

Assessment of chemical properties and hydro-geochemical coefficients at the Qareh Sou Basin, Golestan Province, Iran

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Abstract This paper focuses on the Qareh Sou Basin in Golestan Province, Iran. Golestan Province is the third largest cereal producer in Iran and water scarcity and salinity are major problems in this area. This study attempts to facilitate the comprehension of system behavior with respect to water quality issues and hydro-geochemical coefficients within the Qareh Sou Basin. This study was carried out during the year 2010. Various parameters, such as pH, EC, chloride, sulfate, bicarbonate, sodium, potassium, calcium and magnesium have been determined for evaluation purposes. Then, Ca/Mg , Na/Cl , $\text{Mg}/(\text{Ca} + \text{Mg})$, Ca/HCO_3 , $(\text{Ca} + \text{Mg})/(\text{HCO}_3 + \text{SO}_4)$, $(\text{Na} + \text{K})/\text{Cl}$, $(\text{Ca} + \text{Mg} + \text{Na} + \text{K})/\text{Cl}$, $\text{HCO}_3 + \text{SO}_4$, $\text{Ca} + \text{Mg}$ and chloro-alkaline indices (CAI) were calculated. Results show that cation exchange probably is an important factor in the hydrochemistry and silicate mineral weathering. Also, CAI-1 plot against CAI-2 demonstrates that most of samples have positive values which suggest normal ion exchange in the system. The carbonic acid is the main agent of calcite, limestone and dolomite weathering which occurs in some stations. According to Chadha's diagram, the type of water is determined as Ca–Mg–HCO₃.

Keywords Hydro-geochemical coefficients · Chadha's diagram · Chloro-alkaline indices (CAI) · Cation exchange · Qareh Sou Basin

Introduction

Water scarcity and salinity are major problems in the reduction of crop production in the arid and semi-arid regions of Iran. Golestan Province is the third largest cereal producer in Iran (Kiani and Abbasi 2009). Moreover, one of the ten targets of the Millennium Development Goals Report (Department of Economic 2006) is the proportion of people without sustainable access to safe drinking water decrease to half by the year 2015. Increasing scarcity of freshwater resources is driving many countries in the arid and semi-arid regions towards using marginal-quality water for agriculture and related activities (Srinivasan and Reddy 2009).

The quality of water is largely controlled by a discharge–recharge pattern, nature of host and associated rocks as well as contaminating activities. Moreover, the nature and amount of dissolved species in natural water is strongly influenced by mineralogy and solubility of rock-forming minerals (Raymahashay 1996). The quality of a river at any point reflects several major influences, including the lithology of the basin, atmospheric inputs, climatic conditions, and anthropogenic inputs (Shrestha and Kazama 2007). The creation of strategies for preventing, control and removing kinds of biological and chemical pollutions in different places of rivers and refineries leads to the promotion of water quality and consumers' health care (Wang et al. 2007).

Rivers and streams are heterogeneous at different spatial scales. This heterogeneity may be attributed to a number of factors including anthropogenic input, local environmental conditions, water discharge, water velocity and degree of temporal variability of surface water chemistry (Qadir et al. 2008). Considering the important contribution of rivers to the main water resources in inland areas for drinking,

