175	50.14	71.57
K	1-39	7.85	12.86	1-126	42.73	33.136
Cl	26-243	77.5	93.95	30-834	209.09	91.79
NO ₃	2-48	14.42	12.51	35-487	121.91	100.15
CO ₃	0-48	3.42	13.31	0-56	21.30	21.24
HCO ₃	160-488	340.21	93.95	160-508	80.09	97.77
SO ₄	8-97	35.28	27.97	18-168	38.79	55.49

All unites have their measurement in mg/l except, 'T' is expressed in °C, 'EC' is expressed in µS/cm, 'TH and CaH' are expressed in mg/l as CaCO₃, SD=standard deviation, BDL =below detection level

post-monsoon and pre-monsoon seasons were found within the safe limit. Regarding the values of TDS, TH, Na⁺, Cl⁻ and NO₃ 67, 65, 88, 73 and 55% samples respectively in shallow aquifer and TDS, TH, Cl⁻ and NO₃ 91, 64, 88 and 54% samples respectively in deep aquifer were found safe.

HYDRO-GEOCHEMISTRY OF THE AQUIFERS

The Hydro-geochemical Facies

The determination of hydro-chemical facies was carried out as per the Piper trilinear diagram (1944) using

Aquachem 4.0 software to assess the nature of hydro-geochemistry of both the aquifers. The piper diagram directly deciphers the groundwater quality, and as a result it is commonly used as an effective tool to specify different water-types. In general, piper diagram reveals six types with nine combinations, according to ionic placement in the diamond field (Figure 2). Plots of analytical data (Figure 2) of the water samples collected from shallow aquifer clustered in the divisions 1,2,4 and 5 of Piper diagram, which showed that alkali earths exceed alkalis, weak acids exceeds strong acid and carbonate hardness (secondary alkalinity) exceeds 50% (Table 4) type of hydro-geochemistry.

Table 3. Distribution of water samples within the drinking water standards collected from shallow and deep aquifers

Physical and unconfined aquifer chemical Parameters (mg/l)	WHO standards for drinking water, 2004 (maximum permissible limit)	Shallow aquifer Samples within safe limit (%)	Deep aquifer Samples within safe limit (%)
pH	6.5 - 9.5	100	100
EC	-	-	-
TDS	1000	67	91
TH	500	65	64
Ca	-	-	-
Mg	-	-	-
Na	200	88	100
K	-	-	-
Cl	250	73	88
NO ₃	50	55	54
CO ₃	-	-	-
HCO ₃	-	-	-
SO ₄	250	100	100

All unites have their measurement in mg/l except, 'T' is expressed in °C, 'EC' is expressed in µScm, 'TH and CaH' are expressed in mg/l as CaCO₃

Table 4. Water-types for shallow aquifer samples from Naokari and Manikgarh limestone mine area

Well ID	Pre 2010	Post 2010
DW1	Mg-Ca-Na-HCO ₃ -Cl	Mg-Ca-HCO ₃ -CO ₃ -Cl
DW2	Mg-Ca- HCO ₃	Mg-Ca-Cl-NO ₃ -HCO ₃
DW3	Mg-Ca-HCO ₃ -Cl	Mg-Ca-Cl-HCO ₃
DW4	Mg-Ca-HCO ₃ -Cl	Mg-Ca- HCO ₃ -Cl
DW6	Ca-Mg-Na-Cl-HCO ₃	Ca-Cl-SO ₄
DW7	Na-Mg-Ca-Cl-HCO ₃	Na-Mg-Ca-HCO ₃ -Cl
DW8	Mg-Na- HCO ₃ -Cl	Na-Mg- HCO ₃ -Cl
DW9	Mg-Na-Cl- HCO ₃	Na-Mg- HCO ₃ -Cl
DW17	Mg-Na-Ca-Cl-HCO ₃	Mg-Ca-Na-HCO ₃
DW 5	Ca-Mg- HCO ₃ -Cl	Mg-Ca-K-SO ₄ - HCO ₃ - NO ₃
DW10	Mg-Ca- HCO ₃	Mg-Ca-HCO ₃
DW11	Mg-Ca- HCO ₃ -Cl	Ca-Mg-Cl- HCO ₃ -SO ₄ -NO ₃
DW12	Mg-Ca- HCO ₃ -Cl	Mg-Ca- HCO ₃
DW13	Ca-Mg- HCO ₃	Ca-Mg- HCO ₃ -Cl
DW14	Mg-Ca- HCO ₃ -Cl	Ca-Mg- HCO ₃ -Cl
DW15	Mg-Ca- HCO ₃	Mg-Ca- HCO ₃
DW16	Mg-Ca- HCO ₃ -Cl	Ca-Mg- HCO ₃ -Cl

1. Alkaline earths exceed alkalis
2. Alkalis exceed alkaline earths
3. Weak acids exceed strong acids
4. Strong acids exceed weak acids
5. Carbonate hardness exceeds 50%
6. Non carbonate hardness exceeds 50%
7. Non carbonate alkalis exceeds 50%
8. Carbonate alkalis exceeds 50%
9. No one cation-anion pair exceeds 50%

The water-types revealed through Piper diagram are presented in **Table 4 and 5**. The data shows that Mg²⁺ is the dominant cation followed by Ca²⁺ and Na⁺. Mg²⁺ is dominant in 64.70% samples and both Ca²⁺ and Na⁺ in 35.29% of samples in shallow aquifer. In deep aquifer

samples Mg²⁺ is dominant in 42.30% samples and both Ca²⁺ and Na⁺ in 57.70% of samples. HCO₃⁻ is the most dominant anion (78% samples) followed by Cl⁻ and SO₄²⁻. It is observed that in almost all pre-monsoon shallow aquifer samples from Naokari limestone mine area alkaline earths (Ca + Mg) exceed alkalis (Na + K), except one sample from Awarpur village (DW7). 100% pre-monsoon shallow aquifer samples from Naokari limestone mine area have weak acids (CO₃ + HCO₃) exceed the strong acids (SO₄+Cl +F). 25% of samples exhibit that non carbonate hardness (secondary alkalinity) exceeds 50% i.e. chemical properties of the groundwater are dominated by alkalis and strong acids. In pre-monsoon season from Naokari limestone mine

Table 5. Water-types for Deep aquifer samples from Naokari and Manikgarh limestone mine area

Well ID	Pre 2010	Post 2010
BW1	Mg-Na- HCO ₃	Mg-Na-Ca- HCO ₃ -Cl
BW2	Na-Mg-Ca- HCO ₃	Na-Mg-Ca- HCO ₃ -Cl
BW3	Ca-Mg- HCO ₃	Mg-Ca-Na- HCO ₃
BW4	Na-Ca- HCO ₃ -Cl	Ca-Mg- HCO ₃
BW5	Mg-Ca- Na-Cl-HCO ₃	Ca-Na-SO ₄ -HCO ₃ -Cl
BW6	Mg-Ca- HCO ₃	Ca-Mg- HCO ₃ -Cl
BW7	Na-Mg- HCO ₃	Mg-Na-HCO ₃
BW8	Mg-Na-Ca- HCO ₃	Na-Mg-HCO ₃
BW9	Ca-Mg-Na- HCO ₃ -Cl	Ca-Mg-HCO ₃ -Cl
BW11	Mg- HCO ₃ -SO ₄ Cl	Ca-Mg-HCO ₃
BW14	Na-Mg- HCO ₃ -CO ₃	Ca-Mg-Cl-HCO ₃
BW10	Ca-Mg-HCO ₃	Ca-Mg-HCO ₃
BW12	Mg-Ca- HCO ₃	Mg-Ca-HCO ₃ -Cl
BW13	Mg-Ca- HCO ₃	Ca-Mg-Cl-NO ₃ - HCO ₃

