



Classification, hydrochemical characterization, and quality assessment of groundwater of coastal aquifer at Sari–Neka plain, Northern Iran

Houshang Khairy¹ · Mysore Ramachandraiah Janardhana²

Received: 6 November 2020 / Accepted: 11 November 2021 / Published online: 2 December 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract

Lack of data on the hydrogeochemistry of coastal aquifers around the south Caspian Sea warranted the present hydrochemical and quality assessment studies. The study involving classical integrated methods, multivariate statistical analyses, and GIS applications was carried out on the groundwater encountered in coastal Sari–Neka plain, Mazandaran Province, Northern Iran. The present survey indicates that the groundwater encountered at majority (~68%) of the sampling locations is of $\text{Na}^+ - \text{SO}_4^{2-}$ category and constitutes deep meteoric percolation type and the same at the remaining ~32% of the sampling locations relates to $\text{Na}^+ - \text{HCO}_3^-$ category and belongs to shallow meteoric percolation class. The groundwater situated at ~64% and ~36% of the sampling locations belongs, respectively, to freshwater and brackish water categories. The groundwater is specified by $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. It pertains to $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{HCO}_3^-$, mixed, and $\text{Na}^+ - \text{Cl}^-$ hydrochemical facies. Reverse cation–anion-exchange process was found dominant at majority (~76%) of the sampling sites. Dissolved solids were originated chiefly from connate brine water confined to the aquifer sedimentary beds, dissolution of aquifer materials, ion-exchange, and different anthropogenic sources. Groundwater encountered at ~71% and ~27% of the bore well locations belongs to good and excellent categories of drinking water, while that at ~73% of the sampling locations pertains to (C3S1) irrigation water class of Richards (Diagnosis and improvement of saline and alkali soils (USDA. Agriculture handbook, Vol. 60). U.S. Department of Agriculture, Washington DC, 1954). The results of the present study are useful for planning sustainable management and protection of the groundwater in coastal areas, especially around the Caspian Sea, and serve as a database for international researchers.

Keywords Hydrogeochemistry · Multivariate statistical analyses · Sources of dissolved solids · Groundwater quality · Sari–Neka plain · Northern Iran

Introduction

In coastal regions of several countries (e.g., Spain, Greece, Cyprus, Hong Kong, Turkey, Iran, Nigeria, Australia, USA, and India), groundwater encountered in different geological settings exhibits diversified hydrochemical features, and quality-wise constitutes a few graded categories of water meant for irrigation and drinking purposes. Furthermore, the groundwater confined to coastal aquifers/alluvial plains are exposed to diverse levels of salinization, and are attributed

to the involvement of one or more terrain—specific contaminants (e.g., seawater, brine/saline water interfaced/ underlying fresh groundwater horizon, connate [palaeo-marine] water trapped in aquifer rocks, and various pollutants of anthropogenic origin) (Brown and Misut 2010; Cheng and Ouazar 2003; Ergil 2000; Gholami et al. 2015; Gilabert-Alarcón et al. 2018; Giménez and Morell 1997; Jamshidzadeh 2020; Janardhana and Khairy 2019; Khairy and Janardhana 2013, 2014; Kim et al. 2004; Kreitler 1993; Liu et al. 2017; Ozler 2003; Petalas and Diamantis 1999; Vandenbohede and Lebbe 2012).

Insufficient understanding of the hydrogeochemistry of coastal aquifers around the south Caspian Sea makes it necessary to do this survey. The present work deals with the characterization, classification, and quality assessment of the groundwater encountered in coastal alluvial plain from Sari to Neka, in Mazandaran province, Northern Iran. The

✉ Houshang Khairy
h.khairy@du.ac.ir

¹ School of Earth Science, Damghan University, Damghan, Iran

² Department of Geology, Yuvaraja's College, University of Mysore, Mysore 570005, India

present investigation was carried out based on the classical methods of interpretation of hydrochemical data, multivariate statistical analyses of the physicochemical parameters of the groundwater, and GIS techniques. The obtained data provide details on the groundwater with respect to the physicochemical characteristics, source-wise and salinity-wise categorization, classifications, degree of evolution, natural mechanisms controlling hydrochemistry, hydrochemical features, ion-exchange processes, sources of dissolved solids, and standard of groundwater for human consumption and agricultural needs.

Materials and methods

Study area

The study region is located in a coastal plain land between Sari and Neka townships in the eastern part of Mazandaran province, Iran (Fig. 1a). The study area, designated as Sari–Neka plain, is limited in the south by the foothills of Alborz Mountain range and in the north by the Caspian Sea coastline. The flow lines of the Siahroud river in the west and Nekaroud river in the east were selected by the present authors to demarcate the adjacent boundaries of the study area. Sari–Neka plain (Fig. 1b) covers an area of ~985 km²

and extends from 36°32′ to 36°52′ latitudes and 52°56′ to 53°25′ longitudes. The ground level elevation, near the southern boundary, is about 136 m above mean sea level (m.s.l.) and the same at the northern boundary is at an elevation of about 26 m below m.s.l. (i.e., at the present level of the Caspian Sea). The coastal geomorphic features of the Mazandaran Province include plateaus, alluvial fans, and flood plains (Vahdati Daneshmand and Saidi 1991).

The study area consists of a thick sequence of unconsolidated-to-semi-consolidated marine, deltaic, and fluvial deposits of Tertiary and Quaternary age. Sand and clay are the major fractions of the sediments, with relatively lesser amounts of silt and calcareous material. Exploratory bore wells reveal the extension of the sedimentary beds to a depth of more than 250 m (SazabShargh 2010). Jackson et al. (2002) consider that the sedimentary formation of the study area was possibly accumulated in the post-Oligocene foreland basin setting of Caspian Sea. The study area was developed consequently of the regression of the Caspian Sea, which, at one period, protracted till the foothill region of the Alborz mountains (Dewan and Famouri 1964). This evolutionary feature of the study region indicates that the sedimentary beds may hold a significant amount of palaeo-marine water.

The groundwater flows from south to north. Near the shoreline, the water table is encountered at a depth of 2–3 m

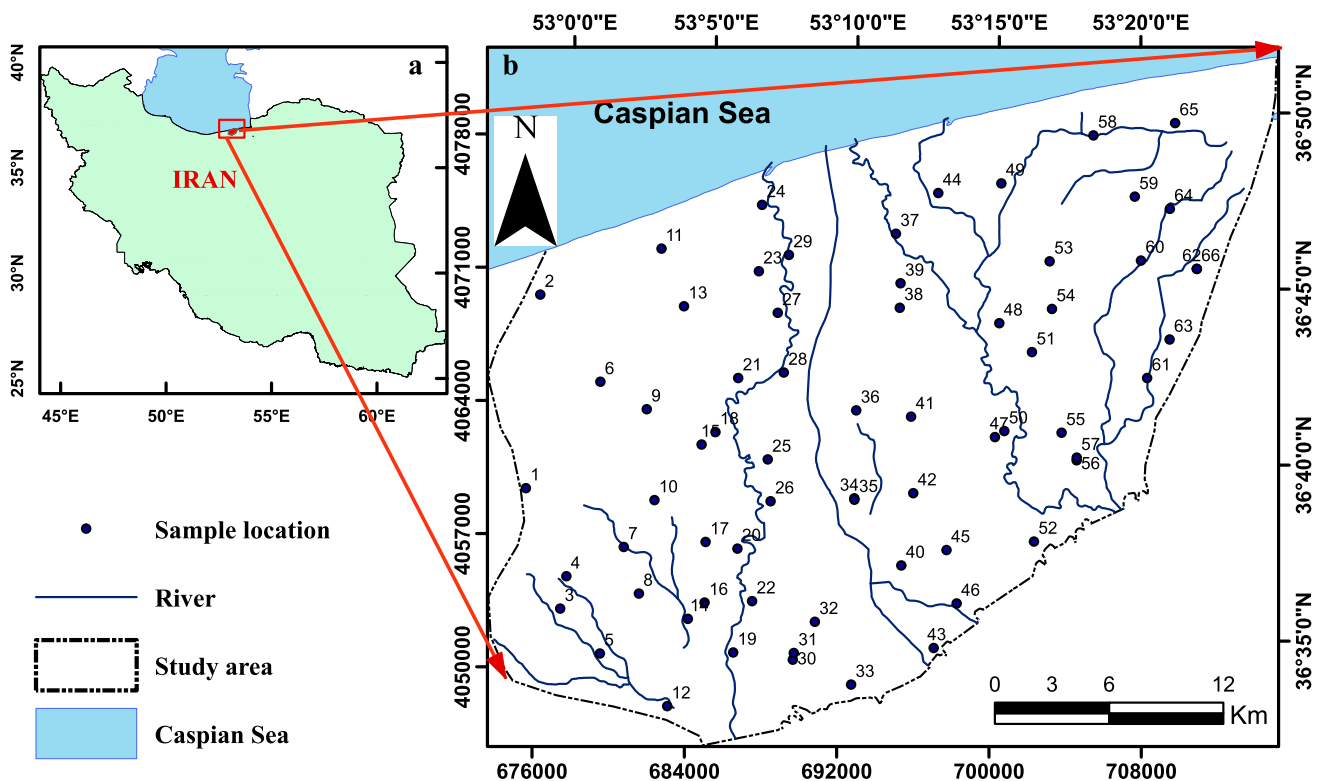


Fig. 1 Location of the study area (a) and plan showing the groundwater sampling spots (bore well locations) in the study area (b)

below the ground level and the same at the southern part of the study region is encountered at a depth of 100–110 m below the ground level. The precipitation in the territory varies from 500 to 800 mm/year and the climate is essentially sub-humid (Source: Iranian Meteorological Organization). The majority of the population makes use of the groundwater for drinking purposes, while about 40% of the agricultural activities are carried out utilizing the groundwater (SazabShargh 2010).

Sampling and hydrochemical analysis

During the month of October 2017, 66 groundwater samples were collected in duplicate at 66 bore wells of the groundwater quality network of the Sari–Neka aquifer (Fig. 1b) by the Mazandaran Regional Water Authority (MRWA) staff. Before collecting the water samples, the water was pumped out from bore wells for about 10 min to remove stagnant groundwater. Prior to sampling, water was filtered through 0.45 Millipore membrane. Portable electrical conductivity and pH meter (WW COND 340i, Germany) were made use of for measuring Electrical Conductivity (EC) and pH of the groundwater at the sampling sites. Cation analysis was done by acidifying 100 ml of filtered groundwater sample with nitric acid, while un-acidified groundwater samples were utilized for the analyses of anion contents. The laboratory tasks were done during a week after sampling. Chemical analysis of the groundwater samples, following the standard procedure (APHA 1995), was accomplished at MRWA, Sari city, Iran. Charge Balance Error (CBE) in each sample as percent was computed following below mentioned mathematical expression (Freeze and Cherry 1979) and were well within the desirable limits of $\pm 5\%$:

$$\text{CBC} = \left[\left(\sum (Zm_c) - \sum Zm_a \right) / \left(\sum (Zm_c) + \sum Zm_a \right) \right] \times 100,$$

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

GIS analysis

The hard copy of the topographic map (1:25,000) of the study area, published by the National Cartographic Center of Iran, was digitized using ARCGIS 10.5 version software for preparation of the base map of the study area. The exact places of the sampling spots (i.e., bore well locations) were determined in the field using Garmin GPSMAP 64sx, and accurate placement of latitudes and longitudes was carried out using a GIS platform. Plans showing the areal extent of availability of the groundwater with desirable and permissible limits of the concentration of TDS, Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^- prescribed for potable water by Institute of Standards and Industrial Research of

Iran (ISIRI) (2009) and the plan depicting the areal extent of occurrence of three types of potable water (demarcated based on the Water Quality Index) were created utilizing ArcGIS software.

Multivariate statistical analysis

During the present study, SPSS (Version 18) software package was used to carry out multivariate statistical analyses of the analytical data of 12 physicochemical variables (viz., EC, TDS, pH, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) of the groundwater samples ($n=66$) of the study area. The multivariate statistical analyses comprise: (1) Computation of Spearman's correlation coefficient matrices to establish affinity between pairs of physicochemical parameters in the samples for identification of various origins of dissolved solids in the groundwater, (2) Principal Component Analysis (i.e., R-mode factor analysis) of the analytical data to determine and decipher relationships within physicochemical parameters of the groundwater and to extract the agents controlling the chemistry of groundwater (Davis 2002), and (3) Hierarchical Cluster Analysis (HCA) of the hydrochemical variables using Ward's linkage procedure (Ward 1963) to find multivariate resemblances in groundwater chemistry and to group the objects (viz., physicochemical variables of the groundwater) into specific domains, so that the entities within a domain are the same but dissimilar compared to other clusters (Singh et al. 2005).

The normality of distribution of the physicochemical variables in the groundwater was ensured by Kolmogorov–Smirnov and Shapiro–Wilk tests (Nematollahi et al. 2018). The tests revealed that the P values of the analytical data are less than 0.05, thus indicating the regular statistical distribution of the physicochemical variables of the samples.

Estimation of water quality index

Groundwater's suitability for the domestic needs of the study region was appraised from the calculated values of Water Quality Index (WQI). The determination of WQI is a ranking approach that represents the combined effect of discrete physicochemical variables of natural waters on the entire standard of freshwater (Mitra 1998). The WQI of the groundwater samples were computed following the procedure from the published literature (e.g., Saba and Umar 2016; Tarawneh et al. 2019).

The selection of the “Hydrochemical variables” for computation of WQI was made based on their relative significance in defining the water quality for drinking consumption. During the present study, the analytical results of 11 hydrochemical variables of the water samples, namely, pH, TH, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^- , were selected. The highest weight

number, which is 5, was assigned to 6 hydrochemical variables (viz., TDS, Ca^{2+} , Na^+ , K^+ , HCO_3^- , and NO_3^-) as their higher concentration can cause significant deterioration of quality of potable water. Weight number 4 was provided to pH as its values away from 7 indicate the deteriorated quality of the potable water. Weight number 3 was allocated to Mg^{2+} and Cl^- , as these hydrochemical variables are known to cause less damage to the quality of potable water. Weight number 2 was assigned to TH, as its higher values can indicate limited deterioration of the quality of potable water. The lowest weight number 1 was allotted to SO_4^{2-} as the latter is known to cause insignificant deterioration of quality of potable water (Sajil Kumar et al. 2013). Weight numbers provided to the selected hydrochemical variables are shown in Table 1.

Calculation of the value of "Relative Weight" (W_i) of the hydrochemical variables was carried out as stated by the formula

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i},$$

where w_i is the weight number allotted to the i th hydrochemical variable, W_i is the "Relative weight" of the i th hydrochemical variable, and n is the whole number of selected hydrochemical variables ($n = 11$). The obtained values of W_i of the hydrochemical variables are provided in Table 1.

Computation of the value of "Quality rating" of the i th hydrochemical variable (q_i) was established using the following mathematical expression:

$$q_i = \frac{C_i}{S_i} \times 100,$$

where C_i represents the concentration of i th hydrochemical variable in the considered groundwater sample, and S_i is the permissible limit of the concentration of the i th hydrochemical variable as per the guidelines of ISIRI (2009) for potable water.

Calculation of the value of "Sub-Index" of the i th hydrochemical variable (SI_i) of the considered groundwater samples was carried out according to the following equation:

$$SI_i = W_i \times q_i.$$

Calculation of the value of WQI of the considered groundwater sample was established using the following equation:

$$\text{WQI} = \sum_{i=1}^n SI_i.$$

Evaluation of the groundwater quality for agricultural uses

Assessment of groundwater standard for agricultural use was carried out on the basis of the values/ratings generated from ten parameters and three parameter-based bivariate diagrams devised by prominent investigators. The considered parameters and diagrams can reveal salinity- and alkalinity-related and ion-specific hazards of irrigation waters to soil and vegetation. Table 2 provides the framework for the appraisal of the groundwater quality for agricultural purposes.

