

Hydrochemical processes and groundwater quality assessment in North eastern region of Jordan valley, Jordan

Mohammad Salim Mohammad Tarawneh^{a,*}, M.R. Janardhana^b, Mohamed Muzamil Ahmed^c

^a INWRDAM, Jordan

^b Department of Geology, Yuvaraja's College, University of Mysore, Mysuru, Karnataka, India

^c UBDT College of Engineering, Davanagere, Karnataka, India

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ABSTRACT

Hydrochemical studies carried out on the groundwater in north eastern part of Jordan valley, Jordan, revealed the confinement of groundwater to two partly overlapping Upper Cretaceous and Tertiary-Quaternary aquifers. Values of Base Exchange Index (r_1) and Meteoric Genesis Index (r_2) indicate that the groundwater is essentially Na-SO₄ type and belongs mainly to the category of Deep Meteoric Percolation type. Major processes responsible for the hydrochemistry of groundwater are: weathering of carbonate and silicate minerals aided by H₂CO₃ and H₂SO₄, oxidation of sulphide minerals, domestic waste water, irrigation return flow, reverse and direct ion exchange reactions as well as connate saline water. Values of Water Quality Index indicate the occurrence of excellent and good quality potable water at majority of bore well locations. The groundwater belongs essentially to (C3S1) and (C4S2) irrigation water classes of Richards (1954) and is suitable for cultivation of semi-salt tolerant and salt tolerant crops.

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1. Introduction

Groundwater is a precious resource especially in arid and semi-arid regions of the globe due to limited occurrence of surface water resources. Stress on the available groundwater resource becomes acute owing to the demand by various sectors thus putting the quality at risk. Groundwater quality parameters exhibit considerable spatial variability and in many regions of the world groundwater quality is strongly influenced by anthropogenic activities and its pollution has become a severe problem for society at large (Bardossy, 2006).

Many regions in Asia are experiencing unprecedented rapid development resulting in great pressures on environment and sustainable management of natural resources (Xiaohong Chen et al., 2008). Jordan, located in southwest Asia, is one among the most fresh water deficient countries in the world owing to the prevailing semi-arid to arid climatic conditions. The demand for the limited available surface and groundwater in the country is continuously on the rise due to native population growth (2.2–2.5% growth/year) and massive influx of

refugees into the country leading to tenfold increase in population of Jordan since 1951 (Hirzallah, 1973). The present scenario of water shortage can get further amplified due to the envisaged installation of nuclear power plant and processing of oil shale. At present, the country is receiving, on average, 400 mm/a of rainfall (8.2 BCM of water/a), out of which, about 91.8% (7.5 BCM) is lost due to evaporation. Only 8.2% of the annual precipitation is available for both infiltration (4.8%; 390 MCM) and surface runoff (3.4%; 280 MCM) (MWI-GTZ, 2005).

Understanding the hydrogeochemistry of groundwater and water quality is important for sustainable development and effective management of groundwater resources in any given terrain. Groundwater of any aquifer has unique chemistry acquired as a result of chemical alteration of meteoric water recharging the system (Back, 1996; Drever, 1982). The groundwater chemistry is controlled mainly by the cumulative consequence of interaction of groundwater with rocks, dissolution of soluble mineral species, ion exchange reactions, and various types of anthropogenic activities (Faure, 1998). The present note provides physico-chemical characteristics and hydrochemical features of the groundwater in the northeastern region of Jordan valley, Jordan, and evaluates the suitability of the groundwater for drinking and agricultural purposes.

* Corresponding author.

E-mail address: Msmt19806044@yahoo.com (M.S.M. Tarawneh).

2. Study area

The study region is located in the north eastern part of Jordan valley and the latter is situated in the north western part of Jordan (Fig. 1a). It extends from Yarmouk river in the north to Suleikhat area in the south and from Jordan river in the west to escarpment foot hills in the east. The study region, covering an area of 504.3 km², lies between 32°41' and 32°18' N latitude and 35°42' and 35°33'E longitude (Fig. 1b). In the study area, the topography changes gradually from rugged hilly terrain in the east to gently sloping plains of Jordan river valley in the west; the general slope varies from 51° in the east to almost 0° in the west; and the elevation reduces gradually from 860 m above msl in the east to 328 m below msl in the west. The Jordan river is at the lowest elevation of 328 m below msl. The study area witnesses arid to semi-arid climatic condition marked by hot summer and warm winter. The maximum temperature during summer reaches 40°. In winter season, night temperature may drop to around 10 °C. The rainfall period starts in October and ends in March and the amount of precipitation vary from 200 mm/a in dry years to 650 mm/a in rain-rich years. The average rain fall amounts to 400 mm/a. The humidity ranges from 30% during

summer to 70% in winter and the average potential evaporation is around 2100 mm/a. The study area is characterized by the presence of several E to W oriented alluvial fans and the water from these channels flows in westerly direction and drains into the Jordan valley during the rainy season. In the western part of the study area Jordan river flows through the valley from north to south and ultimately joins Dead Sea.

In the study area lithounits/unconsolidated sediments range in age from Upper Cretaceous to Recent and include present day soils; alluvial fans, calcrete and marl of Quaternary age; conglomerate, limestone, chalk and cherty limestone of Tertiary age and limestone and dolomite of Cretaceous age. In the northern central part the study area, basalts of Upper Tertiary and Quaternary ages are also encountered. In the study area, Upper Cretaceous and Tertiary sedimentary rocks were subjected to gentle folding and are traversed by a prominent N-S trending regional fault, which is known as Dead Sea Transform Fault. The sedimentary rocks are also traversed by NW-SE trending tensional faults, E-W trending dextral shears and NE-SW trending compressional structures.

The study area comprises 2 aquifer complexes: Upper Cretaceous aquifer complex and Tertiary-Quaternary aquifer complex (Salameh and Bannayan, 1993). According to Salameh and Bannayan (1993)

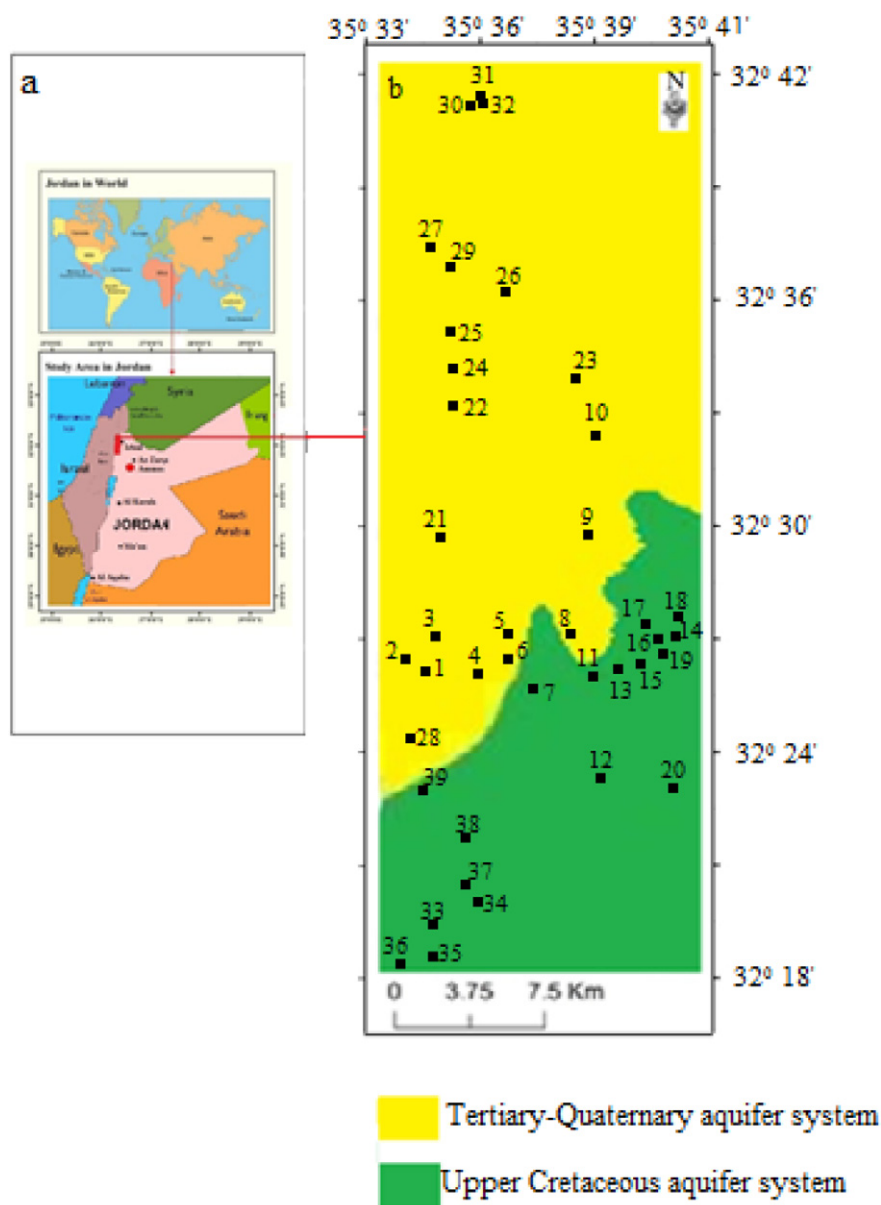


Fig. 1. Location map of the study area (a) and the plan showing the locations of bore wells in the Cretaceous and Tertiary-Quaternary aquifers (b).

and Bandel and Salameh (2013) the Upper Cretaceous aquifer complex outcrops in the southern part and covers a large area in the highland region (central and western side of the study area) (Fig. 1b). It can be subdivided into lower Ajlun aquitard/aquifer and upper Ajlun aquifer systems. The lower Ajlun aquifer system consists of Late Cretaceous marl, limestone, dolomite and shale. The upper Ajlun aquifer system is made up of Late Cretaceous limestone, chalk, marl, chert, silicified dolomite, limestone, dolomite, oyster-rich limestone and phosphorite. Tertiary-Quaternary aquifer complex is encountered in the northern and western parts of the study area (Fig. 1b). In the central and northern parts, it consists of marl, chalk, marly limestone, chert, limestone, glauconite and sandstone of Tertiary age. In the western part (Jordan valley region), the aquifer consists of alluvial deposits composed of sand, gravel, conglomerate, travertine and evaporates of Quaternary age and limestone and sandstone of Tertiary age. The marl facies of the Quaternary deposits (e.g., 30–40 m thick Lisan Marl Formation) contains several kinds of evaporate minerals, including gypsum and anhydrite (Hirzallah, 1973) and is the main controlling factor of the groundwater salinity within the Jordan valley region.

3. Materials and methods

3.1. Hydrochemical analysis

Groundwater samples were collected during the summer, 2016 (sample nos. 1 to 39) and winter, 2017 (sample nos. 40 to 78) seasons at 39 bore well locations, covering the study area (Fig. 1b). The groundwater samples were collected (in duplicate) in pre-washed polypropylene sampling bottles. Groundwater was collected after pumping the wells for about 10 min and rinsing the bottles twice with the water to be sampled. Water was filtered through 0.45 µm millipore membrane filters to separate suspended particles. Water samples meant for cation analyses were acidified with HNO₃ to decrease the pH. The filtered samples were stored at 4 °C and the analytical work was completed within 10 days from the date of sampling. Electrical conductivity (EC µS/cm) and pH were measured in the field using portable conductivity and pH meters, after recalibration with standard buffer solutions. During the analytical work, concentration of HCO₃⁻ in groundwater was determined by acid titration method, as prescribed by the American Public Health Association (APHA, 1998). Other major anions (SO₄²⁻, Cl⁻ and NO₃⁻) were analysed by ion chromatograph. Major cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) were analysed by atomic absorption spectrometer, after calibration of the instrument with known standards. Concentrations of the Total Dissolved Solids (TDS) and Total Hardness (TH) were estimated as per the procedure provided by Raghunath (2007). Analytical precision was maintained by running the known standard after analysing 15 samples. The overall precision, expressed as Percent Relative Standard Deviation (RSD), was found within 5% for all the analysed samples. Charge Balance Errors (CBE) were calculated according to the following formula (Freeze and Cherry, 1979) and were found within the permissible limit of ±10%.

$$CBE = \left[\left(\sum Zm_c - \sum Zm_a \right) / \left(\sum Zm_c + \sum Zm_a \right) \right] \times 100$$

where Z is the ionic valence, m_c is the molarity of cation species and m_a is the molarity of anion species.

3.2. Computation of Water Quality Index (WQI) of the groundwater

Assessment of the quality of the groundwater for drinking purposes was carried out based on the values of Water Quality Index (WQI) and the latter was computed by assigning specific weight to individual physico-chemical parameters. WQI is defined as a rating that reflects the composite influence of different physico-chemical parameters of water (Sahu and Sikdar, 2008). It is an important tool for demarcating

groundwater quality for drinking purposes (Tiwari and Mishra, 1985; Singh, 1992; Subba Rao, 1997; Mishra and Patel, 2001; Naik and Purohit, 2001; Singh et al., 2006; Boateng et al., 2016). Computation of Water Quality Index (WQI) of the groundwater samples collected during both summer and winter seasons was carried out in 4 steps, following the procedure provided by Saba and Umer (2016).

In the first step, each one of the considered 11 parameters (pH, TDS, TH, Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻, Cl⁻ and NO₃⁻) of the groundwater was provided with a “weight” number (wi), and in the present case, 1 to 5. These numbers denote the parameter’s significance in defining the overall status of the quality of the water for drinking purposes. In the present study, the “weight” numbers given to the physico-chemical parameters are: 5 to NO₃⁻; 4 to pH, TDS, SO₄²⁻ and HCO₃⁻; 3 to Cl⁻; 2 to TH, Ca²⁺ and Mg²⁺; and 1 to K⁺ and Na⁺ (Table 1).