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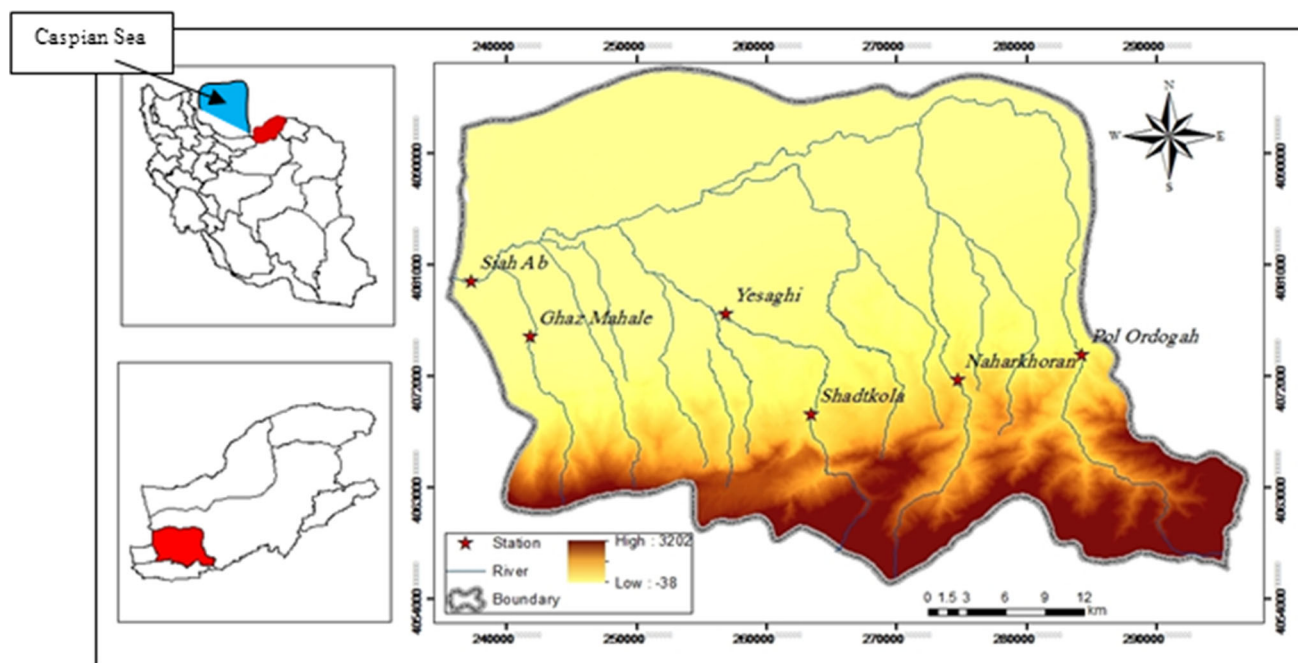


Fig. 1 The map depicts Qareh Sou Basin in North of Iran and sampling stations are located on the basin map

irrigation and industrial purposes, it is imperative to have reliable information on water quality for effective and efficient water management (Bhuiyan et al. 2011). Anthropogenic activities result in a significant decrease in surface water quality of aquatic systems in watersheds (Massoud et al. 2006). According to the FAO guidelines, the salinity of surface water for irrigation did not cause great restrictions; however, many of these waters could create potential permeability problems (Rasouli et al. 2012). Traditional approaches to assessing river water quality are based on the comparison of experimentally determined parameter values with the existing local normative (Debels et al. 2005). Rivers and their basins are highly important parts of the natural heritage. Rivers have been utilized by mankind for thousands of years to the extent that few of them are now in their natural condition (Ngoye and Machiwa 2004). There is a growing concern about the potential effects of extensive land-use change and resultant changes in hydrological conditions on the availability and quality of the water from this watershed (Garizi et al. 2011).

In this study, the Qareh Sou Basin in Golestan Province in Iran was chosen for water quality assessment. Therefore, this study attempts to facilitate the understanding of system behavior with respect to water quality issues and hydro-geochemical coefficients within the Qareh Sou Basin. The objectives of this study are: (1) to examine the variations of river water quality parameters recorded during 2010 and (2) to identify the hydro-geochemical coefficient of the river water.

Materials and methodology

Study area

This paper focuses on the southern part of the Caspian Sea. Qareh Sou Basin (Fig. 1) has an area of 1,637.65 km² along the north mountainside of the Alborz Mountains which is regarded as having the most important nutrients of Qareh Sou River and from the west it extends to Gorgan and from the south it reaches the Alborz Mountains, and finally ends in the Caspian Sea at a village called Qareh Sou (Jahanshahi 2000). The bed of Qareh Sou River is different with a source and estuary which follows from the geological status of this region. With respect to its morphology, the river is divided into mountain and level land (Hanafi 1997).

