



## Hydrogeochemical evaluation of springs water for drinking, agricultural, and industrial purposes in Alvand heights of Hamedan, west of Iran

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### Abstract

Alvand heights can be considered a suitable site for reserving a significant volume of water. The main contributors to this potential are lithology (mainly comprised of igneous rocks and metamorphism), erosion performance, and tectonic forces regarding their roles in feeding hard formations. In the present study, the hydrogeology and hydrogeochemistry of water resources in Alvand heights are evaluated. Also, the effect of geological formations on the quality of these resources is investigated. For hydrogeochemical studies of water resources of hard formations of Alvand heights and their suitability for drinking, agricultural, and industrial uses in the study area, 27 water samples were collected from the region's springs and subjected to chemical analyses. The predominant water type in all samples is the bicarbonate-calcium. Generally, the water quality of the springs for domestic and drinking purposes is in good condition in terms of hardness such that the samples have no permanent hardness and are soft water based on the total hardness. Based on various indicators (i.e., SAR, EC, Na<sup>+</sup>%, and RSC), the water quality of the springs was assessed as very good for agricultural use and irrigation. Evaluating these indicators showed that most springs have corrosive and invasive waters. Moreover, the hydrochemical composition of the region's aquifers is mainly affected by geological and geochemical factors, including weathering of igneous rocks, metamorphism, feldspar minerals (especially plagioclase and orthoclase), and biotite.

**Keywords:** Water Chemistry; Alvand Springs; Igneous And Metamorphic Rocks; Effect Of Lithology On Water Quality; Hamedan; Iran.

### Introduction

Today, access to quality drinking water is considered a major challenge in many societies (Lone et al., 2021). Population growth and water demand have intensified the necessity and importance of groundwater resources as one of the most important sources of freshwater supply. Groundwater makes up only 20% of the world's freshwater, which is equivalent to 0.61% of the world's total water (Singh et al., 2019). Increasing and uncontrolled use of alluvial aquifers and the water level decline in these aquifers have urged to find other groundwater sources in hard formations. Therefore, exploration and exploitation of water resources in the aquifers of hard formations are currently of special importance regarding the urgent need for drinking water supply in urban areas. Besides, the quality of these resources is higher compared to alluvial

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resources. Aquifers formed in hard formations are vital in some areas (e.g., Africa), as they are their only considerable water reserves (Setlur et al., 2019). Hard Formation aquifers can supply water to scattered populations, small to medium-sized villages, or suburbs of larger cities. Groundwater aquifers in hard formations are more often of better quality than surface water and contribute to population well-being and economic development. These aquifers are especially important in arid and semi-arid regions where surface water resources are seasonal and limited to land adjacent to major rivers. In this respect, large parts of Africa, South America, Asia, and Australia rely on these groundwater resources (Lachassagne et al., 2021).

Therefore, groundwater exploration, detection, and potentiality mapping in this type of formation are of great importance. Iran has a semi-arid climate with an average annual rainfall of about 250 mm. This rainfall level is less than one-third of the average annual rainfall in the world (Nazaripour et al., 2011). Also, this country's temporal and spatial rainfall distributions do not have a uniform pattern. As a result, in most parts of the country, we always face the problem of water shortage (Nakhaei, 2009). Although groundwater resources in the Formation aquifer are hard to form, they are of great strategic importance in many parts of the world because they provide unique water reserves for human and agricultural use (Singhal & Gupta, 2010).

Hard rock formations are sedimentary, metamorphic, and igneous rocks with partial primary porosity or no primary porosity. These formations can store water due to weathering and a developing system of secondary fracture porosity. Hence, these formations are also known as jointed rocks. Also, these formations cover more than 20% of the current land surface (Witherspoon et al., 1980). Although these aquifers make up for a small share of groundwater resources, many studies have been recently conducted on these resources due to the global water shortage. Such intense attention shows the importance of these aquifers due to the inherent characteristics of hard formations. Regarding the inherent properties of hard formations, in areas with the potential to make aquifers, their soluble materials might affect the hydrochemistry of these aquifers.

Aquifers in hard formations are usually shallow and form at the initial 100 m above the ground. Since these aquifers are hydraulically distinct, they are called discontinuous aquifers (Lachassagne, 2008). In hard formations such as granite massifs, the number of fractures in rock mass decreases from its surface to the depth, and fracturing severity declines. As a result, dense rocks act as impermeable bedrock, and a free aquifer is formed in the upper parts of the granite rock mass with more intense weathering. There are examples of these aquifers in the Alvand mountains in the Ganjnameh region (southwest of Hamedan, Iran) (Ghobadi, 2017). Unlike alluviums, where the volume of water stored is equivalent to 10 to 15% of the alluvium volume, this percentage is less than 2% in hard rocks. The discharge of wells or springs in these formations is between 0.5 and 50 liters per second (L/s). This discharge is affected by rainfall, intensity-duration of rainfall, the proximity of wells with major fractures, distance to water sources, size and degree of upstream waterways, regolith thickness, topography, and geomorphology of the well site (Houston, 1992).