Results and discussion

Physicochemical characteristics of groundwater

The pH values of the groundwater samples ($n = 66$) vary from 6.8 to 9.1 (av. = 7.3) and indicate that majority (~85%) of samples are mildly alkaline (Table 3). The values of TDS and EC of the groundwater vary, respectively, from 372 to 2595 mg/l (av. = 1061 mg/l) and from 520 to 3630 $\mu\text{S}/\text{cm}$ (av. = 1484 $\mu\text{S}/\text{cm}$). Total hardness (TH) of the groundwater varies from 115 to 1285 mg/l (av. 339 mg/l). Based on the classification proposed by Sawyer and McCarty (1967), the groundwater at the majority (~74%) of the sampling locations can be designated as very hard class (TH > 300 mg/l). At the remaining ~22% and ~4% of the sampling locations, the groundwater belongs to hard water (TH: 150–300 mg/l) and moderately hard water (TH: 75–150 mg/l) classes, respectively. The groundwater, on average and in terms of meq/l, is specified by $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and

Table 1 "Weight" numbers and "relative weight" assigned to hydrochemical variables of the groundwater samples for computation of the values of Water Quality Index of the groundwater samples

Hydrochemical parameter	Permissible limits (mg/l) ISIRI (2009)	Weight (w_i)	Relative weight (W_i)
pH	6.5–9	4	0.093
TDS	1500	5	0.116
TH	500	2	0.047
Ca	300	5	0.116
Mg	150 ^a	3	0.070
Na	200	5	0.116
K	200 ^a	5	0.116
Cl	400	3	0.070
SO_4	400	1	0.023
HCO_3	600 ^a	5	0.116
NO_3	50	5	0.116
		$\Sigma W_i = 43$	$\Sigma W_i = 1$

^aWHO (1997)

Table 2 Parameters and parameter-based bivariate diagrams devised for quality assessment of natural waters for irrigation purposes

Parameters and parameter-based bivariate diagrams	Reference
Salinity Hazard= Values of EC (µS/cm)	Richards (1954)
Sodium Adsorption Ratio (SAR) = $\frac{Na^+}{\sqrt{\frac{(Ca^{2+}+Mg^{2+})}{2}}}$	Bouwer (1978)
Residual Sodium Carbonate (RSC) = $(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+} + K^+)$	Lloyd and Heathcote (1985)
Kelley's Ratio (KR) = $Na^+ / (Ca^{2+} + Mg^{2+})$	Kelley (1951)
Exchangeable Sodium Percentage (ESP) = $[100(-0.0126 + 0.01475 \times SAR)] / [1 + (-0.0126 + 0.01475 \times SAR)]$	Tijani (1994)
Percent Sodium (% Na) = $[(Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + K^+)] \times 100$	Wilcox (1955)
Permeability Index (PI) = $[(Na^+ + \sqrt{HCO_3^-}) / (Ca^{2+} + Mg^{2+} + Na^+)] \times 100$	Doneen (1964)
Chloride Hazard (CH)= concentration of Cl ⁻	Doneen (1964)
Bicarbonate Hazard (BH)= concentration of HCO ₃ ⁻	Mandel and Shiftan (1981)
Magnesium Hazard (MH) = $Mg^{2+} / (Ca^{2+} + Mg^{2+}) \times 100$	Lloyd and Heathcote (1985)
Bivariate EC (µS/cm) versus %Na diagram	Wilcox (1955)
Bivariate PI versus (Tz ⁺ + Tz ⁻) diagram	Doneen (1964)
Bivariate SAR versus EC (µS/cm) diagram	Richards (1954)

All ionic concentrations utilized for above calculation are stated in meq/l

HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻. Average concentration of individual cations to total concentration of cations is 45.07% Na⁺, 34.80% Ca²⁺, 20.06% Mg²⁺, and 0.06% K⁺. On average, the anions are composed of 51.62% HCO₃⁻, 30.14% Cl⁻, 16.12% SO₄²⁻, and 2.11% NO₃⁻. The average concentration of (Na⁺ + K⁺) (6.76 meq/l) is lower than that of (Ca²⁺ + Mg²⁺) (8.02 meq/l) and the average concentration of (HCO₃⁻ + SO₄²⁻) (10.10 meq/l) is higher than that of (Cl⁻ + NO₃⁻) (4.72 meq/l). The average concentration of total ions (Tz⁻ + Tz⁺) equals 29.8 meq/l.

Classification of groundwater

Generally speaking, there are various classifications of groundwater. The principal ones are based on: Cl⁻, SO₄²⁻, and HCO₃⁻ contents; quantities of Base Exchange Index (r₁); quantities of Meteoric Genesis Index (r₂); and concentration of TDS (i.e., salinity).

Categorization of groundwater depending on Cl⁻, SO₄²⁻, and HCO₃⁻ contents

Groundwaters, according to their Cl⁻, SO₄²⁻, and HCO₃⁻ contents, can be classified as normal chloride (Cl⁻ < 15 meq/l), normal sulfate (SO₄²⁻ < 6 meq/l), and normal bicarbonate (HCO₃⁻ content between 2 and 7 meq/l) types (Soltan 1998). In 66 samples, 38 groundwater samples are affiliated to chloride, sulfate, and bicarbonate water types. Out of the 66 groundwater samples, 65, 62, and 39 samples represent

normal chloride, normal sulfate, and normal bicarbonate types. Furthermore, out of 66 samples, 62 samples belong to both chloride and sulfate water types, 38 are related to both sulfate and bicarbonate groups, and 39 belong to both chloride and bicarbonate types. The above data show that the groundwater at ~98% of the sampling sites belongs to chloride type, at ~94% of the sampling locations are of sulfate type, and at ~59% of the bore well locations belongs to bicarbonate group.

Categorization of groundwater based on the base exchange index (r₁)

Base Exchange Index (r₁) as the criterion, Matthes (1982) grouped the groundwater into two categories viz, “Na⁺-SO₄²⁻” and “Na⁺-HCO₃⁻” types. The value of r₁ is arrived at with the following expression:

$$r_1 = (Na^+ - Cl^-) / SO_4^{2-} \text{ (concentrations of all ions in meq/l).}$$

The computed r₁ values of the water samples collected at 66 sampling sites are given in Table 4 and the same data are also presented graphically in Fig. 2a. The r₁ values of the groundwater samples at 44 bore well locations designate them as of Na⁺-SO₄²⁻ type as their r₁ values are < 1. At the remaining 22 bore well locations, r₁ values of the groundwater samples are > 1 and thus belong to Na⁺-HCO₃⁻ group.

Table 3 Physicochemical characteristics of the groundwater samples ($n=66$)

S.No.*	pH	EC	TDS	TH	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	NO ₃
1	7.1	1838	1314	575	120.2	66.8	151.7	4.3	518.6	148.8	230.4	6.2
2	7.4	3630	2595	655	216.4	28.0	528.8	4.3	353.9	662.4	652.3	49.6
3	7.2	1030	736	330	110.2	13.4	80.5	4.3	323.4	124.8	78.0	6.2
4	7.4	1211	866	420	140.3	17.0	82.8	4.3	427.1	115.2	70.9	12.4
5	7.8	520	372	130	40.1	7.3	57.5	2.0	91.5	96.0	53.2	0.0
6	6.9	3240	2317	1285	190.4	196.9	149.4	5.1	366.1	873.6	283.6	6.2
7	7.4	725	518	185	34.1	24.3	78.2	2.7	244.1	52.8	67.4	6.2
8	7.5	866	619	350	80.2	36.5	34.5	3.1	274.6	100.8	63.8	6.2
9	7.4	2010	1437	580	130.3	62.0	183.9	4.3	732.2	148.8	159.5	130.2
10	7	1456	1041	565	100.2	76.6	69.0	4.3	488.1	110.4	141.8	31.0
11	7.3	2100	1502	190	50.1	15.8	367.8	4.3	610.2	244.8	166.6	18.6
12	7.2	1390	994	530	150.3	37.7	71.3	4.3	518.6	57.6	141.8	18.6
13	7.4	1310	937	520	100.2	65.6	57.5	4.3	427.1	187.2	70.9	43.4
14	7.2	1210	865	500	150.3	30.4	46.0	4.3	427.1	67.2	124.1	6.2
15	7.3	1102	788	440	120.2	34.0	46.0	4.3	427.1	110.4	53.2	6.2
16	6.9	1302	931	460	150.3	20.7	82.8	4.3	427.1	144.0	99.3	37.2
17	7.3	1196	855	510	120.2	51.0	34.5	4.3	427.1	129.6	70.9	6.2
18	7	1077	770	465	120.2	40.1	27.6	4.3	396.6	96.0	70.9	6.2
19	7.2	844	603	315	100.2	15.8	46.0	3.1	347.8	57.6	46.1	12.4
20	7.5	1073	767	350	110.2	18.2	80.5	4.3	366.1	86.4	95.7	18.6
21	6.9	1758	1257	615	150.3	58.3	114.9	4.3	610.2	182.4	124.1	55.8
22	6.9	1139	814	440	150.3	15.8	52.9	4.3	488.1	76.8	53.2	0.0
23	7.2	1188	849	280	50.1	37.7	137.9	4.3	457.6	100.8	70.9	18.6
24	7.2	1234	882	455	120.2	37.7	69.0	4.3	457.6	48.0	92.2	6.2
25	7.7	820	586	255	80.2	13.4	69.0	3.1	213.6	96.0	88.6	0.0
26	7	1018	728	250	90.2	6.1	114.9	4.3	396.6	19.2	106.4	6.2
27	7	1326	948	475	110.2	48.6	80.5	4.3	518.6	96.0	88.6	12.4
28	6.8	1580	1130	655	206.4	34.0	57.5	4.3	573.6	57.6	177.3	6.2
29	7.3	1565	1119	420	110.2	35.2	160.9	4.3	549.2	163.2	106.4	6.2
30	7.3	825	590	305	90.2	19.4	46.0	3.1	366.1	33.6	46.1	18.6
31	7.2	1022	731	410	120.2	26.7	41.4	4.3	396.6	81.6	63.8	18.6
32	7.2	862	616	360	116.2	17.0	29.9	3.1	414.9	9.6	49.6	24.8
33	7.3	816	583	300	100.2	12.2	46.0	3.1	396.6	19.2	35.5	18.6
34	7.1	930	665	360	80.2	38.9	46.0	3.5	366.1	28.8	88.6	31.0
35	7.5	791	566	205	60.1	13.4	85.1	2.7	366.1	19.2	42.5	0.0
36	7.3	1203	860	290	30.1	52.3	137.9	4.3	457.6	86.4	88.6	24.8
37	7.4	3020	2159	150	40.1	12.2	620.7	5.1	854.2	67.2	514.1	0.0
38	7.4	2010	1437	200	60.1	12.2	367.8	4.7	549.2	91.2	319.1	18.6
39	7.2	2060	1473	195	70.1	4.9	379.3	4.7	732.2	67.2	248.2	0.0
40	6.9	1260	901	505	120.2	49.8	52.9	4.3	610.2	19.2	70.9	43.4
41	9.1	1864	1333	285	92.2	13.4	287.4	4.3	109.8	144.0	475.1	0.0
42	7.5	1785	1276	430	80.2	55.9	206.9	4.3	396.6	172.8	265.9	43.4
43	7	900	644	385	110.2	26.7	27.6	3.1	427.1	38.4	35.5	43.4
44	7.5	1503	1075	245	80.2	10.9	229.9	4.3	335.6	206.4	177.3	12.4
45	7.3	1387	992	475	116.2	45.0	92.0	4.3	500.3	38.4	163.1	31.0
46	7.1	728	521	315	90.2	21.9	18.4	2.7	335.6	24.0	35.5	18.6
47	7.2	1634	1168	620	120.2	77.8	85.1	4.3	506.4	192.0	134.7	55.8
48	7.2	1220	872	495	100.2	59.5	48.3	4.3	549.2	48.0	70.9	12.4
49	7.3	1468	1050	395	100.2	35.2	149.4	4.3	427.1	52.8	223.4	18.6
50	6.9	1830	1308	630	140.3	68.1	126.4	4.3	701.7	134.4	134.7	55.8
51	6.9	1236	884	460	150.3	20.7	66.7	4.3	482.0	67.2	99.3	31.0

Table 3 (continued)

S.No.*	pH	EC	TDS	TH	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	NO ₃
52	6.9	1348	964	310	90.2	20.7	160.9	4.3	427.1	81.6	159.5	37.2
53	7.2	1452	1038	465	100.2	52.3	114.9	4.3	549.2	62.4	141.8	31.0
54	7.6	1380	987	465	70.1	70.5	98.9	4.3	518.6	52.8	141.8	0.0
55	7.1	1330	951	355	120.2	13.4	137.9	4.3	396.6	62.4	187.9	24.8
56	7	1249	893	415	140.3	15.8	89.7	4.3	549.2	9.6	106.4	31.0
57	7.5	1537	1099	405	100.2	37.7	160.9	4.3	427.1	28.8	265.9	18.6
58	7.4	2800	2002	115	30.1	9.7	586.2	4.7	976.3	206.4	265.9	0.0
59	7.4	2830	2023	210	50.1	20.7	551.8	0.0	732.2	292.8	354.5	18.6
60	8	1178	842	175	30.1	24.3	183.9	4.3	305.1	48.0	195.0	0.0
61	7.3	2040	1459	310	80.2	26.7	321.9	4.3	396.6	81.6	425.4	18.6
62	7.3	1729	1236	250	50.1	30.4	275.9	4.3	671.2	91.2	141.8	0.0
63	7.3	1534	1097	405	110.2	31.6	160.9	8.2	396.6	57.6	262.4	18.6
64	7.4	1885	1348	480	100.2	55.9	206.9	4.3	457.6	124.8	301.3	12.4
65	7.4	2830	2023	305	60.1	37.7	505.8	4.7	732.2	273.6	368.7	18.6
66	7.3	1728	1236	450	170.3	6.1	183.9	4.3	732.2	33.6	152.4	0.0
Ave	7.3	1484	1061	399	102.6	34.7	152.5	4.1	469.8	115.2	159.1	19.5
Max	9.1	3630	2595	1285	216.4	196.9	620.7	8.2	976.3	873.6	652.3	130.2
Min	6.8	520	372	115	30.1	4.9	18.4	0.0	91.5	9.6	35.5	0.0

S. No* sample number; all ions, TH and TDS are in mg/l; EC in µS/cm

Categorization of groundwater depending on the values of meteoric genesis index (r_2):

Meteoric Genesis Index (r_2) of the water samples gathered from the study region was computed using the following equation:

$$r_2 = [(Na^+ + K^+) - Cl^-] / SO_4^{2-} \text{ (concentrations of all ions in meq/l).}$$

The r_2 values of the water samples gathered at 66 sampling sites are provided in (Table 4) and the same data are presented in Fig. 2b. The results show that at 43 bore well locations, the groundwater belongs to deep meteoric percolation type (r_2 values < 1) and the groundwater at the remaining 23 sampling sites is of shallow meteoric percolation type (r_2 values > 1) (Soltan 1998).

Comparison of r_1 and r_2 values implies that at 43 sampling sites, the groundwater is allied to $Na^+ - SO_4^{2-}$ type and constitutes the deep meteoric percolation type. Out of the remaining 23 sample locations, the groundwater at 22 locations related to “ $Na^+ - HCO_3^-$ ” type and conform to shallow meteoric percolation type, and at BW No. 40 locations, the groundwater is of $Na^+ - SO_4^{2-}$ type but constitutes shallow meteoric percolation type. Based on the above information, the groundwater encountered at a large number of the sampling sites belongs to $Na^+ - SO_4^{2-}$ type and constitutes deep meteoric percolation type.