Sampling and analysis

Six hydrometer stations were used for the sampling of Qareh Sou (Table 1). For examination of Qareh Sou's water quality during 2010, sampling regime were done in 10 stages in different seasons. Overall, 58 samples were analyzed from six stations. Electrical conductivity (EC), total dissolved solid (TDS) and pH were measured by a water checker portable meter (hatch model HQ40D53000000). The bicarbonate (HCO_3^-) had been measured by the alkalinity measurements method. Sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chlorine (Cl^-) and sulfate (SO_4^{2-}) were measured

Table 1 Characteristics of hydrometric stations

Station	River	Altitude (m)	Longitude	Latitude
Naharkhoran	Ziarat	500	54°28′32″	36°45′53″
Shadtkola	Shastkola	150	54°21′00″	36°44′12″
Siah Ab	Qareh Sou	−26	54°3′16″	36°49′35″
Pol Ordogah	Garmabdasht	465	54°34′56″	36°47′5″
Ghaz Mahale	Kurdkoy	5.5	54°6′24″	36°47′17″
Yesaghi	Yesaghi	6	54°16′27″	36°48′31″

by graphite atomic absorption (furnace 4100) using standard methods (APHA 1998).

Results and discussion

General physicochemical characteristics

Table 2 provides a statistical summary of the chemical parameters analyzed for this study. If the anion–cation balance is <5 %, the chemical analysis is assumed to be good. If the balance is much >5 % then the analysis is poor (inaccurate). Other constituents present were not used to calculate the ionic balance which includes the high concentration of H⁺ ions and organic ions (Hounslow 1995). The anion–cation balance of all water samples in the current research work ranged from −10.80 to 1.06 % which is <5 %, indicating the accuracy of the experimental chemical analyses, absence of any other major chemical constituents, absence of high H⁺ ion concentration and absence of significant amounts of organic ions. Height of the sampling stations ranged from −26 to 500 m from sea level. The pH ranged from 6.72 to 8.47. It was shown that water changes from acidic to alkaline. TDS values <450, 450–2,000 and >2,000 mg/l represent the irrigation water as ‘none’, ‘slight to moderate’ and ‘severe’, respectively (UCCC 1974). According to this standard, the Qareh Sou Basin water classified as ‘none’, and ‘slight to moderate’.

Table 2 Statistical summary of the chemical species (in mg/l) from samples in the studied area

Variables	Mean	Variance	Minimum	Q1	Q3	Maximum
Ca (mg/l)	61.71	580.52	28.05	42.08	78.65	116.20
Mg (mg/l)	34.91	256.13	12.15	25.52	42.53	82.64
Na (mg/l)	38.47	2,697.24	2.30	4.21	78.22	208.30
K (mg/l)	3.93	17.09	0.78	1.17	5.76	16.03
HCO ₃ (mg/l)	240.83	3,554.26	122.00	195.31	274.64	439.30
SO ₄ (mg/l)	87.71	6,601.12	20.20	30.52	121.32	456.30
Cl (mg/l)	60.32	5,586.88	7.09	7.09	92.18	319.10
TDS (mg/l)	451.00	65,238.80	205.00	264.34	626.51	1,195.00
pH	7.90	0.15	6.72	7.39	8.17	8.47
EC (mS/cm)	644.35	133,140.49	292.92	377.52	895.01	1,707.15

Hydro-geochemical coefficients

To carry out the investigation, chemical properties were characterized according to its major constituents; and some of the most hydro-geochemical coefficients were calculated. Table 3 provides a statistical summary of these coefficients for the Qareh Sou Basin.

