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Groundwater geochemistry of the volcanic rocks in Torud-Chahshirin magmatic belt

Jalal Dolatabadi, Hadi Jafari *, Sajjad Moradi Nazarpoor, Somayeh Zarei Doudeji, Rahim Bagheri

Faculty of Earth Sciences, Shahrood University of Technology, Shahrood, Iran

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Abstract
The increasing population and growing water demands have drawn global research attention to alternative water sources such as hard rocks aquifers. They play a crucial role in arid regions, where water resources are scarce. This study focuses on the volcanic belt of Torud–Chahshirin, situated in the south of Shahrood (Northeast Iran), to assess the geochemistry of water resources. This volcanic belt holds significant importance as it serves as the only water source for surrounding villages. Sampling was conducted during two wet (February 2017) and dry (July 2018) seasons from 34 springs and qanats and physico-chemical parameters (electrical conductivity, pH, temperature, major ions and heavy metals) and stable isotopes (^{18}O and ^{2}H) were measured. Spatial analysis revealed increasing electrical conductivity and temperature with reduction of pH along the flow path, primarily due to the dissolution of evaporate minerals (fracture filling halite and gypsum) and weathering of the silicates that enhanced the concentration of SiO_2 with reduction in altitude along the flow pathways. Temporal changes in major ions indicated higher levels of ions in February as compared to July due to progress in dissolution and weathering processes. Halite and gypsum dissolution and weathering of silicate minerals were determined as the main mechanisms controlling the geochemistry of the groundwater in this area. The concentration of heavy metals followed the order of Rh < Sb < Se < Mo < Sc < Ba < Li < Sr. They mainly sourced from geogenic origins, emerging in concentrations below WHO drinking standard except for Sr. Isotopic studies (^{18}O and ^{2}H) revealed that groundwater from the volcanic belt closely resembles local rainfall, suggesting that local water resources originate primarily from local atmospheric precipitations.

Keywords: Hydrogeochemistry; Stable isotopes; Heavy metals; Hard rocks.

Introduction

Water supply scarcity represents one of the most critical global challenges, necessitating comprehensive water quality assessments. This issue has gained increasing prominence in recent researches. Groundwater resources in semi-arid and arid regions face particular challenges mainly groundwater depletion due to excessive extractions (Hu et al., 2019; Jahanshahi et al., 2025a; Jahanshahi et al., 2025b). These areas are significantly impacted by minimal precipitation and elevated evaporation rates, which consequently lead to increased ionic dissolution and salinity in groundwater systems (Shojaei Baghini et al., 2020; Singhal et al., 2010; Bagheri et al., 2021; Boosalik et al., 2022).

Volcanic aquifers are recognized as premium water sources for human consumption in some regions (Wotany et al., 2013; Awaleh et al., 2017). Overall, the quality of water from volcanic rocks is good due to the minimum contact of water with the rock matrix and low solubility of

* Corresponding author e-mail: h_jafari@shahroodut.ac.ir

the silicate minerals. In general, the quality of water from volcanic sources is the best of all (Hem, 1985). The range of total dissolved solids (TDS) varies from 100 to 50000, averaging as 500 milligrams per liter (mg/l). Chloride ions typically maintain low concentrations in volcanic aquifers due to their primary sources being sea and evaporitic minerals, which are generally absent in volcanic formations. This characteristic chemical signature distinguishes volcanic groundwater systems from other hydrogeological environments (Hounslow, 2018). Additionally, the concentration of heavy metals is another subject that affects the quality of the groundwater. Uranium concentration, as one of the important heavy metals, is a serious issue in the quality of the water from volcanic sources (Aiuppa et al., 2003).

Hydrochemistry of the water from volcanic sources is an interesting research worldwide. Assessment of groundwater quality in a structurally deformed granitic terrain in Hyderabad (India) showed the high concentration of Fe, Be, Co, Pb, U, Zn, Mn, and Al mainly from granite weathering (Satyanarayanan et al., 2007). Results showed that groundwater overexploitation caused the deterioration of water quality for human use. Gastmans et al. (2010) explained that weathering of the silicate minerals in volcanic rocks constitute the minor source of water bicarbonate. Many researches showed the effect of volcanic formations on groundwater (Obiefuna & Sheriff, 2011; Al-Ahmadi, 2013; Kurdehlachin et al., 2018; Yazdizadeh et al., 2019; Bahadori et al., 2019). Recently, stable isotopes (^{18}O and ^{2}H) in combination with chemical data (chemo-isotopic approaches) have gained more interests to finding groundwater origins (e.g. Jahanshahi & Zare, 2017; Mali et al., 2022). The method has been followed to study geochemistry and origin of groundwater in the study area of Torud-Chahshirin magmatic belt.

Torud-Chahshirin volcanic belt, located south of Shahrood (Semnan province, Iran), was selected to evaluate the geochemistry of groundwater as a case of hard rock aquifer. These volcanic water reservoirs are particularly important, as they provide the only source of water for the surrounding villages. In this regard, the study was aimed to investigate the chemical and isotopic signatures of groundwater resources in volcanic belt of Torud-Chahshirin using a chemo-isotopic approach. Spatio-temporal variations of physical and chemical parameters, detectable heavy metals and origin of groundwater resources based on stable isotopes were also studied.

Materials and Methods

To clarify all processes affecting geochemistry of groundwater in the study area, a detail methodological framework was designed (Fig.1). The methodology involved three steps including: 1) sampling, 2) preparing data and 3) interpretation of results. Step-by-step methodology is described schematically in Figure 1.