The second step involved is the calculation of “relative weight” (Wi) of each physico-chemical parameter, according to the following equation:

$$Wi = \frac{wi}{\sum_{i=1}^n wi}$$

where Wi is the relative weight of the ith parameter; wi is the weight assigned to ith parameter and n is the number of parameters. Table 1 provides the calculated values of the relative weight of individual physico-chemical parameters for computation of the values of WQI of the groundwater samples of the present study.

The third step involved is the calculation of “quality rating” (qi) for each parameter, according to the following equation:

$$qi = (Ci/Si) \times 100$$

where qi is the quality rating of the ith parameter; Ci is the value/concentration of ith parameter and Si is the value of permissible limit of the considered ith parameter, according to the guidelines of WHO (1997).

The fourth step involved is the calculation of the value of “Sub-Index” (Sli) of ith parameter and computation of sum-total of sub-indices of all parameters (i.e., Water Quality Index), according to the following equations:

$$Sli = Wi \times qi$$

$$WQI = \sum_{i=1}^n Sli$$

where Sli is the Sub-Index of the ith parameter; Wi is the relative weight of the ith parameter; qi is the quality rating of the ith parameter, n is the number of parameters, and WQI is the Water Quality Index.

Table 1

Weight and relative weight assigned to the measured physico-chemical parameters of the groundwater of the study area.

Physico-chemical parameters	WHO (1997)	Weight factor (wi)	Relative weight (Wi)
pH	8.5	4	0.1212
TDS	1500	4	0.1212
TH	500	2	0.0606
Ca	200	2	0.0606
Mg	501	2	0.0606
Na	200	2	0.0606
K	200	1	0.0303
Cl	600	3	0.0909
SO ₄	600	4	0.1212
HCO ₃	600	4	0.1212
NO ₃	50	5	0.1515
		wi = 33Σ	Wi = 1Σ

3.3. Assessment of the quality of the groundwater for irrigation purposes

Suitability of the groundwater for irrigation uses was evaluated based on the computed values/ratings provided by the following parameters and bivariate diagrams.

Salinity (Richards, 1954) = Values of EC ($\mu\text{S}/\text{cm}$)

Chloride Hazard (CH; Doneen, 1964) = Concentration of Cl^-

Bicarbonate Hazard (BH; Mandel and Shiftan, 1981) = Concentration of HCO_3^-

Sodium Adsorption Ratio (SAR; Bower, 1978) = $\frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}$

Residual Sodium Carbonate (RSC; Lloyd and Heathcote, 1985) = $(\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})$

Kelley's Ratio (KR; Kelley, 1951) = $\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$

Magnesium Hazard (MH; Lloyd and Heathcote, 1985) = $[\text{Mg}^{2+} / (\text{Ca}^{2+} + \text{Mg}^{2+})] \times 100$

Exchangeable Sodium Percentage (ESP; Tijani, 1994) = $[100 (-0.0126 + 0.01475 \times \text{SAR})] / [1 + (-0.0126 + 0.01475 \times \text{SAR})]$

Percent Sodium (%Na; Wilcox, 1948; Wilcox, 1955) = $\text{Na}^+ + \text{K}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+) \times 100$

Permeability Index (PI; Doneen, 1964) = $[(\text{Na}^+ + \sqrt{\text{HCO}_3^-}) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)] \times 100$

Bivariate EC ($\mu\text{S}/\text{cm}$) versus % Na diagram (Wilcox, 1955)

Bivariate PI versus ($\text{Tz}^+ + \text{z}^-$) diagram (Doneen, 1964) and Bivariate SAR versus EC ($\mu\text{S}/\text{cm}$) Diagram (Richards, 1954).

(All ionic concentrations used for calculation are expressed in meq/l .)

4. Results and discussion

4.1. Physico-chemical characteristics of the groundwater

Hydrochemical analysis of the groundwater samples collected during the summer ($n = 39$) and winter ($n = 39$) seasons was carried out according to the procedure provided in Section 3.1 and the obtained results are given in Tables 2 and 3, respectively. The physico-chemical features of the groundwater were evaluated based on the hydrochemical data of the groundwater samples and the same are presented in Table 4. From the data provided in Table 4, it is seen that the physico-chemical features (barring one feature) of the groundwater during both summer and winter seasons qualitatively do not differ. During both seasons, the groundwater was found to be slightly alkaline. During the summer season, cation abundance-wise, the groundwater was characterized by, on average, $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ whereas the same during the winter season was found to be $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. However, during both seasons the anions, on average, maintained the same order of abundance, viz., $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. Thus, Na^+ among the cations and Cl^- among the anions were found

Table 2
Physico-chemical characteristics of the groundwater samples ($n = 39$) collected during the summer season.

BW no.	Sample no.	A*	B*	EC	PH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	TDS	TH	$\text{Tz}^+ + \text{z}^-$
1	1	33.2	-270	1622	7.6	77.3	73.5	160.1	5	328	81	293.1	117.2	988.65	494.6	34.83
2	2	31.4	-283	950	7.85	85	45	70	5	168.1	60.2	331.7	6.3	605.45	397	22.76
3	3	32.9	-253	1820	8.47	80.5	59	190.1	11.8	350.2	145.9	140.2	1.4	909	443.15	32.87
4	4	47.2	-198	1543	7.6	106.7	78.7	180	5.6	318.1	104.1	446.9	97.8	1114.45	589.42	40
5	5	49.3	-170	1105	8.1	84.8	58.1	78.9	4.1	195.1	104.9	318.8	3.7	689	450.21	25.66
6	6	54	-160	4312	7.16	148.1	110.8	298.8	238.7	815.8	204.9	419.8	102.6	2339.5	824.53	71.86
7	7	70.2	-120	1176	7.73	88.3	59.2	69.9	10.5	101.2	100	331.8	146.7	741.7	463.22	25.43
8	8	78.4	-84	764	7.14	72.9	40	39.7	4	44.9	5.4	408.7	7.3	418.55	346.25	17
9	9	111.3	105	806	7.3	65	38.2	39.8	2.7	45.2	70.2	319.2	3.1	423.8	319.12	16.26
10	10	103.2	118	735	7	70	45.1	39.8	2.6	41.7	89.2	344.6	1.8	462.5	359.91	17.78
11	11	92.4	75	1315	7.34	114.2	58.5	69.7	7	100.5	103.6	447.1	39.6	716.65	525.35	26.79
12	12	160	90	1149	7.1	95	51	60.8	2.8	82.9	81.1	408.9	25.3	508.35	446.6	22.88
13	13	96.3	112	2055	7.75	96	108.6	118.9	0.7	205.9	64.3	689.6	5.9	945.1	685.26	37.65
14	14	108.5	290	2189	7.7	121.6	70.2	179.8	10	342.8	160.3	305.8	22.3	1059.9	591.82	38.51
15	15	102.2	250	9345	7.12	546	312.4	799.2	90.1	1744.8	1551	511.2	6.8	5305.9	2645.84	181
16	16	104.3	270	3766	7.62	148.1	155.8	418.9	30.1	741.2	341.8	664.3	15.5	2183.55	1009.03	78.81
17	17	99.2	275	3228	7.22	215.8	96.2	359.2	14	312.8	610.3	741.3	48.8	2027.75	933.92	69.37
18	18	104.2	310	1265	7	118	40.2	81	1.9	101.5	49	472.6	3.1	631	459.82	24.53
19	19	106	264	3733	7.58	129.9	151.9	365.5	8	668.1	496.1	395.8	45.1	2062.5	947.54	71.87
20	20	181.5	332	754	7.3	96	31.3	14.72	0.702	29.75	32.2	432.5	17.73	438.652	368.33	16.96
21	21	34.6	-227	1387	6.1	144	56.6	200.56	17.95	326.9	158.88	434.9	4.89	1127.23	592.06	40.95
22	22	18	-140	837	7.3	120.4	38.1	28.29	4.69	72.88	80.6	433.1	2.4	563.91	457.21	21.44
23	23	94.4	127	652	8.25	63.4	33.7	25.53	3.12	45.6	37.45	312.31	68.4	433.355	296.67	15.47
24	24	14.4	-132	1056	7.6	72	45.61	72.25	30.03	110.1	79.3	335.5	4.1	581.14	367	21.67
25	25	12.7	-137	785	7.9	74	41.28	61.71	3.91	94.6	40.32	396.4	2.36	516.38	354.25	20
26	26	48.3	-141	838	8.1	92.6	37.2	28.29	3.91	43.78	89.1	392.8	13.6	504.88	384.02	18.82
27	27	35.1	-130	1347	8.2	74	41.3	61.65	3.87	94.56	40.32	396.5	2.35	516.3	354.33	20
28	28	37.2	-240	1510	7.95	117.3	48.37	108.12	13.65	180.5	117.3	402.2	36.51	822.85	491.57	29.73
29	29	37.5	-128	3389	7.1	233.81	178.44	292.8	39.81	430.17	890.4	535.61	49.33	2382.56	1316.1	80.72
30	30	26.2	-221	3384	7.2	160	78.2	414	35.1	595.1	361.93	457.48	73.11	1946.18	720.6	66.63
31	31	25.9	-228	3812	7.28	183.61	120.2	414	15.6	700.12	361.93	445.32	73.11	2091.23	951.85	73.61
32	32	30.1	-220	3180	7	232	36.36	323.86	39.1	574	252.95	414.77	39.1	1704.75	729.1	58.814
33	33	68	-183	1080	7.5	71.2	40.6	61	4.7	98.6	62	276.2	26.7	502.9	344.46	18.73
34	34	65	-142	751	7.2	73.4	30.3	30	5.8	57.1	22.1	288.4	35	397.9	307.73	15.02
35	35	74.2	-187	1287	7.4	81.9	67.6	95.4	5	244.3	92.5	316.1	42	786.75	481.91	28.78
36	36	84.3	192	3100	7.4	94	136.8	370.3	54.6	672	398.4	408.7	42.3	1972.75	795.88	68.48
37	37	73.8	-132	950	8.1	60	49.2	55.2	11.7	87.5	110.4	268.4	12	520.2	351.72	19.19
38	38	84	-123	681	8.2	58	38.4	23	1.56	45.5	14.88	317.2	15.6	355.54	302.44	14.2
39	39	42.3	-204	1516	8	136	66	101.2	8.9	217	67.2	512.4	66.4	918.9	610.6	33.98
Avr	-	-	-	1927	7.5	120.5	73.5	164.1	19.4	293	198.2	404.3	34	1108	602.8	39.5

A*: depth of water table in m below ground surface. B*: ground surface in m below (-) or above (+) mean sea level. TDS, TH and major ions in mg/l . EC in $\mu\text{S}/\text{cm}$. $\text{Tz}^+ + \text{z}^-$: in meq/l .

Table 3

Physico-chemical characteristics of the groundwater samples (n = 39) collected during the winter season.