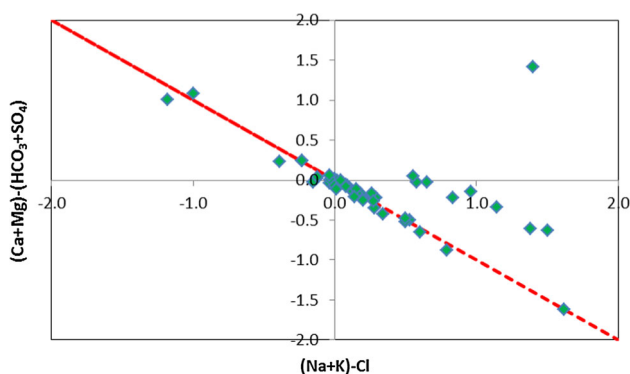
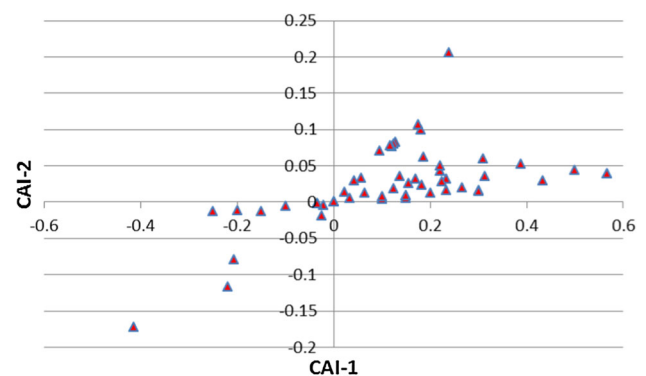
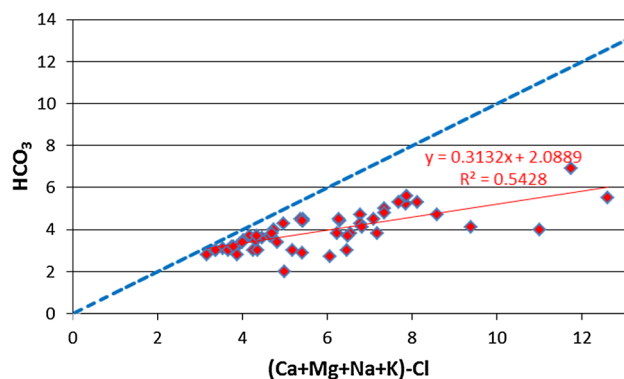
To assess the possible role of ion exchange in the hydrochemistry of the Qareh Sou Basin, (Ca + Mg)–(HCO₃ + SO₄) in meq/l was plotted against (Na + K)–Cl in meq/l (Fig. 2). The (Ca + Mg)–(HCO₃ + SO₄) provides the sum of the cations Ca and Mg from sources other than their respective carbonates and sulfates, whereas (Na + K)–Cl provides the total concentration of the cations K and Na from sources other than their respective chlorides in the system. If cation exchange involving Na and the other major cations occurs in the system, one would expect that a plot of (Ca + Mg)–(HCO₃ + SO₄) in the ordinate axis, against (Na + K)–Cl in the abscissa would result in a straight line of slope at approximately −1. For the absence of these reactions in significant quantities to influence the hydrochemistry, all points will plot close to the origin (Jalali 2007). It is obvious from the plot that cation exchange is probably an important factor in the hydrochemistry at Qareh Sou.

A plot of the sum of the major cations, minus their respective chlorides against HCO₃ (Fig. 3) appears to corroborate this assertion, suggesting that silicate mineral weathering does take place. Data points close to the 1:1 line (the blue dotted line) are attributed to carbonate mineral weathering. Since the basin is made of sedimentary units, the presence and dissolution of carbonate and sulfate minerals might also play variable roles in the hydrochemistry (Yidana and Yidana 2010).

Chloro-alkaline indices (CAI), calculated using Eqs. 1 and 2, were further used to constrain the possible ion exchange reactions taking place in the system. If cation exchange occurs between Ca and Mg in the host rock and K and Na in water, both indices are expected to be positive.

Table 3 Statistical summary of the hydro-geochemical coefficients

Variables	Mean	Variance	Minimum	Q1	Q3	Maximum
Ca/Mg	1.20	0.25	0.37	0.82	1.58	2.44
Na/Cl	0.94	0.53	0.33	0.74	0.89	4.77
Mg/(Ca + Mg)	0.47	0.01	0.29	0.38	0.54	0.72
Ca/HCO ₃	0.77	0.04	0.37	0.62	0.93	1.31
(Ca + Mg)–(HCO ₃ + SO ₄)	0.23	0.26	–1.18	–0.01	0.54	1.62
(Na + K)–Cl	–0.10	0.17	–1.62	–0.22	0	1.41
(Ca + Mg + Na + K)–Cl	5.79	4.31	3.16	4.28	6.81	12.61
HCO ₃ + SO ₄	5.62	4.03	3.24	4.11	6.84	12.78
Ca + Mg	5.85	4.21	3.21	4.32	7.31	11.65
CIA-1	0.07	0.09	–1.21	0	0.22	0.56
CIA-2	0.01	0.002	–0.17	0	0.04	0.20

**Fig. 2** Scatter plot of (Ca +Mg)–(HCO₃ + SO₄) against (Na + K)–Cl**Fig. 4** Scatter plot of CIA-1 against CIA-2**Fig. 3** Scatter plot of (Ca +Mg + Na + K)–Cl against HCO₃