Springs have recently become extremely important regarding their role in meeting the increasing demands for drinking water (Bhat et al., 2020). Springs are essential for the livelihoods of mountain communities worldwide (Tambe et al., 2011; Risko, 2018; Bhat & Pandit, 2018). Springs are less well-known in the scientific literature, despite their numerous benefits and services. Thus, the need for an in-depth look at the stressors and various health threats to the spring ecosystem is ignored (Barquin & Scarsbrook, 2008; Nelson, 2008; Unmack & Minckley, 2008). Springs have recently received much attention also regarding their role in ecosystem services, e.g., in the climate change threat scenario forecasted for the Himalayas (IPCC, 2014; Gupta & Kulkarni, 2017). Although springs play a vital role in water security, their role in promoting socioeconomic characteristics and overall development has been rarely

discussed at the policy and governance levels (Springer et al., 2008; Kreamer et al., 2014; Gupta & Kulkarni, 2017). Springs developed at the intersection of groundwater with the ground surface are of special importance for studying groundwater in hard formations as they directly reflect the internal characteristics of the aquifer (Kresic & Stevanovic, 2010).

To date, several studies have been conducted on spring waters worldwide (Ryan & Meiman, 1996; Prasad & Bose, 2001; Ragno et al., 2007; Michalik, 2008; Ako et al., 2012; Shigut et al., 2017). For instance, Barbieri et al., (2017, 2019) evaluated the principal geochemical processes and the contamination of anthropogenic and natural sources' impact on the quality of the aquifer system groundwater used for agricultural and domestic purposes. Hydrogeological and geological settings can be used to predict discharge properties and spring water quality. Groundwater characteristics, in special hydrogeochemical properties, show its principal source, water type, the mechanism of its formation, interaction between the water and rock, and the groundwater reservoir's environment (Sun et al., 2014; Saxena & Ahmed, 2001; Taheri et al., 2017; Zhang et al., 2020). The spring waters hydrochemistry delivers evidence concerning the interaction between water and rock along flow paths (Kanduč et al., 2012). Similarly, groundwater's regional and local hydrology can be determined with springs information (Larsen et al., 2001). Thus, the principal cause of spring water pollution is geological and anthropogenic factors (Jang et al., 2016; Iqbal et al., 2017; Mostaza- Colado et al., 2018; Khalid, 2019). In this respect, irrigation water quality can be assessed by widely used indices such as sodium percentage (Na%), sodium adsorption ratio (SAR), and residual sodium carbonate (RSC) (Li et al., 2016; Tahmasebi et al., 2018; Verma et al., 2017; Abdulhusein, 2018; Khalid, 2019, Xu et al., 2019).

Hard formations include all rocks that lack primary porosity and do not have sufficient transmissibility to extract significant volumes of groundwater (Singhal, 2008). These formations include magmatic rocks from granites to basics, metamorphic rocks, and many sedimentary rocks such as broken shales, greywackes, sandstones, conglomerates, and some carbonate rocks.

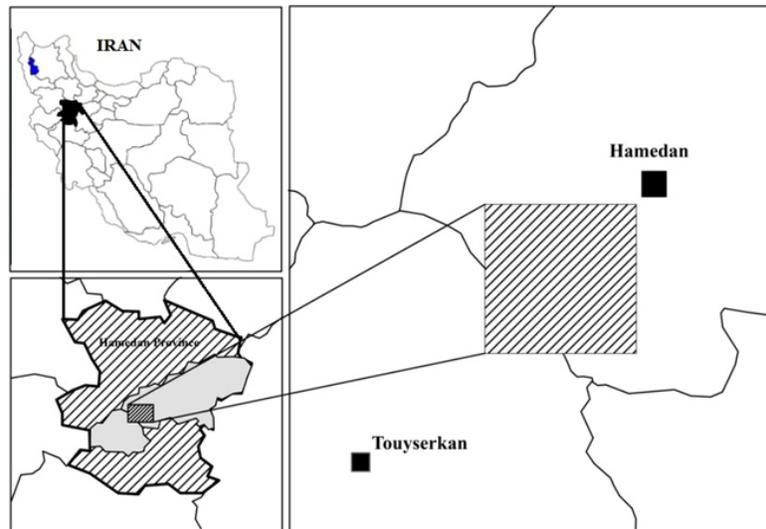
The present study investigates the characteristics and mechanisms governing the hydrochemistry of springs in Alvand heights and the effect of geological units, evaluation of groundwater chemical changes affected by geological formations, and water resources classification for drinking, irrigation, and industrial uses. Also, it is trying to explore geological units and sources of springs and determine the type of springs.

### **Study area setting**

The study area is located in Hamadan province and between the cities of Hamadan and Tuyserkhan. This region is situated in coordinates of 48°21'38" to 48°29'15" E and 34°41'57" to 34°47'69" N. The access path to the study area is an asphalt road connecting Hamedan-Shahrestaneh-Tuyserkhan (Fig. 1).

In terms of structural divisions and stratigraphy, the study area is located in the Sanandaj-Sirjan zone, which belongs to a larger tectonic province called Central and Northern Iran (Sepahi, 1999). This zone is one of Iran's most turbulent and most active construction zones and has gone through important phases of metamorphism and magmatic activity up to the Cenozoic.

Sanandaj-Sirjan zone can be divided into northern and southern parts from the Golpayegan area (Darvishzadeh, 1991). The northern part includes the important phases of the Cimmerian and Late Cretaceous (Laramide) orogeny, in which several intrusive massifs (e.g., Alvand, Boroujerd, Arak, and Malayer) have been formed. This part is called the Hamedan-Orumiyeh segment (Eftekhari-Nezhad, 1980).



**Figure 1.** Location of the study area

Most of the exposed rocks in the study area are igneous and metamorphic, and no sedimentary rock is seen. The metamorphic rocks in this area belong to the Mesozoic, and igneous rocks result from Laramide orogeny (Sepahi, 1999).