BW no.	Sample no.	A*	B*	EC	PH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	TDS	TH	Tz ⁺ + z ⁻
1	40	31.1	-270	1512	7.1	61	55	122.5	1	254	54	220	88.2	745.7	378	26.36
2	41	30.2	-283	820	7.4	72.3	31	66	2	122.1	41.2	310.2	5.2	494.9	307.85	18.59
3	42	31.9	-253	1623	7.9	82.5	50	151.8	3.2	275.2	123	123.2	1	748.3	411.25	27.4
4	43	45	-198	1456	7.3	90.7	66.3	162.8	6.1	241.3	93	412	76	942.2	498.58	34.06
5	44	47	-170	984	7.6	65	48.2	79.2	2.3	144	90	285	2.1	573.3	360.12	21.43
6	45	49.7	-160	3125	6.82	121.6	112.2	242.9	154.8	745.2	143.2	390.2	88.2	1803.2	764.02	62.03
7	46	66.2	-120	1045	7.2	91	32.8	45	5.2	90.2	72.5	288	108	588.7	361.98	19.9
8	47	75.4	-84	613	6.9	62	37.8	42.7	2.2	47.2	8.9	350.2	5.2	381.1	309.98	15.49
9	48	107.8	105	722	6.8	58.9	36.7	36.7	2.2	38	71.5	240.1	5.2	369.25	297.72	14.2
10	49	97.8	118	652	6.7	58.2	47.4	33.1	1.5	43	49	315	2.7	392.4	339.84	15.76
11	50	88.4	75	1102	7.4	96.3	50.9	72.5	8.1	85.4	88.6	387.5	41.2	636.75	449.44	23.69
12	51	155	90	963	6.87	82.9	44	51.2	2	75.6	75.6	330.6	22	518.6	387.65	19.56
13	52	91.1	112	1633	7.6	90.7	88.3	95.3	0	179.9	58.7	572.3	10.2	809.25	588.78	31.92
14	53	103.2	290	1858	7.5	102.3	60	125.4	3.3	278.2	118.7	275.4	12.5	838.1	501.75	30.76
15	54	98.6	250	8962	6.7	488.6	210.7	744.7	40.2	1552	1312.5	455	5.2	4581.4	2085.37	154.59
16	55	100.7	270	3510	7.4	128	107.9	382.6	11.5	663.3	247.6	602.9	12.3	1854.65	762.39	66.48
17	56	98.9	275	3120	7.3	196	75.8	327	9.7	271.1	589.2	689	38.2	1851.5	800.78	62.47
18	57	101.3	310	1101	6.7	89.8	35	68.7	0.75	88	51	438.7	3	555.6	368	21.19
19	58	102.1	264	3518	7.3	100	115.7	316.2	5.1	612.6	410.8	338	40	1769.4	724.37	60.74
20	59	173.4	332	688	7.1	97.8	24.8	22.6	0	32.2	35.8	385.5	12.5	418.45	346.18	16.1
21	60	34.5	-227	1231	6.55	129	49.2	175.8	10	258	122.8	386.4	3.5	941.5	524.22	34.74
22	61	17.2	-140	776	6.87	111	36	35.9	4	73	62.3	348.9	2.1	498.75	425.1	19.32
23	62	93.3	127	630	7.8	68	30	28.6	2.5	41.2	38.9	278.2	48.3	396.6	293	14.51
24	63	13.7	-132	972	7.2	67	42.3	61	17.2	101.5	52.8	285.3	3.6	488.05	340.93	18.68
25	64	11.3	-137	690	7.3	68	39.8	50.4	1.56	54.3	30.6	314.9	3.4	405.51	333.18	16.28
26	65	47.3	-141	775	7.66	77.2	35	38.1	3	42	71.2	289.2	11	422.1	336.5	16.08
27	66	33.4	-130	1211	7.45	72.5	40.8	48.3	2.8	92.8	42	358.2	2.2	480.5	348.53	18.61
28	67	34.7	-240	1483	7.52	101.5	42	88.4	8.8	115.3	82.6	338	28.6	636.2	425.95	23.64
29	68	35.1	-128	3195	6.74	214.7	142	212.6	14.2	389	815.8	478.2	41.5	2068.9	1118.95	68.75
30	69	24.6	-221	3284	7	145.2	62.1	387.5	20.1	520.1	310.5	412	55.8	1707.3	617.61	58.75
31	70	25.7	-228	3750	6.95	171	91.5	385.2	7.2	623.5	305.8	395.2	58.1	1839.9	802.65	64.67
32	71	27.2	-220	3085	7.1	189.7	33.7	302.4	30	485.4	192.3	345	30.2	1436.2	612.42	50.18
33	72	67.3	-183	994	7.2	75.6	33.8	67	41	75	52.8	223.3	22	478.85	327.58	17.8
34	73	63.2	-142	712	7	68.7	24.6	36.8	5.2	52.8	24.6	289.3	37.2	394.55	272.61	14.56
35	74	72	-187	1124	7.1	83.2	49.7	85.6	3.2	233.6	80.3	325	38.5	736.6	411.77	26.38
36	75	81.4	192-	2986	7.2	92.7	104	352.1	33.4	602.4	312.3	356.3	39.1	1714.15	658.15	59.62
37	76	72	-132	877	7.85	48.2	38	58.9	9.5	52.3	72	248	14	416.9	276.3	15.64
38	77	82.5	-123	668	7.75	56.3	32.1	28.7	0.85	35.7	22.9	263.3	19.2	327.4	272.36	12.84
39	78	41.8	-204	1491	7.6	118.1	51	115.7	6.33	174	41	418	48.2	763.33	504.35	28.78
Avr	-	-	-	1767.7	7.2	107.5	59.2	147.3	12.3	252.8	165.8	352.8	27.8	949.4	511.4	33.9

A*: depth of water table in m below ground surface. B*: ground surface in m below (-) or above (-) mean sea level. TDS, TH and major ions in mg/l. EC in $\mu\text{S}/\text{cm}$. Tz⁺ + z⁻: in meq/l.

to dominate in the major ion chemistry of the groundwater during both summer and winter seasons. In the groundwater of both seasons, the average concentration of (Ca²⁺ + Mg²⁺) was higher than that of (Na⁺ + K⁺) and among the anion pairs the average concentration of

(HCO₃⁻ + SO₄²⁻) was higher than that of (Cl⁻ + NO₃⁻). The average concentration of total ions (Tz⁺ + z⁻) of the groundwater of the summer season was found to be comparatively higher (39.64 meq/l) than that of the winter season (33.91 meq/l).

Table 4

Physico-chemical features of the groundwater samples collected during the summer (n = 39) and winter (n = 39) seasons.

	Summer season	Winter season
pH	6.1 to 8.47 (avr. = 7.5)	6.55 to 7.9 (avr. = 7.2)
EC	652 $\mu\text{S}/\text{cm}$ to 9345 $\mu\text{S}/\text{cm}$ (avr. = 1922.2 $\mu\text{S}/\text{cm}$)	613 $\mu\text{S}/\text{cm}$ to 8962 $\mu\text{S}/\text{cm}$ (avr. = 1768.9 $\mu\text{S}/\text{cm}$)
TDS	355.54 mg/l to 5305.9 mg/l (avr. = 1108.8 mg/l)	327.4 mg/l to 4581.4 mg/l (avr. = 949.68 mg/l)
TH	296.67 mg/l to 2645.84 mg/l (avr. = 600.5 mg/l)	272.36 mg/l to 2085.37 mg/l (avr. = 510.3 mg/l)
Average decreasing order of abundance of ions (meq/l)	Na > Mg > Ca > K and Cl > HCO ₃ > SO ₄ > NO ₃	Na > Ca > Mg > K and Cl > HCO ₃ > SO ₄ > NO ₃
Average contribution of individual cations to total concentration of cations (meq/l)	36.06% Na, 30.96% Mg, 30.46% Ca and 2.51% K	37.62% Na, 31.6% Ca, 28.96% Mg and 1.83% K
Average contribution of individual anions to total concentration of anions (meq/l)	42.54% Cl, 33.67% HCO ₃ , 20.99% SO ₄ and 2.78% NO ₃	42.7% Cl, 34.2% HCO ₃ , 20.43% SO ₄ and 2.6% NO ₃
Average concentration of (Ca + Mg) versus average concentrations of (Na + K)	Concentration of (Ca + Mg) (12.15 meq/l) is higher than that of (Na + K) (7.63 meq/l)	Concentration of (Ca + Mg) (10.3 meq/l) is higher than that of (Na + K) (6.72 meq/l)
Average concentration of (HCO ₃ + SO ₄) versus average concentration of (Cl + NO ₃)	Concentration of (HCO ₃ + SO ₄) (10.76 meq/l) is higher than that of (Cl + NO ₃) (8.92 meq/l)	Concentration of (HCO ₃ + SO ₄) (9.23 meq/l) is higher than that of (Cl + NO ₃) (7.66 meq/l)
Average (Ca + Mg) content versus average (Na + K) content	(Ca + Mg) content (61.4%) is higher than that of (Na + K) content (38.6%)	(Ca + Mg) content (60.55%) is higher than that of (Na + K) content (39.45%)
Average (HCO ₃ + SO ₄) content versus average (Cl + NO ₃) content	(HCO ₃ + SO ₄) content (54.7%) is higher than that of (Cl + NO ₃) content (45.3%)	(HCO ₃ + SO ₄) content (54.64%) is higher than that of (Cl + NO ₃) content (45.36%)
Average concentration of (Tz ⁺ + z ⁻)	39.46 meq/l	33.91 meq/l

4.2. Classification of groundwater

In recent published literature, the groundwaters encountered at various regions are being classified based on various parameters. They include classification based on Cl^- , SO_4^{2-} and HCO_3^- content, classification based on Base Exchange Index (r_1) and classification based on Meteoric Genesis Index (r_2).

4.2.1. Classification of groundwater based on Cl^- , SO_4^{2-} and HCO_3^- content

The groundwater, based on its Cl^- , SO_4^{2-} and HCO_3^- content, can be classified as normal chloride (Cl^- content < 15 meq/l), normal sulphate (SO_4^{2-} content < 6 meq/l) and normal bicarbonate (HCO_3^- content, from 2 to 7 meq/l) water types (Soltan, 1998). In the study area, among the 39 groundwater samples collected during the summer season, 21 samples are found to belong to all three water types (viz., normal chloride, normal sulphate and normal bicarbonate water types). Out of the 39 groundwater samples of the summer season, 33, 31 and 25 samples belong, respectively, to normal chloride, normal sulphate and normal bicarbonate water types. Among the 39 groundwater samples collected during the winter season, 28 groundwater samples belong to all three types. Out of the 39 groundwater samples of the winter season, 33, 32 and 33 samples belong, respectively, to normal chloride, normal sulphate and normal bicarbonate water types.

4.2.2. Classification of the source of groundwater based on Base Exchange Index (r_1)

Mathess (1982) proposed the classification of the source of groundwater based on the values of the Base Exchange Index (r_1). Base Exchange Index (r_1) is calculated according to the following equation:

$$r_1 = (\text{Na}^+ - \text{Cl}^-) / \text{SO}_4^{2-} \text{ (in meq/l)}.$$

If the values of r_1 are <1, the source of the groundwater is considered as $\text{Na}^+ - \text{SO}_4^{2-}$ type and when the values of r_1 are >1, the groundwater is visualized as $\text{Na}^+ - \text{HCO}_3^-$ type.

The r_1 values of the groundwater samples collected during the summer and winter seasons are graphically shown in Fig. 2. The r_1 values of the groundwater samples collected during the summer season are <1 in 38 samples, and in one sample (sample no. 8) the r_1 value is >1 (Table 5). The groundwater samples collected during the winter season also reveal similar r_1 values, i.e., r_1 values of 38 samples are <1 and r_1

Table 5

Classification of the groundwater samples based on the values of Base Exchange Index (r_1).

Value of Base Exchange Index	No. of groundwater samples		Significance
	Summer season	Winter season	
$r_1 < 1$	38	37	Na- SO_4 type
$r_1 > 1$	1	2	Na- HCO_3 type

values of two samples (sample nos. 47 and 64) are >1 (Table 5). This data indicate that, barring at two groundwater sampling locations, the groundwater of the study area belongs to $\text{Na}^+ - \text{SO}_4^{2-}$ type. Three samples (nos. 8, 47 and 64) collected from two sampling locations (BW no. 8 and 25) during the summer and winter seasons are found to belong to $\text{Na}^+ - \text{HCO}_3^-$ type. Hence, the source of groundwater of the study area, for all practical purposes, can be considered as $\text{Na}^+ - \text{SO}_4^{2-}$ type.

4.2.3. Classification of groundwater source based on Meteoric Genesis Index (r_2)

The source of the groundwater is evaluated based on the values of Meteoric Genesis Index (r_2) and the latter is calculated according to the following equation:

$$\text{Meteoric Genesis Index } (r_2) = [(\text{K}^+ + \text{Na}^+) - \text{Cl}^-] / \text{SO}_4^{2-} \text{ (in meq/l)}.$$

If the values of r_2 are <1, the source of groundwater is considered as “deep meteoric percolation type”. If the values of r_2 are >1, the groundwater source belongs to “shallow meteoric percolation type” (Soltan, 1998).

In the study area, the r_2 values of the groundwater samples collected during the summer and winter seasons are shown graphically in Fig. 3. The obtained data indicate that, among the 39 groundwater samples collected during the summer season, 38 samples and 1 sample belong, respectively, to the category of deep meteoric percolation type and shallow meteoric percolation type (Table 6). Among the 39 groundwater samples collected during the winter season, 35 samples and 4 samples belong, respectively, to deep meteoric percolation type and shallow meteoric percolation of type (Table 6). The 4 groundwater samples belonging to the category of shallow meteoric percolation type include 2

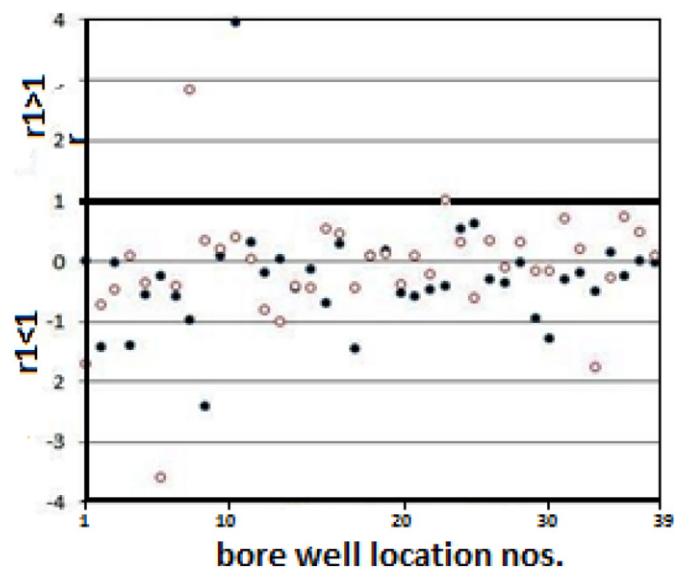


Fig. 2. Base Exchange Index (r_1) of the groundwater samples collected during the summer (●) and winter (○) seasons at 39 bore well locations.

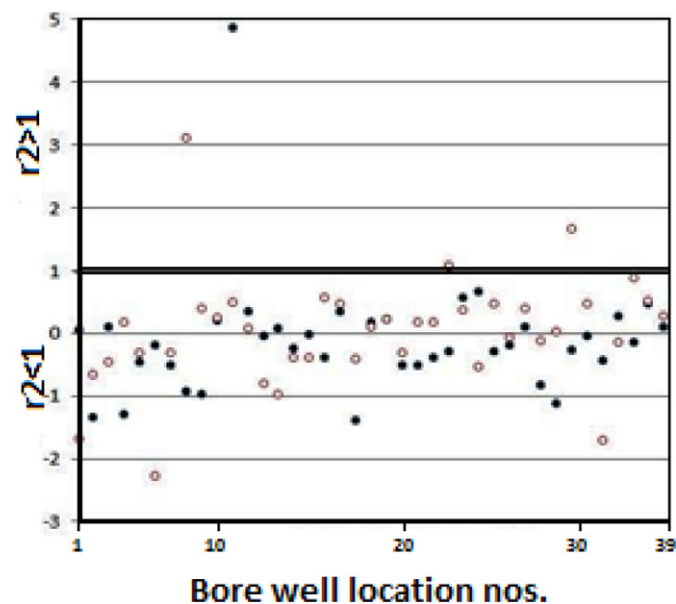


Fig. 3. Meteoric Genesis Index (r_2) of the groundwater samples collected during the summer (●) and winter (○) seasons at 39 bore well locations.