Categorization of groundwater depending on TDS concentration

Davis and Wiest (1966) categorized natural waters based on the concentration of Total Dissolved Solids (TDS) into freshwater (TDS < 1000 mg/l), brackish water (TDS between 1000 and 10,000 mg/l), saline water (TDS between 10,000 and 1,00,000 mg/l), and brine water (TDS > 1,00,000 mg/l). The water samples gathered at 66 sampling sites in the study region belong to two types: freshwater and brackish water. Freshwater type of groundwater appeared at 38 places, whereas the brackish water type is found at 28 sites. Table 5 provides the locations of the bore wells yielding fresh and brackish ground waters in the study area.

Degree of evolution

The dissolved load in groundwater increases in proportionate to its length of flow (Freeze and Cherry 1979) and anion chemistry reveals the degree of its evolution in the subsurface environment (Chebotarev 1955). The average analytical data of the groundwater samples show relatively higher levels of HCO_3^- (7.77 meq/l) followed by Cl^- (4.40 meq/l), SO_4^{2-} (2.48 meq/l), and NO_3^- (0.32 meq/l). Samples containing bicarbonate as the principal anion, as in the present case, imply the zone of dynamic groundwater movement and least residence time.

Table 4 Calculated parameters of the groundwater samples for classification of the groundwater and assessment of natural mechanisms controlling the hydrochemistry and sources of dissolved solids in the groundwater

S.No	r_1^*	r_2^*	Gibb's ratio ₁	Gibb's ratio ₂	CAI [*] I	CAI [*] II	C-ratio*	Ca/HCO ₃	Ca/SO ₄	Mg HCO ₃	Mg/SO ₄	(Na+K)/Tz + HCO ₃	(Ca+Mg)/ HCO ₃	(Ca+Mg)/(Na+K)	Na/Cl
1	0.03	0.07	0.60	0.37	-0.70	-0.21	0.73	0.71	1.94	0.65	1.77	0.37	1.35	1.71	1.02
2	0.33	0.34	0.70	0.22	-0.83	-0.22	0.30	1.86	0.78	0.40	0.17	0.64	2.26	0.57	1.25
3	0.50	0.54	0.47	0.29	-0.23	-0.07	0.67	1.04	2.12	0.21	0.42	0.35	1.25	1.83	1.59
4	0.67	0.71	0.32	0.19	0.12	0.03	0.74	1.00	2.92	0.20	0.58	0.31	1.20	2.26	1.80
5	0.50	0.52	0.59	0.10	-2.14	-0.34	0.43	1.33	1.00	0.40	0.30	0.50	1.73	1.02	1.67
6	-0.08	-0.08	0.19	0.10	0.13	0.02	0.25	1.58	0.52	2.70	0.89	0.21	4.28	3.88	0.81
7	1.36	1.43	0.33	0.12	-0.60	-0.09	0.78	0.42	1.55	0.50	1.82	0.48	0.92	1.07	1.79
8	-0.14	-0.10	0.35	0.11	-0.60	-0.09	0.68	0.89	1.91	0.67	1.43	0.18	1.56	4.43	0.83
9	1.13	1.16	0.43	0.19	-0.64	-0.14	0.79	0.54	2.10	0.42	1.65	0.41	0.97	1.43	1.78
10	-0.44	-0.39	0.33	0.08	-1.08	-0.13	0.78	0.62	2.18	0.79	2.74	0.22	1.41	3.63	0.75
11	2.22	2.24	0.86	0.39	-0.47	-0.23	0.66	0.25	0.49	0.13	0.25	0.81	0.38	0.24	3.40
12	-0.75	-0.66	0.21	0.15	0.35	0.07	0.88	0.88	6.25	0.36	2.58	0.23	1.25	3.30	0.77
13	0.13	0.16	0.57	0.21	-0.70	-0.21	0.64	0.71	1.28	0.77	1.38	0.20	1.49	3.99	1.25
14	-1.07	-0.99	0.22	0.11	0.01	0.00	0.83	1.07	5.36	0.36	1.79	0.17	1.43	4.74	0.57
15	0.22	0.27	0.29	0.11	-0.41	-0.06	0.75	0.86	2.61	0.40	1.22	0.19	1.26	4.17	1.33
16	0.27	0.30	0.38	0.19	0.16	0.04	0.70	1.07	2.50	0.24	0.57	0.29	1.31	2.48	1.29
17	-0.19	-0.14	0.28	0.14	-0.06	-0.01	0.72	0.86	2.22	0.60	1.56	0.14	1.46	6.34	0.75
18	-0.40	-0.35	0.24	0.14	0.20	0.03	0.76	0.92	3.00	0.51	1.65	0.12	1.43	7.10	0.60
19	0.58	0.65	0.43	0.21	-0.34	-0.08	0.83	0.88	4.17	0.23	1.08	0.25	1.11	3.03	1.54
20	0.44	0.51	0.28	0.10	-0.61	-0.08	0.77	0.92	3.06	0.25	0.83	0.34	1.17	1.94	1.30
21	0.39	0.42	0.25	0.23	0.40	0.12	0.72	0.75	1.97	0.48	1.26	0.29	1.23	2.41	1.43
22	0.50	0.57	0.83	0.16	-1.44	-0.30	0.83	0.94	4.69	0.16	0.81	0.21	1.10	3.65	1.53
23	1.90	1.96	0.38	0.14	-0.85	-0.15	0.78	0.33	1.19	0.41	1.48	0.52	0.75	0.92	3.00
24	0.40	0.51	0.22	0.08	-0.28	-0.03	0.88	0.80	6.00	0.41	3.10	0.25	1.21	2.93	1.15
25	0.25	0.29	0.74	0.13	-2.05	-0.35	0.64	1.14	2.00	0.31	0.55	0.38	1.46	1.66	1.20
26	5.00	5.27	0.60	0.21	-0.10	-0.03	0.94	0.69	11.26	0.08	1.25	0.51	0.77	0.98	1.67
27	0.50	0.55	0.34	0.11	-0.10	-0.02	0.81	0.65	2.75	0.47	2.00	0.28	1.12	2.63	1.40
28	-2.08	-1.99	0.76	0.81	0.06	0.04	0.89	1.10	8.59	0.30	2.33	0.17	1.39	5.02	0.50
29	1.18	1.21	0.43	0.15	-0.44	-0.08	0.73	0.61	1.62	0.32	0.85	0.46	0.93	1.18	2.33
30	1.00	1.11	0.75	0.35	-1.02	-0.34	0.90	0.75	6.43	0.27	2.29	0.25	1.02	2.93	1.54
31	0.00	0.06	0.54	0.32	-0.15	-0.06	0.79	0.92	3.53	0.34	1.29	0.19	1.26	4.29	1.00
32	-0.50	-0.10	0.32	0.17	-0.07	-0.02	0.97	0.85	29.02	0.21	7.00	0.16	1.06	5.22	0.93
33	2.50	2.70	0.61	0.34	-0.05	-0.02	0.94	0.77	12.51	0.15	2.50	0.26	0.92	2.89	2.00
34	-0.83	-0.68	0.38	0.14	-0.30	-0.04	0.91	0.67	6.67	0.53	5.33	0.22	1.20	3.45	0.80
35	6.25	6.43	0.33	0.21	0.20	0.06	0.94	0.50	7.50	0.18	2.75	0.48	0.68	1.09	3.08
36	1.94	2.01	0.37	0.19	-0.32	-0.07	0.81	0.20	0.83	0.57	2.39	0.51	0.77	0.95	2.40

Table 4 (continued)

S.No	r_1^*	r_2^*	Gibb's ratio ₁	Gibb's ratio ₂	CAI _I [*]	CAI _{II} [*]	C-ratio [*]	Ca/HCO ₃	Ca/SO ₄	Mg/HCO ₃	Mg/SO ₄	(Na+K)/Tz+	(Ca+Mg)/HCO ₃	(Ca+Mg)/(Na+K)	Na/Cl
37	8.93	9.02	0.61	0.40	0.03	0.01	0.91	0.14	1.43	0.07	0.71	0.90	0.21	0.11	1.86
38	3.68	3.75	0.62	0.38	0.05	0.03	0.83	0.33	1.58	0.11	0.53	0.80	0.44	0.25	1.78
39	6.79	6.87	0.42	0.23	0.22	0.06	0.90	0.29	2.50	0.03	0.29	0.81	0.32	0.23	2.36
40	0.75	1.02	0.65	0.27	-0.58	-0.19	0.96	0.60	15.01	0.41	10.25	0.19	1.01	4.19	1.15
41	-0.30	-0.26	0.45	0.25	0.11	0.03	0.38	2.56	1.53	0.61	0.37	0.69	3.17	0.45	0.93
42	0.42	0.45	0.40	0.16	-0.34	-0.08	0.64	0.62	1.11	0.71	1.28	0.51	1.32	0.94	1.20
43	0.25	0.35	0.23	0.24	0.48	0.15	0.90	0.79	6.88	0.31	2.75	0.14	1.10	6.02	1.20
44	1.16	1.19	0.54	0.21	-0.28	-0.07	0.56	0.73	0.93	0.16	0.21	0.67	0.89	0.48	2.00
45	-0.75	-0.61	0.32	0.10	-0.20	-0.03	0.91	0.71	7.25	0.45	4.63	0.30	1.16	2.31	0.87
46	-0.40	-0.26	0.56	0.31	-0.03	-0.01	0.92	0.82	9.01	0.33	3.60	0.12	1.15	7.24	0.80
47	-0.03	0.00	0.68	0.40	-0.07	-0.03	0.67	0.72	1.50	0.77	1.60	0.24	1.49	3.25	0.97
48	0.10	0.21	0.85	0.17	-2.03	-0.48	0.90	0.56	5.00	0.54	4.90	0.18	1.10	4.48	1.05
49	0.18	0.28	0.72	0.40	-0.21	-0.09	0.86	0.71	4.55	0.41	2.64	0.46	1.13	1.20	1.03
50	0.61	0.65	0.43	0.21	0.00	0.00	0.80	0.61	2.50	0.49	2.00	0.31	1.10	2.25	1.45
51	0.07	0.15	0.52	0.17	-0.89	-0.22	0.85	0.95	5.36	0.22	1.21	0.25	1.16	3.06	1.04
52	1.47	1.53	0.80	0.52	-0.18	-0.10	0.80	0.64	2.65	0.24	1.00	0.53	0.89	0.87	1.56
53	0.77	0.85	0.30	0.10	-0.78	-0.08	0.87	0.56	3.85	0.48	3.31	0.35	1.03	1.82	1.25
54	0.27	0.37	0.85	0.05	-11.11	-0.63	0.89	0.41	3.18	0.68	5.27	0.32	1.09	2.11	1.07
55	0.54	0.62	0.86	0.37	-0.79	-0.35	0.83	0.92	4.62	0.17	0.85	0.46	1.09	1.16	1.13
56	4.50	5.05	0.44	0.17	-0.46	-0.09	0.98	0.78	35.02	0.14	6.50	0.33	0.92	2.07	1.30
57	-0.84	-0.65	0.88	0.21	-2.43	-0.57	0.92	0.71	8.34	0.44	5.17	0.47	1.16	1.14	0.93
58	4.19	4.21	0.85	0.25	-1.37	-0.47	0.79	0.09	0.35	0.05	0.19	0.92	0.14	0.09	3.40
59	2.30	2.30	0.45	0.44	0.17	0.04	0.66	0.21	0.41	0.14	0.28	0.85	0.35	0.18	2.40
60	2.50	2.61	0.48	0.16	-0.48	-0.10	0.83	0.30	1.50	0.40	2.00	0.70	0.70	0.43	1.45
61	1.17	1.24	0.89	0.33	-1.13	-0.41	0.79	0.62	2.35	0.34	1.29	0.69	0.95	0.44	1.17
62	4.21	4.27	0.92	0.33	-1.40	-0.49	0.85	0.23	1.32	0.23	1.32	0.71	0.45	0.41	3.00
63	-0.33	-0.16	0.59	0.18	-0.80	-0.17	0.84	0.85	4.59	0.40	2.17	0.47	1.25	1.12	0.95
64	0.19	0.23	0.95	0.21	-2.42	-0.65	0.74	0.67	1.92	0.61	1.77	0.49	1.28	1.05	1.06
65	2.04	2.06	0.94	0.38	-0.87	-0.42	0.68	0.25	0.53	50.33	25.00	0.78	0.51	0.28	2.11
66	5.29	5.44	0.71	0.65	-0.26	-0.12	0.94	0.71	12.15	25.22	77.27	0.47	0.75	1.11	1.86
Avg							0.78					0.40	1.14	2.30	

r_1^* base exchange index, r_2^* Meteoric Genesis Index, CAI^{*} Chloro-Alkaline Index, C-ratio^{*} HCO₃⁻/(HCO₃⁻ + SO₄²⁻)

All ionic ratios are in meq/l

Fig. 2 Base Exchange Index (r1) (a) and Meteoric Genesis Index (r2) (b) of groundwater samples

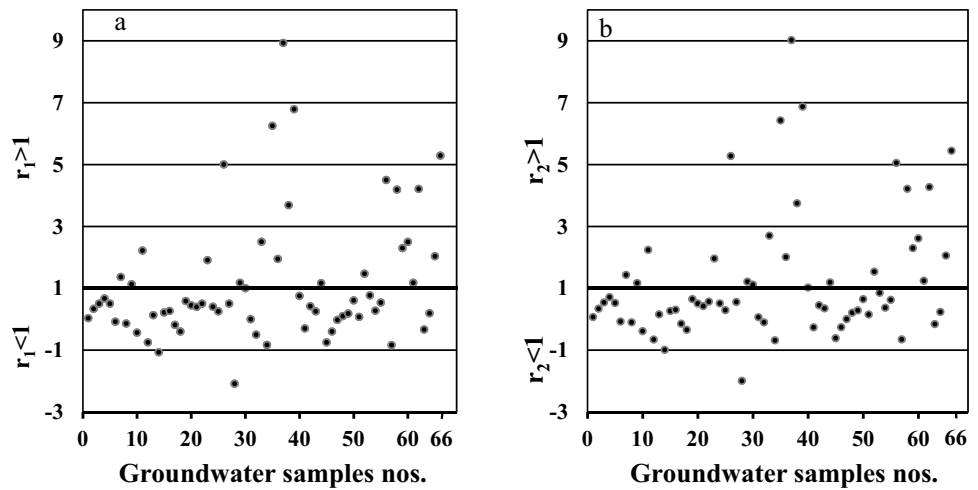
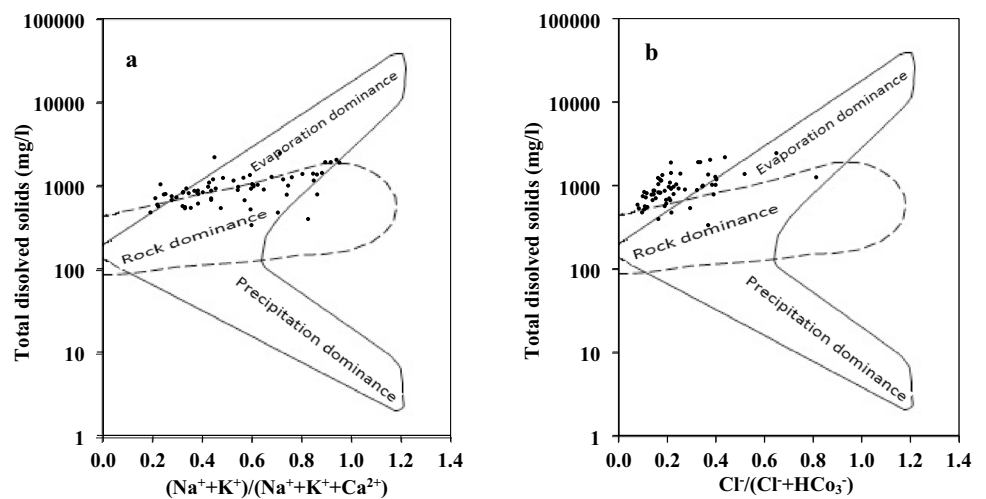