Alvand Plutonic Complex and its metamorphic halo are restricted by Touyserkan from the southeast, Assadabad from the northwest, and Hamedan from the east. Its surroundings have an area of about 700 km<sup>2</sup>, about 400 km<sup>2</sup> of which consists of plutonic igneous rocks. The shape of the Alvand intrusive mass is almost elliptical. However, its central part is almost narrow, and its two sides are more voluminous (Fig. 3).

This plutonic mass comprises granitoids, especially porphyroid granites (monzogranite-granodiorite) from mesocratic to leucocratic. Darker granitoids (i.e., tonalities) and lighter granitoids (i.e., holographic granitoids) comprise a small mass volume (Sepahi, 1999).

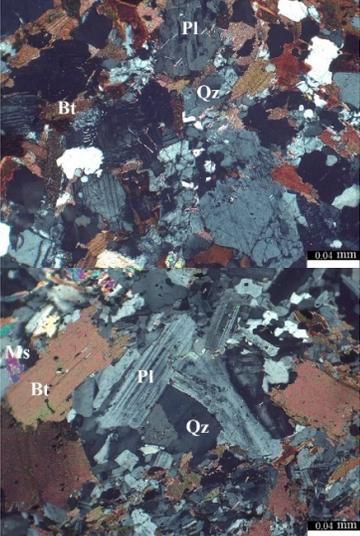
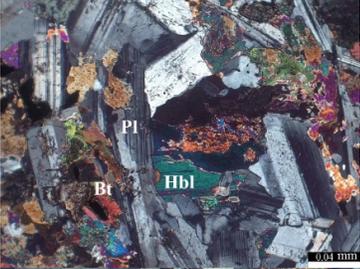
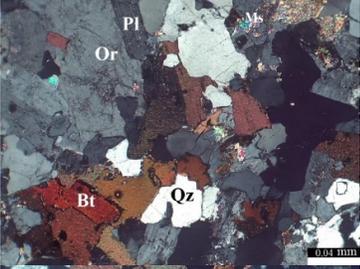
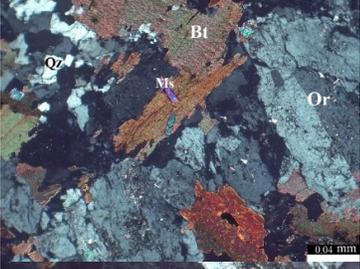
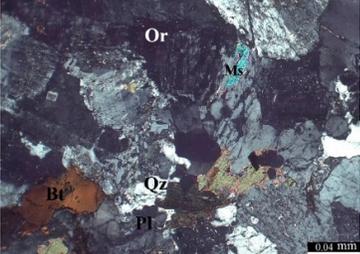
Pegmatite and tourmaline-bearing aplites also have a considerable abundance in the study area. These dikes are also seen in granite mass and metamorphic halo margins. In addition to pegmatite and applet dikes, other veins containing quartz-aluminosilicate, quartz-sphene (titanium), quartz-rutile, quartz-actinolite, quartz-apatite, and quartz-epidote (13) are also observed.

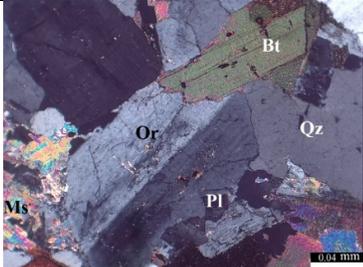
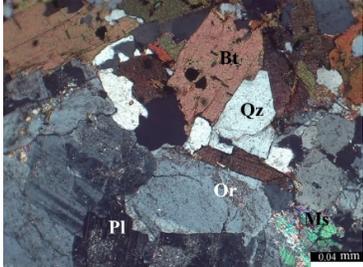
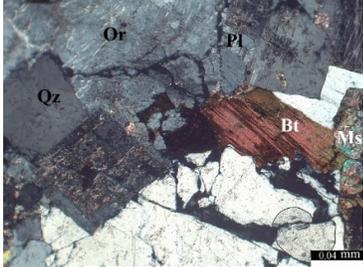
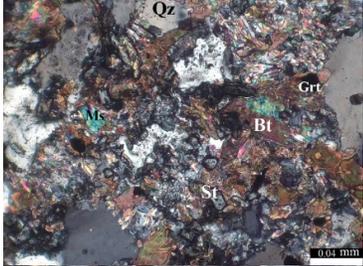
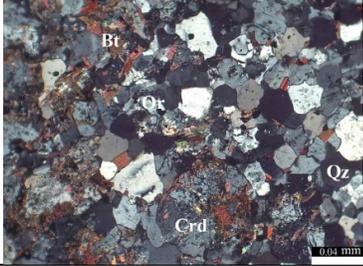
According to Valizadeh and Cantagrel (1975), the age of biotite in Alvand basalt rocks is 90-78 million years, while this age is 70-75 and 100 million years for biotites in porphyroid granites and muscovite in pegmatites, respectively. Therefore, based on these traditions, the plutonism activity of Alvand belongs to the Middle to Upper Cretaceous and early Tertiary periods. However, in a recent study, Shahbazi et al., (2010) estimated the age of these rock masses as the middle Jurassic.