Table 6
Classification of the groundwater samples based on the values of Meteoric Genesis Index (r_2).

Value of Meteoric Genesis Index	No. of groundwater samples		Significance
	Summer season	Winter season	
$r_2 < 1$	38	35	Deep meteoric percolation type
$r_2 > 1$	1	3	Shallow meteoric percolation type

samples collected from bore well no. 8 during the summer and winter seasons and 2 samples collected from bore wells no. 25 and 33 during the winter season.

Thus, in the study area, source-wise, the groundwater belongs essentially to deep meteoric percolation type and only at 3 bore well locations (BW nos. 8, 25 and 33) the groundwater source is found to belong to shallow meteoric percolation type. At these 3 bore well locations, the aquifers are possibly receiving significant amount of downward percolating fresh surface water flowing along well defined alluvial fans (wadies).

4.3. Groundwater types

The groundwater is usually classified based on TH, EC, TDS or $\text{Cl}^-/(\text{CO}_3^{2-} + \text{HCO}_3^-)$ molar ratio (Simpson's ratio). In the present investigation the groundwater of the study area has been classified based on EC values of the groundwater samples collected during the summer ($n = 39$) and winter ($n = 39$) seasons. According to Saxena et al. (2003), waters with EC values $<1500 \mu\text{S}/\text{cm}$, between 1500 and $3000 \mu\text{S}/\text{cm}$ and $>3000 \mu\text{S}/\text{cm}$ are considered, respectively, as "fresh", "brackish" and "saline" waters. The EC values of the groundwater samples of the study area indicate that, during the summer season, the groundwater at 22, 7 and 10 bore well locations belongs, respectively, to fresh water type (type 1), brackish water type (type 2) and saline water type (type 3) groundwater (Table 7). During the winter season, the groundwater at 25, 5 and 9 bore well locations belongs, respectively, to fresh water type, brackish water type and saline water type groundwater (Table 7). The above data reveal that, during the winter season, the groundwater at a few bore well locations was found comparatively less salinized. For example, the brackish water type groundwater encountered at bore well locations nos. 4, 28 and 39 during the summer season was found to be fresh water type during the winter season. Likewise, the saline water type groundwater encountered at bore well location no. 36 during the summer season was found to be brackish water type during the winter season. The observed decrease in the salinity of the groundwater at the above mentioned bore well locations during the winter season can be attributed either to dilution of the

groundwater aided by downward percolating surface/rain water or to decrease in the intensity of evaporation or to both.

With regard to hydrochemical composition of the above identified 3 types of groundwater, two features are found conspicuously different in the two end members of the groundwater types, viz., in fresh water type and saline water type groundwaters. The fresh water type groundwater, in terms of meq/l and on average, is characterized by $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ and the average concentration of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ in it is higher than that of $(\text{Cl}^- + \text{NO}_3^-)$. The saline water type groundwater, on the contrary, is characterized by, on average, $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$ and in it the average concentration of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ is lower than that of $(\text{Cl}^- + \text{NO}_3^-)$. However, in all three types of groundwater, the average concentration of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ was found to be higher than that of $(\text{Na}^+ + \text{K}^+)$.

4.4. Hydrochemical features of the groundwater

The trilinear Piper diagram (Piper, 1944) is widely used for determining the relationships between the various dissolved constituents in water and for identification of ionic types and hydrochemical facies of water. On the diamond shaped central field of the Piper diagram, the groundwater samples collected during the summer season plot in 6 fields (1, 3, 4, 5, 6 and 9) (Fig. 4). All groundwater samples plot in the field 1 and indicate that in all samples alkaline earth metals ($\text{Ca}^{2+} + \text{Mg}^{2+}$) exceed alkali metal cations ($\text{Na}^+ + \text{K}^+$). About 31% of the samples plot in the field 3 and indicate dominance of weak acid (HCO_3^-) over strong acids ($\text{SO}_4^{2-} + \text{Cl}^-$). The remaining ~69% the samples plot in the field 4 and indicate that in these samples the concentration of strong acids exceeds the same of the weak acid. About 31% of the samples plot in the field 5 suggesting that in these samples the carbonate hardness (secondary alkalinity) exceeds 50%. Only ~18% of the samples plot in the field 6 and indicate that in these samples the non-carbonate hardness (secondary salinity) exceeds 50%. About 51% of the samples plot in the field 9 and this data indicate that the groundwater representing these samples possess an intermediate (mixed) chemical character with none of the cation-anion pairs dominating its chemical composition. In the triangular fields of the cations of the Piper diagram, about 25%, 2% and 73% of the samples plot, respectively, in the fields of magnesium type, calcium type and no dominant cationic type (Fig. 4). In the triangular fields of the anions, about 31%, 44% and 25% of the samples plot, respectively, in the fields of bicarbonate type, chloride type and no dominant anionic type (Fig. 4). Hydrochemical facies-wise, ~51% of the samples belong to mixed facies [mixed character of Ca-Mg-Cl hydrochemical facies (Back, 1996) and the remaining ~31% and ~18% of the samples belong, respectively, to Ca-Mg- HCO_3 and Ca-Mg- SO_4 facies.

The hydrochemical features, ionic types and hydrochemical facies of the groundwater samples collected during the winter season are found

Table 7

Bore wells (shown as bold nos.) yielding fresh water (Type 1), brackish water (Type 2) and saline water (Type 3) categories of groundwater during the summer and winter seasons. Sample nos are provided in bracket.

Groundwater type	Borewells yielding specified type of groundwater (summer season)	Borewells yielding specified type of groundwater (winter season)
Fresh water type (Type 1) groundwater	2 (2), 5 (5), 7 (7), 8 (8), 9 (9), 10 (10), 11 (11), 12 (12), 18 (18), 20 (20), 21 (21), 22 (22), 23 (23), 24 (24), 25 (25), 26 (26), 27 (27), 33 (33), 34 (34), 35 (35), 37 (37) and 38 (38) Total 22 borewells	2 (41), 4 (43), 5 (44), 7 (46), 8 (47), 9 (48), 10 (49), 11 (50), 12 (51), 18 (57), 20 (59), 21 (60), 22 (61), 23 (62), 24 (63), 25 (64), 26 (65), 27 (66), 28 (67), 33 (72), 34 (73), 35 (74), 37 (76), 39 (77) and 39 (78) Total 25 borewells
Brackish water type (Type 2) groundwater	1 (1), 3 (3), 4 (4), 13 (13), 14 (14), 28 (28) and 39 (39) Total 7 borewells	1 (40), 3 (42), 13 (52), 14 (53) and 36 (75) Total 5 borewells
Saline water type (Type 3) groundwater	6 (6), 15 (15), 16 (16), 17 (17), 19 (19), 29 (29), 30 (30), 31 (31), 32 (32) and 36 (36) Total 10 borewells	6 (45), 15 (54), 16 (55), 17 (56), 19 (58), 29 (68), 30 (69), 31 (70) and 32 (71) Total 9 borewells

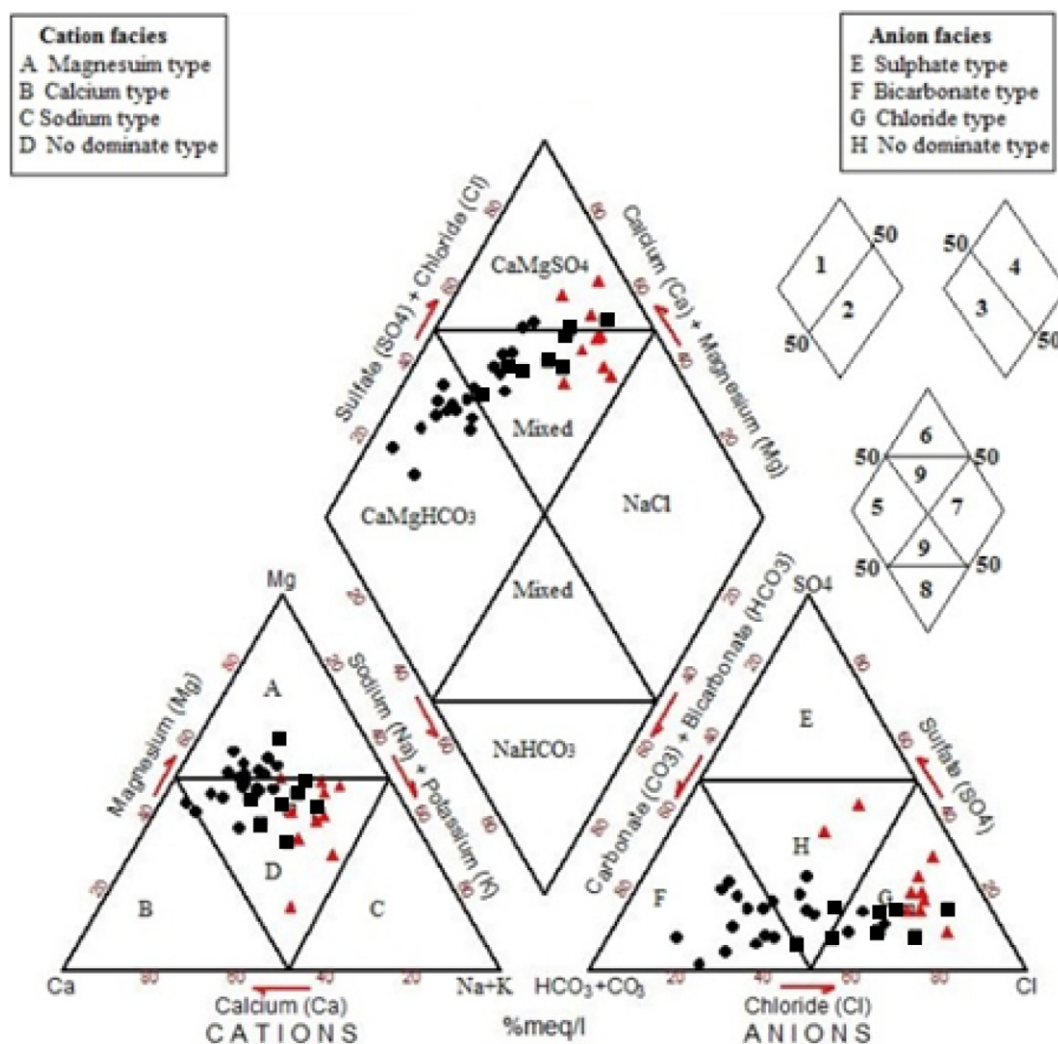


Fig. 4. Piper trilinear diagram showing the hydrochemical characteristics and hydrochemical facies of the groundwater based on the hydrochemical data of 39 groundwater samples collected during the summer season. Fresh (●), brackish (■) and saline (▲) water categories of groundwater samples (after Piper, 1944).

almost similar to those of the groundwater samples collected during the summer season. Tables 8 and 9 provide the details of the hydrochemical data of the groundwater samples collected during both summer and winter seasons for comparison purposes.

4.5. Natural mechanisms controlling the hydrochemistry

It is well known that the natural mechanisms controlling the hydrochemistry of groundwater include mineral dissolution and

weathering, atmospheric precipitation, and evaporation and fractional crystallization. Importance of individual natural mechanisms involved in the acquisition of dissolved solids in groundwater can be deciphered from the plots of the hydrochemical data of the groundwater samples on two diagrams of Gibbs (1970) viz., (1) bivariate TDS versus Gibbs's ratio I [weight ratio of $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$] and (2) TDS versus Gibbs's ratio II [weight ratio of $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$] diagrams. Table 10 provides the values of Gibbs's ratio I and II of the groundwater samples collected during the summer season. On the Gibbs's diagram 1,

Table 8
Hydrochemical features of the groundwater samples collected during the summer (n = 39) and winter (n = 39) seasons based on the plots of hydrochemical data on Piper (1944) diagram.

Field no. of the Piper diagram (1–9)	Characteristic feature indicated by the Piper diagram's fields (1–9)	No. of plots of the groundwater samples of the summer season in each field	No. of plots of the groundwater samples of the winter season in each field
1	Alkaline earths (Ca + Mg) exceed alkalis (Na + K)	39 samples (22 fresh; 7 brackish; 10 saline)	39 samples (25 fresh; 5 brackish; 9 saline)
2	Alkalis exceed alkaline earths	–	–
3	Weak acid (HCO_3) exceed strong acids ($\text{SO}_4 + \text{Cl}$)	12 samples (12 fresh)	11 samples (11 fresh)
4	Strong acids exceed weak acid	27 samples (9 fresh; 8 brackish; 10 saline)	28 samples (13 fresh; 5 brackish; 10 saline)
5	Carbonate hardness (secondary alkalinity) exceeds 50%	12 samples (12 fresh)	11 samples (11 fresh)
6	Non-carbonate hardness (secondary salinity) exceeds 50%	7 samples (2 fresh; 2 brackish; 3 saline)	6 samples (2 brackish; 4 saline)
7	Non-carbonate alkali (primary salinity) exceeds 50%	–	–
8	Carbonate alkali (primary salinity) exceeds 50%	–	–
9	None of the cation and anion pairs exceeds 50%	20 samples (7 fresh; 6 brackish; 7 saline)	22 samples (13 fresh; 3 brackish; 5 saline)

Table 9

Ionic types and hydrochemical facies of the groundwater samples collected during the summer (n = 39) and winter (n = 39) seasons based on the plots of hydrochemical data on Piper (1944) diagram.