Study area description

The study area of Torud-Chahshirin is situated in Semnan province, northeast Iran, at approximate longitude of 54° and latitude of 40°. The study area experiences an annual long-term average precipitation of 37.5 mm and a temperature of 30°C (Dolatabadi, 2019). Torud-Chahshirin magmatic belt spans approximately 1,250 square kilometers with an altitude of around 1,850 meters above sea level. The study area corresponds to geological formations from the Oligocene and Eocene periods (Fig. 2). The predominant rock types in this area are Gabbro and Granite (Khajehzadeh, 2009). Schist with carbonate rock, dolomite, and marl with gypsum exists to the south of the study area. Furthermore, to the south and southwest, there is a composition of carbonate rock with shale. The geological structure of the study area was primarily influenced by fault systems. The activity of hydrothermal fluids and faults has led to the formation of silicic and argillic alteration zones (Fig. 2).

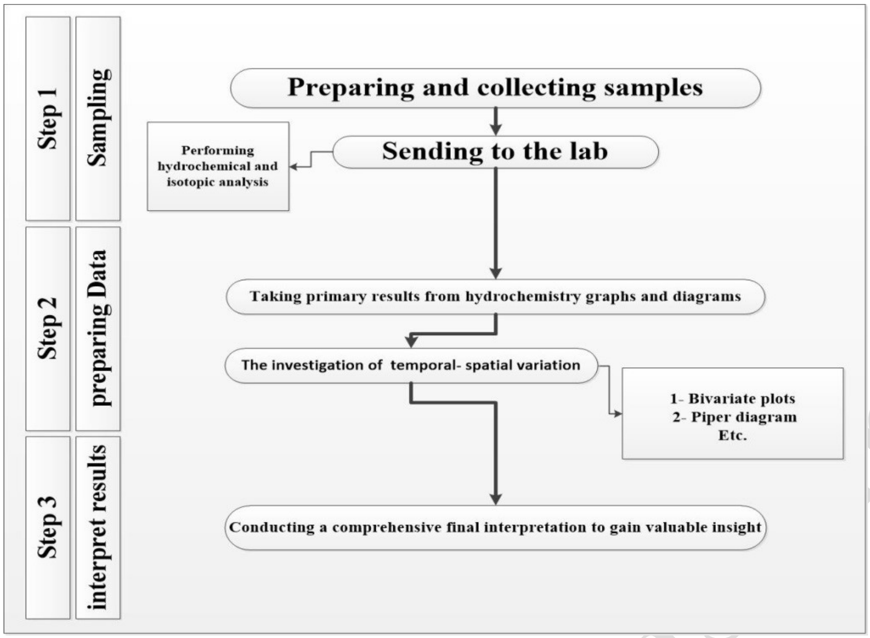

Figure 1. Methodological framework designed to study geochemistry of groundwaters in Torud-Chahshirin volcanic belt

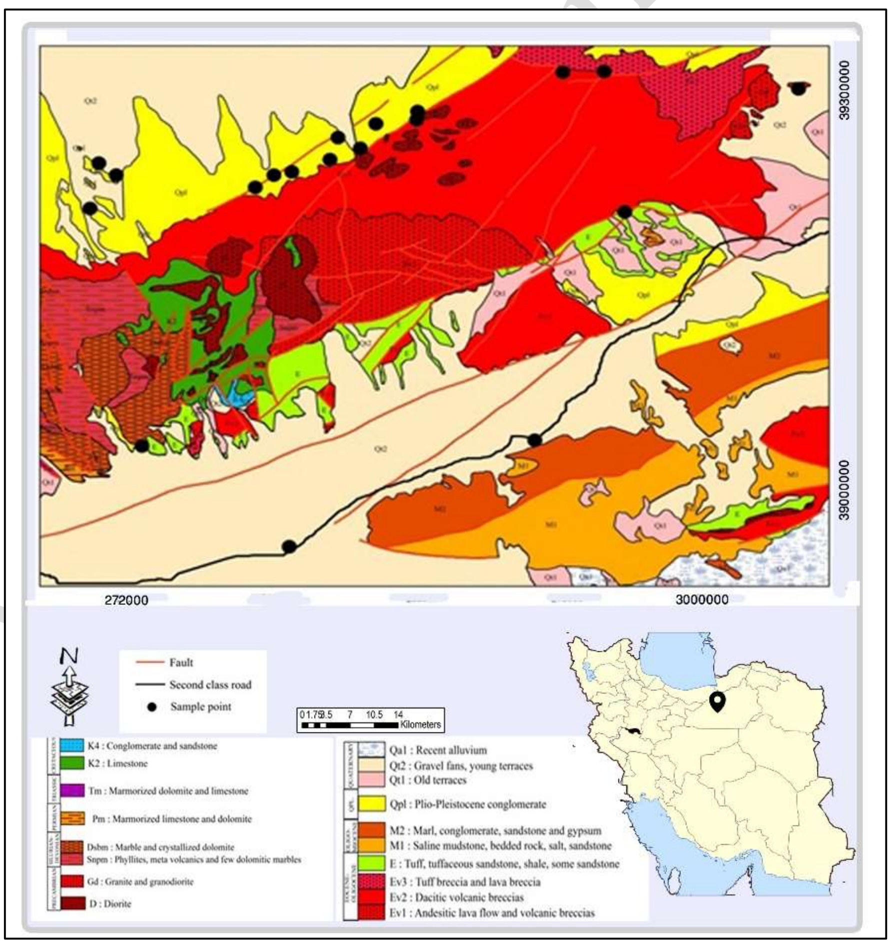

Figure 2. The geological map of the study area (GSI, 1976), representing the location of groundwater samples

Sampling and Analysis

In total, 34 water samples from qanats and springs were collected during wet (February 2017) and dry (July 2018) seasons. Electrical conductivity (EC), temperature and pH were measured in-situ and the samples were transported to the Water and Environment Lab of Shahrood University of Technology. The samples were analyzed for major ions (Na, Ca, K, Mg, Cl, SO4, HCO3). Heavy metals (Ba, Li, Mo, Rb, Sb, Sc, Se, and Sr) were measured in Zarazma Lab and stable isotopes (^{18}O and ^{2}H) were analyzed in Mesbah Energy laboratory. The locations of the groundwater samples are displayed in Figure 2, and the results of the analyses are presented in Table 1.