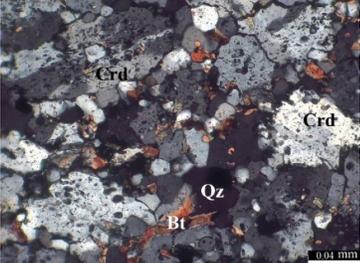
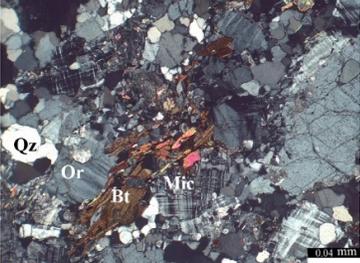
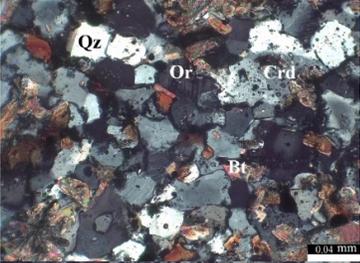
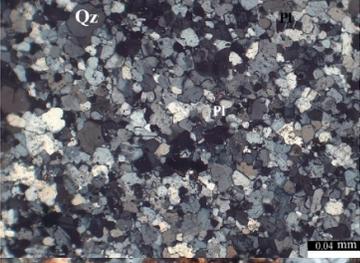
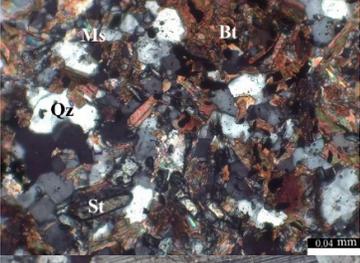
Contact metamorphic rocks, including spotted schists and hornfels, surround the Alvand intrusive mass. These rocks have formed due to the thermal effect of basic and acidic masses penetrating older rocks (Sepahi, 1999). The apparent thickness of these rocks at outcrops is 4-5 km, and even 10 km in some parts, especially in the southeast of Alvand rock mass (Zareian et al., 1952).

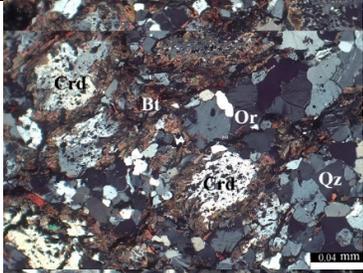
In the Hamedan region, there are various types of regional metamorphic rocks, including slate, phyllite, schists, amphibolites, and migmatites. The age of Hamedan metamorphism is Jurassic or younger (Dehghan et al., 1947). Sadeghian (1994) believes that the metamorphism of the study area is of medium Barrovian pressure-temperature type (i.e., kyanite-sillimanite). This author attributes the area's metamorphism age to the Jurassic and probably older during the Late Cimmerian phase. The rocks' names, mineralogy, and microscopic cross-section photos are given in Table 1.

**Table 1.** Name of rocks, mineralogy, and microscopic section images of the studied samples

No.	Rock name	Mineralogy	Microscopies views of the rock sections under XPL
Sp 1 Sp 2	Plagiogranite	Qz, Plg, Bt, Ms, Mic	
Sp 3	Trondhjemite (plagiogranite)	Qz, Plg, Bt, Ms, Grt	
Sp 4	Gabbro	Plg, Bt, Hbl	
Sp 5	Monzogranite	Qz, Plg, Or, Bt, Ms, Grt	
Sp 6	Syenogranite	Qz, Plg, Or, Bt, Ms, Mic	
Sp 7	Syenogranite	Qz, Plg, Or, Bt, Ms	

Sp 12	Syenogranite	Qz, Plg, Or, Bt	
Sp 13	Monzogranite	Qz, Plg, Or, Bt	
Sp 14	Alkali feldspar Granite	Qz, Plg, Or, Bt	
Sp 8 Sp 9 Sp 15	Staurolite-Cordierite-Hornfels	Qz, Plg, Or, Bt, Crd, Str	
Sp 16	Garnet-Staurolite-Hornfels	Qz, Bt, Ms, Grt, Str	
Sp 10 Sp 11 Sp 17 Sp 26	Cordierite hornfels	Qz, Plg, Or, Bt, Crd	

Sp 18	Cordierite hornfels	Qz, Plg, BtCrd, Opak	
Sp 19	Alkali feldspar Granite	Qz, Or, Bt, Ms, Mic, Sfan	
Sp 20	Cordierite hornfels	Qz, Or, Bt, Crd	
Sp 21	Plagiogranite (aplite)	Qz, Plg, Bt, Ms	
Sp 22	Staurolite Hornfels	Qz, Plg, Bt, Ms, Str, Tur	
Sp 23	Granodiorite	Qz, Plg, Or, Bt, Ms, Mic	

Sp 24	Cordierite hornfels	Qz, Plg, Or, Bt, Ms, Crd, Tur	
Sp 25	Cordierite hornfels	Qz, Or, Bt, Crd	
Sp 27	Granite porphyroid	Qz, Plg, Or, Bt, Ms, Tur	

Aquifers in hard formations are formed in broken and weathered rocks. In these aquifers, the fracture density decreases with depth. Fractures control many of the hydraulic properties of these aquifers (Muchingami et al., 2019). Groundwater resources in igneous rocks and crystallized metamorphism are often limited to crushed and weathered rocks that extend to a depth of 50 m (Guihéneuf et al., 2014). Due to the function of structural processes in the region, many fracture systems have formed in the region's intrusive massifs. As a result, free aquifers have formed in these plutonic masses.

According to Singhal (1999), in hard-formation aquifers, a weathered layer called regolith develops on the crystallized rocks, suitable for groundwater accumulation. Thick and wide weathered layers can form potential aquifers. If a permanent water resource is available, a thin layer (5 to 7 m) can be a good source of water storage. The weathering profile from top to bottom in crystalline rocks consists of four zones: Zone A is made up of sand or clay sands. These hardened works are several meters thick. Zone B is a saprolite layer where secondary clay minerals are accumulated. This zone is known for its high porosity and low permeability and can be up to 30 m thick. Zone C, called Saprock, is gradually weathered downward and is up to 30 m thick. Finally, Zone D is a fractured source rock with low porosity and moderate permeability.