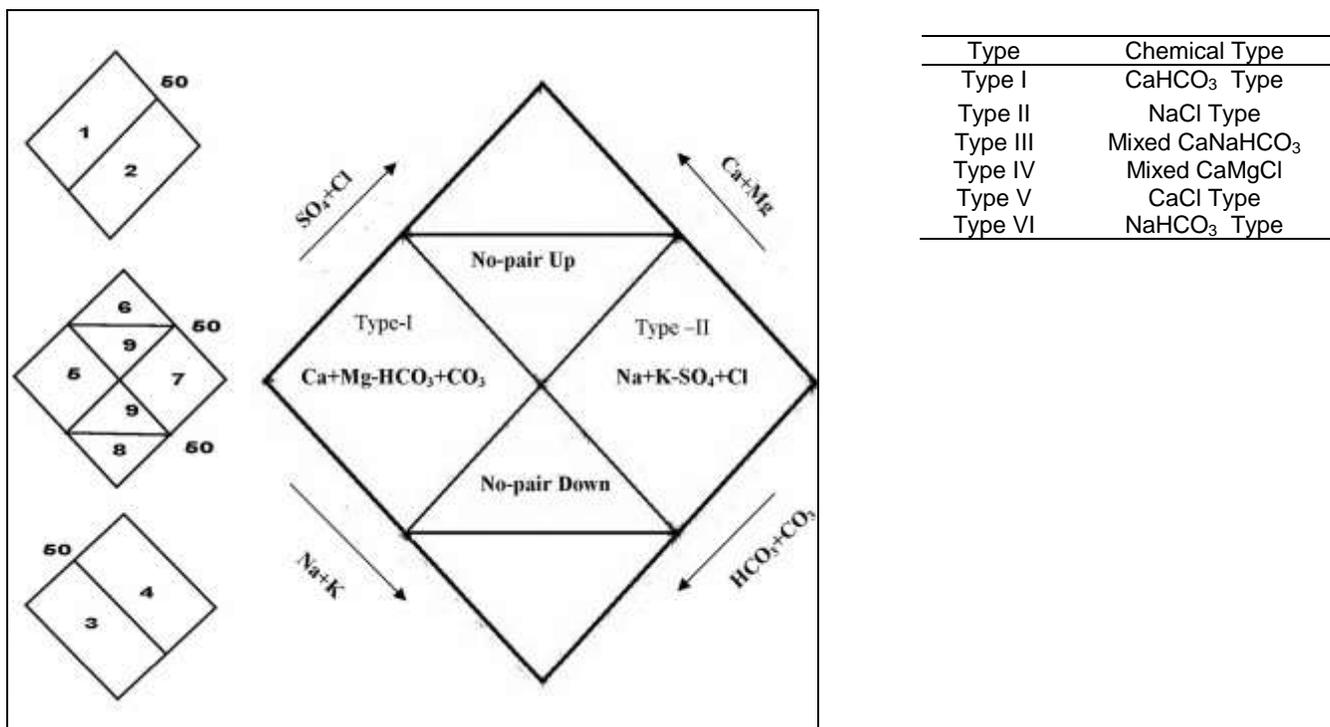


Figure 2. Characteristic features of Piper Diagram

area 61.11% of deep aquifer samples show alkaline earths (Ca + Mg) exceeds the alkalis (Na + K). About 63.64% of deep samples reveal that weak acids ($\text{CO}_3 + \text{HCO}_3$) exceed strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$). Remaining 36.36% samples divulge strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) exceed weak acids ($\text{CO}_3 + \text{HCO}_3$).

Similarly all the pre-monsoon shallow aquifer samples from Manikgarh limestone mine area exhibit that the alkaline earths (Ca + Mg) exceeds alkalis (Na + K) as well as weak acids ($\text{CO}_3 + \text{HCO}_3$) exceed strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$). While 73 % deep aquifer samples reveal alkaline earths (Ca + Mg) exceeds alkalis (Na + K) and all the samples represent that the weak acids ($\text{CO}_3 + \text{HCO}_3$) exceed strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$).

It is observed from 50% post-monsoon shallow aquifer samples of Naokari limestone mine area that the alkaline earths (Ca + Mg) exceed alkalis while 50% show alkalis (Na + K) exceed alkaline earths (Ca + Mg). 33.33% post-monsoon shallow aquifer samples from Naokari limestone mine area have weak acids ($\text{CO}_3 + \text{HCO}_3$) exceed the strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) while remaining 66.67% samples show strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) exceed weak acids ($\text{CO}_3 + \text{HCO}_3$). 38% of samples exhibit that non carbonate hardness (secondary alkalinity) exceeds 50% i.e. chemical properties of the groundwater are dominated by alkalis and strong acids. Also, 38% of samples exhibit that no one cation-anion exceeds 50%. In post-monsoon season, from Naokari limestone mine area 50.09% of deep aquifer samples show alkaline earths (Ca + Mg) exceed the alkalis (Na+K). About 75% of deep aquifer samples reveal that weak acids ($\text{CO}_3 + \text{HCO}_3$) exceed strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$). Remaining 50% samples divulge strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) exceed weak acids ($\text{CO}_3 + \text{HCO}_3$).

Correspondingly all the post-monsoon shallow aquifer samples from Manikgarh limestone mine area exhibit that the alkaline earths (Ca + Mg) i.e. 100% exceeds alkalis (Na + K) as well as weak acids ($\text{CO}_3 + \text{HCO}_3$) i.e. 52.94% exceed strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) i.e. 47.06%. While 100% deep aquifer well samples reveal alkaline earths (Ca + Mg) exceeds alkalis (Na + K) and also 50% samples represent that the weak acids ($\text{CO}_3 + \text{HCO}_3$), strong acids ($\text{SO}_4 + \text{Cl} + \text{F}$) i.e. 50%.

From another point of view 71 % of the plots clustered in Type I (Ca+MgCO₃+HCO₃) facies of the Piper's diagram. This might be attributed to hydro-geochemistry of the shallow aquifer was mainly controlled by dissolution of carbonate minerals in pre monsoon seasons 2010.

Plots of analytical data of the water samples collected from deep aquifer clustered in the divisions 1,2,3,4 of Piper diagram (Figure 4) in pre-monsoon season, representing equal dominance of alkaline earths and alkali, dominance of weak acid, carbonate hardness and non carbonate alkali. Plots of analytical data of the water samples collected from the same aquifer in post

monsoon seasons clustered in the divisions of 1, 4, 5 which indicated equal dominance of alkaline earths and alkali, dominance of strong acids, equal dominance of carbonate hardness and non carbonate hardness and dominance of non-carbonate alkali (Table 4) type of hydro-geochemistry.