However, if both indices are negative, it indicates a reverse cation exchange (Schoeller 1965; Kumar et al. 2007). Figure 4 shows the scatter plot of CIA-1 against CIA-2, in which most of the samples indicate positive values for both indices, suggesting a normal ion exchange in the system. However, in some cases, the indices are negative, especially in Siah ab station, suggesting reverse ion exchange in

the system. Cation exchange is feasible when exchange sites such as clay minerals are known to be present.

$$\text{CIA-1} = [\text{Cl} - (\text{Na} + \text{K})]/\text{Cl} \quad (1)$$

$$\text{CIA-2} = [\text{Cl} - (\text{Na} + \text{K})]/(\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3) \quad (2)$$

A plot of (Mg + Ca) against (HCO₃ + SO₄) was used to assess the effects of carbonate and sulfate mineral dissolution in the system. Data points that are close to the 1:1 line are attributed to carbonate and sulfate mineral weathering. Those that above the 1:1 line resulted from the effects of the reverse ion exchange processes in the system. Data points that fall below the equiline are deemed to have also resulted from the dissolution of carbonates and sulfates (Yidana and Yidana 2010). In Fig. 5, most of the points fall around the 1:1 line, which is attributed to carbonate and sulfate mineral weathering. Some of them are above the equiline signifying the effects of cation exchange and silicate mineral weathering and some of them which fall below the equiline are deemed to have also resulted from the dissolution of carbonates and sulfates at the Qareh Sou Basin.

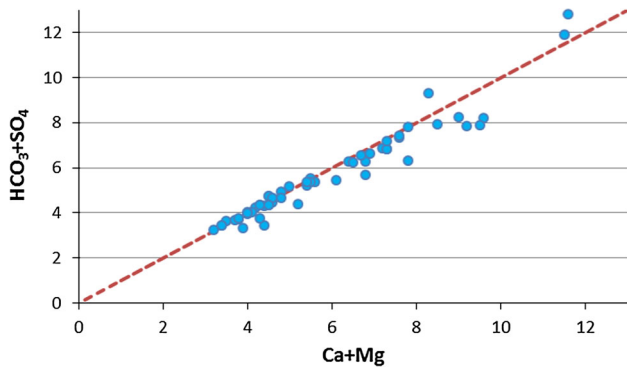


Fig. 5 Scatter plot of (Mg + Ca) against (HCO₃ + SO₄)