Lachassagne et al., (2021) explained the structure of aquifers in hard formations as follows: Hydraulic conductivity and storage in hard formations are mainly the results of weathering processes. Consequently, the aquifers of the hard formations further develop up to 100 m below ground level. In places where they are partially weathered or not fully eroded, they include the following sections: 1) Saprolite is an unreinforced aerated layer with water storage capacity but relatively low permeability and 2) a permeable crushed layer immediately below the crushed pseudo-permeable layer. To a lesser extent, weathering and deeper hydraulic conductivity occur in non-weathering rocks at the margins or within old geological discontinuities (e.g., lithological boundaries, joints, ditches, and veins).

Most of the springs in this area are faults and drain the free aquifers of the region (Ghobadi,

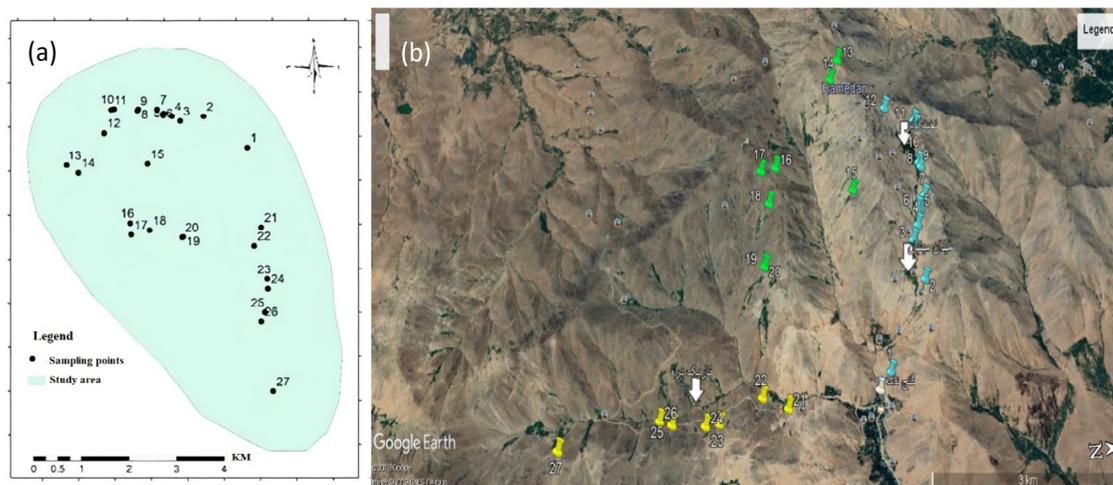
2017). The general direction of groundwater movement in the southern slopes of Alvand is approximately from south-southwest to north-northeast (Ghobadi, 2017).

Due to the lack of piezometers, aqueducts, and wells in the study area, the springs are the only indicator of the area's hydrogeological conditions and reflect the aquifer's internal conditions. The position of the springs was captured by a GPS device through several stages of the site visit. Also, during these visits, the flow of the springs was measured by the floating body method. In addition, lithological surveys were performed at the source of the springs. Fig. 4 presents some of these springs. In this study, springs were selected based on spatial distribution, accessibility of springs, flow rate, type of use, and lithological differences of reservoir rocks for the preliminary studies. Some springs were selected in the route of Ganjnameh, Meidan Mishan, Takhte Nader, and Kalaghlan Shelter, which is a high-traffic route due to mountaineering activities. Hence, the water of the springs in this route is widely used for drinking. There are several other selected springs along the Tarik Dareh ski slope route. Due to people's high flow and easy access, these springs are also used for drinking. The reservoir rocks of the first route are mainly igneous rocks, while the springs in the Tarik Dareh route are mainly in metamorphic rocks. The flow of selected springs varies from 0.5 L/s to 7 L/s. Due to lithological changes and differences in reservoir rocks, springs with a low flow were also sampled.

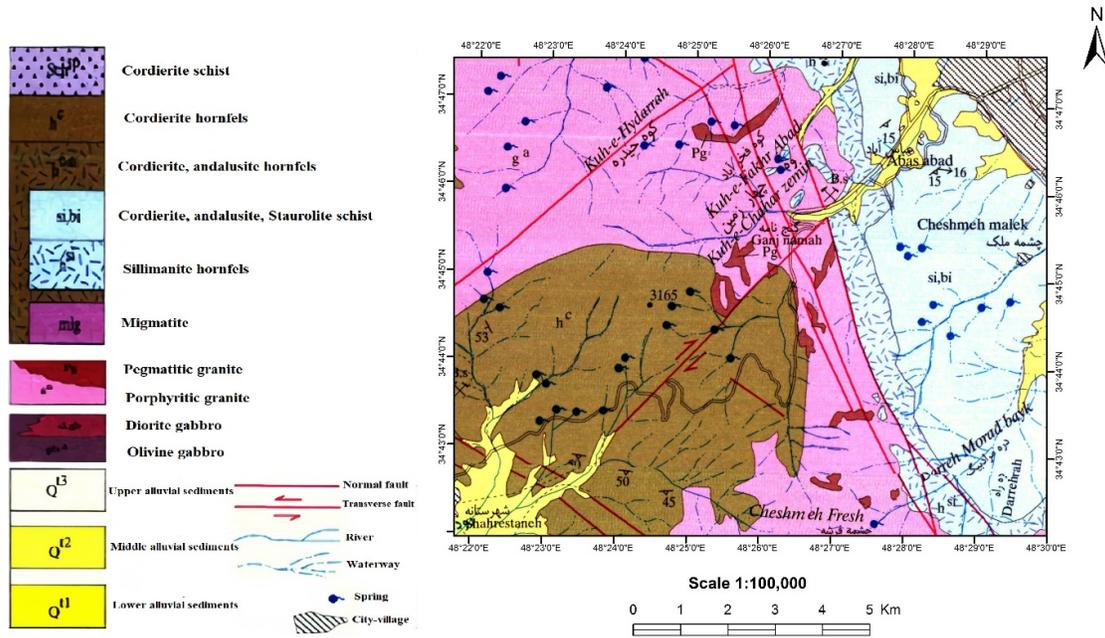
The existence of many springs and the significant volume of some of these springs is a clear sign of reserves and groundwater resources in the region. Almost all manifestations of springs are seen in connection with faults and fractures in the region. They also appear in contact with anaerobic and impermeable rocks as impermeable bedrock and a weathered rock mass with many fractures, together forming free aquifers of Alvand heights. Fig. 4 presents some of the springs in Alvand heights.