Ion exchange process in the aquifers

The ion exchange between the ground water and its host environment during residence or travel can be understood by studying the chloroalkaline indices i.e.

$$\text{CAI} [(\text{Cl}^- - \text{Na}^+ + \text{K}^+) / \text{Cl}^-] \text{ and } \text{CAII} [(\text{Cl}^- - \text{Na}^+ + \text{K}^+) / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-)].$$

100% of the water samples collected from shallow aquifers and deep aquifers in both post-monsoon and pre-monsoon seasons had positive CA-I and CA-II values. Positive chloroalkaline indices is due to base exchange (Na^+ and K^+ ions in water are exchanged with Mg^{2+} and Ca^{2+} ions) reaction (Schoeller, 1965 and 1967).

Mechanism controlling ground water chemistry

Gibbs's diagrams representing the ratios of $[\text{Na} + : (\text{Na}^+ + \text{Ca}^{2+})]$ and $[\text{Cl} : (\text{Cl} + \text{HCO}_3)]$ as a function of TDS, are widely employed to assess the functional source of dissolved chemical constituents, such as precipitation dominance, rock dominance and evaporation dominance (Gibbs, 1970). Gibbs's plot (Figure 7) of analytical data of the ground water samples collected from shallow aquifer clustered at the region of rock dominance. This might be attributed to chemical weathering of rock forming minerals is the major driving force in controlling ground water chemistry. Gibbs's diagram plot (Figure 8) of analytical data of the water samples exhibit that chemical weathering of rock forming minerals is the main causative factor in the evolution of chemical composition of groundwater occurring in all the lithological domains of study area, which is later influenced by anthropogenic activities. The ratio of cations $\text{Na}^+ : (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- : (\text{Cl}^- + \text{HCO}_3^-)$ are spread from the rock domain towards the zone of precipitation dominance indicating the existence of rock water interactions which is a major source of dissolved ions in the groundwater.

Analysis of irrigation water samples

The electrical conductivity and Na^+ have a fundamental role in suitability of water for irrigation. According to Saleh et al., (1999) the excess salinity reduces the osmotic activity of plants and hence interferes with the absorption of water and nutrients from the soil. The excess amount of dissolved ions affects the physical and the chemical setup of agricultural soil. In addition, salts affect the

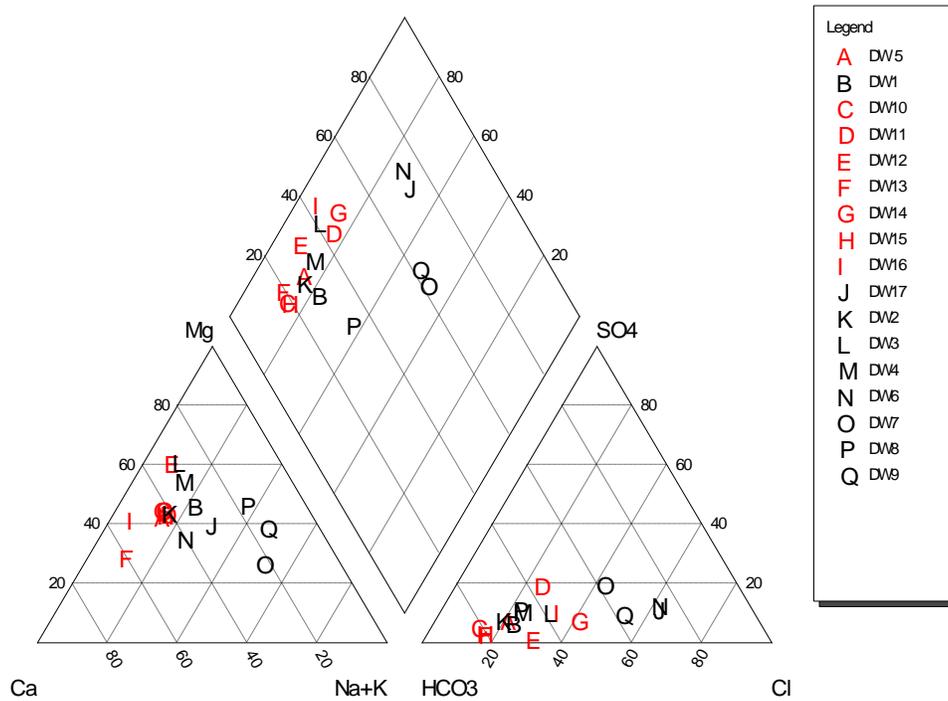


Figure 3. Piper diagram plot of the water samples collected from shallow aquifer (Pre-monsoon 2010 samples)
 (Note: samples from Manikgarh area samples shown by Red colour and Naokari area samples shown by Black colour in piper diagram)

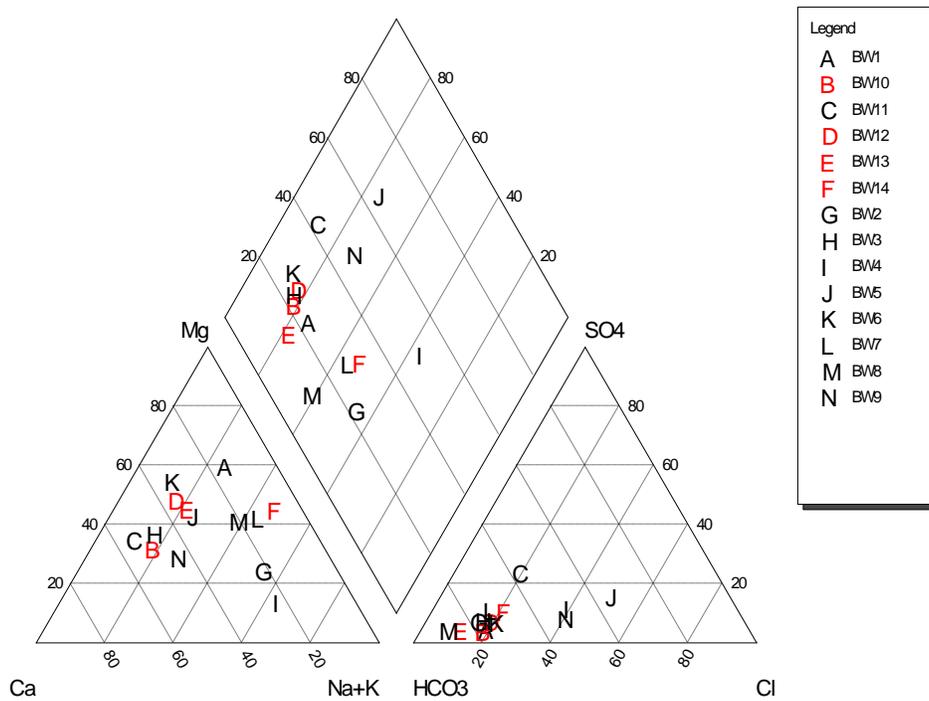


Figure 4. Piper diagram plot of the water samples collected from Deep aquifer (Pre-monsoon 2010 samples)