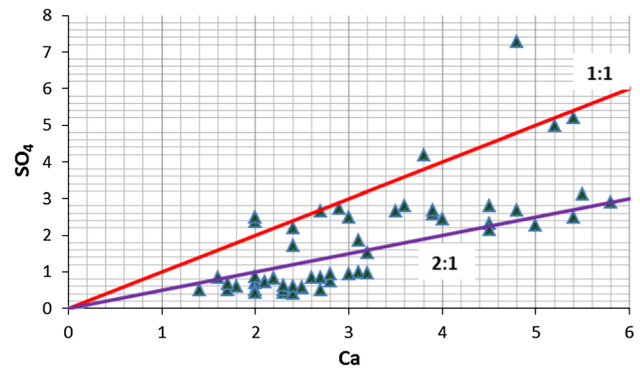


Fig. 7 Scatter plot of Ca against SO₄

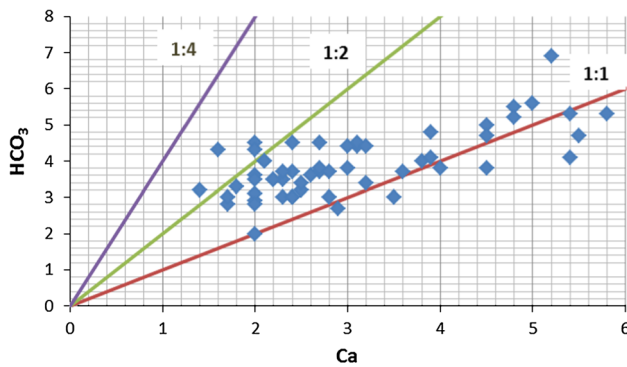


Fig. 6 Scatter plot of Ca against HCO₃

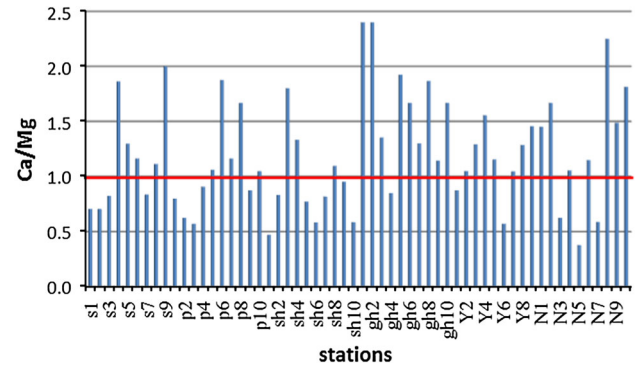


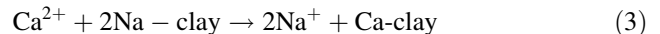
Fig. 8 Ca/Mg ratio at the sampling stations

The dissolution of calcite or dolomite can be mediated by either carbonic or sulfuric acid. The presence of carbonic and sulfuric acids facilitates weathering reactions. If carbonic acid is the agent in the weathering of calcite, the molar ratio of Ca to HCO₃ ions is 1:2, whereas for dolomite weathering it is 1:4. The mediation of sulfuric acid in the weathering of calcite would result in a Ca:SO₄ ratio of almost 1:1 (Garrels and McKenzie 1967). In this study, in the scatter plot of the relationship between Ca and HCO₃ (Fig. 6), some of the points fall between the 1:2 and 1:4 line but most are around the 1:1 line and between the 1:2 and 1:1 line, indicating that the carbonic acid is the agent in the weathering of calcite. The scatter plot for Ca and SO₄ (Fig. 7) does not establish any relationship that would suggest the mediation of sulfuric acid in the weathering of calcite in the system.

In surface and ground waters, Ca/Mg equivalent ratios were >1. Girdhar and Yadav (1982) have reported that lower Ca/Mg ratio in water and soil solution affected soils induces dispersion and subsequently decreases crop yields (Afzal et al. 2000). The Ca/Mg ratio for all stations has been shown in Fig. 8, the diagram depicts almost half of the sample values are >1 and the rest of the samples are

<1, which indicates that water condition in most of stations is relatively acceptable.

In surface and ground waters, the average Na/Cl equivalent ratios were >2, indicating a sodium source other than halite, such as albite, or natural softening according to the following equation (Afzal et al. 2000):



As shown in Fig. 9, Na/Cl ratio at the sampling stations, are often less than 2, indicating the absence of a source other than halite for sodium at the Qareh Sou Basin. In the surface and ground waters, the average Mg/(Ca + Mg) ratio was >0.5, indicating weathering of limestone and dolomite (Afzal et al. 2000). The Mg/(Ca + Mg) ratio for the Qareh Sou Basin suggests the weathering of limestone and dolomite occurs in some stations (Fig. 10). The average of Ca/HCO₃ equivalent ratio is >0.5, indicating natural CO₂ dissolution of calcite (Afzal et al. 2000). As shown in Fig. 11, Ca/HCO₃ ratio at most of the sampling stations is >0.5 and can indicate natural CO₂ dissolution of calcite.

To classify the water and to identify the hydro-chemical processes, a Chadha’s diagram (Chadha 1999) is used. This diagram is a somewhat modified version of the Piper