Ionic types and hydrochemical facies	No. of groundwater samples of the summer season	No. of the groundwater samples of the winter season
Ionic types		
A Magnesium type	10 samples (9 fresh; 1 brackish)	6 samples (5 fresh; 1 brackish)
B Calcium type	1 sample (1 fresh)	1 sample (1 fresh)
C Sodium or potassium type	–	–
D No dominant cationic type	28 samples (11 fresh; 7 brackish; 10 saline)	32 samples (19 fresh; 4 brackish; 9 saline)
E Sulphate type	–	–
F Bicarbonate type	12 samples (12 fresh)	12 samples (12 fresh)
G Chloride type	17 samples (3 fresh; 6 brackish; 8 saline)	17 samples (6 fresh; 4 brackish; 7 saline)
H No dominant anionic type	10 samples (6 fresh; 2 brackish; 2 saline)	10 samples (7 fresh; 1 brackish; 2 saline)
Hydrochemical facies		
1. CaMgHCO ₃	12 samples (12 fresh)	11 samples (11 fresh)
2. CaMgSO ₄	7 samples (2 fresh; 2 brackish; 3 saline)	6 samples (2 brackish; 4 saline)
3. NaCl	–	–
4. Mixed	20 samples (7 fresh; 6 brackish; 7 saline)	22 samples (13 fresh; 3 brackish; 5 saline)

30 groundwater samples of the summer season plot essentially in the weathering dominance field and the remaining 9 samples plot in the evaporation dominance field and outside its boundary (Fig. 5a). On the Gibbs's diagram 2, the plots of the groundwater samples of the summer season are encountered mainly along the boundary line between the weathering dominance and evaporation dominance fields (Fig. 5b). The above data of Gibbs's diagrams 1 and 2 indicate that the

hydrochemistry of the groundwater is controlled mainly by mineral dissolution and weathering (chemical interaction between groundwater and aquifer rocks), and to some extent, by evaporative concentration process. Plots of the hydrochemical data of the groundwater samples (n = 39) of the winter season on Gibbs's diagrams 1 and 2 also indicate that rock weathering and evaporation practically controlled the hydrochemistry of the groundwater of the study area.

Table 10

Calculated parameters for assessment of hydrochemical processes and values of parameters considered for assessment of the quality of groundwater for irrigation purposes.

Sample No	Gibbs ratio-I	Gibbs ratio-II	CAI-I	CAI-II	$\frac{(\text{Na}^+ + \text{K}^+)}{\text{Tz}^+}$	$\frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{\text{HCO}_3^-}$	$\frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{(\text{Na}^+ + \text{K}^+)}$	CH Cl [–] (meq/l)	SAR	RSC	BH HCO ₃ [–] (meq/l)	KR	MH	ESP	%Na	PI
1	0.68	0.52	0.24	0.27	0.42	2.07	1.40	9.37	3.12	–5.18	4.80	0.69	61.31	3.23	41.5	53.98
2	0.46	0.3	0.33	0.24	0.28	1.47	2.52	4.80	1.52	–2.56	5.43	0.38	46.87	0.97	28.38	48.65
3	0.71	0.71	0.14	0.26	0.48	3.89	1.04	10	3.91	–6.64	2.29	0.92	54.98	4.32	48.93	56.8
4	0.63	0.44	0.12	0.1	0.40	1.62	1.49	9.08	3.22	–4.56	7.32	0.65	55.14	3.37	40.12	53.37
5	0.49	0.4	0.36	0.27	0.28	1.73	2.56	5.57	1.61	–3.85	5.22	0.37	53.31	1.1	28.01	45.63
6	0.78	0.64	0.18	0.32	0.53	2.41	0.87	23.3	4.51	–9.75	6.88	0.78	55.49	5.11	53.45	52.68
7	0.47	0.21	–0.14	–0.04	0.26	1.71	2.82	2.89	1.42	–3.9	5.43	0.32	52.77	0.82	26.13	43.34
8	0.37	0.12	–0.42	–0.07	0.21	1.04	3.81	1.28	0.92	–0.27	6.7	0.24	47.76	0.1	20.76	49.46
9	0.39	0.14	–0.39	–0.07	0.22	1.22	3.57	1.29	0.96	–1.2	5.23	0.26	49.48	0.16	21.85	49.12
10	0.37	0.1	–0.5	–0.08	0.19	1.28	4.03	1.19	0.91	–1.6	5.64	0.23	51.77	0.08	19.84	45.61
11	0.4	0.18	–0.11	–0.03	0.23	1.44	3.29	2.87	1.31	–3.25	7.32	0.28	46.05	0.67	23.26	42.08
12	0.4	0.15	–0.14	–0.03	0.23	1.34	3.31	2.36	1.24	–2.29	6.70	0.29	47.22	0.57	23.17	44.85
13	0.55	0.23	0.11	0.05	0.27	1.22	2.67	5.88	1.96	–2.54	11.30	0.37	65.34	1.61	27.24	44.84
14	0.6	0.54	0.17	0.19	0.40	2.37	1.47	9.79	3.2	–6.91	5.01	0.65	49.03	3.34	40.36	50.87
15	0.61	0.77	0.25	0.31	0.41	6.36	1.43	49.8	6.73	–44.9	8.38	0.65	48.81	7.98	40.99	42.73
16	0.75	0.54	0.1	0.12	0.48	1.87	1.07	21.17	5.7	–9.49	10.89	0.89	63.67	6.68	48.21	55.73
17	0.63	0.31	–0.78	–0.27	0.46	1.54	1.17	8.93	5.03	–6.65	12.15	0.83	42.62	5.81	45.93	55.47
18	0.41	0.17	–0.23	–0.07	0.27	1.19	2.59	2.9	1.64	–1.5	7.74	0.38	36.21	1.15	27.84	49.33
19	0.74	0.63	0.15	0.17	0.45	2.94	1.18	19.08	5.12	–12.6	6.48	0.83	66.06	5.92	45.68	52.61
20	0.13	0.1	0.22	0.02	0.08	1.04	11.2	0.85	0.33	–0.31	7.09	0.08	35.2	–0.77	8.15	41
21	0.6	0.46	0.01	0.015	0.43	1.67	1.29	9.34	3.58	–4.78	7.12	0.73	39.58	3.87	43.51	55.14
22	0.21	0.12	0.35	0.08	0.13	1.29	6.81	2.08	0.57	–2.09	7.1	0.13	34.52	–0.41	12.8	37.31
23	0.31	0.12	0.08	0.016	0.17	1.16	5.02	1.30	0.64	–0.85	5.11	0.18	46.97	–0.3	16.6	47.54
24	0.58	0.24	–0.24	–0.1	0.34	1.34	1.89	3.14	1.63	–1.9	5.5	0.42	51.35	1.13	34.57	51.99
25	0.46	0.17	–0.02	–0.019	0.28	1.09	2.56	2.70	1.41	–0.64	6.49	0.37	48.17	0.82	28.04	53.17
26	0.25	0.1	–0.06	–0.009	0.14	1.20	5.81	1.25	0.62	–1.29	6.43	0.15	40.1	–0.33	14.67	41.96
27	0.46	0.17	–0.02	–0.01	0.28	1.09	2.56	2.70	1.41	–0.64	6.5	0.37	48.19	0.82	28.01	53.14
28	0.5	0.32	0.02	0.01	0.34	1.50	1.95	5.15	2.11	–3.3	6.59	0.47	40.73	1.82	33.79	49.74
29	0.58	0.44	–0.11	–0.05	0.34	3.02	1.93	12.29	3.49	–17.7	8.78	0.47	55.98	3.75	34.11	39.93
30	0.73	0.56	–0.11	–0.11	0.56	1.93	0.76	17	6.69	–7.01	7.49	1.23	44.89	7.92	56.55	63.75
31	0.7	0.61	0.08	0.09	0.48	2.62	1.04	20	5.8	–11.8	7.3	0.93	52.17	6.8	48.93	55.64
32	0.61	0.58	0.08	0.1	0.51	2.15	0.96	16.4	5.21	–7.83	6.79	0.96	20.71	6.04	50.76	58.09
33	0.47	0.26	0.01	0.008	0.28	1.52	2.48	2.82	1.43	–2.36	4.53	0.38	48.33	0.84	28.67	50
34	0.32	0.16	0.11	0.031	0.18	1.30	4.26	1.63	0.73	–1.46	4.73	0.21	40.71	–0.17	18.97	46.32
35	0.55	0.43	0.38	0.34	0.30	1.87	2.27	6.98	1.88	–4.55	5.18	0.42	57.86	1.49	30.54	46.25
36	0.81	0.62	0.08	0.1	0.52	2.40	0.92	19.2	5.68	–9.4	6.7	1	70.8	6.65	52.08	58.01
37	0.52	0.24	–0.08	–0.02	0.27	1.61	2.62	2.5	1.27	–2.7	4.4	0.33	57.74	0.61	27.55	47.26
38	0.29	0.12	0.2	0.04	0.14	1.17	5.86	1.3	0.57	–0.9	5.2	0.16	52.45	–0.41	14.56	46.19
39	0.44	0.29	0.25	0.14	0.27	1.46	2.66	6.2	1.77	–3.9	8.4	0.35	44.71	1.33	27.26	43.65

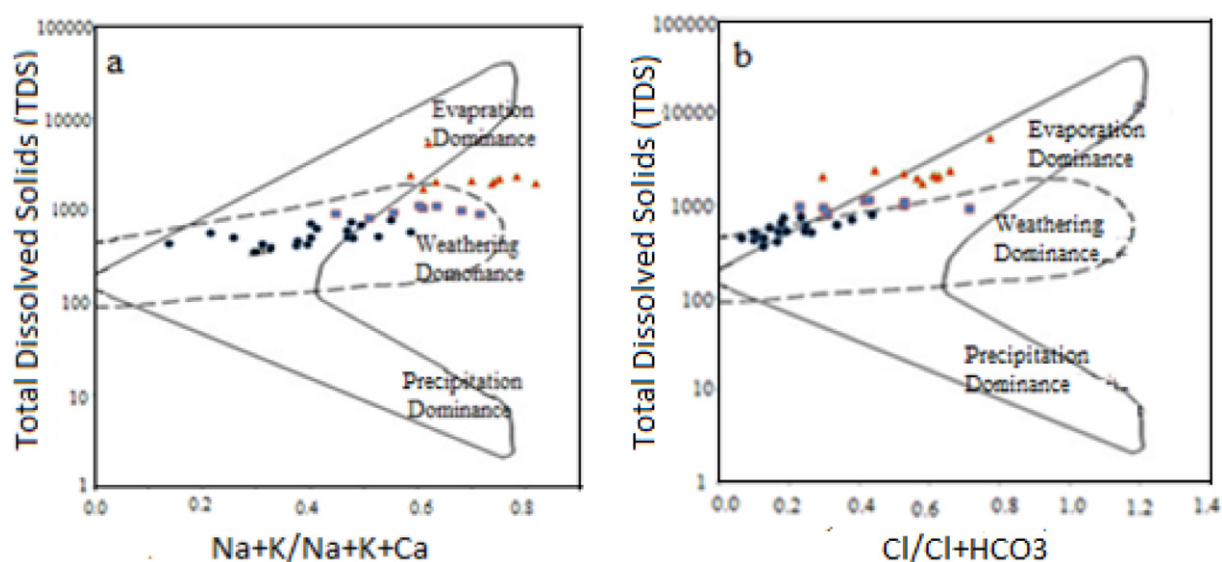


Fig. 5. Bivariate TDS versus Gibbs's ratio I (a) and TDS versus Gibbs's ratio II (b) diagrams (Gibbs, 1970). Fresh water (●), brackish water (■) and saline water (▲) types of the groundwater samples of the summer season.

4.6. Ion exchange reactions

Ion exchange reactions between the exchanger (usually clay minerals) of the aquifer matrix and the groundwater during its residence or movement processes invariably modify the concentration of certain pre-existing dissolved solids, which were derived from one or more solute acquisition mechanisms (prominent among them being rock weathering). The nature of the ion exchange process can be deciphered based on the values of two chloro-alkaline indices (CAI) [also known as Schoeller, 1977 indices] of the groundwater. Positive and negative values of CAI-I and CAI-II indicate, respectively, the involvement of direct cation exchange (Base Exchange) and reverse cation anion exchange (chloro-alkaline disequilibrium) reactions.

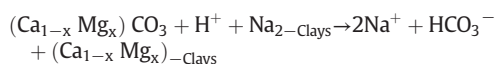
CAI-I and CAI-II are expressed as:

$$\text{CAI-I} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / \text{Cl}^- \text{ (in meq/l)}$$

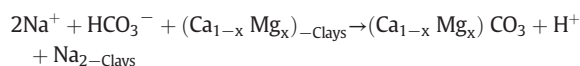
$$\text{CAI-II} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^-) \text{ (in meq/l)}$$

Ion exchange reactions can be expressed by the following two reactions (Cardona et al., 2004).