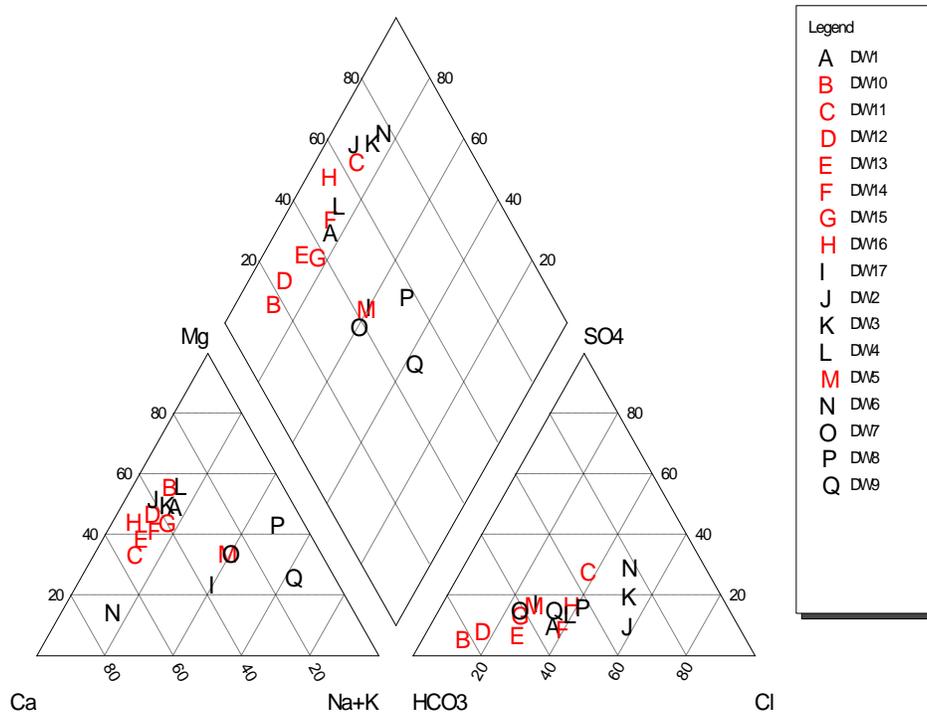


Figure 5. Piper diagram plot of the water samples collected from Shallow aquifer (Post-monsoon 2010 samples)

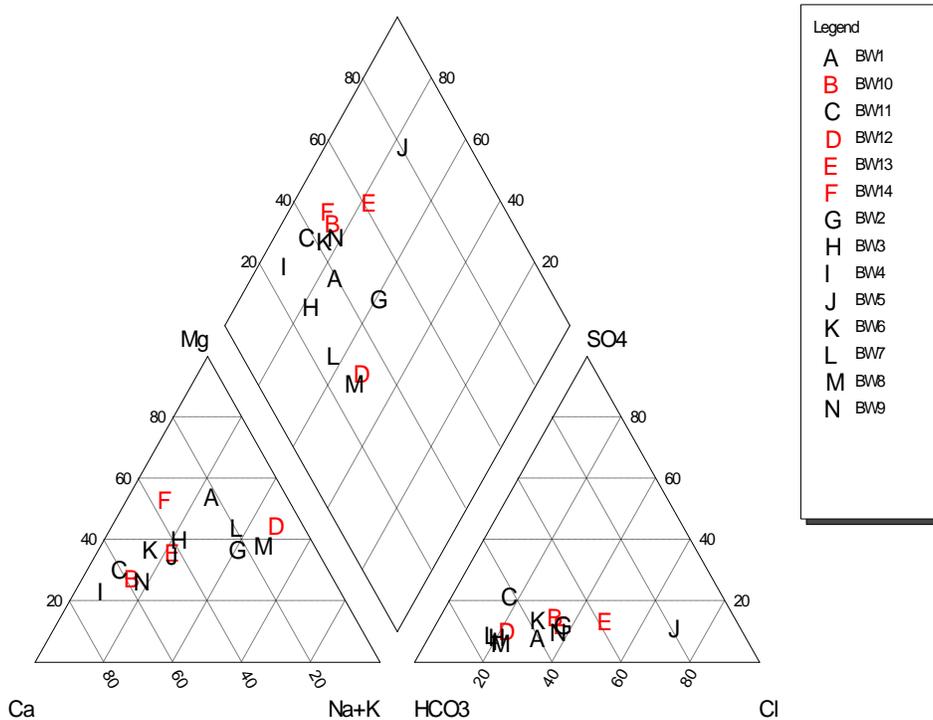


Figure 6. Piper diagram plot of the water samples collected from Deep aquifer (Post-monsoon 2010 samples)

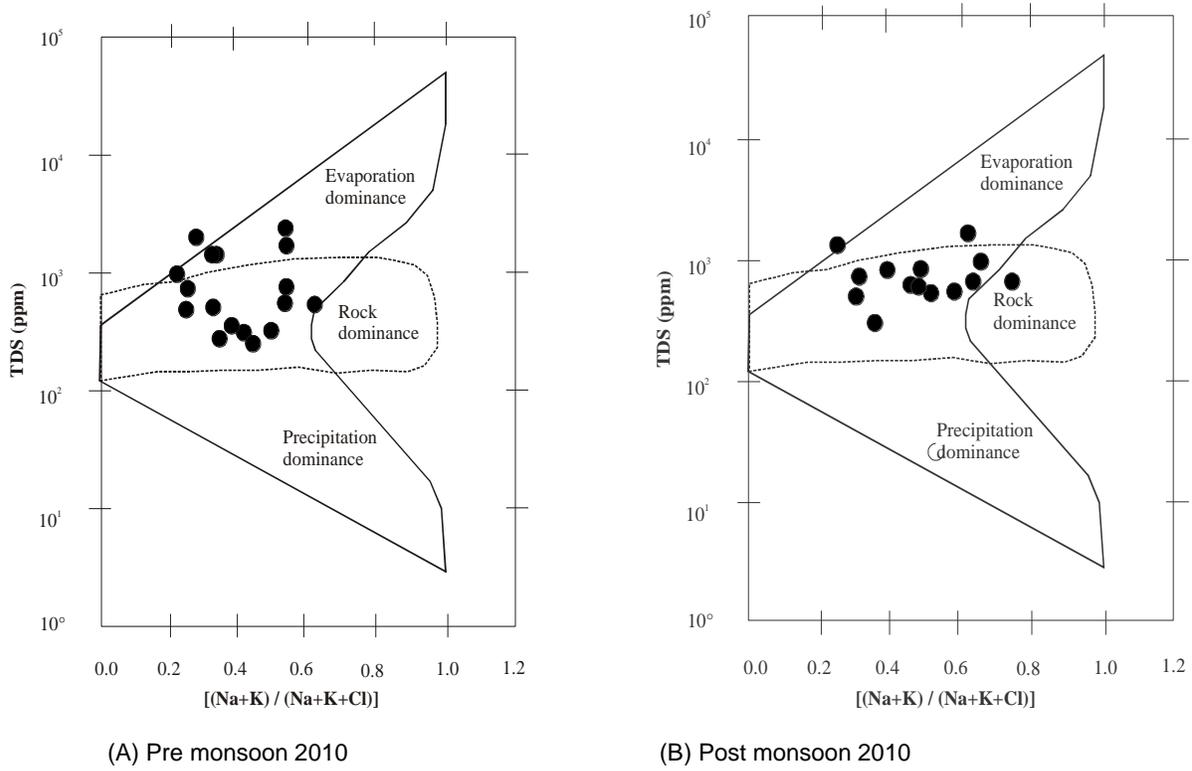


Figure 7. Gibb's diagram plot of the water samples collected from shallow aquifer