Table 1. Physico-chemical parameters of the groundwater samples from Torud -Chahshirin area in February 2017 (wet season) and July 2018 (dry season)

Month	Sample	Parameters										
		T (°C)	EC (μS/cm)	pH	TDS (ppm)	Na (epm)	K (epm)	Mg (epm)	Ca (epm)	HCO_3 (epm)	Cl (epm)	SO_4 (epm)
February 2017	W4	16.5	683	7.96	817.5	7.72	0.015	1.85	0.31	4.3	1.59	1.92
	W5	18.3	1715	7.5	1791.9	10.78	0.116	3.87	13.04	4.3	6.63	18.21
	W6	18.8	2950	7.95	2715.6	22.17	0.061	4.24	9.46	2.1	24.67	15.05
	W7	17.2	735	8.05	648.55	5.32	0.016	2.88	2.30	3.9	3.26	3.13
	W9	11.3	1024	8.01	791.8	7.00	0.107	1.29	2.69	3.0	1.94	6.25
	W10	10.8	724	8.16	578.1	4.74	0.043	1.26	2.44	2.7	1.29	3.96
	W11	6.3	1186	8.35	1037.5	8.78	0.025	2.56	2.70	3.8	1.17	9.9
	W12	4.5	604	8.26	478.82	4.36	0.022	0.76	1.29	2.2	0.96	2.29
	W13	5.5	1120	8.18	903.94	6.10	0.030	2.69	2.82	2.3	1.28	8.32
	W14	6.4	726	8.26	622.84	4.78	0.028	1.26	2.08	2.6	1.86	3.41
	W16	7.1	578	7.93	492.5	3.46	0.023	0.95	2.13	2.7	1.63	2.3
	W17	12.4	632	8.25	549.07	6.18	0.023	0.45	1.56	3.0	1.03	3.06
	W18	10.4	1005	8.07	923.9	9.06	0.063	1.21	3.56	2.9	1.25	8.29
	W19	10.8	1025	8.12	952.77	8.89	0.053	1.32	4.36	2.5	1.77	9.94
July 2018	W1	20.5	2520	7.52	2053.68	17.20	0.057	2.92	13.00	3.5	15.06	13.37
	W2	18.5	1355	7.27	864.62	5.40	0.025	1.51	4.78	3.6	1.15	6.93
	W3	21.5	1814	7.6	975.18	12.09	0.028	0.58	1.40	3.5	6.77	3.66
	W4	26	885	7.76	572.46	5.97	0.026	0.25	0.31	4.2	1.60	1.7
	W5	30.5	2636	7.25	1808.79	10.89	0.103	2.00	9.50	4.8	2.65	18.79
	W6	26.5	4452	7.54	2261.94	22.22	0.075	2.87	6.70	1.8	23.11	12.5
	W7	23.5	1026	7.6	653.31	5.09	0.023	2.44	1.68	3.4	3.01	2.82
	W8	24.2	1716	7.78	1011	9.68	0.028	1.72	3.34	2.6	3.64	7.95
	W9	18.5	1365	7.13	875.05	6.93	0.069	1.23	3.34	3.5	1.99	6.59
	W10	19.8	946	7.82	599.29	4.78	0.026	0.96	1.90	2.8	1.27	4.02
	W11	17.5	1618	7.69	995.39	8.49	0.031	2.52	2.59	3.5	1.09	9.07
	W12	19	777	7.91	508.79	4.36	0.024	0.89	1.23	3.3	0.90	2.22
	W13	17.7	1478	7.5	977.82	6.94	0.020	3.05	4.15	3.2	1.53	8.71
	W14	19.8	928	7.69	561.88	4.75	0.028	0.97	1.82	2.7	1.75	3.1
	W15	19.3	665	7.68	429.55	3.87	0.022	1.02	1.78	2.7	1.24	1.58
	W16	17.3	686	7.54	441.25	3.86	0.025	0.71	2.25	2.9	1.21	1.55
	W17	24.8	824	7.98	557.17	5.69	0.022	0.44	1.31	3.1	1.02	2.91
	W18	19.7	1275	7.74	929.78	7.88	0.026	1.02	3.06	3.9	1.31	7.61
	W19	19.7	1339	7.68	906.40	7.42	0.041	1.07	3.43	2.9	1.56	8.13

Data Interpretation

In order to explore the time and space distribution of hydrochemical parameters, spatio-temporal variations of EC, pH, temperature and ions were investigated along the flow path in two seasons. Composite plots were used to assess the effects of human activity and geological impact on groundwater chemistry and to determine the origin and mixing of groundwater (Mazore, 2004). Schoeller and Piper diagrams were used to analyze the hydrochemical processes and to display the hydrochemical facies of the groundwater. In summary, a variety of hydrochemistry diagrams and bivariate plots were applied to identify dominant hydrochemical processes in the study area. Isotopic data (^{18}O and ^{2}H) were interpreted in relation to global and local meteoric water lines to identify the origin of groundwater in Torud-Chahshirin volcanic belt.

Results and Discussion

Results of the hydro-chemistry methods

Table 2 presents the mean values of the parameters collected in wet (February 2017) and dry (July 2018). Overall, it is evident that the mean values generally increased from February to July. This increase can be likely attributed to enhancement of dissolution and weathering processes and reduction in recharge volume, as well. The mean value of EC is 1287 µS/cm, and according to the mean value of TDS (907 ppm), the TDS-EC relationship of the study area can be expressed as:

TDS (ppm) = 0.7 EC (µS/cm)

According to Freeze & Cherry (1979), the standard range for silica (SiO_2) in hard rock aquifers is typically between 10 and 30 mg/l. However, in the study area, the mean value of silica concentration was measured 30 mg/l, exceeding the global mean. This anomaly may be attributed to the weathering of plagioclase, quartz, biotite, pyroxene, and amphibole in contact with the circulating water.