1. Direct cation exchange reaction



2. Reverse cation anion exchange reaction



In the study area, during the summer season (2016) the groundwater at 24 and 15 bore well locations was characterized by positive and negative values of both CAI I & II respectively (Table 10). Groundwater samples collected during the winter season (2017) indicate that the groundwater at 17 and 22 bore well locations was characterized by positive and negative values of both CAI I and II, respectively. This data indicate that the groundwater during the summer season was witnessing direct cation exchange and reverse cation anion exchange reactions, respectively, at 24 and 15 bore well locations. During the winter season, the groundwater was witnessing direct cation exchange and reverse cation anion exchange reactions, respectively, at 17 and 22 bore well locations. This data indicate dominance of direct cation exchange reaction between the groundwater and the host environment during the summer season (2016), whereas in the winter season (2017) the groundwater was witnessing reverse cation anion reaction at relatively more number of bore well locations.

During the direct cation exchange reaction, part of the Ca^{2+} ($\pm \text{Mg}^{2+}$) content of the groundwater gets exchanged with Na^+ ($\pm \text{K}^+$) content of the clay minerals of the aquifer matrix, thereby causing enrichment of the groundwater with Na^+ ($\pm \text{K}^+$) at the expense of part of its Ca^{2+} ($\pm$

Table 11
Correlation matrix of the measured parameters of the groundwater samples (n = 39) of the summer season.

	EC (μS/cm)	pH	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	TDS (mg/l)	TH (mg/l)
EC (μS/cm)	1											
pH	-0.26	1										
Ca ²⁺ (mg/l)	0.90	-0.36	1									
Mg ²⁺ (mg/l)	0.91	-0.19	0.81	1								
Na ⁺ (mg/l)	0.96	-0.30	0.83	0.87	1							
K ⁺ (mg/l)	0.58	-0.23	0.40	0	0.48	1						
Cl ⁻ (mg/l)	0.97	-0.25	0.84	0.89	0.96	0.59	1					
SO ₄ ²⁻ (mg/l)	0.90	-0.27	0.91	0.91	0.87	0.37	0.84	1				
HCO ₃ ⁻ (mg/l)	0.42	-0.33	0.45	0.45	0.43	0.13	0.31	0.40	1			
NO ₃ ⁻ (mg/l)	0.15	-0.01	0.03	0.11	0.18	0.29	0.17	0.04	0.02	1		
TDS (mg/l)	0.98	-0.30	0.90	0.93	0.96	0.56	0.96	0.93	0.44	0.17	1	
TH (mg/l)	0.95	-0.29	0.94	0.95	0.90	0.44	0.91	0.96	0.47	0.08	0.96	1

Mg²⁺) content. During the reverse cation anion exchange reaction, part of the Na⁺ (±K) content of the groundwater gets exchanged with Ca²⁺ (±Mg²⁺) content of the clay minerals of the aquifer matrix, thus causing enrichment of the groundwater with Ca²⁺ (±Mg²⁺) at the expense of equivalent amount of its Na⁺ (±K⁺) content.

4.7. Interelemental relationships

Several sources involved in accumulation of dissolved solids in groundwaters are usually identified based on the relative abundance of individual ions, and their ratios and correlations. Correlation analysis was carried out between 12 analysed parameters (pH, EC, TDS, TH, Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻, Cl⁻ and NO₃⁻) of the groundwater samples collected during the summer season and the obtained correlation matrices are provided in Table 11.

Among the parameters, EC and TDS exhibit strong positive correlation ($r > 0.9$) with Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, Cl⁻ and TH and moderate positive correlation with HCO₃⁻ ($r = 0.42$) and K⁺ ($r = 0.58$). Strong positive correlation is also observed between Ca²⁺ and Mg²⁺ ($r = 0.81$), Ca²⁺ and Na⁺ ($r = 0.83$), and Mg²⁺ and Na⁺ ($r = 0.87$), and moderate positive correlation between HCO₃⁻ and Ca²⁺ ($r = 0.45$), HCO₃⁻ and Mg²⁺ ($r = 0.45$), and HCO₃⁻ and Na⁺ ($r = 0.43$). This data indicate that part of the concentrations of Ca²⁺, Mg²⁺ and Na⁺ was derived from weathering of silicate minerals aided by carbonic acid as weathering agent. Strong positive correlation is also observed between Ca²⁺ and SO₄²⁻ ($r = 0.91$), and Mg²⁺ and SO₄²⁻ ($r = 0.91$). This relationship suggest derivation of significant concentrations of Ca²⁺ and Mg²⁺ from dissolution of carbonates aided by sulphuric acid. Further, Cl⁻ shows strong positive correlation with Na⁺ ($r = 0.96$) and moderate positive correlation with K⁺ ($r = 0.59$). This data may suggest derivation of significant amount of alkalis from Cl⁻ salts of the evaporate accumulations in sedimentary beds of the aquifer.

The correlation matrices also indicate strong positive correlation of Cl⁻ with SO₄²⁻ ($r = 0.84$), Ca²⁺ (0.84), Mg²⁺ (0.89) and Na⁺ (0.96). Likewise, SO₄²⁻ exhibits strong positive correlation with Ca²⁺ ($r = 0.91$), Mg²⁺ ($r = 0.91$) and Na⁺ ($r = 0.87$), and moderate positive correlation with HCO₃⁻ ($r = 0.40$). The observed strong positive correlations between Cl⁻, SO₄²⁻, Na⁺, Ca²⁺, Mg²⁺ and HCO₃⁻ indicate the presence of another source of these ions, that is, the connate saline (palaeomarine) water trapped in sedimentary beds of the aquifer, which now constitutes the admixed component of the groundwater. The computed correlation matrices of 12 physico-chemical variables of the groundwater samples collected during the winter season also suggest that bulk of the ionic load of the groundwater was provided by the same aforesaid sources, viz., carbonate and silicate mineral weathering, Na⁺ and K⁺-bearing Cl⁻ salts of the evaporites and connate saline water component of the sedimentary rocks.

4.8. Sources of dissolved solids in groundwater

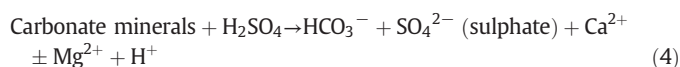
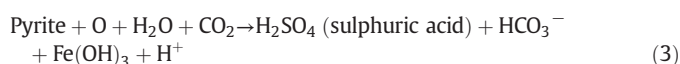
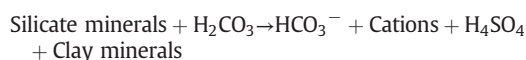
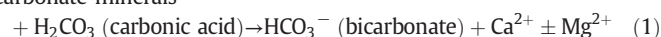
It is well known that mineral dissolution/weathering, ion exchange processes, and input from atmospheric, soil and anthropogenic sources are the major solute acquisition mechanisms controlling the concentration of chemical constituents in groundwater (Berner and Berner, 1987). In the study area, considerable amount of connate saline (palaeomarine) water trapped in the sedimentary rocks of the aquifers constitutes another additional, but relatively minor source of Na⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻, SO₄²⁻, Mg²⁺ and Ca²⁺ ions. The following paragraphs of this section provide a brief account of the major contributors of anions (HCO₃⁻, SO₄²⁻, Cl⁻ and NO₃⁻) and cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) to the groundwater of the study area.

It is known that concentrations of bicarbonate (HCO₃⁻) and sulphate (SO₄²⁻) encountered in groundwaters are generated during weathering/dissolution of minerals aided by carbonic acid (H₂CO₃) and sulphuric acid (H₂SO₄) and oxidation of sulphide minerals in the presence of O and H₂O. Among the weathering agents (viz., H₂CO₃ and H₂SO₄),

carbonic acid is derived from dissolution of atmospheric CO₂, oxidation of organic matter and root respiration (Berner and Berner, 1987), whereas the sulphuric acid is generated as a consequence of oxidation of sulphide minerals.

During weathering of silicate and carbonate minerals and oxidation of sulphide minerals, generation of either one or two acids among three acids (viz., HCO₃⁻, SO₄²⁻ and H₂SO₄) depends on the participating mineral and weathering agent. For example, dissolution of carbonate minerals aided by H₂CO₃ generates only one anion, viz., HCO₃⁻, whereas the same carbonate minerals when getting dissolved in the presence of sulphuric acid, generate both HCO₃⁻ and SO₄²⁻. The following reactions involved during weathering/oxidation of minerals indicate the generation of (a) HCO₃⁻ (Eqs. (1) and (2)), (b) SO₄²⁻ (Eq. (5)), (c) HCO₃⁻ and SO₄²⁻ (Eq. (4)) and (d) H₂SO₄ and HCO₃⁻ (Eq. (3)).

Carbonate minerals



In groundwaters, the individual concentrations of HCO₃⁻ and SO₄²⁻ reflect, respectively, the intensity of participation of carbonic acid and sulphuric acid during weathering/dissolution process. The relative intensity of participation of these two weathering agents during weathering process witnessed by the groundwater of any given terrain can be evaluated from the values of HCO₃⁻/(HCO₃⁻ + SO₄²⁻) equivalent ratio (C-ratio, Brown et al., 1996). In the study area, the values of C-ratio of the groundwater samples collected during both summer and winter seasons vary from 0.21 to 0.98 and their average value equals 0.73. This data indicate that, in comparison with the sulphuric acid, the carbonic acid has played relatively major role during the weathering process.

In the study area, Cl⁻ content of the groundwater was derived mainly from connate saline water of the sedimentary rocks, Cl⁻-bearing soluble salts of the evaporites and anthropogenic sources. Values of Na⁺/Cl⁻ molar ratio of the groundwater samples found very close or equal to 1 are usually taken into consideration while confirming the derivation of Cl⁻ from dissolution of Cl⁻-bearing salts. In the study area, the values of Na⁺/Cl⁻ molar ratio of the groundwater samples vary from 0.55 to 1.74, and among them, the values of Na⁺/Cl⁻ molar ratio of several groundwater samples vary very close to 1 (i.e., from 0.95 to 1.05). This data may be taken into consideration to confirm the derivation of part of the concentration of Cl⁻ in the groundwater from soluble Cl⁻-bearing salts of the evaporite beds encountered in sedimentary rocks of the Tertiary-Quaternary aquifer.

Among the groundwater samples, samples collected at 6 bore well locations (BW nos. 6, 15, 16, 19, 31 and 36) are found to contain very high concentrations of Cl⁻ (>18 meq/l). Further, at these bore well locations, the groundwater samples are also found to contain very high concentrations of Na⁺ (10 to 34 meq/l). The observed high concentration of Cl⁻ (and Na⁺) in the groundwater at these bore well locations has to be attributed partly to inputs from anthropogenic activities (e.g., domestic waste water and irrigation return flow).

In the groundwater of the study area, NO₃⁻ content was derived exclusively from anthropogenic sources and the latter may include: nitrogenous fertilizers, human and animal waste, biocombustion and

nitrification of organic N and NH_4 (Savoe and Prospero, 1989; Carling and Hammar, 1995; Min et al., 2003).

Alkaline earths (Ca^{2+} and Mg^{2+}) encountered in groundwaters are derived usually from a few sources, and among them, mineral weathering usually constitutes the major source. In the study area, during mineral weathering processes, carbonate minerals must have contributed significant amount of alkaline earths to the cationic load of the groundwater and this presumption finds support from the observed (a) prominent occurrence of carbonate rocks (limestone and dolomite) among the lithounits of the aquifers and (b) significant presence of SO_4^{2-} content in the groundwater.

The values of certain ionic ratios of the hydrochemical data of the groundwater samples provide clues for identification of the sources of alkaline earths. The considered ionic ratios can indicate whether the alkaline earths of the groundwater were derived either exclusively from carbonate mineral dissolution or from multiple sources, including carbonate minerals.

In groundwater samples, alkaline earths derived from exclusive dissolution of carbonate minerals can be identified from the obtained values of the $\text{Ca}^{2+}/\text{HCO}_3^-$, $\text{Mg}^{2+}/\text{HCO}_3^-$, $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and $\text{Mg}^{2+}/\text{SO}_4^{2-}$ molar ratios obtained from hydrochemical data. During weathering process, dissolution of calcite, dolomite and carbonates (a mixture of calcite and dolomite, in proportions ranging from 0 to 100% of each mineral), aided by either carbonic acid or sulphuric acid, can be identified based on the following theoretically deduced values of $\text{Ca}^{2+}/\text{HCO}_3^-$, $\text{Mg}^{2+}/\text{HCO}_3^-$, $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and $\text{Mg}^{2+}/\text{SO}_4^{2-}$ molar ratios, resulting from the dissolution of calcite/dolomite/mixture of carbonate minerals.

- Values of $\text{Ca}^{2+}/\text{HCO}_3^-$ molar ratio will be equal to 0.50 for calcite; 0.25 for dolomite and vary from 0.25 to 0.50 for carbonates.
- Values of $\text{Mg}^{2+}/\text{HCO}_3^-$ molar ratio will be equal to 0.25 for dolomite and vary from 0 to 0.25 for carbonates.
- Values of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ molar ratio will be equal to 1.00 for calcite; 0.50 for dolomite and vary from 0.50 to 1.00 for carbonates.
- Values of $\text{Mg}^{2+}/\text{SO}_4^{2-}$ molar ratio will be equal to 0.50 for dolomite and vary from 0 to 0.50 for carbonates.

The values of the molar ratios of $\text{Ca}^{2+}/\text{HCO}_3^-$, $\text{Mg}^{2+}/\text{HCO}_3^-$, $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and $\text{Mg}^{2+}/\text{SO}_4^{2-}$ of the groundwater samples collected during the summer (sample nos. 1 to 39) and winter (sample nos. 40 to 78) seasons vary, respectively, from 0.42 to 3.27; from 0.32 to 3.10; from 0.56 to 32.40; and from 0.51 to 29.60. These values of the above considered molar ratios of the groundwater samples of the study area, when compared with the theoretically deduced values of the same molar ratios resulting from dissolution of carbonate minerals (calcite or dolomite or carbonates), are found to be higher in all groundwater samples, barring the values of a few molar ratios in sample nos. 13, 19, 56 and 75. The above data clearly indicate that the alkaline earths of the groundwater of the study area were derived not only from carbonate mineral dissolution, but also from other sources.