Table 5 Classification of the groundwater encountered at the bore well locations ($n = 66$) based on TDS content

Groundwater type	Bore wells yielding the specified type of groundwater
Freshwater TDS: < 1000 mg/l	Bore well nos: 3–5, 7, 8, 12 to 20, 22–27, 30–36, 40, 43, 45, 46, 48, 51, 52, 54–56, and 60 Total: 38 bore wells
Brackish water TDS: Between 1000 and 10,000 mg/l	1, 2, 6, 9–11, 21, 28, 29, 37 to 39, 41, 42, 44, 47, 49, 50, 53, 57–59, and 61–66 Total: 28 bore wells

Fig. 3 Bivariate TDS versus Gibbs’s ratio I diagram (a) and TDS versus Gibbs’s ratio II diagrams (b)

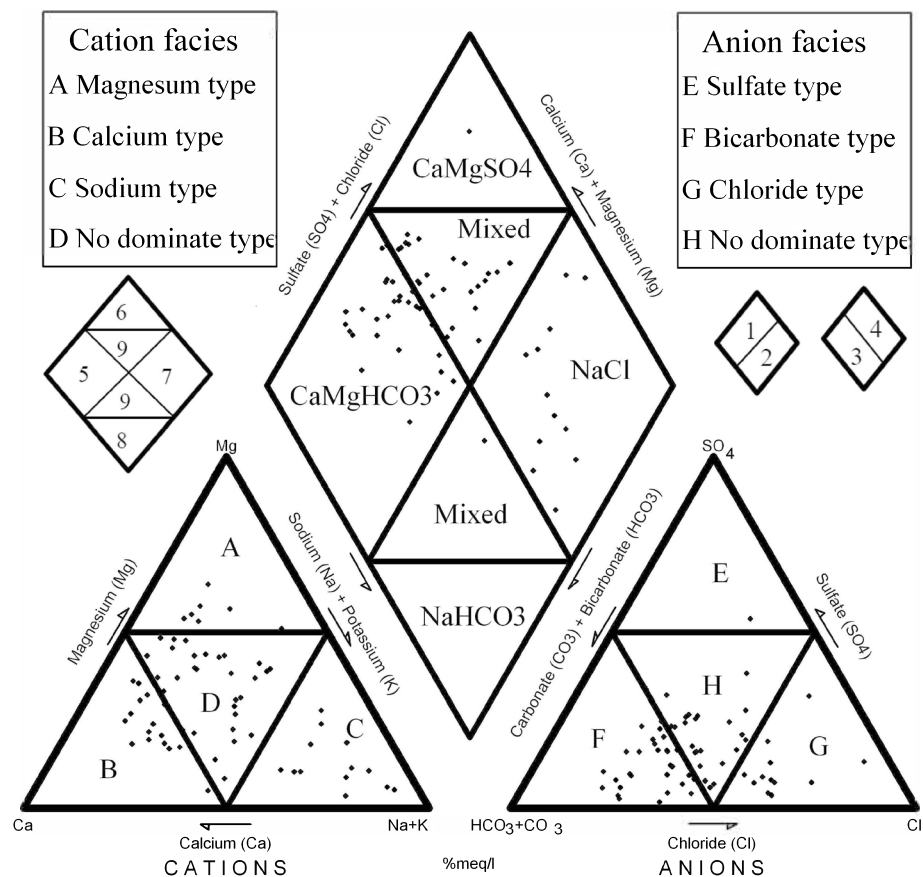


Natural mechanisms controlling hydrochemistry

Plots of hydrochemical data on graphs of TDS versus Gibbs’s ratio I $[(Na + + K +)/(Na + + K + + Ca^{2+})]$ and TDS versus Gibbs’s ratio II $[Cl^{-}/(Cl^{-} + HCO_3^{2-})]$ (Gibbs 1970) give a clue on the sources of dissolved solids in the groundwater. These diagrams reveal the importance of three major natural mechanisms controlling water chemistry, viz., mineral weathering, atmospheric precipitation,

and evaporation and fractional crystallization. On the graph of TDS versus Gibbs’s ratio I (Table 4; Fig. 3a), the samples plot mainly in the rock dominance and evaporation dominance fields. On the bivariate TDS versus Gibbs’s ratio II diagram (Table 4; Fig. 3b), the samples plot mainly near and above the boundary lines of rock dominance and evaporation dominance fields. The above data indicate that the hydrochemistry of the groundwater is controlled mainly by rock weathering reactions and

Fig. 4 Piper trilinear diagram (Piper 1944) showing the hydrochemical characteristics and hydrochemical facies of the groundwater samples



minimally by evaporation processes (Khairy and Janardhana 2013; Şehnaz et al. 2020). The samples which did not plot in the specified domains may indicate the influence of anthropogenic sources (Adimalla and Venkatayogi 2017).

Hydrochemical facies

The plot of the Hydrochemical data of the groundwater samples ($n=66$) on Piper diagram (Piper, 1944) (Fig. 4) show that, cation facies-wise, 16 samples are calcium type, 14 samples are sodium type, 7 samples are magnesium type, and in 29 samples, none of the cations dominates. Anion facies-wise, 28 samples are bicarbonate type, 12 samples are chloride type, 1 sample is sulfate type, and in 25 samples, none of the anion ions dominates. Among the groundwater samples, hydrochemical facies-wise, 27 samples belong to $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ facies, 13 samples belong to $\text{Na}^+\text{-Cl}^-$ facies, and 26 samples belong to mixed facies (i.e., $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$ hydrochemical facies of Back, 1966).

Ion-exchange reactions

It is observed that groundwater encountered at different locations of a given terrain, barring rare exceptions, participates in ion-exchange reactions with clay minerals (exchanger) of

the aquifer matrix (Cardona et al. 2004). The type of ion-exchange reaction (i.e., either direct cation-exchange reaction or reverse cation–anion-exchange reaction) witnessed by the water at a given location may vary seasonally, but invariably depends on its hydrochemical composition.

Ion-exchange reactions witnessed by water at the 66 sampling sites were evaluated based on the values of Chloro-Alkaline Indices (CAI-I and II) of the groundwater samples. The CAI values were computed according to the equations provided by Schoeller (1977) and the obtained data are provided in Table 4. The data reveal that during the sampling season, the water at 50 sampling sites was specified by negative CAI-I and II values implying the water in these locations was witnessing reverse cation–anion reaction. At the remaining 16 sampling sites, the groundwater samples were characterized by positive values of CAI-I and II and the latter designate direct cation-exchange reaction of waters with clay minerals (exchanger) of the aquifer matrix.

It is well known that direct cation-exchange reaction provides a certain amount of alkalies while a similar amount of alkaline earths is being removed from the groundwaters. Reverse cation–anion-exchange reaction involves the addition of a certain amount of alkaline earths and simultaneous removal of similar amount of alkalies from the groundwater. In the study region, the ion-exchange reactions resulted in a

significant addition of alkaline earths and removal of similar amounts of alkalies. These data suggests that the ion-exchange process can be considered as one among the few sources of alkaline earths to the groundwater of the study region (Jamshidzadeh 2020; Nematollahi et al. 2018).

Multivariate statistical analyses

Correlation matrix

Correlation analysis has a pivotal role in the hydrogeochemical investigation. The correlation matrix can demonstrate the dependence between different parameters, thus revealing the association between different variables and controlling factors. A correlation coefficient near 1 or at 1 demonstrates a good positive relationship and a correlation coefficient around zero shows no relationship between two variables at a significant level of $p < 0.05$. Generally, the parameters with $r > 0.7$ show a strong correlation, and r between 0.5 and 0.7 indicates moderate correlation (Şehnaz et al. 2020). The computed correlation matrices of the analyzed physicochemical variables ($n = 12$) of the groundwater samples are provided in Table 6. Among the variables, EC shows high positive correlation with TDS (0.99), Na^+ (0.81), and Cl^- (0.88), and moderate positive correlation with K^+ (0.67), HCO_3^- (0.61), and SO_4^{2-} (0.54). Likewise, TDS shows high positive correlation with Na^+ (0.79), and Cl^- (0.88) and moderate positive correlation with K^+ (0.66), HCO_3^- (0.58), and SO_4^{2-} (0.53). Na^+ shows high positive correlation with Cl^- (0.86), moderate positive correlation with K^+ (0.54), and weak positive correlation with HCO_3^- (0.37) and SO_4^{2-} (0.41). K^+ shows moderate positive correlation with Cl^- (0.63) and weak positive correlation with HCO_3^- (0.47) and SO_4^{2-} (0.32). Mg^{2+} shows weak positive correlation with Ca^{2+} (0.25), HCO_3^- (0.23), and SO_4^{2-} (0.24) and very

weak positive correlation with K^+ (0.14). Ca^{2+} shows very weak positive correlation with K^+ (0.15) and HCO_3^- (0.11). HCO_3^- shows weak-to-very weak positive correlation with K^+ (0.47), Na^+ (0.37), Mg^{2+} (0.23), and Ca^{2+} (0.11). Likewise, SO_4^{2-} shows weak-to-very weak positive correlation with K^+ (0.32), Na^+ (0.41), and Mg^{2+} (0.24). Cl^- shows high-to-moderate positive correlation with Na^+ (0.86) and K^+ (0.63). The observed high positive correlation between EC and TDS, high-to-moderate positive correlation between Na^+ , K^+ , and Cl^- and their weak positive correlation with Mg^{2+} , HCO_3^- , and SO_4^{2-} , and weak-to-very weak positive correlation of Mg^{2+} with Ca^{2+} , K^+ , HCO_3^- , and SO_4^{2-} may confirm the presence of connate saline water in the Quaternary deposits of the aquifer (Khairy and Janardhana 2013).

In groundwaters, a significant amount of alkaline earths is derived essentially from mineral weathering/dissolution aided by H_2CO_3 and H_2SO_4 , and in such cases, alkaline earths ($\text{Ca}^{2+} \pm \text{Mg}^{2+}$) exhibit very high-to-high positive correlation with HCO_3^- and SO_4^{2-} . In the present study, the alkaline earths were found to exhibit weak-to-extremely weak correlation with HCO_3^- and SO_4^{2-} . The observed poor positive correlation of alkaline earths with genetically related acids (i.e., HCO_3^- and SO_4^{2-}) can be explained if the net contributions of alkaline earths from ion-exchange processes witnessed by the groundwater are considered. As mentioned in the section of ion-exchange reactions, the groundwater was found witnessing reverse cation–anion-exchange reaction with exchanger (clay minerals) of the aquifer matrix at 50 out of 66 groundwater sampling locations. This reverse cation–anion-exchange reaction at majority of the sampling sites provided the significant concentration of alkaline earths to the groundwater. Hence, the observed weak-to-very weak positive correlation of alkaline earths with HCO_3^- and SO_4^{2-} has to be attributed to

Table 6 Correlation coefficient matrix of the physicochemical variables of the groundwater samples ($n = 66$)

	EC	pH	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
EC	1.00											
pH	0.06	1.00										
TDS	0.99^a	0.06	1.00									
TH	0.22	-0.46 ^a	0.21	1.00								
Ca^{2+}	0.08	-0.55 ^a	0.09	0.81^a	1.00							
Mg^{2+}	0.23	-0.21	0.19	0.73^a	0.25 ^b	1.00						
Na^+	0.81^a	0.36 ^a	0.79^a	-0.27 ^b	-0.32 ^a	-0.13	1.00					
K^+	0.67^a	-0.10	0.66^a	0.19	0.15	0.14	0.54 ^a	1.00				
HCO_3^-	0.61^a	-0.26 ^b	0.58^a	0.24	0.11	0.23	0.37 ^a	0.47 ^a	1.00			
SO_4^{2-}	0.54 ^a	0.17	0.53 ^a	0.16	0.02	0.24	0.41 ^a	0.32 ^a	0.13	1.00		
Cl^-	0.88^a	0.22	0.88^a	0.02	-0.09	0.06	0.86^a	0.63^a	0.33 ^a	0.38 ^a	1.00	
NO_3^-	0.14	-0.33 ^a	0.10	0.40 ^a	0.29 ^b	0.40 ^a	-0.06	-0.04	0.13	0.07	0.01	1.00

^aCorrelation is significant at the 0.01 level

^bCorrelation is significant at the 0.05 level

the significant derivation of alkaline earths from the ion-exchange process.

Factor analysis

Factor analysis is a multivariate statistical approach that can be used for studying the correlation between a set of variables (Yu and He 2006). The essential objective of the factor analysis is to discover the role of each variable and also simplify the structure of the pure data. Kaiser–Meyer–Olkin (KMO) Measure of Sampling Adequacy (MSA) is calculated in SPSS and is often used to distinguish if a dataset is “suitable” for factor analysis. In this research, a KMO value of 0.52 was attained, so the hydrochemical data are proper to carry out Principal Component Analysis (PCA). PCA was used as a factor analysis method with considering of varimax rotation technique and eigenvalue > 1 (Yang et al. 2016). Factor analysis of the analytical data of the physicochemical variables of the groundwater brought to light 4 factors with Eigenvalues > 1. These factors have been extracted from the principal factor matrix after varimax rotation. These independent factors account for 80.57% of the total variance of the data set (Table 7). Factor-1 accounts for 31.19% of the total variance and has strong positive loadings of TDS (0.936), Na⁺ (0.927), and Cl⁻ (0.894), moderate positive loadings of EC (0.680) and SO₄²⁻ (0.601) and weak positive loading of HCO₃⁻ (0.429) and very weak positive loadings of K⁺ (0.22) and Mg²⁺ (0.12). The strong-to-very weak positive loadings of Na⁺, Cl⁻, HCO₃⁻, SO₄²⁻,

Table 7 Principal and R-mode varimax-rotated factor loadings of the physicochemical variables of the groundwater samples

Variables	Varimax-rotated factor matrix			
	Factor-1	Factor-2	Factor-3	Factor-4
EC	0.663	0.171	0.125	0.600
pH	0.341	-0.316	-0.692	-0.191
TDS	0.936	0.225	0.177	0.094
TH	0.001	0.969	0.144	0.122
Ca ²⁺	-0.121	0.742	0.261	0.051
Mg ²⁺	0.108	0.814	-0.013	0.140
Na ⁺	0.930	-0.313	0.096	0.028
K ⁺	0.234	0.310	0.537	-0.369
HCO ₃ ⁻	0.424	-0.165	0.744	0.300
SO ₄ ²⁻	0.602	0.629	-0.219	0.065
Cl ⁻	0.916	0.044	-0.064	-0.093
NO ₃ ⁻	0.006	0.242	0.125	0.854
Eigenvalues	3.757	3.011	1.534	1.412
% Variance	31.312	25.089	12.782	11.769
Cumulative %	31.312	56.402	69.183	80.952

Extraction method: Principal component analysis; Rotation method: Varimax with Kaiser normalization.