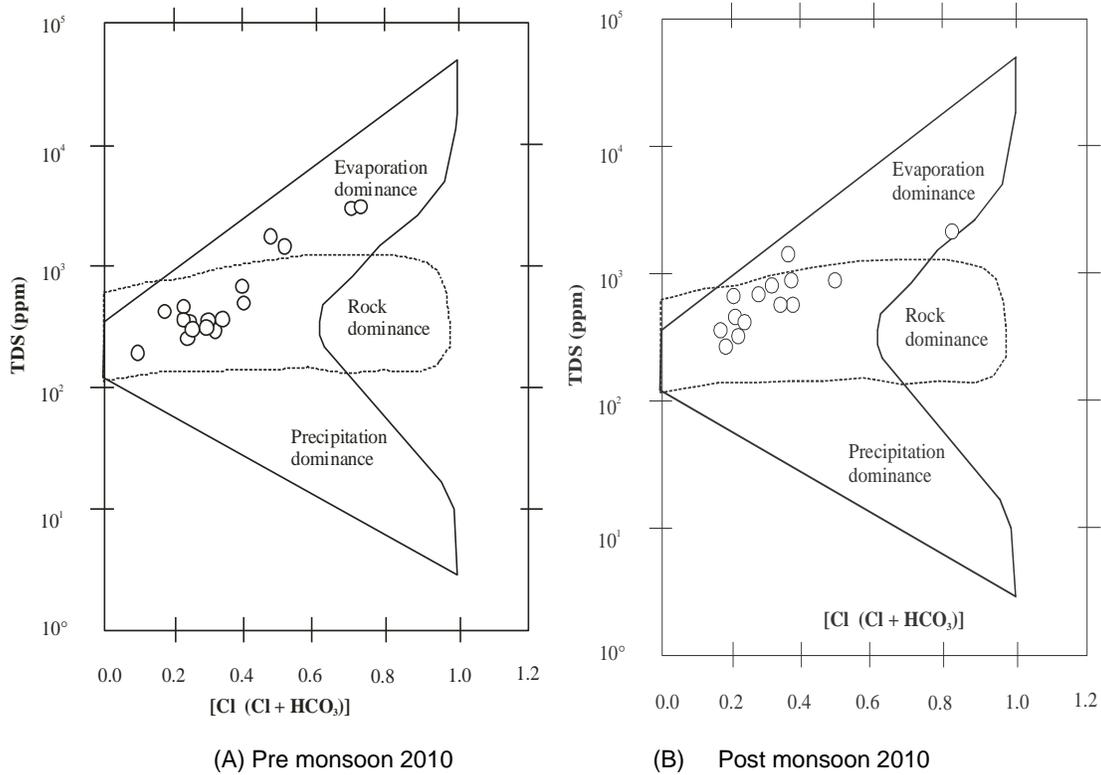


Figure 8. Gibb's diagram plot of the water samples collected from deep aquifer

growth of plants directly and also indirectly affect the soil structure, permeability and aeration (Subba Rao, 2006).

Sodium hazards

Values of residual sodium carbonate (RSC), percentage sodium (%Na) and sodium adsorption ratio (SAR) of the collected samples are described in Table 5. RSC is a measurement that compares the concentration of Ca^{2+} and Mg^{2+} to HCO_3^- and CO_3^{2-} . It also determines when Ca^{2+} and Mg^{2+} (macro nutrients) precipitation can occur in the soil and results in additional Na^+ dominance of soil cation exchange sites.

In the present study, the suitability of groundwater has been checked for irrigation purpose using the Sodium Adsorption Ratio (SAR) $\{\text{SAR} = \text{Na}^+ / \sqrt{[(\text{Ca}^{++} + \text{Mg}^{++})/2]}\}$ and the US Salinity Laboratory diagram (1954) (Figure 9.1 to 9.4). In addition, the Percent Sodium (%Na), Residual Sodium Carbonate (RSC), Residual Sodium Bicarbonate (RSBC), Soluble Sodium Percentage (SSP), Corrosivity Ratio (CR), Kelley's Ratio (KR) and permeability Index (PI) have been also estimated which decides its suitability for irrigation purpose. Thus, suitability of groundwater from the study area for irrigation purpose is calculated and the data are presented in Table 6 and 7).

Sodium Adsorption Ratio (SAR)

A high sodium concentration changes soil properties and reduce soil permeability. The suitability of water for irrigation purpose is determined by the mathematical equation:

$\text{SAR} = \text{Na} / \sqrt{\text{Ca} + \text{Mg}/2}$. (Where, ions are expressed as meq/l.)

Water with SAR value ≤ 10 is considered as of excellent quality, 10 to 18 is good, between 18 to 26 is fair and above 26 is said to be unsuitable for irrigation. The calculated SAR values from Naokari and Manikgarh limestone mine areas are less than 10 meq/l [pre monsoon 2010 (shallow aquifer: 0.116 to 1.586; deep aquifer: 1.198 to 1.875) post monsoon 2010 (deep aquifer: 0.103 to 1.90; Bore well: 0.121 to 1.226). In general, the plots of the groundwater samples from both from Naokari and Manikgarh limestone mine areas fall in $\text{C}_2\text{-S}_1$ and $\text{C}_3\text{-S}_1$ category, which indicate the water of medium to high salinity-low sodium type and can be utilized for irrigation with very little danger of exchangeable sodium (Murkute, 2014).

Residual Sodium Carbonate (RSC)

RSC value (in meq/l) is calculated as $\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{++} + \text{Mg}^{++})$. A high RSC value in water leads to an increase in the adsorption of sodium on soil (Eaton 1950). RSC level less than 1.25meq/l is considered safe,

where as water with RSC of 1.25 – 2.50meq/l is within marginal range and RSC value of water sample 2.50 meq/l or greater is considered too high making the water unsuitable for irrigation use. The maximum RSC value of groundwater sample is noted from pre-monsoon deep aquifer sample, collected from BW2- Asan kh village located in Naokari limestone mine area. In pre-monsoon 2010, shallow aquifers having 10.782 to -0.317 and deep aquifer ranging -7.544 to 2.052, in post-monsoon 2010, shallow aquifer is -16.663 to 1.704 and deep aquifer ranging from 24.341 to 0.729. RSC value negative which may be attributed to excess Ca^{2+} and Mg^{2+} in irrigation water.

Percent Sodium (%Na)

The % Na is widely used for evaluating the suitability of water quality for irrigation (Wilcox, 1955). This value is defined by the expression: $\% \text{Na} = \text{Na} + \text{K} / (\text{Ca} + \text{Mg} + \text{Na} + \text{K}) \times 100$. High % Na in irrigation water causes exchange of sodium in water, and exchange of calcium and magnesium contents in soil having poor internal drainage. The % Na, < 60 represents safe water while it is unsafe if > 60 (Eaton, 1950). The % Na values from Naokari and Manikgarh limestone mine areas do not exceed the limit of 60 as stated by Eaton (1950), except the one bore well sample (BW4- Village Sonurli from Naokari limestone mine area. [Pre-monsoon 2010 (shallow aquifer: 7.95 to 52.39; deep aquifer: 12.09 to 65.30) post-monsoon 2010 (shallow aquifer: 6.62 to 61.76; deep aquifer: 9.43 to 47.96). As per this criterion the groundwater from Naokari and Manikgarh limestone mine areas is safe for irrigation purpose.