## Materials and Methods

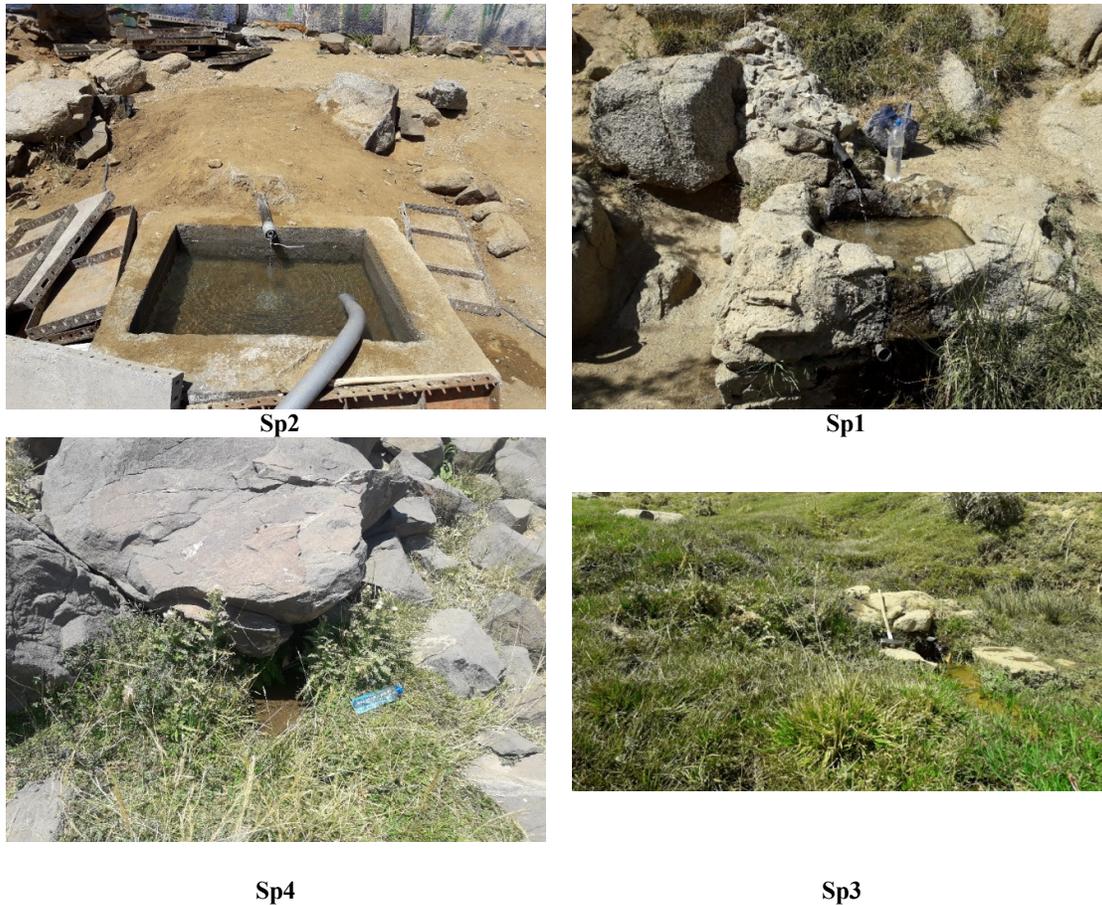
Hydrogeology and hydrogeochemistry of the water resources of Alvand heights based on information obtained through preliminary studies, field visits, interpreting geological maps, determining the sampling stations, and taking water samples. The field study's steps included determining the springs' location, taking photos of springs in the region, measuring the discharge of springs, and collecting samples of reservoir rock from each spring for lithological studies. Thin sections were prepared from these rock samples and studied in the lithology laboratory of Bu Ali Sina University. The location of the sampling stations is shown in Fig. 2.



**Figure 2.** a) Location of sampling points from Alvand Heights (taken from 1:100,000 Tuyserkan geological map, Geological Survey of Iran) and b) Satellite image of sampling location from Alvand Heights



**Figure 3.** Geological map of the study area (from 1:100,000 Tuyserkan geological map, Eshraghi & Mahmoudi Gharai, 2003)



**Figure 4.** (continued)



Sp9



Sp6



Sp13 & Sp14



Sp12



Sp24



Sp22

Figure 4. (continued)



Sp26



Sp25



Sp27

**Figure 4.** Some springs of this study

Sampling from the water resources of the study area was performed in three steps. Half-liter plastic containers were used for sampling, and the containers were washed with water from the same spring before sampling. The samples' water pH was reduced to prevent the possible precipitation of heavy metals by adding a few drops of concentrated nitric acid. The samples were immediately transferred to the ICP laboratory of the Iranian Chemical Research Institute located in Tehran province for heavy metal analysis.