Spatio-temporal variations of physico-chemical parameters

Figure 3 illustrates the spatial variation of electrical conductivity (EC) in the study area during the both wet and dry seasons. The results indicate that EC values were generally higher in February as compared to July. Furthermore, the southern portion of the study area exhibited the highest EC values during both seasons.

To further analyze the spatial distribution of EC, Figure 4 illustrates the correlation between elevation and EC. EC demonstrates an inverse correlation with elevation. This relationship can be attributed to increases in flow paths at lower elevations that enhance residence time of groundwater in contact with geological materials and enhancement for dissolution and weathering processes. The processes contribute to increased EC values in lower altitude regions.

Table 2. The mean values of the chemical data in groundwater samples from Torud-Chahshirin area for wet (February) and dry (July) seasons

Parameter (mean)	TDS (ppm)	SiO2 (ppm)	HCO_3 (ppm)	SO_4 (ppm)	Cl (ppm)	Ca (ppm)	K (ppm)	Mg (ppm)	Na (ppm)	pH	EC (µS/cm)
February	887.3	-	192.3	269.7	125.5	75.4	1.73	22.9	196.1	8.1	1018.5
July	926.3	30.5	195.5	311.3	134.3	71.3	1.58	18.5	189.5	7.6	1556.6

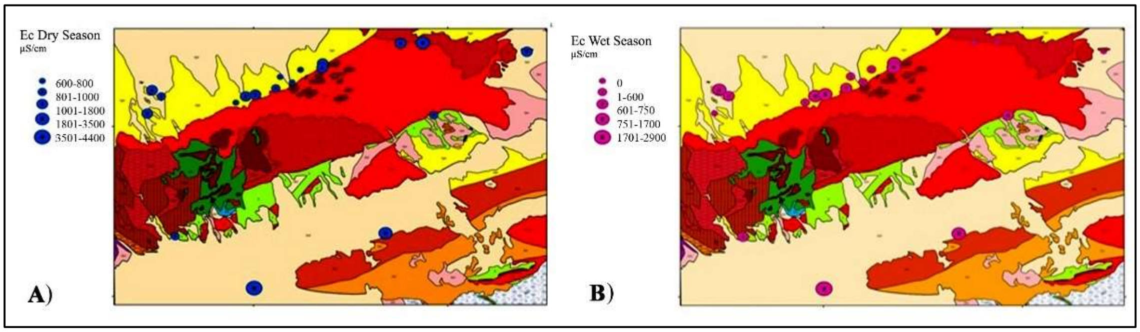

Figure 3. Spatial variations of EC during February (A) and July (B) seasons

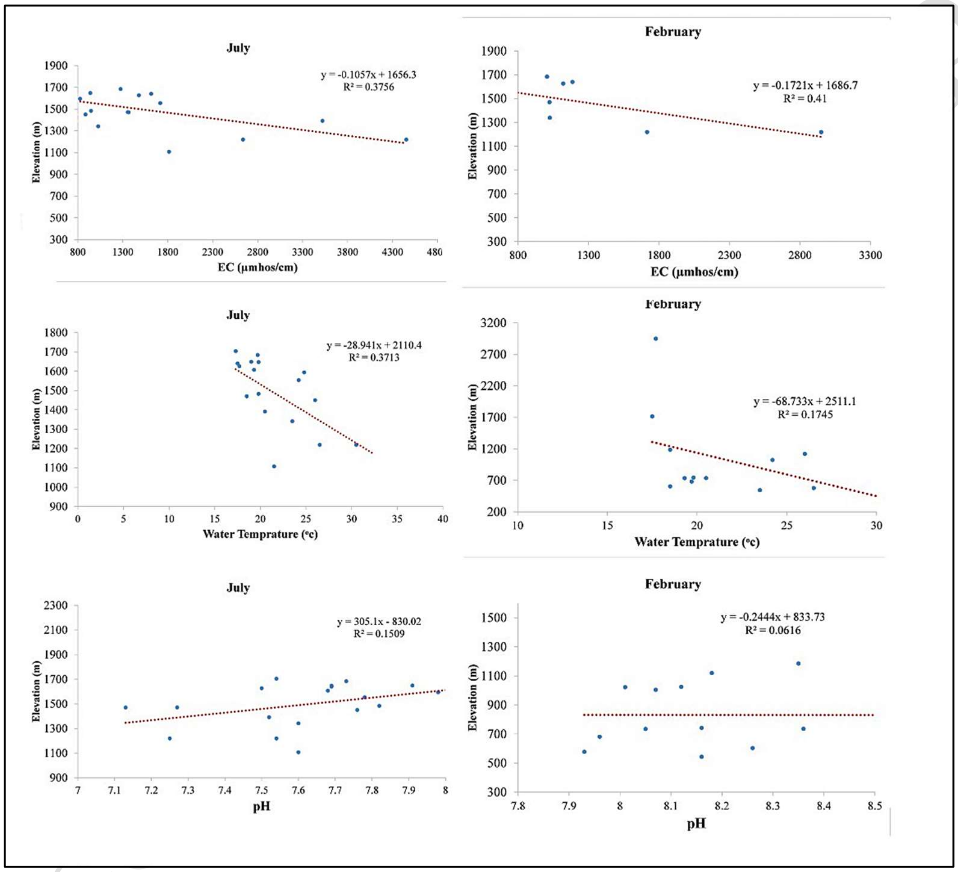

Figure 4. Variations of EC, pH and temperature of the groundwater samples with elevation during wet (February) and dry (July) seasons

Figure 4 shows the correlation between elevation and temperature in groundwaters from Torud-Chahshirin volcanic belt for both wet (February) and dry (July) seasons. Overall, the average temperatures are 11 degrees °C in February increased to 21°C in July. A consistent increase in temperature is observed with decreasing elevation in response to the extended flow path and increased residence time. In addition, seasonal temperature variations suggest that the aquifer is relatively shallow, influenced by the surface air temperature.