PI

In the study area, PI values fall in class I of Doneen (1964) sample from pre-monsoon 2010 shallow aquifer in between 48.749 to 110.69 and deep aquifer 31.761 to 86.562 (Table 4, 5). In post-monsoon 2010, shallow aquifer shows 17.827 to 77.051 and deep aquifer are in between 33.173 to 85.138 (Table 6, 7). On the basis of computed PI values, it can be understood that the groundwater from Naokari and Manikgarh limestone mine areas is suitability for the irrigation purpose.

$\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio

$\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio of the 57.14% of collected irrigation water samples in post-monsoon and 71.43% of collected irrigation water samples in pre-monsoon were less than one. It indicated that, these were Mg^{2+} dominated water. In Mg^{2+} dominated water the potential effect of Na^+ may be slightly increased (FAO, 1994) might be due to Mg^{2+} induced Ca^{2+} deficiency caused by high levels of exchangeable Mg^{2+} in soil. Ca^{2+} appears to reduce

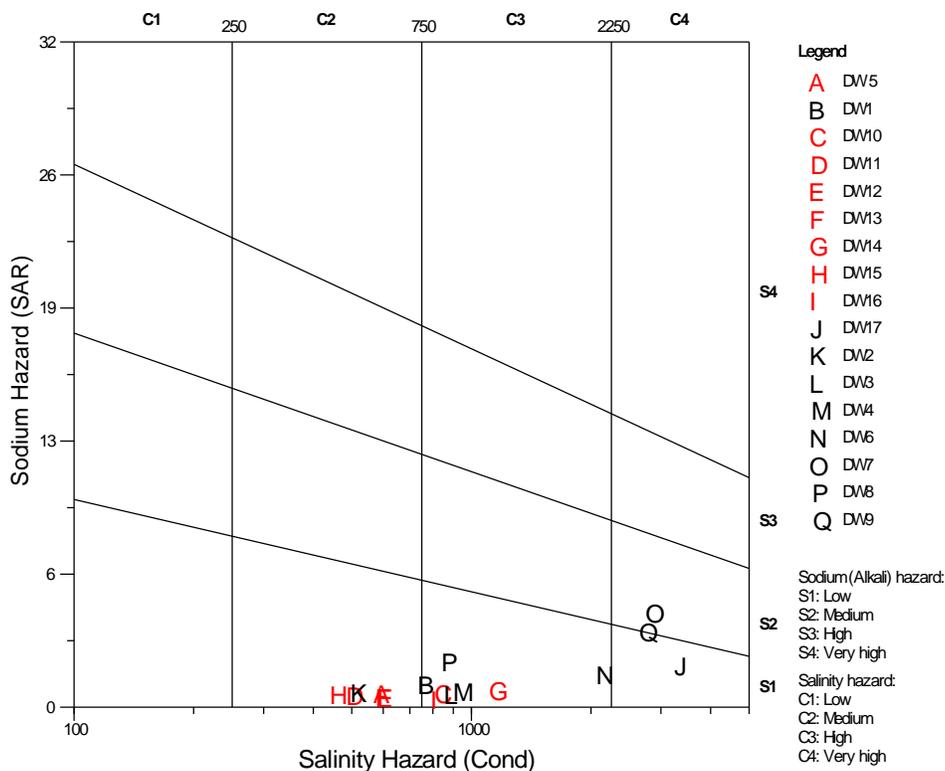


Figure 9.1. US Salinity Diagram of groundwater samples from Naokari and Manikgarh limestone mine areas (Pre-monsoon 2010 Shallow aquifer)

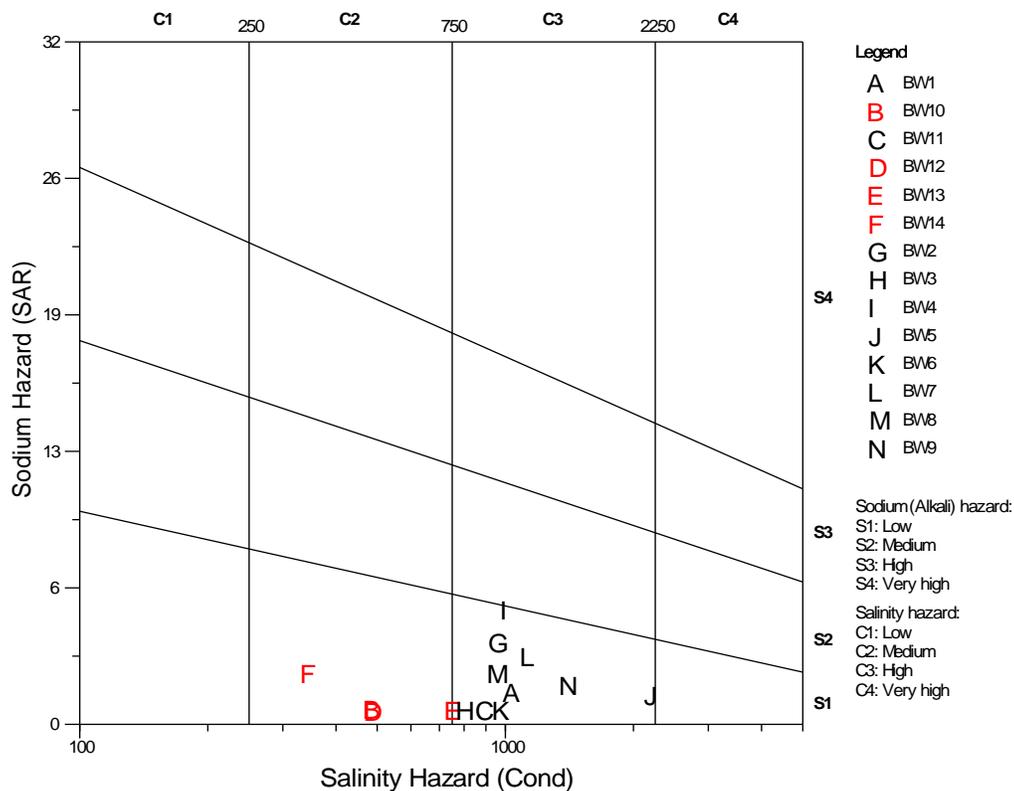


Figure 9.2. US Salinity Diagram of groundwater samples from Naokari and Manikgarh limestone mine areas (Pre-monsoon 2010 Deep aquifer)