The collected samples were transferred to the hydrological laboratory of Hamadan Regional Water Company to determine pH, EC, and the concentration of water-soluble cations and main anions (i.e., sulfate, chlorine, carbonate, bicarbonate, potassium, sodium, magnesium, and calcium ions). RockWorks, AqQA, and CHEMISTRY software were used to draw quality diagrams.

#### *Hydrochemical water resources of Alvand heights*

Studying groundwater is important from both quantitative and qualitative perspectives. Despite enough groundwater in many parts of Iran, they are not suitable to use. Studying groundwater

chemistry provides information on the retention time of water in the earth, its effect on the soil and rock mass that passes through it, the minerals hidden in the ground, and its origin based on the water cycle (Todd & Mays, 2005). Groundwater is the most important source for drinking, irrigation, and industrial use in arid and semi-arid regions. Regarding the quality changes in groundwater resources due to natural processes or human activities, maintaining the quality and management of these resources is possible only by examining their hydrochemical aspects. Geological formations, precipitation and balance between evaporation and precipitation salts in the catchment, seasonal changes in runoff volume, and weathering conditions and type are among the natural factors affecting the quality of water resources. The results of the analysis of groundwater samples in Alvand heights are presented in Table 2.

### *Determining the origin, type, and facies of water resources*

In this study, based on anions and cations concentrations (meq/lit), some graphs related to water quality were drawn in RockWorks, AqQA, and CHEMISTRY computer programs to determine the type and facies of water resources.

### Piper diagram

In Piper diagrams, large amounts of data can be analyzed based on their relative concentrations rather than actual concentrations (Fetter, 1999). The percentage of anions and cations is transferred in triangular fields and their combined position in the rhombic field. Fig. 5 shows a diagram drawn for the springs of Alvand Heights.

**Table 2.** The results of chemical analysis of water samples taken from Alvand heights (units of ions in meq/lit)

No	EC	TDS	PH	CO <sub>3</sub>	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	anions	Ca	Mg	Na	K	sum cation
Sp1	45	30.15	7.74	0	0.2	0.2	0	0.4	0.3	0.1	0.01	0	0.41
Sp 2	75	48	7.95	0	0.4	0.3	0	0.7	0.4	0.3	0.02	0	0.72
Sp 3	84	52.92	7.9	0	0.5	0.3	0	0.8	0.4	0.3	0.11	0	0.81
Sp 4	46	28.98	7.85	0	0.3	0.1	0	0.4	0.2	0.2	0.01	0	0.41
Sp 5	46	28.98	8.07	0	0.2	0.2	0	0.4	0.3	0.1	0.01	0	0.41
Sp 6	41	25.83	7.7	0	0.3	0.1	0	0.4	0.3	0.1	0	0	0.4
Sp 7	52	32.76	8.5	0.09	0.3	0.1	0	0.49	0.3	0.14	0.06	0	0.5
Sp 8	61	38.43	8.61	0.1	0.3	0.2	0	0.6	0.4	0.2	0.01	0	0.61
Sp 9	68	42.84	7.21	0	0.4	0.2	0	0.6	0.3	0.2	0.11	0	0.61
Sp 10	62	39.06	7.56	0	0.3	0.3	0	0.6	0.3	0.2	0.11	0	0.61
Sp 11	68	42.84	7.55	0	0.3	0.3	0	0.6	0.3	0.2	0.11	0	0.61
Sp 12	147	92.61	7.94	0	0.8	0.4	0.05	1.25	0.6	0.5	0.17	0	1.27
Sp 13	34	21.42	7.4	0	0.2	0.1	0	0.3	0.2	0.08	0.03	0	0.31
Sp 14	61	38.43	8.01	0	0.3	0.2	0.03	0.53	0.3	0.2	0.04	0	0.54
Sp 15	99	62.37	9.1	0.2	0.4	0.3	0.02	0.92	0.4	0.3	0.23	0	0.93
Sp 16	31	19.53	7.73	0	0.2	0.1	0	0.3	0.2	0.05	0.06	0	0.31
Sp 17	43	27.09	7.66	0	0.3	0.1	0	0.4	0.2	0.2	0.01	0	0.41
Sp 18	119	74.97	7.96	0	0.7	0.4	0.02	1.12	0.7	0.3	0.13	0	1.13
Sp 19	79	49.77	8.32	0.1	0.4	0.3	0	0.8	0.4	0.3	0.11	0	0.81
Sp 20	73	45.99	9.38	0.3	0.2	0.2	0	0.7	0.3	0.2	0.21	0	0.71
Sp 21	242	152.46	7.52	0	2	0.2	0.45	2.65	2.1	0.5	0.07	0.01	2.68
Sp 22	110	69.3	7.21	0	0.5	0.2	0.35	1.05	0.9	0.1	0.06	0	1.06
Sp 23	97.8	61.614	7.73	0	0.7	0.2	0	0.9	0.5	0.3	0.12	0	0.92
Sp 24	90.6	57.078	8.15	0	0.55	0.25	0.12	0.92	0.75	0.05	0.13	0	0.93
Sp 25	87.33	55.02	7.75	0	0.58	0.22	0.04	0.84	0.56	0.17	0.12	0	0.85
Sp 26	73.6	46.368	7.37	0	0.5	0.2	0	0.7	0.44	0.15	0.12	0	0.71
Sp 27	90.2	56.826	7.97	0	0.5	0.2	0.1	0.8	0.4	0.1	0.31	0	0.81