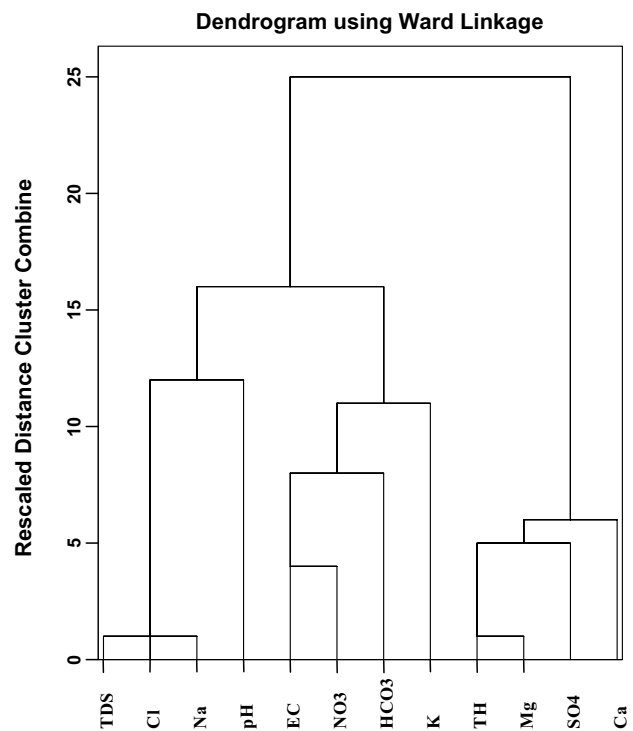


Fig. 5 Dendrogram showing clustering of hydrogeochemical variables of the groundwater samples

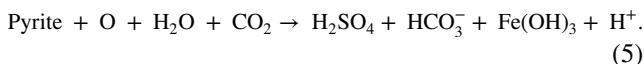
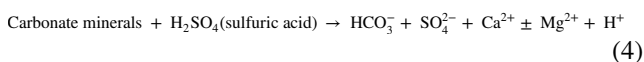
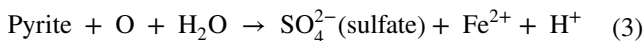
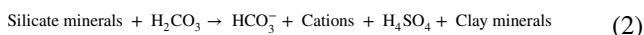
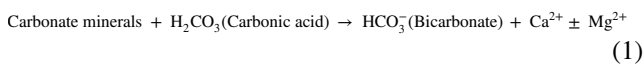
K⁺, and Mg²⁺ of the Factor-1 may be related to connate saline water of the sedimentary layers of the aquifer, which now constitutes the admixed component of the groundwater. Factor-2 accounts for 25.2% of the total variance and has strong positive loadings of TH (0.969), Mg²⁺ (0.809), and Ca²⁺ (0.742) and moderate positive loading of SO₄⁻² (0.623). The high-to-moderate positive loadings of Ca²⁺, Mg²⁺, and SO₄⁻² of the Factor-2 may indicate derivation of significant concentration of alkaline earths from weathering of carbonate minerals, including dolomite. Factor-3 accounts for 12.74% of the total variance and has moderate positive loadings of HCO₃⁻ (0.742) and K⁺ (0.550) and weak positive loading of Ca²⁺ (0.253). The observed positive loadings of HCO₃⁻, K⁺, and Ca²⁺ of the Factor-3 may indicate derivation of a certain amount of K⁺ of the groundwater from weathering of K-bearing silicate minerals aided by carbonic acid. Factor-4 accounts for 11.43% of the total variance, and has strong positive loading of NO₃⁻ (0.828) and moderate positive loading of EC (0.567). High positive loading of NO₃⁻ of the Factor-4 may indicate the presence of the same in the groundwater as a consequence of pollution caused by anthropogenic inputs (e.g., nitrogenous fertilizers, industrial effluents, human and animal waste, and bio-combustion).

Cluster analysis

Cluster analysis performed on physicochemical variables of the groundwater samples brought to light two major clusters (Fig. 5). Cluster 1 consists of EC, pH, Na^+ , HCO_3^- , and NO_3^- . Cluster 2 includes Ca^{2+} , Mg^{2+} , and SO_4^{2-} . Variables of the cluster 1, especially Na^+ , HCO_3^- , and NO_3^- , may indicate their derivation from connate saline (palaeomarine) water of the sedimentary beds of the aquifer, weathering of alkali feldspars aided by carbonic acid, and inputs of anthropogenic sources, which include animal and human waste and fertilizers. Variables of cluster 2 suggest an influx of significant amounts of alkaline earths through dissolution of carbonate minerals, including dolomite, aided by H_2SO_4 . The grouping of three variables of cluster 1 (i.e., Ca^{2+} , Mg^{2+} , and SO_4^{2-}) is consistent with the loadings of factor-2 of the factor analysis data provided earlier in the section of Factor analysis.

Sources of dissolved solids in groundwater

In natural system dissolution of carbonate, silicate, and sulfide minerals and consequent generation of HCO_3^- , SO_4^{2-} and H_2SO_4 are represented by the following reactions:



In ground waters of the study area, the carbonic acid (H_2CO_3) played a predominant part in comparison to sulfuric acid (H_2SO_4) during dissolution process as could be made out from the average value of > 0.50 of $\text{HCO}_3^-/(\text{HCO}_3^- + \text{SO}_4^{2-})$ equivalent ratio (C-ratio; Brown et al. 1996). The source of Cl^- ion could either be saline water trapped in the basin or anthropogenic inputs or both. The connate saline water, now admixed with the groundwater, in reality, constitutes the Caspian seawater of Quaternary age. The admixed connate water component of the groundwater can provide a significant concentration of Cl^- and Na^+ and relatively lesser quantities of other major

ions to the groundwater. The amount of ionic load received by the groundwater from the admixed component of the connate saline water at any given location of the study area depends on its quantity and hydrochemical composition. The hydrochemical composition of the Caspian seawater of Quaternary age is not known, but it may not differ significantly from the hydrochemical composition of the present-day Caspian seawater. The present-day Caspian seawater, on average, contains in (meq/l) $\text{Ca}^{2+} = 44.00$; $\text{Mg}^{2+} = 19.20$; $\text{Na}^+ = 100.80$; $\text{K}^+ = 2.60$; $\text{HCO}_3^- = 3.40$; $\text{SO}_4^{2-} = 2.70$; $\text{Cl}^- = 158.80$ (Khairy and Janardhana 2013).

In the study area, anthropogenic inputs (from the agricultural field and domestic wastewater) rendered the groundwater at several localities significantly saline. For example, six samples (BW nos. 2, 37, 38, 41, 59, and 61) contain high concentration of Cl^- , ranging from 319.1 to 652.3 mg/l (av. = 456.75 mg/l) (Table 3). At these sites, the water also contains elevated concentration of Na^+ , varying from 206.9 to 620.7 mg/l (av. = 433.15 mg/l) (Table 3). The observed high concentrations of Cl^- and Na^+ at several localities were possibly originated from anthropogenic inputs.

High concentrations of Ca^{2+} and Mg^{2+} might have been originated from three sources: mineral weathering, ion-exchange process, and palaeomarine water in the basin. During the weathering process, minerals belonging to both carbonate and silicate mineral groups can provide alkaline earths. Hence, it is necessary to identify the mineral group(s) involved during weathering events, based on the hydrochemical data of the groundwater samples.

Groundwater samples of the study area contain significant concentration of sulfate and the latter may be considered to indicate the participation of carbonate minerals during weathering events. During mineral dissolution/weathering process, Ca^{2+} and Mg^{2+} derived exclusively from the dissolution of carbonates (calcite and/or dolomite) may be recognized by comparing the 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 related to weathering of carbonates (mixtures of calcite and dolomite in proportions ranging from 0 to 100% of each mineral) which vary, respectively from 0.25 to 0.50, from 0 to 0.25, from 0.5 to 1.00, and from 0 to 0.50 (Khairy and Janardhana 2013).

In this study region, the values of one or two of the above-mentioned molar ratios (viz., $\text{Ca}^{2+}/\text{HCO}_3^-$, $\text{Ca}^{2+}/\text{SO}_4^{2-}$, $\text{Mg}^{2+}/\text{HCO}_3^-$, and $\text{Mg}^{2+}/\text{SO}_4^{2-}$) in 30 groundwater samples are within the limits of the theoretically deduced values (TDV) of molar ratios originated from the exclusive dissolution of carbonates. For example, the values of $\text{Ca}^{2+}/\text{HCO}_3^-$ molar ratio in seven samples vary from 0.25 to 0.42 (TDV = 0.25 to 0.50). The values of $\text{Mg}^{2+}/\text{HCO}_3^-$ molar ratio in 20 samples range from 0.03 to 0.25 (TDV = 0 to 0.25). The values of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ molar ratio in five samples

vary from 0.52 to 0.93 (TDV = 0.50 to 1.00). The values of the Mg^{2+}/SO_4^{2-} molar ratio in nine samples vary from 0.17 to 0.37 (TDV = 0 to 0.50). These values of molar ratios in the identified 30 groundwater samples support the derivation of alkaline earths from the exclusive dissolution of carbonates. Molar ratios of the remaining samples possibly point to the derivation of alkaline earth from dissolution of silicate rocks.

The presence of significant concentrations of HCO_3^- in the samples validates the participation of silicate minerals during weathering process and they can further be confirmed from the values of certain molar ratios of the hydrochemical data. For example, the values of $(Na^+ + K^+)/Tz^+$, $(Ca^{2+} + Mg^{2+})/HCO_3^-$, and $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ molar ratios reveal the dissolution of minerals of carbonate and/or silicate groups (Sarin et al. 1989). In the present case, the values (Table 4) of the above-mentioned molar ratios suggest the chemical weathering of minerals of both silicate and carbonate groups as the source of alkaline earths (Singh et al. 2005). The plots of the values of Mg^{2+}/Na^+ and Ca^{2+}/Na^+ molar ratios (Fig. 6) on the graph of Gaillardet et al. (1999) indicate the effect of weathering of both carbonate and silicate minerals in the course of the accession of cations (Singh et al. 2012). Also, the groundwater witnessed an influx of alkaline earth during the ion-exchange process.

The alkali content of the samples might have been originated from four sources: weathering of alkali feldspars, ion-exchange processes, admixed connate saline water, and anthropogenic inputs. The values of Na^+/Cl^- molar ratio of the samples were considered and it was found that 50 out of 66 samples have values > 1 implying significant participation

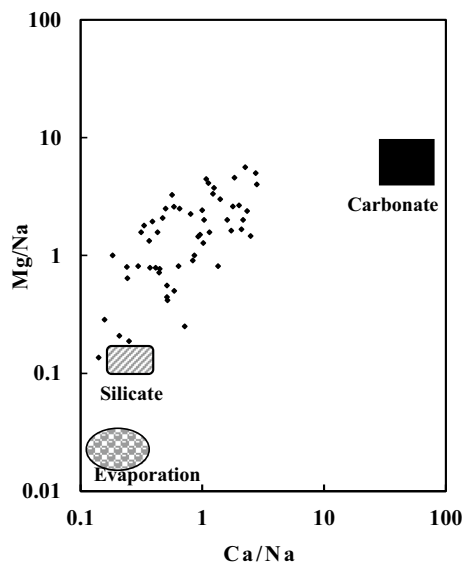


Fig. 6 Bivariate Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ diagram (Gaillardet et al. 1999) showing the plots of the hydrochemical data of the groundwater samples

of alkali feldspars during weathering process (Stallard and Edmond 1983; Meybeck 1987; Morgan and Stumm 1996). At the remaining 16 bore well sites, the water might have acquired $Na^+ \pm K^+$ during the ion-exchange process.

Groundwater samples contain, on average, high concentration of Na^+ (av = 152.50 mg/l) and low concentration of K^+ (av = 4.1 mg/l) among cations. The observed domination of Na^+ over K^+ and low concentration K^+ may be attributed to the Na^+ -rich and K^+ -poor nature of the dissolved solids in the connate saline water component of the groundwater and anthropogenic inputs. Other reasons for the observed difference in the concentrations of Na^+ and K^+ include: high mobility of Na^+ vis-à-vis K^+ during mineral weathering (Milliot 1970), ion-exchange process, and participation of a limited amount of K-feldspars during weathering process in comparison with Na-bearing aluminosilicates.

Suitability of the groundwater for drinking purpose

The suitability of the groundwater of the study area for drinking purpose was evaluated following two different methods. The first method involved comparison of the values/concentrations of 11 physicochemical variables (viz., pH, TDS, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) of the groundwater samples (Table 3) with the permissible limits of the values/concentrations of the same physicochemical variables prescribed by Institute of Standards and Industrial Research of Iran (ISIRI 2009) for potable water (Table 8). The second method of evaluation was based on the computed values of the water quality index (WQI) of the groundwater samples.

The permissible limits of the values/concentrations of physicochemical variables prescribed by ISIRI (2009) for drinking water are: pH (6.5–9), TDS (1500 mg/l), TH (500 mg/l), Ca^{2+} (300 mg/l), Mg^{2+} (150 mg/l), Na^+ (200 mg/l), K^+ (200 mg/l), HCO_3^- (600 mg/l), SO_4^{2-} (400 mg/l), Cl^- (400 mg/l), and NO_3^- (50 mg/l). In the present studies, the values/concentrations of pH in 1 sample, TDS in 7 samples, TH in 14 samples, Mg^{2+} in 1 sample, Na^+ in 14 samples, HCO_3^- in 12 samples, SO_4^{2-} in 2 samples, Cl^- in 4 samples, and NO_3^- in 4 samples exceed the permissible limits prescribed by ISIRI (2009). Concentrations of Ca^{2+} and K^+ in all groundwater are within the prescribed limits of the ISIRI (2009). Table 8 provides the details of the groundwater samples having values/concentrations of physicochemical variables exceeding the prescribed limits suggested by ISIRI (2009).

Figure 7 shows the areal distribution of groundwater with desirable and permissible limits of concentrations of Mg^{2+} (A), Na^+ (B), HCO_3^- (C), SO_4^{2-} (D), Cl^- (E), NO_3^- (F), TDS (G), TH (H), and pH (I) recommended by ISIRI (2009).

The values of the WQI of the groundwater samples, which were calculated based on the approach explained in

Table 8 Assessment of the quality of the groundwater for drinking purpose based on the permissible limits of the hydrochemical variables prescribed by ISIRI (2009) for potable water

Hydrochemical parameter	Desirable limits (ISIRI 2009)	Maximum permissible limits (ISIRI 2009)	Groundwater samples exceeding maximum permissible limits (ISIRI 2009)
pH	6.5–8.5	6.5–9	Sample nos: 41 Total: 1 (~2%)
TDS	1000 mg/l	1500 mg/l	Sample nos: 2, 6, 11, 37, 58, 59, and 65 Total: 7 (~11%)
TH	200 mg/l	500 mg/l	Sample nos: 1, 2, 6, 9, 10, 12, 13, 14, 17, 21, 28, 40, 47, and 50 Total: 14 (~21%)
Ca ²⁺	300 mg/l	300 mg/l	Nil
Mg ²⁺	30 mg/l	150 ^a mg/l	Sample nos: 6 Total: 1 (~2%)
Na ⁺	200 mg/l	200 mg/l	Sample nos: 2, 11, 37- 39, 41,42, 44, 58, 59, 61, 62, 64, and 65 Total: 14 (~21%)
K ⁺	–	200 mg/l	Nil
HCO ₃ ⁻	200 ^a mg/l	600 ^a mg/l	Sample nos: 9, 11, 21, 37, 39, 40, 50, 58, 59, 62, 65, and 66 Total: 12 (~18%)
SO ₄ ²⁻	250 mg/l	400 mg/l	Sample nos: 2 and 6 Total: 2 (~3%)
Cl ⁻	250 mg/l	400 mg/l	Sample nos: 2, 37, 41, and 61 Total: 4 (~6%)
NO ₃ ⁻	–	50 mg/l	Sample nos: 9, 21, 47, and 50 Total: 4 (~6%)

^aWHO (1997)

the section of methodology, are provided in Table 9. In the published literature (e.g., Tarawneh et al. 2019), the values of WQI of waters are grouped into five classes, which correspond to five types of potable water (Table 10). Details of the groundwater samples belonging to the above-mentioned water classes are provided in Table 11. The obtained data designate that, in the study region, groundwater fitting to “excellent”, “good”, and “poor” water classes are encountered, respectively, at 37, 28, and 1 sampling sites (Table 10). Figure 8, which is prepared based on the values of the WQI of the groundwater samples, shows the spatial distribution of potable groundwater belonging to “excellent”, “good”, and “poor” categories.