The spatial variation of pH with respect to elevation is shown in Figure 4. Overall, the pH remained stable for the both wet and dry seasons. However, a decrease in the average pH was observed at lower altitudes. This decrease can be attributed to dissolution and weathering of sulfide minerals in volcanic rocks where the water infiltrates and circulates through the fractures and comes in contact with these minerals.

The relationship between major ions and TDS as an indicator of groundwater movement along the flow path is depicted in Figures 5. These figures reveal significant variations in cation and anion concentrations, which are contributed to increase in flow path. However, the rates of increase in anions and cations concentrations differ between February and July, generally due to reduction in recharge rates and then groundwater velocity in dry seasons.

Figures 6 illustrate the relationship between SiO_2-elevation and SiO_2-TDS during the dry season. An increase in SiO_2 is observed as elevation decreased or TDS enhanced. This may be attributed to the increase in residence time and progress in weathering of silicate minerals (e.g. plagioclase), leading to an increase in silica concentrations along the flow path based on the following equation:

$$2NaCaAl_3Si_5O_{16} + 6CO_2 + 9H_2O \rightarrow 2Ca^{2+} + 2Na^{+} + 6HCO_3^{-} + 4SiO_2 + 3Al_2Si_2O_5(OH)_4 \downarrow \quad \text{Eq.1}$$

Temporal variations of EC, pH, temperature are shown in Figure 7, providing insights into the changes in two wet and dry seasons. In comparison with wet season, enhancements in EC and temperature values and reduction of pH are observed in dry season as mentioned and discussed earlier.

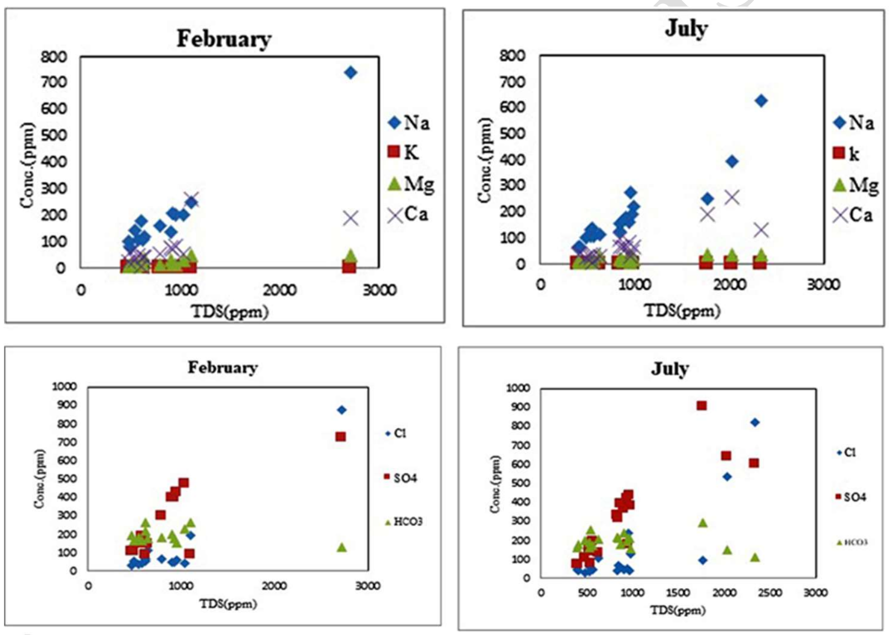

Figure 5. Relationships between total dissolved solids (TDS) and major ions concentrations during the wet (February) and dry (July) sampling periods

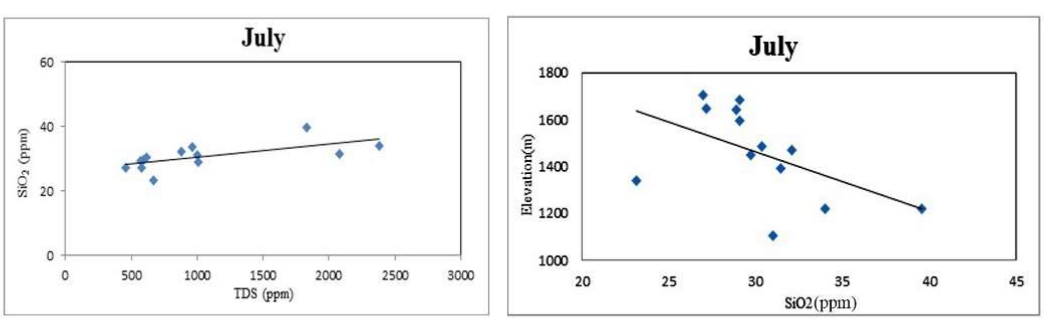

Figure 6. SiO_2-elevation and SiO_2-TDS relationships in Torud-Chahshirin groundwater samples