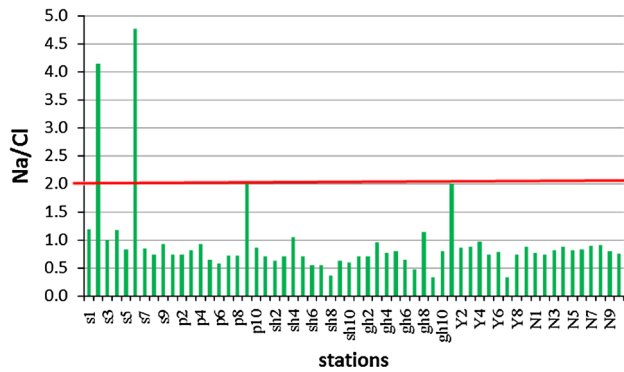


Fig. 9 Na/Cl ratio at the sampling stations

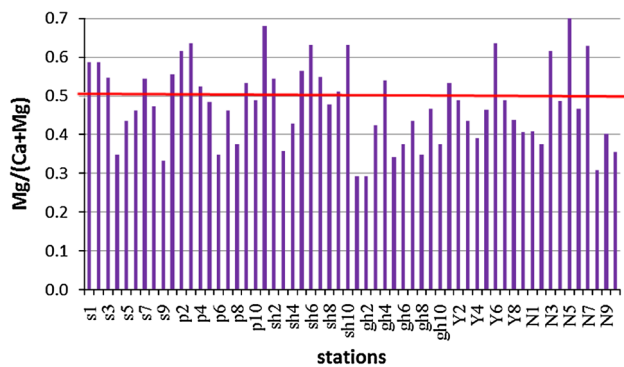


Fig. 10 Mg/(Ca + Mg) ratio at the sampling stations

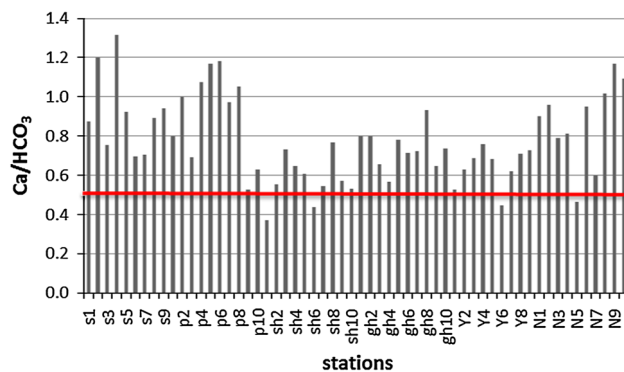


Fig. 11 Ca/HCO₃ ratio at the sampling stations

diagram (Piper 1944) and the expanded Durov diagram (Durov 1948). In Chadha's diagram, samples fall in 2 fields from 8 fields as indicated as green octagon in Fig. 12. The samples from Siahab, Naharkhoran and Pol Ordogah fall in fields 1, which is alkaline earths, and exceed alkali metals. The samples from Yesaghi, Ghazmalleh and Shastkola fall in field 5, which is alkaline earths and weak acidic anions, exceed both alkali metals and strong acidic anions,

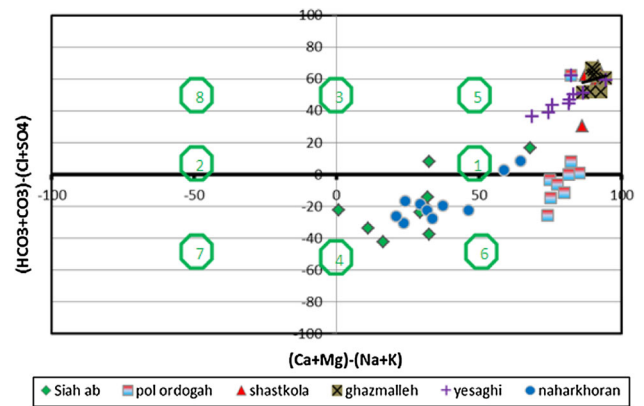


Fig. 12 Classification of samples as per Chadha's at Qareh Sou (1999) Scheme

respectively. The positions of data points in the proposed diagram represent $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ type.

Conclusion

Assessment of the chemical characteristics and hydro-geochemical coefficients of water of the Qareh Sou Basin have been studied on the basis of characteristics of water samples collected from six hydrometer stations during 2010. The possible role of ion exchange in the hydro-chemistry of the Qareh Sou Basin is cation exchange that involves Na and the other major cations in the system. Also, cation exchange occurs between Ca and Mg in the host rock and K and Na in water based on CAI.

Na/Cl ratio indicating human impact on water was relatively weak. Carbonate and sulfate mineral weathering occur in system and carbonic acid is the agent in the weathering of calcite. The presence and dissolution of carbonate and sulfate minerals might also play variable roles in the hydrochemistry, especially in silicate mineral weathering.

Further studies are needed to estimate relationship between trace element and hydro-geochemical coefficients and determining hydro-geochemical coefficients in soil.