Suitability of water for irrigation

Criteria for judging the quality of water for irrigation needs considered here are listed in Tables 9 and 12. The results indicated certain limitations of the usage of the groundwater for irrigation purposes.

Based on the amounts of *Exchangeable Sodium Percentage* (Tijani 1994), groundwater at ~95% of the sampling sites is suitable for irrigation needs (Table 12). Likewise, the ratings provided by the graphs of the data *PI* versus $T_{z+} + z_-$ also suggest that the groundwater encountered at the majority (i.e., ~86%) of the bore well locations belongs to the

Class I category of irrigation water (Table 12). The values/ratings of other parameters and bivariate diagrams brought to light the following specific and valuable information on the possible damage to soil and vegetation due to the excess presence of certain ions/groups of ions in groundwater.

The values/ratings provided by *Salinity hazard* (Richards 1954) show that the region is devoid of excellent category of irrigation water. Good quality groundwater for irrigation purposes is encountered only at ~5% of the bore well locations. At the remaining ~85% and ~10% of the sites, the water allied, respectively, to fair/medium and poor/bad classes (Table 12). The data reveal high-to-very high salinity encountered at majority (~95%) of the sampling sites.

A high content of Na⁺ in irrigation waters can cause the exchange of Na⁺ in water with Ca²⁺ and Mg²⁺ in soil, and this chemical activity can reduce the permeability and internal drainage in soils (Collins and Jenkins 1996; Saleh et al. 1999). Furthermore, the continued application of water with high Na⁺ and HCO₃⁻ can also adversely affect the soil permeability (Doneen 1964; Davis and Wiest 1966; Raghunath 2007). Harmful effects of Na⁺ in irrigation water are also assessed from the values of % Na⁺, *Kelley's ratio*, *Permeability Index* as well from the graph of % Na⁺ versus *EC* ($\mu\text{S}/\text{cm}$) (Wilcox 1955). The classification of water concerning % Na⁺ indicates that the groundwater at ~27% of the sampling locations is not suitable for irrigation purposes (Table 12). According to the ratings of *Kelley's ratio*, the groundwater

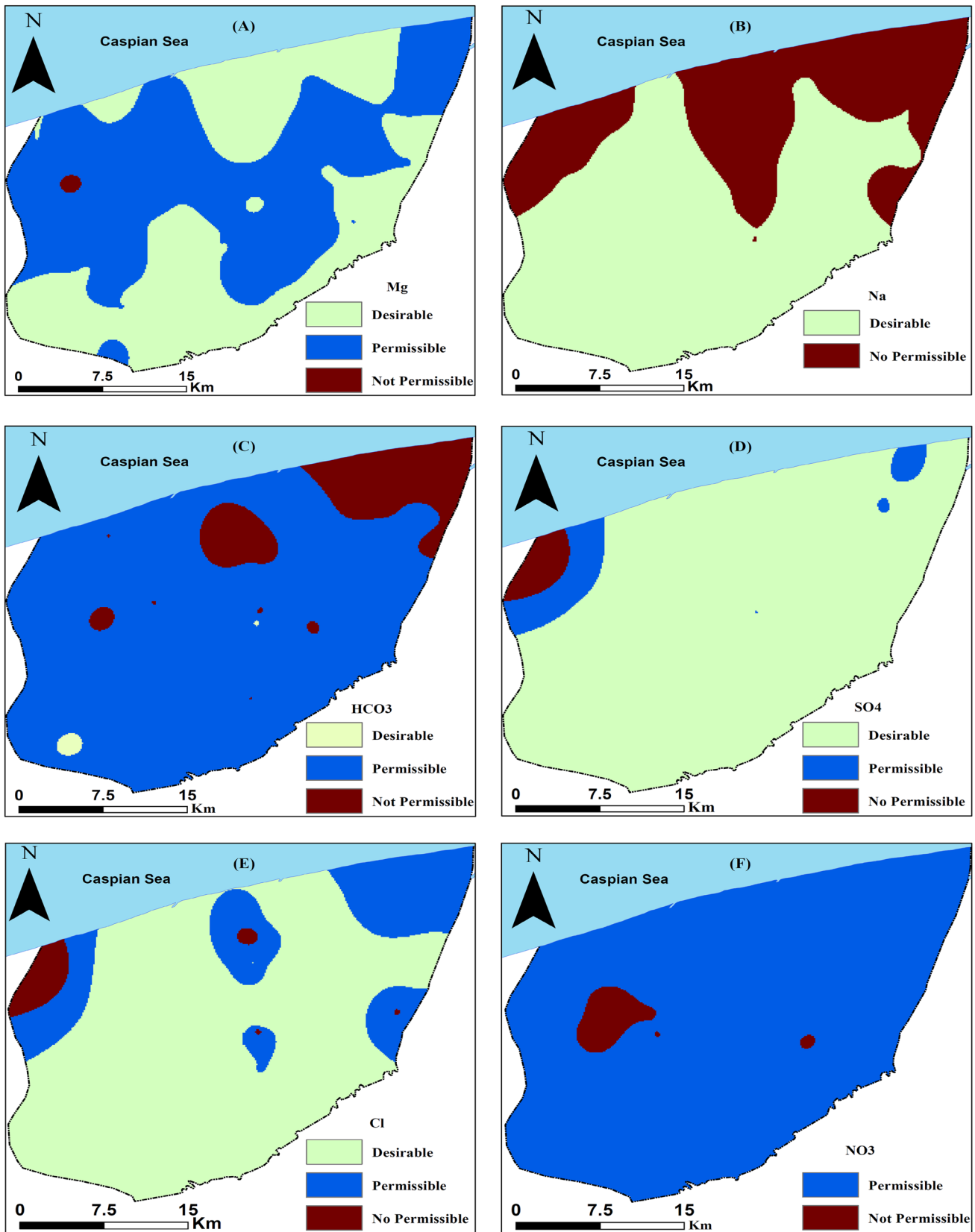


Fig. 7 Plans showing the areal extent of occurrence of the groundwater with desirable and permissible limits of concentrations of Mg^{2+} (A), Na^+ (B), HCO_3^- (C), SO_4^{2-} (D), Cl^- (E), NO_3^- (F), TDS (G), TH (H), and pH (I) prescribed by ISIRI (2009) for potable water

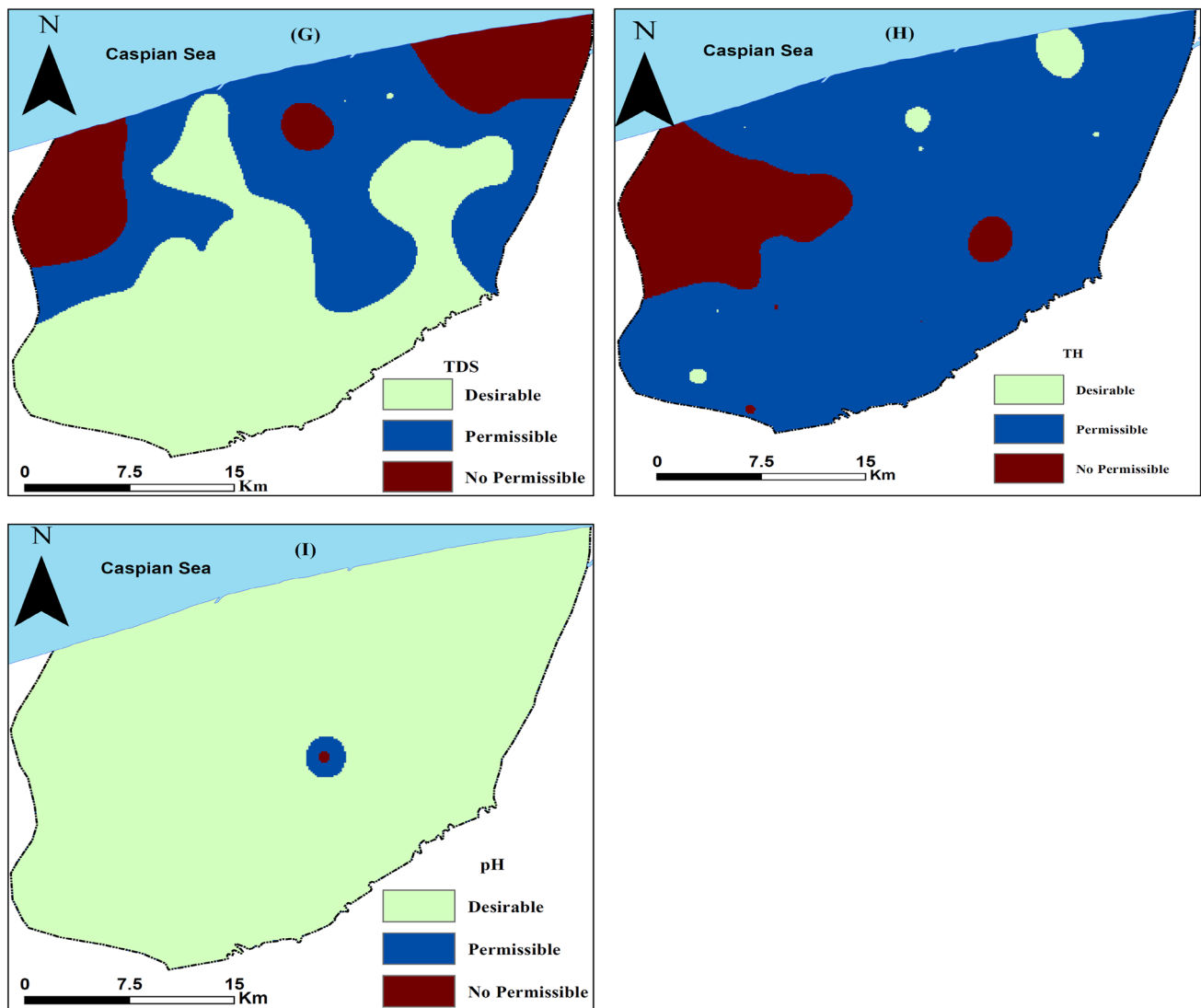


Fig. 7 (continued)

encountered at ~26% of the bore well locations is unsuitable (Table 12). *Permeability Index* data suggest that the groundwater at ~44% of the sampling locations is unsuitable (Table 12). The ratings generated from the plots of the data on the Wilcox diagram indicate that the groundwater encountered at ~8%, ~10%, and 6% of the borewell locations belongs to permissible to doubtful, doubtful to unsuitable, and unsuitable categories of irrigation water, respectively (Table 12). Thus, the ratings provided by % Na^+ , *Kelley's ratio* and *Wilcox diagram* together indicate that the water at ~27% of the sampling sites is marginally suitable/not suitable, whereas ratings inferred from the *Permeability Index* suggest that groundwater extracted from half of the sampling sites is unfit for application in the agricultural field.

The quantity of HCO_3^- and CO_3^{2-} present in excess of Ca^{2+} and Mg^{2+} tend to rise sodium ions in water (Eaton

1950). The values of the related parameter *Residual sodium carbonate* (RSC, Lloyd and Heathcote 1985) at ~7% and ~14% of the bore well sites belong, respectively, to doubtful (marginal quality) (Singh et al. 2012) and not suitable categories (Table 12). Bicarbonate in excess in irrigation waters is considered as harmful to soils. The ratings of the *Bicarbonate hazard* (Mandel and Shiftan 1981) suggest that the groundwater at ~71% of the sampling locations may cause an increasing problem, inducing alkalinity to the soil and at ~27% of the well locations' severe problem (Table 12). The high content of chloride in irrigation waters is also considered as detrimental to soils and plant growth. A high concentration of chloride, combined with excess sodium, promotes the formation of acidic soil. According to the values/ratings of the *chloride hazard*, the groundwater encountered at ~20%

Table 9 Values of the water quality index of the groundwater samples and the values of the irrigation water quality assessing parameters ($n=9$)

S.No	WQI	CH	BH	SAR	RSC	ESP	% Na	KR	MH	PI
1	55.45	6.50	8.50	2.75	- 3.00	2.72	36.85	0.57	47.81	52.57
2	106.90	18.40	5.80	8.98	- 7.30	10.71	63.82	1.76	17.55	70.38
3	35.31	2.20	5.30	1.93	- 1.30	1.56	35.35	0.53	16.66	57.45
4	42.01	2.00	7.00	1.76	- 1.40	1.31	30.63	0.43	16.66	52.05
5	20.46	1.50	1.50	2.19	- 1.10	1.93	49.51	0.96	23.07	73.03
6	80.00	8.00	6.00	1.81	- 19.69	1.39	20.51	0.25	63.02	27.80
7	27.83	1.90	4.00	2.50	0.30	2.37	48.39	0.92	54.04	76.06
8	30.82	1.80	4.50	0.80	- 2.50	- 0.08	18.41	0.21	42.84	42.61
9	90.32	4.50	12.00	3.32	0.40	3.51	41.14	0.69	43.95	58.49
10	51.43	4.00	8.00	1.26	- 3.30	0.60	21.58	0.27	55.74	40.76
11	65.01	4.70	10.00	11.60	6.20	13.69	80.91	4.21	34.20	96.78
12	48.64	4.00	8.50	1.35	- 2.10	0.72	23.24	0.29	29.23	43.91
13	50.41	2.00	7.00	1.10	- 3.40	0.36	20.06	0.24	51.91	39.89
14	40.62	3.50	7.00	0.89	- 3.00	0.06	17.42	0.20	24.99	38.72
15	37.64	1.50	7.00	0.95	- 1.80	0.15	19.34	0.23	31.81	43.02
16	49.42	2.80	7.00	1.68	- 2.20	1.20	28.73	0.39	18.47	48.79
17	39.31	2.00	7.00	0.66	- 3.20	- 0.28	13.63	0.15	41.16	35.44
18	36.29	2.00	6.50	0.56	- 2.80	- 0.44	12.35	0.13	35.47	35.71
19	32.86	1.30	5.70	1.13	- 0.60	0.40	24.82	0.32	20.63	52.86
20	40.05	2.70	6.00	1.87	- 1.00	1.48	34.02	0.50	21.42	56.66
21	65.48	3.50	10.00	2.02	- 2.30	1.68	29.35	0.41	39.01	47.18
23	37.68	1.50	8.00	1.10	- 0.80	0.36	21.49	0.26	14.77	46.20
23	43.01	2.00	7.50	3.58	1.90	3.87	52.18	1.07	55.34	75.34
24	40.85	2.60	7.50	1.41	- 1.60	0.81	25.47	0.33	34.05	47.43
25	28.63	2.50	3.50	1.88	- 1.60	1.49	37.65	0.59	21.56	60.13
26	36.50	3.00	6.50	3.16	1.50	3.29	50.54	1.00	9.99	75.49
27	44.84	2.50	8.50	1.61	- 1.00	1.10	27.53	0.37	42.09	49.35
28	50.24	5.00	9.40	0.98	- 3.70	0.18	16.61	0.19	21.36	35.68
29	49.87	3.00	9.00	3.41	0.60	3.64	45.84	0.83	34.51	64.94
30	34.21	1.30	6.00	1.14	- 0.10	0.43	25.42	0.33	26.22	54.93
31	38.56	1.80	6.50	0.89	- 1.70	0.05	18.89	0.22	26.82	43.50
32	37.08	1.40	6.80	0.68	- 0.40	- 0.25	16.08	0.18	19.44	45.97
33	34.49	1.00	6.50	1.15	0.50	0.44	25.74	0.33	16.66	56.87
34	39.18	2.50	6.00	1.05	- 1.20	0.29	22.50	0.28	44.43	48.37
35	29.65	1.20	6.00	2.58	1.90	2.49	47.90	0.90	26.82	78.84
36	41.85	2.50	7.50	3.52	1.70	3.79	51.30	1.03	74.13	74.07
37	89.14	14.50	14.00	22.04	11.00	23.81	90.04	9.00	33.32	102.48
38	65.57	9.00	9.00	11.31	5.00	13.36	80.12	4.00	24.99	95.00
39	64.13	7.00	12.00	11.81	8.10	13.91	80.99	4.23	10.25	97.86
40	51.85	2.00	10.00	1.02	- 0.10	0.25	19.26	0.23	40.58	44.06
41	54.14	13.40	1.80	7.40	- 3.90	8.81	68.86	2.19	19.29	76.05
42	62.29	7.50	6.50	4.34	- 2.10	4.89	51.44	1.05	53.47	65.63
43	41.86	1.00	7.00	0.61	- 0.70	- 0.36	14.25	0.16	28.56	43.21
44	48.63	5.00	5.50	6.39	0.60	7.54	67.35	2.04	18.36	82.85
45	51.22	4.60	8.20	1.83	- 1.30	1.43	30.19	0.42	38.93	50.84
46	31.26	1.00	5.50	0.45	- 0.80	- 0.60	12.13	0.13	28.56	44.30
47	61.30	3.80	8.30	1.49	- 4.10	0.92	23.50	0.30	51.60	40.88
48	43.04	2.00	9.00	0.94	- 0.90	0.13	18.25	0.21	49.48	42.51
49	50.00	6.30	7.00	3.27	- 0.90	3.44	45.55	0.82	36.70	63.51
50	68.41	3.80	11.50	2.19	- 1.10	1.93	30.80	0.44	44.43	49.13
51	47.32	2.80	7.90	1.35	- 1.30	0.73	24.65	0.32	18.47	47.20