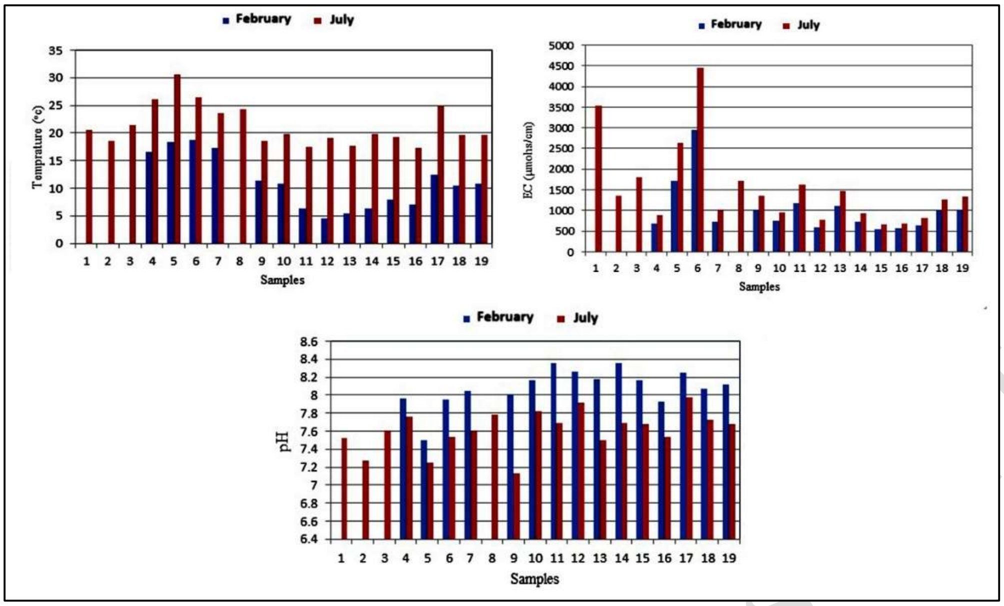

Figure 7. Temporal variations of groundwater temperature, electrical conductivity (EC) and pH during wet (February) and dry (July) seasons, showing increase in EC and temperature and reduction of pH in dry season

Mechanisms controlling groundwater geochemistry

The strong correlation between Na and Cl (Figure 8) with correlation coefficient approaching 1, underscores the main process of the halite (NaCl) dissolution. Direct correlation confirms halite dissolution mainly in fracture filling sediments, as this process releases Na and Cl to the solution in 1:1 ratio (Equation 2).

$$NaCl \rightarrow Na^{+} + Cl^{-} \qquad \text{Eq. 2}$$

Moreover, the excess Na suggests additional sources, potentially from weathering hard rock minerals. The volcanic rocks of the Torud-Chahshirin belt contain abundant plagioclase feldspars (albite–andesine series), as documented in regional geological surveys and confirmed by petrographic descriptions of the study area (Khajehzadeh, 2009). Weathering of plagioclase releases sodium into solution through hydrolysis reactions (Eq. 1). The mechanisms were further confirmed in other hard rock aquifers like Shir-kuh granitoid aquifer (Yazdizadeh et al., 2019) and Mahabad Ryolite aquifer (Kurdehlachin et al., 2018).

The correlation coefficient between Ca and SO_4 (Figure 9) suggests that dissolution of gypsum mineral available in the geological units (M2) and fracture-filling sediments is the primary source for Ca and SO_4 ions (Eq. 3). Furthermore, the relatively stable concentration of bicarbonate (HCO_3) compared to calcium (Ca) provides additional evidence supporting gypsum dissolution as the predominant source of calcium.

$$CaSO_4 \rightarrow Ca^{2+} + SO_4{}^{2-} \qquad \text{Eq. 3}$$

Based on the above explanations, halite and gypsum dissolution and weathering of the silicate minerals are introduced as the main sources of the ions in groundwater resources in Torud-Chahshirin volcanic belt, controlling the geochemistry of water resources in this magmatic region. Based on the Piper diagram (Figure 10), the dominant water types in both wet and dry seasons are Na-SO_4, approving the main mechanisms of halite dissolution and silicate weathering that enhances the Na and gypsum dissolution which releases SO_4 in groundwater resources. The Schoeller semi-logarithmic diagram (Figure 11) reveals parallel lines that indicate similar trends and common origins among the samples (Todd & Mays, 2004). The consistent patterns observed in the major ions further support the hypothesis of a common origin for the all samples in the study area.

The isotopic survey

The groundwater stable isotopes, the local meteoric water line (LMWL) based on Shahrood precipitation samples (Kazemi et al., 2015), and the global meteoric water line (GMWL) are depicted in Figure 12. The most relevant result is that evaporation did not significantly impact the groundwater, as evidenced by the similarity between the groundwater isotopic data and the LMWL. This confirms that the main source of the groundwater samples is the local precipitation. No other sources are identified.

The deuterium excess (D-excess) of the groundwater samples were calculated as the following:

D-excess = $\delta^2H - 8\delta^{18}O$

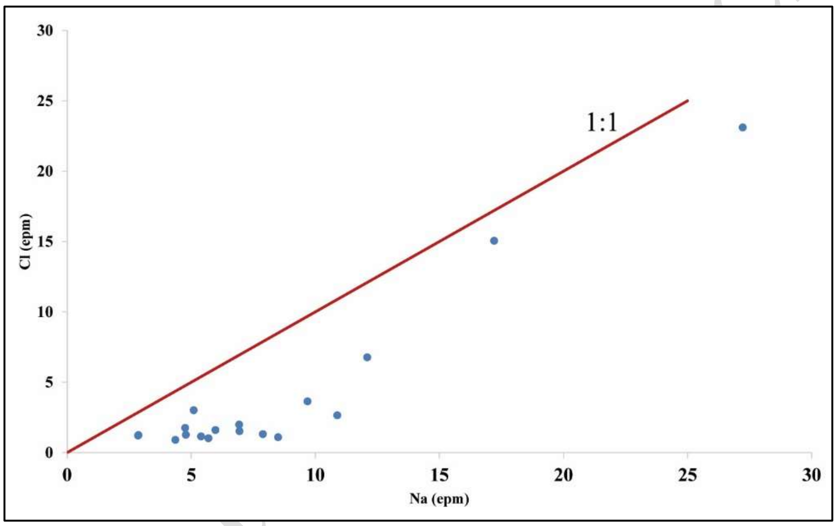

Figure 8. The correlation of the Na and Cl in groundwater samples representing halite dissolution as the main source of the ions