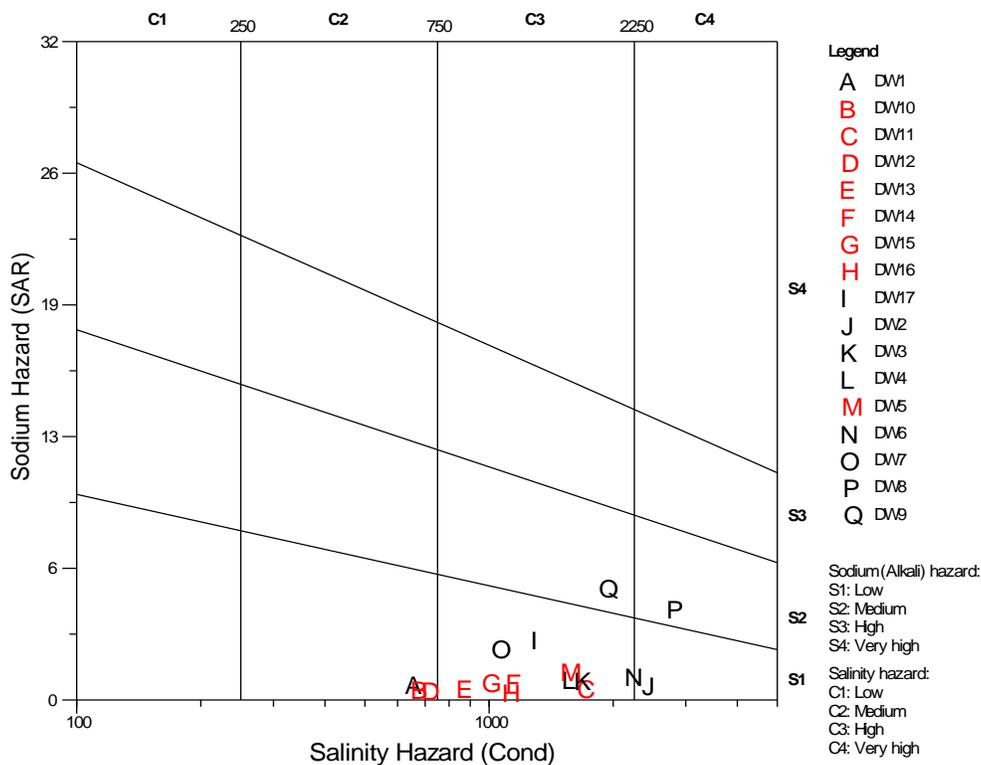


Figure 9.3. US Salinity Diagram of groundwater samples from Naokari and Manikgarh limestone mine areas (Post-monsoon 2010 Shallow aquifer)

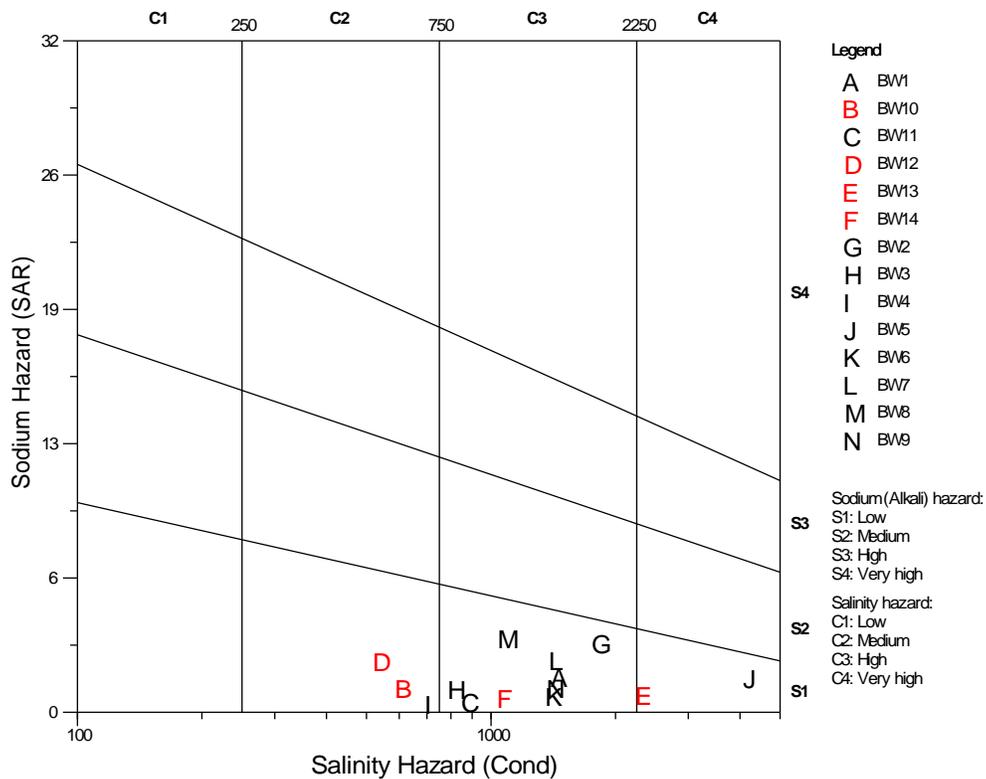


Figure 9.4. US Salinity Diagram of groundwater samples from Naokari and Manikgarh limestone mine areas (Post monsoon 2010 Deep aquifer)

Table 6. Irrigation quality results of groundwater samples (shallow aquifer 2010)

Sample No		SAR	% Na	RSC	RSBC	CR	SSP	KR	PI
1	Pre 2010	0.367	23.36	-1.385	2.809	0.185	23.369	0.276	88.078
	Post 2010	0.250	16.86	-1.592	-0.0223	0.079	16.860	0.198	37.866
2	Pre 2010	0.227	16.89	-1.653	1.060	0.064	16.899	0.198	80.162
	Post 2010	0.233	9.22	-16.663	-4.978	0.680	9.226	0.098	17.827
3	Pre 2010	0.190	11.25	-4.412	2.004	0.247	11.257	0.124	79.552
	Post 2010	0.309	14.05	-10.849	-3.030	0.467	14.055	0.156	24.140
4	Pre 2010	0.248	14.87	-2.130	3.134	0.251	14.879	0.171	85.245
	Post 2010	0.330	15.02	-8.832	1.0386	0.584	15.052	0.170	28.717
5	Pre 2010	0.216	15.51	-1.365	1.513	0.106	15.517	0.179	77.521
	Post 2010	0.464	38.7	-3.609	1.7372	0.370	38.708	0.296	42.424
6	Pre 2010	0.527	25.73	-10.782	-3.872	0.709	25.738	0.271	50.006
	Post 2010	0.375	15.56	-14.122	-11.242	0.483	15.569	0.18	24.072
7	Pre 2010	1.586	52.39	-1.237	3.369	1.105	52.394	1.091	90.574
	Post 2010	0.852	40.46	0.255	2.809	0.260	40.462	0.667	62.025
8	Pre 2010	0.745	37.18	-0.534	4.153	0.226	37.188	0.588	110.69
	Post 2010	1.538	48.9	-2.227	7.032	1.469	48.907	0.853	58.606
9	Pre 2010	1.265	46.5	-4.799	4.989	1.752	46.501	0.681	92.002
	Post 2010	1.900	61.76	1.704	6.146	0.835	61.764	1.470	77.051
10	Pre 2010	0.203	14.76	-0.497	2.628	0.096	14.766	0.164	83.467
	Post 2010	0.159	12.15	-0.981	2.802	0.072	12.153	0.129	44.474
11	Pre 2010	0.180	16.28	-2.0585	0.327	0.067	16.289	0.167	76.008
	Post 2010	0.168	12.59	-8.480	-3.544	0.495	12.592	0.093	23.519
12	Pre 2010	0.140	9.45	-3.090	2.010	0.148	9.4532	0.101	83.775
	Post 2010	0.134	10.71	-2.059	1.3956	0.087	10.719	0.104	38.644
13	Pre 2010	0.147	12.14	-0.317	1.245	0.071	12.142	0.132	68.531
	Post 2010	0.165	12.26	-3.720	-0.101	0.148	12.263	0.115	33.443
14	Pre 2010	0.257	14	-4.994	0.270	0.364	14.007	0.160	58.410
	Post 2010	0.272	14.82	-5.444	-0.344	0.349	14.823	0.166	32.661
15	Pre 2010	0.192	15.63	-0.861	1.441	0.045	15.632	0.179	86.125
	Post 2010	0.280	16.63	-4.076	0.4475	0.165	16.638	0.190	36.779
16	Pre 2010	0.116	7.95	-4.437	-0.982	0.126	7.9546	0.083	48.749
	Post 2010	0.103	6.62	-7.581	-2.316	0.210	6.624	0.061	21.860
17	Pre 2010	0.676	31.21	-4.207	0.974	0.927	31.211	0.448	77.728
	Post 2010	1.00	41.41	-2.626	0.663	0.355	41.410	0.694	57.904