Table 9 (continued)

S.No	WQI	CH	BH	SAR	RSC	ESP	% Na	KR	MH	PI
52	51.16	4.50	7.00	3.97	0.80	4.40	53.41	1.13	27.41	73.07
53	53.13	4.00	9.00	2.32	-0.30	2.11	35.46	0.54	46.22	55.95
54	44.07	4.00	8.50	1.99	-0.80	1.65	32.17	0.46	62.35	53.06
55	48.09	5.30	6.50	3.18	-0.60	3.32	46.25	0.84	15.49	65.26
56	48.88	3.00	9.00	1.91	0.70	1.54	32.57	0.47	15.66	56.56
57	52.03	7.50	7.00	3.48	-1.10	3.72	46.74	0.86	38.26	63.88
58	83.99	7.50	16.00	23.77	13.70	25.26	91.76	11.08	34.77	106.12
59	85.68	10.00	12.00	16.56	7.80	18.81	85.10	5.71	40.46	97.39
60	38.75	5.50	5.00	6.05	1.50	7.11	69.85	2.29	57.13	89.02
61	64.25	12.00	6.50	7.95	0.30	9.47	69.47	2.26	35.47	81.93
62	54.37	4.00	11.00	7.59	6.00	9.03	70.78	2.40	49.99	90.10
63	51.66	7.40	6.50	3.48	-1.60	3.72	47.09	0.86	32.09	63.24
64	58.40	8.50	7.50	4.11	-2.10	4.58	48.69	0.94	47.90	63.11
65	85.48	10.40	12.00	12.59	5.90	14.76	78.38	3.61	50.81	90.62
66	55.44	4.30	12.00	3.77	3.00	4.12	47.39	0.89	5.55	67.43

WQI water quality index, CH chloride hazard (meq/l), BH bicarbonate hazard (meq/l), SAR sodium adsorption ratio, RSC residual sodium carbonate, ESP exchangeable sodium percentage, %Na percent sodium, KR Kelley's ratio, MH magnesium hazard, PI permeability index

Table 10 Classification of groundwater of the study area for drinking purpose based on the range of values of water quality index of the groundwater samples

WQI range	Type of water	No. of groundwater samples (% of total number of samples)
< 50	Excellent water	37 (~ 56%)
50–100	Good water	28 (~ 42%)
100–200	Poor water	1 (~ 2%)
200–300	Very poor water	–
> 300	Unsuitable water	–

Table 11 Assessment of the quality of groundwater for drinking purpose based on the values of WQI of the groundwater samples

Water quality	Groundwater sample nos. with the values of WQI in bracket
Excellent	3 (35.1), 4 (42.1), 5 (20.5), 7 (27.8), 8 (30.8), 12 (48.6), 14 (40.6), 15 (37.6), 16 (49.4), 17 (39.3), 18 (36.2), 19 (32.8), 20 (40.0), 22 (37.7), 23 (43.0), 24 (40.8), 25 (28.6), 26 (36.5), 27 (44.8), 29 (49.9), 30 (34.2), 31 (38.6), 32 (37.1), 33 (34.5), 34 (39.2), 35 (29.6), 36 (41.8), 43 (41.9), 44 (48.6), 46 (31.3), 48 (43.0), 49 (49.9), 51 (47.3), 54 (44.1), 55 (48.1), 56 (48.9), and 60 (38.7)
Good	1 (55.4), 6 (80.0), 9 (90.3), 10 (51.4), 11 (65.0), 13 (50.4), 21 (65.05), 28 (50.2), 37 (89.1), 38 (65.6), 39 (64.1), 40 (51.8), 41 (54.1), 42 (62.3), 45 (51.2), 47 (61.3), 50 (68.4), 52 (51.2), 53 (53.1), 57 (52.0), 58 (84.0), 59 (85.6), 61 (64.2), 62 (54.3), 63 (51.6), 64 (58.4), 65 (85.5), and 66 (55.4)
Poor	2 (106.9)

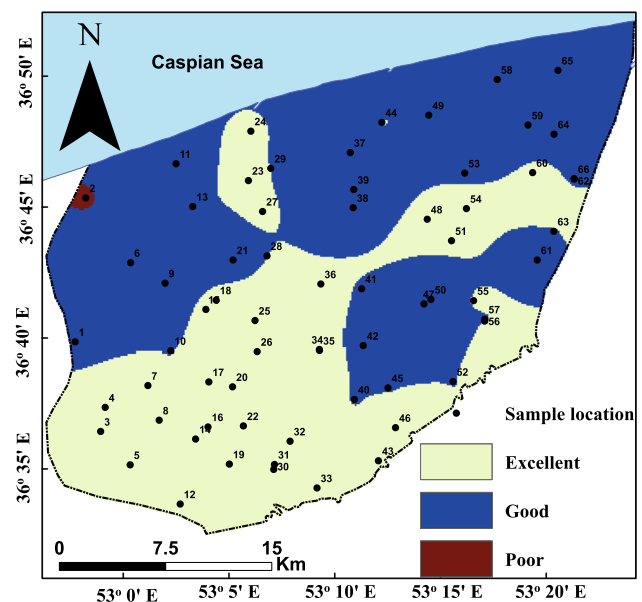


Fig. 8 Plan showing the spatial variation of the quality of the groundwater for drinking purpose based on the values of the Water Quality Index (WQI) of the groundwater samples

and ~7% of the bore well locations belong, respectively, good-to-hazardous, and hazardous-to-very hazardous categories of irrigation water (Table 12).

Mg²⁺-rich irrigation water can cause ill effects on clay dispersion and hydraulic conductivity of soils, thus affecting the agricultural produce in the region. The values of Magnesium hazard (expressed as Mg²⁺ratio—Lloyd and Heathcote 1985; Szabolcs and Darab, 1964) indicate that at ~ 16%

Table 12 Assessment of the quality of the groundwater for irrigation purpose based on the values/ratings of the irrigation water quality assessing parameters ($n = 10$) and parameter-based bivariate diagrams ($n = 3$)

Parameters	Rating	Water class	No of bore wells	Parameters	Rating	Water class	No of bore wells
Salinity (EC(μ S/cm)) (Richards 1954)	< 250	Excellent	Nil	Kelley's Ratio (KR) (Kelley 1951)	< 1	Suitable	49
	250- 750	Good	3		> 1	Unsuitable	17
	750–2250	Fair/medium	56	Mg ratio (Lloyd and Heathcote 1985)	< 50	Suitable	55
	> 2250	Poor/bad	7		> 50	Unsuitable	11
Chloride hazard (CH) (Doneen 1964)	< 5	Very good-to-good	48	PI (Doneen 1964)	< 60	Suitable	37
	5–10	Good to hazardous	13		> 60	Unsuitable	29
	> 10		5	PI vs. Total ions (Doneen 1964)	Class I	Class I	57
Bicarbonate hazard (Mandel and Shiftan 1981)	< 1.5	No problem	1		Class II	Class II	4
	1.5–8.5	Increasing problem	47		Class III	Class III	5
	> 8.5	Severe problem	18	% Na VS. Ec (Wilcox 1955)	Field 1	Excellent-to-good	3
SAR (Bouwer 1978)	< 6	No problem	53		Field 2	Good-to-permissible	47
	6–9	Increasing problem	6		Field 3	Permissible-to-doubtful	5
	> 9	Severe problem	7		Field 4	Doubtful-to-unsuitable	7
RSC (Lloyd and Heathcote 1985)	< 1.25	Suitable	52		Field 5	Unsuitable	4
	1.25–2.5	Doubtful	5	SAR vs. EC (Richards 1954)	C2–S1		3
	> 2.5	Not suitable	9		C3–S1		48
ESP (Tijani 1994)	< 15	Suitable	63		C3–S2		3
	> 15	Unsuitable	3		C3–S3		5
Percentage Sodium % Na (Wilcox 1955)	< 50	Suitable	48		C4–S1		1
	> 50	Not suitable	18	C4–S2		1	
				C4–S3		2	
				C4–S4		3	

of the bore well locations, the groundwater belongs to the unsuitable category of irrigation water (Table 12).

Plots of *EC* (salinity hazard) and *SAR* (alkalinity hazard) values of the groundwater samples of the study area on USSL diagram (Richard, 1954) (Fig. 9) reveal that the groundwater at ~ 78% and ~ 5% of the sampling locations belongs, respectively, to C3-S1 and C2-S1 categories of irrigation water (Table 12). Low sodic (S1) nature of the groundwater indicates that it can be safely used in most types of soils with little danger of development of harmful levels of exchangeable sodium. However, water characterized by high (C3) and very high (C4) salinity prohibits its use on fine-textured soils with minimal drainage. The data obtained from the USSL diagram (Fig. 9) suggest that the

groundwater encountered at ~ 95% and ~ 5% of the bore well locations can be utilized for lands growing, respectively, salt-tolerant and semi salt-tolerant crops.

Figure 10 provides details of spatial distribution of groundwater belonging to seven identified irrigation water classes of Richards (1954). In the study area, groundwater belonging to C3-S1 irrigation water class of Richards (1954) is widely encountered and is located at 48 out of 66 bore well locations (Fig. 10). Groundwater encountered at NW and NE regions of the study area belongs to essentially very high saline irrigation water classes.

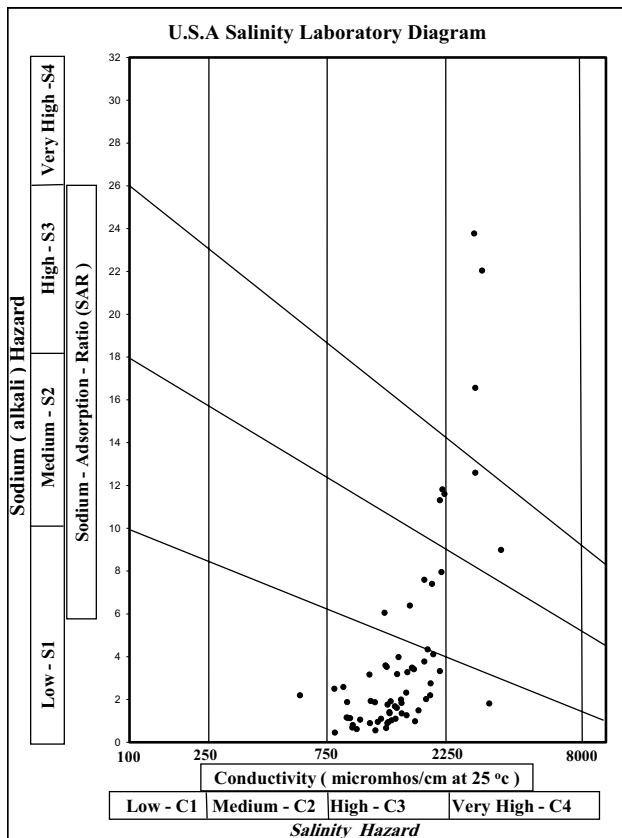


Fig. 9 U.S Salinity Laboratory diagram (Richards 1954) showing the irrigation water classes of groundwater samples

Summary and conclusions

The amalgamation of geological knowledge, geochemical data, and statistical treatment of the hydrochemical data was made use of the classification, characterization, and evaluation of the quality of water of coastal aquifer at Sari–Neka region in Iran for drinking and irrigation needs. Source-wise, groundwater of the studied region at about 68% of the bore well locations constitutes $\text{Na}^+\text{-SO}_4^{2-}$ type and belongs to deep meteoric percolation type. In about 30% of the bore well locations, the groundwater constitutes $\text{Na}^+\text{-HCO}_3^-$ type and belongs to shallow meteoric percolation type. Salinity-wise, at about 64% and at about 36% of the sampling sites, the groundwater belongs to freshwater and brackish water

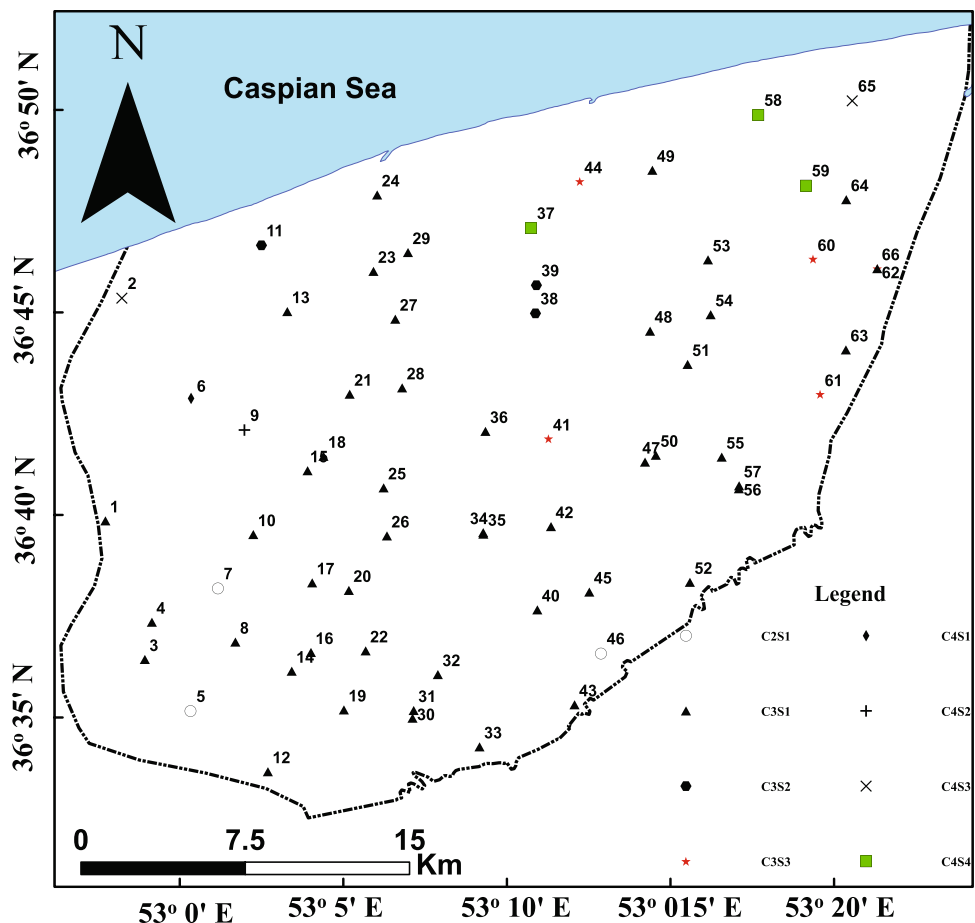
types, respectively. Molar concentrations of various ions show that cations and anions abundances, respectively, are $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. Hydrochemical facies-wise, ~42%, ~41%, and ~17% of the samples belong, respectively, to $\text{Ca}^{2+}\text{Mg}^{2+}\text{HCO}_3^-$, mixed ($\text{Ca}^{2+}\text{Mg}^{2+}\text{Cl}^-$; Back, 1996), and $\text{Na}^+\text{-Cl}^-$ facies.