Values of certain ionic ratios [viz., $(\text{Na}^+ + \text{K}^+)/\text{Tz}^+$; $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$; and $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$] computed from hydrochemical data of the groundwater samples are found informative while evaluating the participation of either one or both among the two mineral groups (viz., carbonates and silicates) during weathering process (Sarin et al., 1989; Singh et al., 2012). The hydrochemical data of the groundwater samples collected during the summer season revealed relatively high values of $(\text{Na}^+ + \text{K}^+)/\text{Tz}^+$ ratio (0.08 to 0.56; av. = 0.38) and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ ratio (1.04 to 6.36; av. 1.83) and low values of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ ratio (0.76 to 11.20; av. 1.59) (Table 10). These values suggest the participation of both carbonate and silicate minerals during the weathering process (Sarin et al., 1989). Further, the observed moderate positive correlation of HCO_3^- with Ca^{2+} ($r = 0.45$) (Table 11) and the location of the plots of the groundwater samples on bivariate $\text{Ca}^{2+}/\text{Na}^+$ versus $\text{Mg}^{2+}/\text{Na}^+$

diagram of Gaillardet et al. (1999) (Fig. 6) also suggest combined influence of carbonate and silicate mineral weathering during solute acquisition processes (Singh et al., 2005).

In the study area, other sources of the alkaline earths of the groundwater include cationic load derived from reverse cation anion exchange reaction involved by the groundwater with the exchanger of the aquifer matrix, and connate saline water trapped in the sedimentary rocks of the aquifer. Contribution of $\text{Ca}^{2+} \pm \text{Mg}^{2+}$ from the reverse cation anion exchange reaction process is revealed from the observed negative values of CAI – I & II of the groundwater samples collected at 15 and 22 bore well locations during the summer and winter seasons, respectively (details provided in Section 4.6). The negative values of CAI – I & II of the groundwater samples confirm the derivation of significant concentration of the alkaline earths from exchanger (clay minerals) of the aquifer.

The $\text{Na}^+ \pm \text{K}^+$ content present in the groundwater of the study area can be attributed to the following sources: Input from direct cation exchange reaction between groundwater and clay minerals of the aquifer matrix, weathering of alkali feldspars, Na^+ and K^+ -bearing soluble salts and input from anthropogenic activities. Further, the connate saline water of the sedimentary rocks of the aquifer constitutes another source of Na^+ and K^+ content of the groundwater.

Contribution of $\text{Na}^+ \pm \text{K}^+$ from ion exchange process is evident from the observed positive values of CAI-I and II of the groundwater samples collected at 24 bore well locations during the summer season and at 17 bore well locations during the winter season (details provided in Section 4.6). Positive values of chloro-alkaline indices indicate the involvement of direct cation exchange reaction, and through this process, the input of $\text{Na}^+ \pm \text{K}^+$ to the groundwater.

$\text{Na}^+ \pm \text{K}^+$ content derived from alkali feldspar weathering and Na^+ and K^+ -bearing soluble salts can be evaluated from the values of Na^+/Cl^- molar ratio of the groundwater samples. Values of Na^+/Cl^- molar ratio >1 indicate derivation of part of Na^+ content of the groundwater from alkali feldspar weathering (Stallard and Edmond, 1983; Meybeck, 1987). If the value of Na^+/Cl^- molar ratio of the groundwater sample equals 1, then it indicates that part of Na^+ content of the groundwater sample was derived from Na-bearing soluble Cl^- salts. In the study area, the values of Na^+/Cl^- molar ratio of 15 out of 39 groundwater samples of the summer season and 22 out of 39 groundwater samples of the winter season are higher than 1. Further, as mentioned earlier, the values of Na^+/Cl^- molar ratio of several groundwater

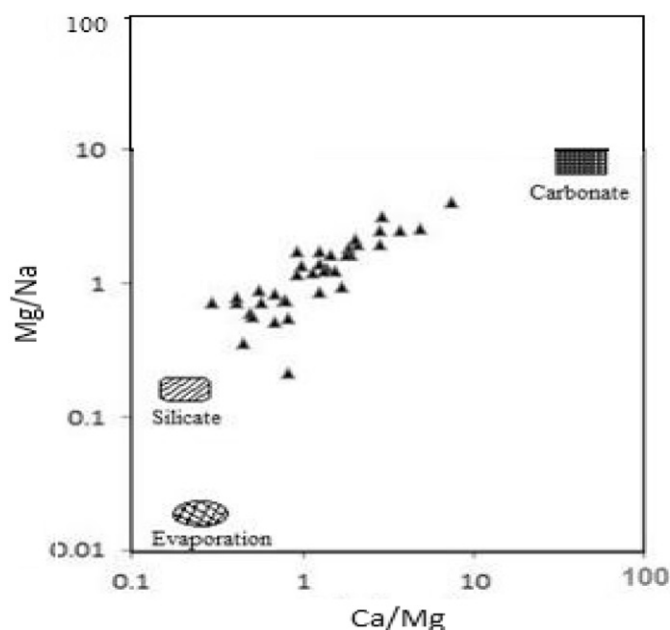


Fig. 6. Plots of the hydrochemical data of groundwater samples of the summer season on the bivariate $\text{Mg}^{2+}/\text{Na}^+$ versus $\text{Ca}^{2+}/\text{Na}^+$ diagram (Gaillardet et al., 1999).

Table 12

Assessment of quality of groundwater for drinking purposes based on the standards of WHO (1997). Total number of groundwater samples examined: 39 in summer season and 39 in winter season.

Permissible limits of physico-chemical parameters of drinking water WHO (1997)	No. of samples exceeding the permissible limits of WHO (1997) (summer season)	No. of samples exceeding the permissible limits of WHO (1997) (winter season)
EC (1500 μ S/cm)	17	14
PH (6.5–8.5)	1	–
Ca ²⁺ (200 mg/l)	4	2
Mg ²⁺ (150 mg/l)	4	1
Na ⁺ (200 mg/l)	11	10
K ⁺ (200 mg/l)	1	–
Cl [–] (600 mg/l)	6	6
SO ₄ ^{2–} (600 mg/l)	3	2
HCO ₃ [–] (600 mg/l)	3	2
NO ₃ [–] (50 mg/l)	8	6
TH (500 mg/l)	16	14
TDS (1500 mg/l)	10	9

samples are found to be very close to 1. Hence, the observed values of Na⁺/Cl[–] molar ratio of groundwater samples (a) exceeding 1 and (b) equal to or very close to 1 indicate, respectively, derivation of part of Na⁺ content of the groundwater samples from (a) weathering of alkali feldspars and (b) Na⁺-bearing soluble Cl[–] salts.

Certain amount of alkalies of the groundwater was probably derived from anthropogenic sources (e.g., irrigation return flow and domestic waste water). This presumption finds support from the observed very high concentrations of Na⁺ (above 15 meq/l) and K⁺ (above 1 meq/l) in groundwater samples collected, respectively, at bore well location nos. 1, 15, 32, and 36 and bore well location nos. 6 and 15. At these bore well locations, the groundwater also contains high concentrations of Cl[–].

4.9. Suitability of groundwater for drinking purposes

Suitability of the groundwater for drinking purposes was evaluated based on the permissible limits of hydrochemical variables prescribed by WHO (1997), and values of computed Water Quality Index (WQI). The first method involved comparison of the values of 11 physico-chemical parameters (pH, EC, TDS, Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃[–], SO₄^{2–}, Cl[–] and NO₃[–]) of the groundwater samples with the values of permissible limits of the same physico-chemical parameters prescribed by WHO (1997) for drinking water. Table 12 provides the details of the (1) WHO (1997) suggested values of the permissible limits of the individual physico-chemical parameters considered for quality assessment of potable water and (2) the number of groundwater samples having the

Table 13

Values of the Water Quality Index (WQI) of the groundwater samples (n = 39) of the summer season.

Water Quality Index	GW sample nos. with the values of WQI in bracket
1. Excellent	2 (37.4), 3 (47.8), 5 (40.4), 8 (30.2), 9 (29.2), 10 (30.1), 12 (42.2), 18 (36.8), 20 (34.3), 22 (34.7), 24 (35.2), 25 (32.9), 26 (36.8), 27 (33.4), 33 (39.8), 34 (38.1), 37 (36.8) and 38 (32.1)
2. Good	1 (52.4), 4 (83.8), 7 (86.6), 11 (69.1), 13 (51.1), 14 (59.3), 16 (96.2), 21 (53), 23 (50.8), 28 (55), 32 (84.3), 35 (54.7), 36 (95.1) and 39 (68.7)
3. Poor	6 (117.5), 17 (101.2), 19 (101.9), 29 (117.9), 30 (102.9) and 31 (111.2)
4. Very poor	15 (212.1)

Bold values indicates borewell no.

Table 14

Values of the Water Quality Index (WQI) of the groundwater samples (n = 39) of the winter season.

WQI	GW sample nos. with the values of WQI in bracket
1. Excellent	41 (31.7), 42 (41.4), 44 (34.4), 47 (27.6), 48 (27.4), 49 (27.5), 50 (49.5), 51 (38.2), 52 (46.5), 53 (47.6), 57 (32.4), 59 (31.6), 60 (46.8), 61 (31.8), 62 (42.8), 63 (31.4), 64 (29), 65 (32.5), 66 (30.9), 67 (45.6), 72 (37), 73 (37.6), 76 (32.9) and 77 (31.4)
2. Good	40 (66.1), 43 (70), 46 (90.2), 55 (80.7), 56 (65.4), 58 (86.7), 69 (88.5), 70 (96), 71 (72.3), 74 (50), 75 (83.9), and 78 (56.6)
3. Poor	45 (100.2), 54 (179.8) and 68 (101.2)

Bold values indicates borewell no.

values of the physico-chemical parameters exceeding the permissible limits prescribed by WHO (1997).

The aforementioned procedure revealed that in the study area, the groundwater drawn at 18 bore well locations (BW nos. 2, 5, 8, 9, 10, 12, 18, 20, 22, 24, 25, 26, 27, 33, 34, 35, 37 and 38) was suitable for drinking purposes during both summer (2016) and winter (2017) seasons. Additionally, the groundwater drawn at 3 bore well locations (BW nos. 11, 23 and 28), which was found unsuitable for drinking purposes during the summer (2016) season, was rendered fit for drinking purposes during the winter (2017) season. The transformation of the quality of the water to potable category during the winter season can be attributed to the observed decrease in the concentration of K⁺ in the groundwater at locations of BW nos. 23 and 28 and decrease in the concentration of Mg²⁺ in the groundwater at the location of BW no. 11 to the levels of permissible limits prescribed by WHO (1997).

Assessment of the quality of the groundwater of the study area for drinking purposes was also carried out based on the values of Water Quality Index (WQI) of the ground water samples. Values of WQI were computed according to the procedure described in Section 3.2. The obtained values of WQI of the groundwater samples (n = 78) are provided in Tables 13 and 14.

In the published literature (e.g., Saba and Umer, 2016) the values of WQI of potable waters are classified into 5 groups, which correspond to 5 water quality classes (Table 15). Table 16 provides the details of the groundwater samples of the study area belonging to the identified 5 water classes during the summer and winter seasons. This data indicate that in the study area, groundwater belonging to “excellent” and “good” water classes was present during the winter season (2016) at 24 and 12 bore well locations, respectively, whereas the groundwater belonging to same water classes was present during the summer season (2017) only

Table 15

Classification of the quantity of water for drinking purposes based on the values of Water Quality Index (WQI).

WQI range	Type of water
50>	Excellent
50–100	Good
100–200	Poor
200–300	Very poor
>300	Unsuitable

Table 16

Assessment of the quality of groundwater for drinking purposes based on the values of the Water Quality Index (WQI) of the groundwater samples collected during the summer (n = 39) and winter (n = 39) seasons.

Water quality	Summer season	Winter season
1. Excellent	18 samples (46.16%)	24 samples (61.54%)
2. Good	14 samples (35.89%)	12 samples (30.77%)
3. Poor	6 samples (15.39%)	3 samples (7.68%)
4. Very poor	1 sample (2.55%)	–

at 18 and 14 bore well locations, respectively. Fig. 7, which was compiled based on the values of WQI of the groundwater samples drawn at 39 bore well locations, shows the spatial variation of the quality of the groundwater of the study area during the summer (Fig. 7a) and winter (Fig. 7b) seasons.

4.10. Suitability of groundwater for irrigation purposes

Assessment of the quality of the groundwater of the study area for irrigation purposes was carried out according to the procedure provided in Section 3.3. The values of EC ($\mu\text{S}/\text{cm}$), concentration of Cl^- (meq/l) and HCO_3^- (meq/l), and ratings/assessment of the parameters and bilateral diagrams considered for evaluation of the quality of the groundwater for irrigation purposes are given in Tables 2, 3, 10 and 17. This data provides the status of the suitability of the groundwater encountered in the study area during summer (2016) and winter (2017) seasons for irrigation purposes.