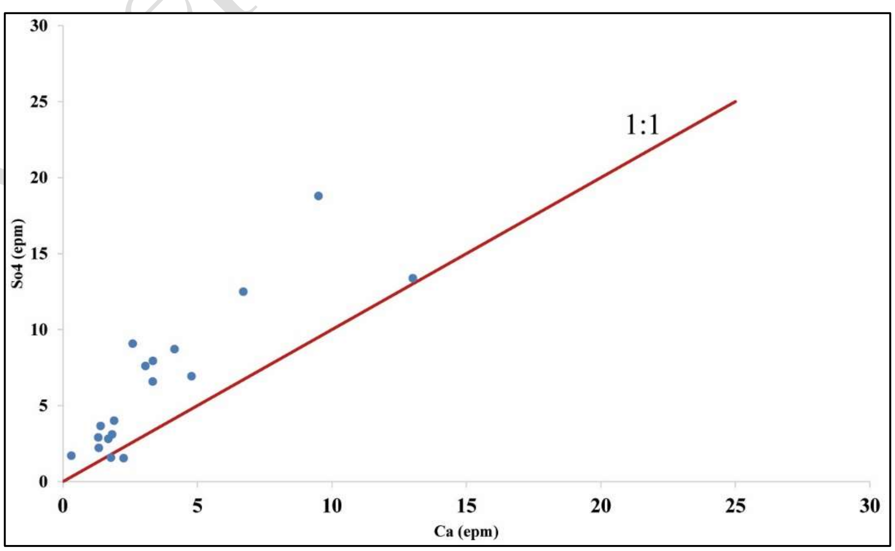

Figure 9. The correlation of the Ca and SO4 in groundwater samples from Torud-Chahshirin area

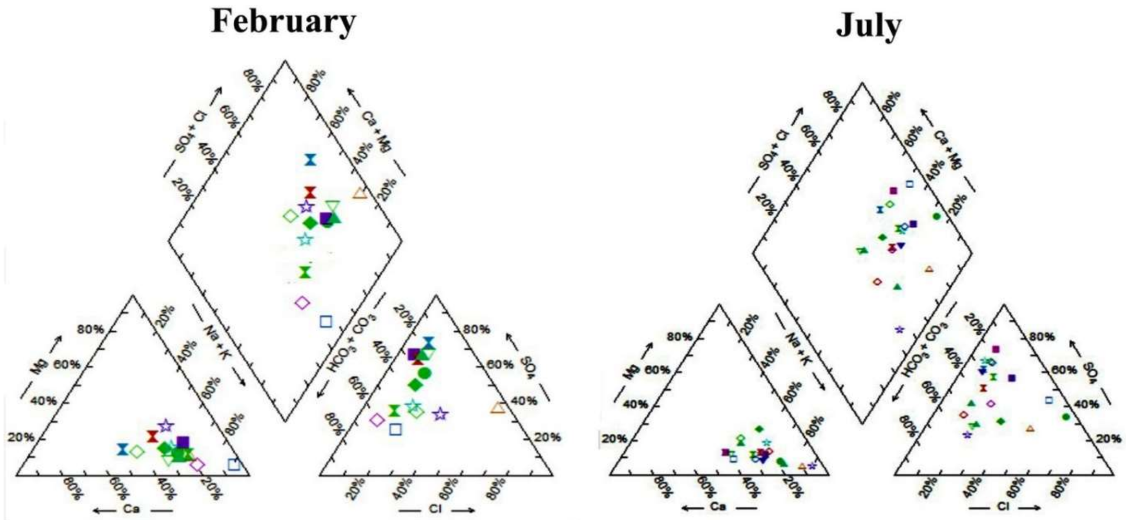

Figure 10. Groundwater samples on Piper diagrams, representing dominant water type of Na-SO4 in both wet and dry seasons

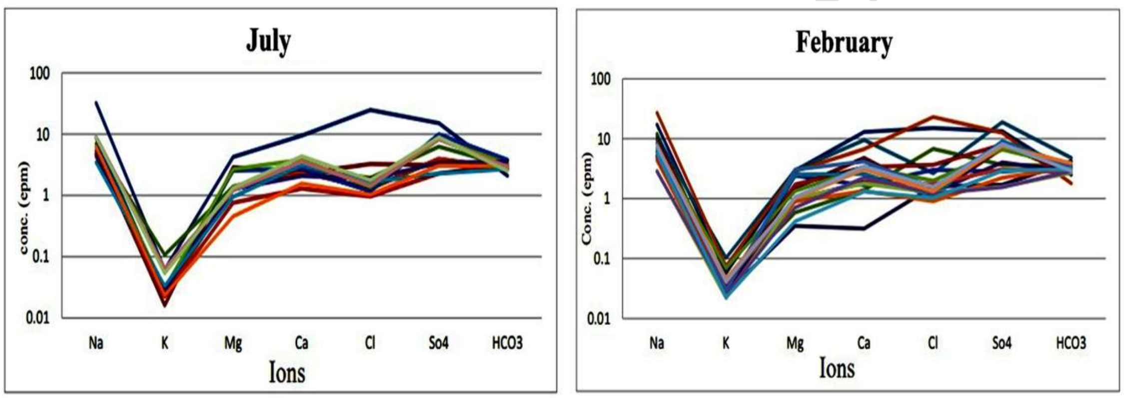

Figure 11. The Schoeller diagrams for wet and dry seasons, showing the common origin of the groundwater samples