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References

- Afzal S, Ahmad I, Younas M, Zahid MD, Khan MH, Ijaz A, Ali K (2000) Study of water quality of Hudiara drain, India–Pakistan. *Environ Int* 26(1):87–96
- APHA (American Public Health Association) (1998) Standard methods for the examination of water and wastewater. American Public Health Association, Port City Press, Maryland

- Bhuiyan MA, Rakib MA, Dampare SB, Ganyaglo S, Suzuki S (2011) Surface water quality assessment in the central part of Bangladesh using multivariate analysis. *KSCE J Civ Eng* 15(6):995–1003
- Chadha DK (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol J* 7:431–439
- Debels P, Figueroa R, Urrutia R, Barra R, Niell X (2005) Evaluation of water quality in the Chillán river (Central Chile) using physicochemical parameters and a modified water quality index. *Environ Monit Assess* 110(1):301–322
- Department of Economic (2006) The Millennium Development Goals Report 2006. United Nations Development Programme
- Durov SA (1948) Natural waters and graphic representation of their compositions. *Akademiya Nauk SSSR Doklady* 59:87–90
- Garizi AZ, Sheikh V, Sadoddin A (2011) Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. *Int J Environ Sci Technol* 8(3):581–592
- Garrels RM, Mackenzie FT (1967) Origin of the chemical compositions of some springs and lakes. In: Stumm W (ed) *Equilibrium concepts in natural water systems*, Advances in Chemistry Series no. 67. American Chemical Society, Washington, DC, pp 222–242
- Girdhar IK, Yadav JSP (1982) Effect of magnesium-rich waters on soil properties, yield, and chemical composition of wheat. *Soil Sci* 134(6):348–353
- Hanafi M (1997) Determination of heavy metals in water of Qareh Su River. Environmental pollution and conservation of sea. School of Marine Science and Technology. Islamic Azad University, North Tehran (in Persian)
- Hounslow W (1995) Water quality data analysis and interpretation. CRC Press Inc, Florida, pp 72–73
- Jahanshahi M (2000) Reported the design of soil and water; self-purification of the Qareh sou river. Gorgan, environment agency (in Persian)
- Jalali M (2007) Hydrochemical identification of groundwater resources and their changes under the impacts of human activity in the Chah basin in western Iran. *Environ Monit Assess* 130(1):347–364
- Kiani AR, Abbasi F (2009) Assessment of the water–salinity crop production function of wheat using experimental data of the Golestan Province, Iran. *Irrig Drain* 58(4):445–455
- Kumar M, Kumari K, Ramanathan AL, Saxena R (2007) A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India. *Environ Geol* 53(3):553–574
- Massoud MA, El-Fadel M, Scrimshaw MD, Lester JN (2006) Factors influencing development of management strategies for the Abou Ali River in Lebanon. I: spatial variation and land use. *Sci Total Environ* 362:15–30
- Ngoye E, Machiwa JF (2004) The influence of land-use patterns in the Ruvu river watershed on water quality in the river system. *Phys Chem Earth* 29(15–18):1161–1166
- Piper AM (1944) A graphic procedure in geochemical interpretation of water analyses. *Am Geophys Union Trans* 25:914–923
- Qadir A, Malik RN, Husain SZ (2008) Spatio-temporal variations in water quality of Nullah Aik-tributary of the river Chenab, Pakistan. *Environ Monit Assess* 140(1):43–59
- Rasouli F, Kiani Pouya A, Cheraghi SAM (2012) Hydrogeochemistry and water quality assessment of the Kor-Sivand Basin, Fars Province, Iran. *Environ Monit Assess* 184(8):4861–4877
- Raymahashay BC (1996) *Geochemistry for hydrologists*. CBS Publisher, New Delhi, p 190
- Schoeller H (1965) *Qualitative evaluation of groundwater resources. Methods and techniques of groundwater investigations and development*. UNESCO, p 54–83
- Shrestha S, Kazama F (2007) Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. *Environ Model Softw* 22(4):464–475
- Srinivasan JT, Reddy VR (2009) Impact of irrigation water quality on human health: a case study in India. *Ecol Econ* 68(11):2800–2807
- UCCC (University of California Committee of Consultants) (1974) *Guidelines for interpretations of water quality for irrigation*. University of California Committee of Consultants, California, USA
- Wang XL, Lu YL, Han JY, He GZ, Wang TY (2007) Identification of anthropogenic influences on water quality of rivers in Taihu watershed. *J Environ Sci* 19(4):475–481
- Yidana SM, Yidana A (2010) Assessing water quality using water quality index and multivariate analysis. *Environ Earth Sci* 59(7):1461–1473