The irrigation water quality assessment parameters and bivariate diagrams revealed diversified assessment/ratings for the groundwater encountered at 39 bore well locations during summer and winter seasons (Table 17). For example, two parameters (viz., Residual Sodium Carbonate and Exchangeable Sodium Percentage) and one bivariate diagram (viz., Permeability Index versus $\text{Tz}^+ + \text{z}^-$ diagram) indicated that the groundwater encountered at all bore well locations is “suitable” for irrigation purposes, but did not specify its suitability for cultivation of diversified crops ranging from salt-sensitive to salt-tolerant categories. The ratings of several other parameters do not support the above assessment and indicated the poor quality of the groundwater at several bore well locations. For example, the ratings provided by the “Magnesium Hazard” parameter indicated that the groundwater at 17 and 15 bore well locations is unsuitable for irrigation purposes during summer and winter seasons, respectively (Table 17). In irrigation waters, high concentration of Mg affects the quality of soil resulting in poor agricultural

returns (Szabolcs and Darab, 1964). Likewise, the values of “Bicarbonate Hazard” parameter revealed that the groundwater at 35 and 4 bore well locations during the summer season can cause, respectively, increasing problem and severe problem to plant growth (Table 17). It is known that excess bicarbonate and carbonate content in irrigation water, combined with sodium, can lead to the formation of alkaline soil. Alkaline soils are known to cause problems to soil and plant growth. Further, the values of the “Salinity” parameter indicated that the groundwater at 10 bore well locations during both summer and winter seasons is of poor/bad quality for irrigation purposes (Table 17). It is known that highly saline irrigation water can lead to the development of saline soil. High salt content in soil, besides affecting the growth of plant directly, also affect the soil structure, permeability and aeration, which indirectly affect the plant growth (Saleh et al., 1999; Singh et al., 2012). The values of “Chloride Hazard” parameter, like “Salinity” parameter, indicate that the groundwater at 9 bore well locations during both summer and winter seasons is hazardous to very hazardous to plant growth (Table 17). Chloride-rich irrigation waters promote the formation of saline soils, which are detrimental to plant growth.

Hydrochemical data of water plotted on bivariate SAR versus EC ($\mu\text{S}/\text{cm}$) diagram (US Salinity Laboratory diagram of Richards, 1954) can provide valuable information on the suitability of the water for irrigation purposes. On the US Salinity Laboratory diagram, about 72% and 28% of the groundwater samples collected during the summer season (2016) plot in the “High Salinity-Low Sodium” (C3S1) and “Very High Salinity-Medium Sodium” (C4S2) irrigation water classes, respectively (Fig. 8 and Table 17). With regard to the groundwater belonging to (C3S1) irrigation water class, it can be said that the irrigation water with low sodium content can be useful for irrigation of almost all soils with little danger of development of harmful levels of exchangeable sodium. But the high salinity of the groundwater prohibits its usage on soils with restricted drainage. About 28% of the groundwater of the study area, which belongs to (C4S2) irrigation water class, is not suitable

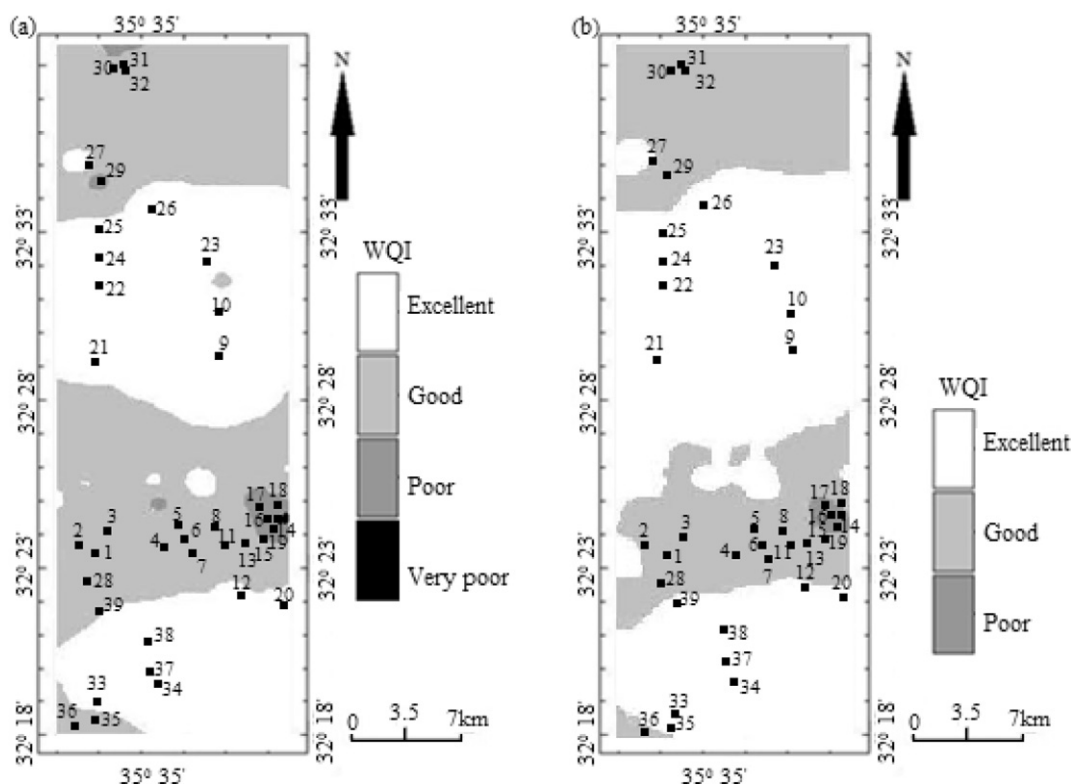


Fig. 7. Plans showing the spatial variation of the quality of the groundwater for drinking purposes based on the values the Water Quality Index (WQI) of the groundwater collected during the summer (a) and winter (b) seasons.

Table 17

Evaluation of the quality of groundwater for irrigation purposes based on the data of irrigation water quality assessment parameters and parameters - based bivariate diagrams.

Water quality assessment parameters	Assessment of water quality	No. of borewells yielding the specified quality of groundwater (summer season)	No. of borewells yielding the specified quality of groundwater (winter season)
Salinity (EC $\mu\text{S}/\text{cm}$) Richards (1954)	Excellent (<250)	–	–
	Good (250–750)	3	8
	Fair/medium (750–2250)	26	21
	Poor/bad (>2250)	10	10
Chloride Hazard (CH) Doneen (1964)	Very good–good (<5 meq/l)	19	22
	Good to hazardous (5–10 meq/l)	11	8
	Hazardous to very hazardous (>10 meq/l)	9	9
Sodium Adsorption Ratio (SAR) Bower (1978)	No problem (<6)	37	36
	Increasing problem (6–9)	2	3
	Severe problem (>9)	–	–
Residual Sodium Carbonate (RSC) Lloyd and Heathcote (1985)	Suitable (<1.25 meq/l)	39	39
	Doubtful (1.25–2.5 meq/l)	–	–
	Unsuitable (>2.5 meq/l)	–	–
Bicarbonate Hazard (BH) Mandel and Shiftan (1981)	No problem (<1.5 meq/l)	–	–
	Increasing problem (1.5–8.5 meq/l)	35	36
	Severe problem (>8.5 meq/l)	4	3
Kelley's Ratio (KR) Kelley (1951)	Suitable (<1)	38	34
	Unsuitable (>1)	1	5
Magnesium Hazard (MH) Lloyd and Heathcote (1985)	Suitable (<50)	22	24
	Unsuitable (>50)	17	15
Exchangeable Sodium Percentage (ESP) Tijani (1994)	Suitable (<15)	39	39
	Unsuitable (>15)	–	–
%Na versus EC diagram Wilcox (1948, 1955)	Excellent to good	12	13
	Good to permissible	15	16
	Permissible to doubtful	–	–
	Doubtful to unsuitable	2	–
	Unsuitable	10	10
Permeability Index (PI) versus ($\text{Tz}^+ + \text{z}^-$) diagram Doneen (1964)	Class I: suitable (PI>75%)	39	39
	Class II: permissible (PI- 25–75%)	–	–
	Class III: unsuitable (PI<25%)	–	–
US Salinity Laboratory diagram (USSL) Richards (1954)	C2S1	–	2
	C3S1	28	27
	C3S2	1	–
	C4S1	–	1
	C4S2	9	8
	C4S3	1	1

as irrigation water under ordinary conditions and can be used only for cultivation of salt tolerant crops.

5. Conclusions

In the study area, the source of the groundwater, according to the values of Base Exchange Index (r_1), belongs to the category of $\text{Na}-\text{SO}_4^{2-}$ type, and according to the values of Meteoric Genesis Index (r_2), belongs mainly to the category of Deep Meteoric percolation type. Salinity-wise, the groundwater encountered at 22, 7 and 10 bore well locations during the summer season and at 25, 5 and 9 bore well locations during the winter season belongs, respectively, to fresh, brackish and saline water categories.

The hydrochemistry of the groundwater, on average, is dominated by Na^+ in cationic abundance and by Cl^- in anionic concentration. Hydrogeochemical facies-wise, about 51% of the groundwater samples collected during the summer season exhibits mixed chemical character of $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{Cl}^-$ hydrochemical facies of Back, 1996 and the remaining ~31% and ~18% of the groundwater samples are characterized by $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{HCO}_3^-$ and $\text{Ca}^{2+}-\text{Mg}^{2+}-\text{SO}_4^{2-}$ hydrochemical facies, respectively.

It is well known that, in ground waters bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) ions are derived from weathering of minerals aided by carbonic acid (H_2CO_3) and sulphuric acid (H_2SO_4) and oxidation of sulphide minerals. In the study area, the values of $\text{HCO}_3^-/(\text{HCO}_3^- + \text{SO}_4^{2-})$ equivalent ratio (C-ratio) of the groundwater samples indicate that, in comparison with the sulphuric acid (H_2SO_4), the carbonic acid (H_2CO_3) involved relatively more active participation during the

mineral weathering process. Cl^- content of the groundwater of the study area was derived mainly from connate saline water, Cl^- -bearing soluble salts of the evaporites encountered in the sedimentary beds of the aquifer, domestic waste water, and irrigation return flow. NO_3^- content of the groundwater of the study area, as elsewhere in ground waters, owes its source exclusively to anthropogenic inputs and the latter may include: nitrogenous fertilizers, domestic and animal waste, biocombustion and nitrification of organic NH_4 and N.

Alkaline earths (Ca^{2+} and Mg^{2+}) of the groundwater were derived mainly from weathering of both carbonate and silicate minerals and, to a lesser extent, from reverse cation anion exchange process and connate saline water of the Quaternary sedimentary beds of the aquifer. Na^+ and K^+ content of the groundwater owes its source mainly to weathering of alkali feldspars, direct cation exchange process, connate saline water and Na^+ and K^+ -bearing soluble Cl^- salts of the evaporite beds of the sedimentary rocks of the aquifer and anthropogenic sources (e.g., domestic waste water, irrigation return flow).

Assessment of the quality of groundwater for drinking purposes, carried out based on the computed values of Water Quality Index (WQI) of the groundwater samples, reveal the presence of excellent and good categories of potable water, respectively, at 18 and 14 bore well locations during the summer season and at 24 and 12 bore well locations during the winter season.

Assessment of the quality of groundwater for irrigation purposes, carried out based on the available quality assessment parameters and parameters-based bivariate diagrams, indicates that the groundwater encountered at 39 bore well locations varies in quality. The groundwater belongs essentially to (C3S1), and to a lesser extent, to (C4S2)

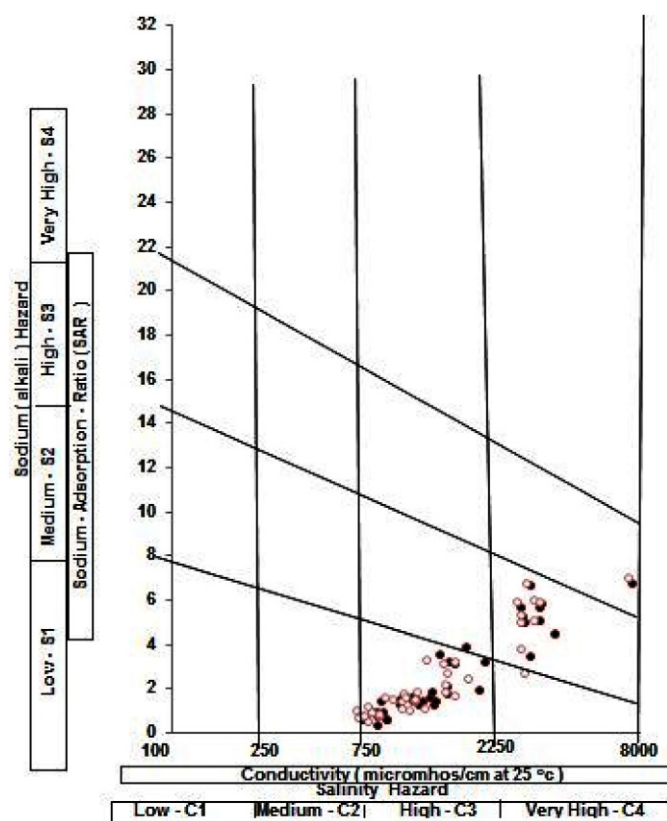


Fig. 8. US Salinity Laboratory diagram (Richards, 1954) showing the irrigation water classes of the groundwater samples collected during the summer (●) and winter (○) seasons.

irrigation water classes of Richards (1954) and is suitable mainly for cultivation of salt tolerant crops and, to a limited extent, semi-salt tolerant crops.

CRediT authorship contribution statement

Mohammad Tarawneh: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **M.R. Janardhana:** Data curation, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Mohamed Muzamil Ahmed:** Funding acquisition, Software, Writing - original draft.

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