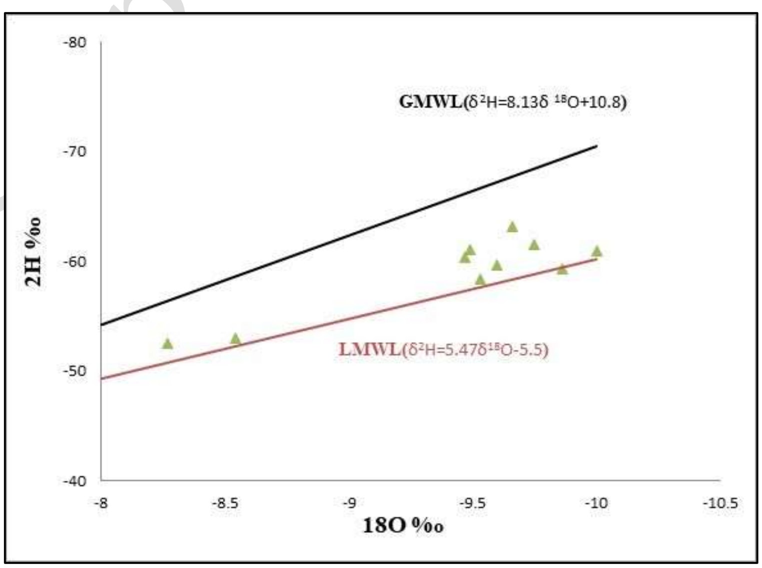

Figure 12. The variations in deuterium (^{2}H) and Oxygen-18 (^{18}O) in the groundwater samples as compared with the local (LMWL) and global (GMWL) meteoric water lines

The values of D-excess vary in the range of 13.6 to 19.5, averaging as 16.3‰. It is a proxy of the humidity of the source region, with lower humidity causing higher D-excess values. The average value of D-excess in the study is close to D-excess of Mediterranean meteoric water line (22‰) that proposes sources of precipitations mainly from Mediterranean air masses with lower humidity as compared with global precipitations (GMWL). D-excess values lower than 22‰ propose probable mixing of the air masses.

Heavy Metals in groundwater

Heavy metals naturally occur in groundwaters, limiting drinking uses of the water as they can create dangerous conditions for human health. The effects of heavy metals extend to the environment and humans. Based on these concerns, 13 groundwater samples were selected and analyzed for heavy metals by ICP-MS. Strontium, selenium, scandium, antimony, rhodium, molybdenum, lithium, and barium were measured in concentrations more than the detectable limit of the instrument (Table 3). Based on the measurement, heavy metal concentration ordered as the following:
Rh < Sb < Se < Mo < Sc < Ba < Li < Sr

The maximum concentration was observed for Strontium (Sr). According to the WHO standard thresholds (Table 3), with the exception of Sr the concentrations of the all analyzed elements were below the permissible limits for drinking uses.

Conclusion

Geochemical characteristics of the groundwater samples in Torud-Chahshirin magmatic belt as a case of hard rock aquifer was assessed based on physico-chemical parameters and stable isotopes measured in wet (February 2017) and dry (July 2018) seasons. The spatio-temporal variations of the parameters confirmed enhancement of the electrical conductivity (EC), silica (SiO_2) and major ions with decrease in elevation that stands for the length of the groundwater flow pathways. Temporal changes in major ions indicated higher levels of ions in July as compared to February due to progress in dissolution and weathering processes.

Table 3. The concentration of heavy metals in groundwater samples from Torud-Chahshirin volcanic belt, compared with the WHO standards

Sample	Barium (ppb)	Lithium (ppb)	Molybdenum (ppb)	Rhodium (ppb)	Antimony (ppb)	Selenium (ppb)	Strontium (ppb)
W1	21.04	102.18	1.82	1.56	5.82	8.25	5560
W2	19.51	36.93	3.59	1.33	4.49	3.77	1620
W3	0.5	40.75	10.26	2.21	2.16	7.89	1120
W4	0.5	17.15	3.85	2.46	4.27	4.05	350
W5	28.65	45.28	3.9	1.59	1.3	6.33	2860
W6	11.49	52.91	4.24	4.99	1.18	17.28	4540
W7	0.5	20.45	4.63	2.22	1.3	6.19	1090
W8	5.9	21.23	9,86	0.5	2.04	4.05	1000
W9	8.0	27.51	6.42	1.61	3.07	3.27	1540
W10	50.74	15.32	0.14	1.53	1.12	4.27	1100
W11	71.7	12.3	1.52	1.85	0.5	4.13	1040
W12	0.5	14.9	3.74	2.21	1.31	2.84	530
W13	0.5	33.69	22.42	3.4	4.9	1.71	1020
Max.	71.7	102.18	22.42	4.99	5.82	17.28	5560
Min.	0.5	12.4	0.14	0.5	0.5	1.71	530
Mean	16.9	33.9	5.9	2.2	2.6	5.7	1797.7
WHO	**700**	-	**70**	-	**20**	**10**	-

The main mechanisms controlling the geochemistry of the groundwater were identified as halite and gypsum dissolution and weathering of the silicate minerals. The processes enhanced major ions and silica in groundwater samples, as the dominant water types were recognized as $Na\text{-}SO_4$.

Isotopic studies based on stable isotopes (^{18}O and ^{2}H) revealed that groundwater from the volcanic belt closely resembles local rainfall. This confirms the main source of the groundwater samples is the local precipitation. No evaporation effects and other sources for groundwater were identified.

The concentration of heavy metals followed the order: Rh < Sb < Se < Mo < Sc < Ba < Li < Sr. They mainly sourced from geogenic origins (weathering of the silicate minerals), emerging in concentrations below WHO drinking standard except for Sr.

This study provides valuable insights into the geochemical characteristics of the groundwater in volcanic belt of Torud-Chahshirin, which is crucial for the sustainable management of vital groundwater resources in this arid region.

Conflicts of interest

There are no conflicts of interest to declare.

Authors' contributions:

Jalal Dolatabadi: Field works, Acquisition of data, Analysis and interpretation of data; Hadi Jafari: Conception and design of study, Supervision, Analysis and interpretation of data, Drafting and revising the manuscript; Sajjad Moradi Nazarpoor: Drafting and revising the manuscript, Analysis of data; Somayeh Zarei Doudeji: Drafting the manuscript, Analysis of data; Rahim Bagheri: Analysis and interpretation of data.

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