possible toxicities due to other ions like Na^+ , Mg^{2+} in the root environment. If the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio is near or less than one, the uptake and translocation of Ca^{2+} from soil water to the above ground parts of the growing crop is diminished due to antagonistic effects of high Mg^{2+} or competition for absorption sites to such an extent that less Ca^{2+} is absorbed.

Concentration of common phytotoxic anions

Values of concentration of common phytotoxic anions (Cl and F) of the collected samples are described in Table 5. In the irrigation water the most common toxicity is from Cl. Cl is not adsorbed or held back by soils, therefore it moves readily with the soil water, is taken up by crops, moves in the transpiration stream, and accumulates in

leaves. If the Cl concentration in the leaves exceeds the tolerance of the crops, injury symptoms develop such as leaf burn or drying of leaf tissue. With sensitive crops, these symptoms occur when leaves accumulate from 0.3 to 1.0% Cl on a dry weight basis, but sensitivity varies among these crops. Usual range of chloride in irrigation water is 0-30 meq/l (FAO, 1994). In the collected irrigation water samples Cl concentration ranged between 28-438 and 28-363 in pre and post monsoon seasons respectively. 22% of the irrigation water samples collected in post-monsoon and 27% of the irrigation water samples collected in pre-monsoon were found within the usual range.

F^- in the soil is generally not harmful. But F^- on plant surfaces may be harmful to plants and grazing animals. BIS (1991) recommended 1mg/l maximum

Table 7. Irrigation quality results of groundwater samples from (deep aquifer 2010)

Sample No		SAR	% Na	RSC	RSBC	CR	SSP	KR	PI
1	Pre 2010	0.511	26.3	-1.016	5.646	0.227	26.302	0.353	50.07877
	Post 2010	0.563	25.19	-5.065	10.458	0.441	25.193	0.324	49.479
2	Pre 2010	1.338	54.73	2.052	4.685	0.190	54.736	1.194	78.54496
	Post 2010	1.141	40.72	-4.0385	11.371	0.637	40.721	0.684	63.745
3	Pre 2010	0.213	16.71	-1.528	1.515	0.123	16.717	0.160	42.58443
	Post 2010	0.358	22.08	-2.261	8.344	0.118	22.087	0.269	54.488
4	Pre 2010	1.875	65.3	0.498	1.978	0.292	65.303	1.869	83.56262
	Post 2010	0.121	9.43	-2.659	10.028	0.111	9.4305	0.090	43.833
5	Pre 2010	0.456	25.61	-7.544	-0.716	0.537	25.615	0.262	34.74854
	Post 2010	0.551	23.38	-24.341	22.929	2.266	23.387	0.199	33.173
6	Pre 2010	0.217	13.31	-2.344	2.837	0.184	13.319	0.150	38.57248
	Post 2010	0.246	15.69	-4.110	10.880	0.288	15.694	0.159	43.797
7	Pre 2010	1.104	44.77	0.377	5.971	0.310	44.772	0.807	65.38937
	Post 2010	0.852	37.54	0.0230	10.871	0.334	37.548	0.592	64.690
8	Pre 2010	0.818	38.5	1.078	5.603	0.108	38.501	0.622	63.55452
	Post 2010	1.226	46.91	0.729	8.867	0.220	46.914	0.880	73.004
9	Pre 2010	0.627	27.96	-3.585	0.527	0.624	27.962	0.385	45.86813
	Post 2010	0.381	18.32	-7.650	14.027	0.320	18.328	0.212	42.816
10	Pre 2010	0.234	19.18	-0.871	1.020	0.065	19.186	0.211	51.17352
	Post 2010	0.372	15.46	-12.763	16.119	0.236	15.469	0.180	37.481
11	Pre 2010	0.206	12.09	-4.899	-1.280	0.182	12.090	0.134	31.76172
	Post 2010	0.152	9.96	-4.1634	10.773	0.172	9.9623	0.102	41.103
12	Pre 2010	0.198	17.31	-0.904	1.562	0.053	17.311	0.191	51.99549
	Post 2010	0.826	47.96	0.6282	3.171	0.041	47.960	0.871	85.138
13	Pre 2010	0.215	22.49	-1.319	2.628	0.079	22.493	0.164	43.51718
	Post 2010	0.257	22.8	-11.517	13.914	0.548	22.807	0.126	34.427
14	Pre 2010	0.826	47.96	-0.970	2.073	0.041	47.960	0.871	70.65757
	Post 2010	0.220	12.08	-5.556	8.0283	0.176	12.088	0.135	40.696

concentrations of F^- in irrigation water. F^- concentration in the collected from shallow aquifer in pre-monsoon seasons water samples ranged between 0.53-7.52 mg/l and samples collected from deep aquifer in post-monsoon seasons range from 0.48-6.28 mg/l. This implied the irrigation waters are not safe from F point of view.

CONCLUSION

Quality of the water samples collected from the deep aquifer found satisfactory in comparison with water samples collected from the shallow aquifer. It was concluded from the Piper diagram plot that hydro-geochemistry of confined aquifer was earth alkaline with increased portion of alkalis and with prevailing bicarbonate. Chloro-alkaline disequilibrium type of ion exchange process was found in shallow aquifer. Chemical weathering of rock forming minerals was the major driving force controlling ground water chemistry as represented by Gibbs diagram plot. Hydro-geochemistry

of deep aquifer in post monsoon season was alkaline with bicarbonate and sulphate chloride and earth alkaline with increased portion of alkalis with prevailing bicarbonate where as in pre-monsoon season. Hydro-geochemistry of the deep aquifer shifted towards alkaline with sulphate and bicarbonate. Ion exchange process in deep aquifer was found Base Exchange type in both the seasons. According to Gibbs's diagram plot chemical weathering of rock forming minerals in post monsoon season and chemical weathering along with evaporation in pre monsoon season were the major driving force controlling hydro-geochemistry of deep aquifer. RSC, %Na, SAR, Ca^{2+}/Mg^{2+} ratio, concentration of Cl, F in irrigation water along with US Salinity Laboratory's and Wilcox's diagrams suggested that the majority of water samples were not good for irrigation during pre monsoon season in comparison to post monsoon season.

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