The bicarbonate (HCO_3^-) content of the groundwater appears to be generated owing to the carbonate and silicate weathering process supplemented by carbonic acid and oxidation of sulfide minerals. Sulfate (SO_4^{2-}) content is probably related to the dissolution of carbonate minerals aided by sulfuric acid (H_2SO_4) and oxidation of sulfide minerals. The average value of C-ratio (0.78) of the groundwater samples indicates the significant role played by the carbonic acid (H_2CO_3) during the weathering process. Cl^- content appears to have two origins: palaeomarine water of the Quaternary formations of the aquifer, now blended with the freshwater and anthropogenic inputs. Alkaline earths were acquired mainly from 3 sources: carbonate and silicate mineral weathering process, and reverse cation–anion-exchange reaction between groundwater and clay minerals of the aquifer and palaeomarine water. Alkalies were provided by feldspars, direct cation-exchange reaction, connate saline water, and anthropogenic inputs.

Water Quality Index (WQI) used as a tool to assess the quality of the groundwater for drinking purposes indicated excellent, good, and poor classes, respectively at 37, 28, and 1 sampling sites. Graphs of the hydrochemical data of the groundwater samples on USSL diagram of Richards (1954) indicate that about 95% of the samples belongs to highly saline (C3) and very highly saline (C4), and alkalinity-wise, low-to-very high sodic (S1 to S4) irrigation water classes, thus implying that the groundwater is suitable for irrigation of land growing salt-tolerant crops. In the remaining ~5% of the sampling sites, groundwater belongs to (C2-S1) irrigation water class and is suitable for the cultivation of semi-salt-tolerant crops.

The present study provides a valuable example for understanding the phenomena of hydrochemical processes and quality assessment of groundwater in parts of the Caspian Sea coastal area that is encountered in five countries. Given that, there are several causes for the deterioration of quality of the groundwater. In terms of salinization, the groundwater samples from the area could potentially represent a variety of water types providing an opportunity to test the performance

Fig. 10 Plan showing the spatial distribution of irrigation water classes of Richards (1954) in the study area



of many of the available methodologies, including classic integrated hydrogeochemical methods, graphical and statistical techniques and GIS analysis for better understanding of the hydrochemical system, and utilization and sustainable management of the groundwater resources of the study area in a more effective way.

Acknowledgements The authors are grateful to Prof. B. Krishna Rao, Mysuru, India for his support and to F. Mahbobi, Mazandaran Regional Water Authority, Sari City, Iran for logistics.

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Adimalla N, Venkatayogi SJEES (2017) Mechanism of fluoride enrichment in groundwater of hard rock aquifers in Medak, Telangana State, South India. *Environ Earth Sci* 76(1):45
 APHA (1995) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, Washington DC, p 100

- Back W (1966) Hydrochemical facies and ground-water flow patterns in the Atlantic Coastal Plain. US Geol. Survey Prof. Paper, p 498
- Bouwer H (1978) Groundwater hydrology. McGraw-Hill Inc, New York
- Brown CJ, Misut PE (2010) Aquifer geochemistry at potential aquifer storage and recovery sites in coastal plain aquifers in the New York City area, USA. *Appl Geochem* 25(9):1431–1452. <https://doi.org/10.1016/j.apgeochem.2010.07.001>
- Brown G, Sharp M, Tranter M (1996) Subglacial chemical erosion: seasonal variations in solute provenance, Haut Glacier d'Arolla, Valais, Switzerland. *Ann Glaciol* 22:25–31
- Cardona A, Carrillo-Rivera J, Huizar-Alvarez R, Graniel-Castro E (2004) Salinization in coastal aquifers of arid zones: an example from Santo Domingo, Baja California Sur, Mexico. *Environ Geol* 45(3):350–366
- Chebotaev II (1955) Metamorphism of natural waters in the crust of weathering—I. *Geochim Cosmochim Acta* 8(1–2):22–48. [https://doi.org/10.1016/0016-7037\(55\)90015-6](https://doi.org/10.1016/0016-7037(55)90015-6)
- Cheng AH, Ouazar D (2003) Coastal aquifer management-monitoring, modeling, and case studies. CRC Press, Berlin
- Collins R, Jenkins A (1996) The impact of agricultural land use on stream chemistry in the Middle Hills of the Himalayas, Nepal. *J Hydrol* 185(1–4):71–86. [https://doi.org/10.1016/0022-1694\(95\)03008-5](https://doi.org/10.1016/0022-1694(95)03008-5)
- Davis J (2002) Statistics and data analysis in geology. Wiley, New York, p 656
- Davis S, De Wiest J (1966) Hydrogeology, vol 2. Wiley, New York
- Dewan M, Famouri J (1964) The soils of Iran. Food and Agriculture Organization of the United Nations
- Doneen LD (1964) Notes on water quality in agriculture. Department of Water Science and Engineering, University of California, Davis
- Eaton FM (1950) Significance of carbonates in irrigation waters. *Soil Sci* 69(2):123–134
- Ergil M (2000) The salination problem of the Guzelyurt aquifer, Cyprus. *Water Res* 34(4):1201–1214. [https://doi.org/10.1016/S0043-1354\(99\)00253-5](https://doi.org/10.1016/S0043-1354(99)00253-5)
- Freeze RA, Cherry J (1979) Groundwater. Prentice-Hall, Englewood Cliffs
- Gaillardet J, Dupré B, Louvat P, Allègre CJ (1999) Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem Geol* 159(1–4):3–30. [https://doi.org/10.1016/S0009-2541\(99\)00031-5](https://doi.org/10.1016/S0009-2541(99)00031-5)
- Gholami V, Aghagholi H, Kalteh AM (2015) Modeling sanitary boundaries of drinking water wells on the Caspian Sea southern coasts, Iran. *Environ Earth Sci* 74(4):2981–2990. <https://doi.org/10.1007/s12665-015-4329-3>
- Gibbs RJ (1970) Mechanisms controlling world water chemistry. *Science* 170(3962):1088–1090. <https://doi.org/10.1126/science.170.3962.1088>
- Gilabert-Alarcón C, Daesslé LW, Salgado-Méndez SO, Pérez-Flores MA, Knöller K, Kretschmar TG et al (2018) Effects of reclaimed water discharge in the Maneadero coastal aquifer, Baja California, Mexico. *Appl Geochem* 92:121–139
- Giménez E, Morell I (1997) Hydrogeochemical analysis of salinization processes in the coastal aquifer of Oropesa (Castellón, Spain). *Environ Geol* 29(1–2):118–131. <https://doi.org/10.1007/s002540050110>
- ISIRI (2009) Chemical specifications of drinking water, ISIRI no. 1053, 5th ed. Institute of Standards and Industrial Research of Iran, Tehran (in Persian)
- Jackson J, Priestley K, Allen M, Berberian M (2002) Active tectonics of the south Caspian basin. *Geophys J Int* 148(2):214–245
- Jamshidzadeh ZJEP (2020) An integrated approach of hydrogeochemistry, statistical analysis, and drinking water quality index for groundwater. *Assessment* 7:781–804
- Janardhana MR, Khairy H (2019) Simulation of seawater intrusion in coastal aquifers: a case study on the Amol-Ghaemshahr coastal aquifer system, Northern Iran. *Environ Earth Sci* 78(24):695. <https://doi.org/10.1007/s12665-019-8711-4>
- Kelley WP (1951) Alkali soils; their formation, properties, and reclamation. Reinold Publication Corporation, New York
- Khairy H, Janardhana MR (2013) Hydrogeochemical features of groundwater of semi-confined coastal aquifer in Amol-Ghaemshahr plain, Mazandaran Province, Northern Iran. *Environ Monit Assess* 185(11):9237–9264. <https://doi.org/10.1007/s10661-013-3248-6>
- Khairy H, Janardhana MR (2014) Hydrogeochemistry and quality of groundwater of coastal unconfined aquifer in Amol-Ghaemshahr plain, Mazandaran Province, Northern Iran. *Environ Earth Sci* 71(11):4767–4782. <https://doi.org/10.1007/s12665-013-2868-z>
- Kim K, Rajmohan N, Kim HJ, Hwang G-S, Cho MJ (2004) Assessment of groundwater chemistry in a coastal region (Kunsan, Korea) having complex contaminant sources: a stoichiometric approach. *Environ Geol* 46(6–7):763–774. <https://doi.org/10.1007/s00254-004-1109-x>
- Kreitler CW (1993) Geochemical techniques for identifying sources of ground-water salinization, edited by K. C. Smoley. CRC Press, Boca Raton
- Liu Y, Jiao JJ, Liang W, Kuang X (2017) Hydrogeochemical characteristics in coastal groundwater mixing zone. *Appl Geochem* 85:49–60
- Lloyd J, Heathcote J (1985) Natural inorganic hydrochemistry in relation to groundwater: an introduction. Oxford University Press
- Mandel S, Shifan Z (1981) Groundwater resources investigation and development. Water Pollution (A Series of Monographs). Academic Press
- Matthess G (1982) The properties of ground-water. Wiley, New York
- Meybeck M (1987) Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am J Sci* 287(5):401–428
- Milliot G (1970) Geology of clays. Springer, New York
- Mitra BK (1998) Spatial and temporal variation of groundwater quality in sand dune area of Aomori Prefecture in Japan. Paper no. 062023. In: 2006 ASAE Annual Meeting
- Morgan JJ, Stumm W (1996) Aquatic chemistry: chemical equilibria and rates in natural waters. Wiley
- Nematollahi MJ, Clark MJR, Ebrahimi P, Ebrahimi M (2018) Preliminary assessment of groundwater hydrogeochemistry within Gilan, a northern province of Iran. *Environ Monit Assess* 190(4):242. <https://doi.org/10.1007/s10661-018-6543-4>
- Ozler MH (2003) Hydrochemistry and salt-water intrusion in the Van aquifer, east Turkey. *Environ Geol* 43(7):759–775. <https://doi.org/10.1007/s00254-002-0690-0>
- Parkhurst D, Appelo C (2011) User's guide to PHREEQC (version 2.18. 5570)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water Resources Investigations Report. USGS Water Resources Investigations Report, pp. 99–4259
- Petalas C, Diamantis I (1999) Origin and distribution of saline groundwaters in the upper Miocene aquifer system, coastal Rhodope area, northeastern Greece. *Hydrogeol J* 7(3):305–316
- Piper A (1944) A graphical procedure in the geochemical interpretation of water analyses. *Am Geophys Union Trans* 25:914–923
- Raghunath HM (2007) Hydrology: principles, analysis and design. New Age International
- Richards L (1954) Diagnosis and improvement of saline and alkali soils (USDA. Agriculture handbook, Vol. 60). US Department of Agriculture, Washington DC
- Saba NU, Umar R (2016) Hydrogeochemical assessment of Moradabad city, an important industrial town of Uttar Pradesh,

- India. *Sustain Water Resour Manag* 2(3):217–236. <https://doi.org/10.1007/s40899-016-0053-8>
- Sajil Kumar PJ, Elango L, James EJ (2013) Assessment of hydrochemistry and groundwater quality in the coastal area of South Chennai, India. *Arab J Geosci* 7(7):2641–2653. <https://doi.org/10.1007/s12517-013-0940-3>
- Saleh A, Al-Ruwaih F, Shehata M (1999) Hydrogeochemical processes operating within the main aquifers of Kuwait. *J Arid Environ* 42(3):195–209
- Sarin M, Krishnaswami S, Dilli K, Somayajulu B, Moore W (1989) Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. *Geochim Cosmochim Acta* 53(5):997–1009
- Sawyer CN, McCarty PL (1967) *Chemistry for sanitary engineers* (2ed.). McGraw-Hill, Berlin
- SazabShargh (2010) Integrating studies of water resources. Sazab Shargh Consulting Engineering, Mashhad
- Schoeller H (1977) *Geochemistry of groundwater. Groundwater studies—an International Guide for Research and Practice*, chapter 15. UNESCO, Paris, pp 1–18
- Şehnaz Ş, Şener E, Davraz A, Varol S (2020) Hydrogeological and hydrochemical investigation in the Burdur Saline Lake Basin, southwest Turkey. *Geochemistry* 80(4):125592
- Singh AK, Mondal G, Singh PK, Singh S, Singh T, Tewary B (2005) Hydrochemistry of reservoirs of Damodar River basin, India: weathering processes and water quality assessment. *Environ Geol* 48(8):1014–1028
- Singh AK, Mondal GC, Singh TB, Singh S, Tewary BK, Sinha A (2012) Hydrogeochemical processes and quality assessment of groundwater in Dumka and Jamtara districts, Jharkhand, India. *Environ Earth Sci* 67(8):2175–2191. <https://doi.org/10.1007/s12665-012-1658-3>
- Soltan ME (1998) Characterisation, classification, and evaluation of some ground water samples in upper Egypt. *Chemosphere* 37(4):735–745. [https://doi.org/10.1016/s0045-6535\(98\)00079-4](https://doi.org/10.1016/s0045-6535(98)00079-4)
- Stallard RF, Edmond JM (1983) Geochemistry of the Amazon: 2. The influence of geology and weathering environment on the dissolved load. *J Geophys Res Oceans* 88(C14):9671–9688. <https://doi.org/10.1029/JC088iC14p09671>
- Tarawneh MSM, Janardhana MR, Ahmed MM (2019) Hydrochemical processes and groundwater quality assessment in North eastern region of Jordan valley, Jordan. *HydroResearch* 2:129–145. <https://doi.org/10.1016/j.hydres.2020.02.001>
- Tijani MN (1994) Hydrogeochemical assessment of groundwater in Moro area, Kwara state, Nigeria. *Environ Geol* 24(3):194–202. <https://doi.org/10.1007/bf00766889>
- Vahdati Daneshmand F, Saidi A (1991) Sari; 1:250,000 scale geological quadrangle map of Iran. Geological Survey of Iran, Tehran
- Vandenbohede A, Lebbe L (2012) Groundwater chemistry patterns in the phreatic aquifer of the central Belgian coastal plain. *Appl Geochem* 27(1):22–36. <https://doi.org/10.1016/j.apgeochem.2011.08.012>
- Ward JJH (1963) Hierarchical grouping to optimize an objective function. *J Am Stat Assoc* 58(301):236–244
- WHO (1997) *Guidelines for drinking-water quality (Surveillance and control of community supplies, Volume 3)*. World Health Organization, Geneva
- Wilcox L (1955) *Classification and use of irrigation waters*, vol 969. US Dept. of Agriculture, Washington D.C.
- Yang Q, Li Z, Ma H, Wang L, Martín JD (2016) Identification of the hydrogeochemical processes and assessment of groundwater quality using classic integrated geochemical methods in the Southeastern part of Ordos basin, China. *Environ Pollut* 218:879–888
- Yu J, He X (2006) *Data statistical analysis and SPSS application*. Posts & Telecommunications Press, Beijing

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.