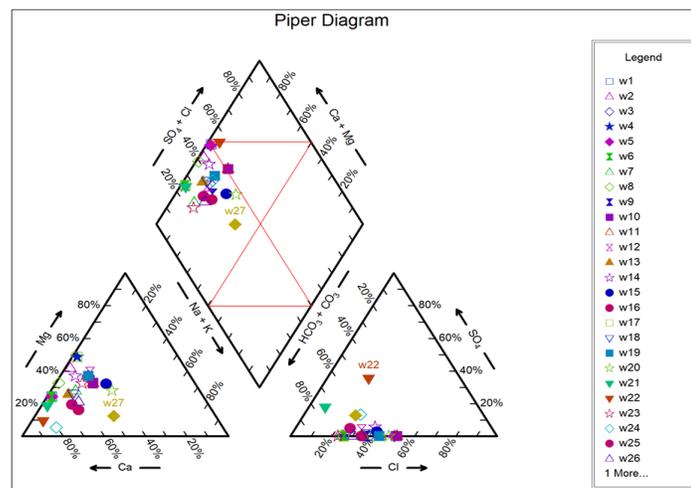
## Durov diagram

A Durov diagram was used to interpret the water samples. This diagram is a more developed Piper diagram used to simultaneously study ionic ratios with the total concentration of soluble solids and the pH of water samples. In the binary diagrams of the studied water samples, the cationic and anionic triangles, the total concentration of soluble solids, and the pH are taken into account. This diagram shows the values of major water cations and anions in meq/l (Fig. 6).

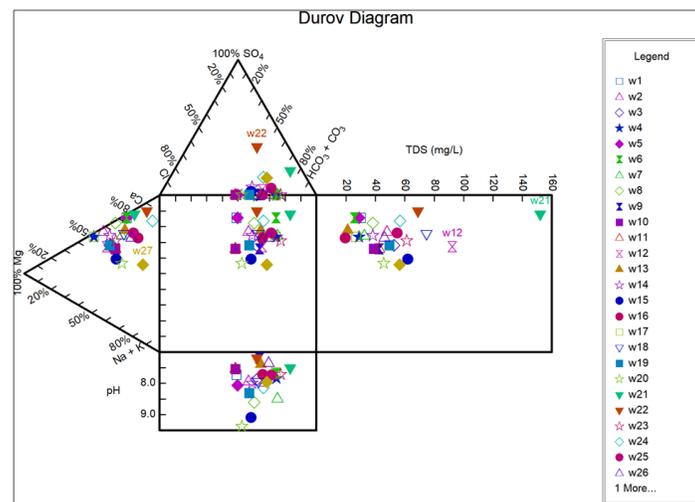
## Stiff diagrams

In the Stiff diagram, each water sample is examined separately. This diagram shows the concentrations of cations and anions in meq/l on the horizontal lines. The larger the area of the resulting shape is, the higher the concentration of solutes in the water will be (Hounslow, 1995).

Stiff diagrams show differences in water samples' hydrochemical facies and total solids concentrations. The results obtained from this diagram can confirm the results obtained from other diagrams. Accordingly, Stiff diagrams of the collected samples were prepared using AQqa software.



**Figure 5.** Piper diagram of groundwater samples taken from Alvand heights



**Figure 6.** Durov diagram of groundwater samples of Alvand heights

*The qualitative study of groundwater resources in terms of drinking water, agriculture, and industry*

In this section, water quality and standard indicators for drinking, agricultural, and industrial purposes are examined.

Groundwater quality for drinking use

Drinking water must have desirable physical properties in terms of color, turbidity, taste, and odor. In addition, it must be chemically healthy for human use and free of harmful microorganisms.

Total hardness is expressed as the sum of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions concentrations in ppm or milligrams per liter and in terms of their equivalent calcium carbonate. This hardness is estimated using the following relation (Hounslow, 1995):

$$\begin{aligned} \text{Total Hardness (in } \frac{\text{mg}}{\text{l}} \text{ CaCO}_3) &= \text{Ca}^{2+} \left( \frac{\text{mg}}{\text{l}} \right) \times \frac{100.08}{40.08} + \text{Mg}^{2+} \left( \frac{\text{mg}}{\text{l}} \right) \times \frac{100.08}{24.31} \end{aligned} \quad (1)$$

Hardness can also be divided into carbonate and non-carbonate hardness. The hardness of calcium and magnesium carbonate lost by boiling is called temporary (or carbonate) hardness. The hardness of calcium/magnesium sulfate and calcium/magnesium chloride that is not eliminated by boiling is called permanent or (non-carbonate) hardness (Hounslow, 1995). Quality of water samples based on hardness and Schuler diagram (Fig. 7) are shown in table 3.

**Table 3** Quality of water samples based on hardness (Durfor & Becker, 1964) and Schuler diagram

NO.	Sampling site	Total hardness	Temporary hardness	Permanent hardness	Water quality based on the total hardness	Schoeller
1	Sp 1	19.92	19.92	0	soft	Good
2	Sp 2	34.79	34.79	0	soft	Good
3	Sp 3	34.79	34.79	0	soft	Good
4	Sp 4	19.86	19.86	0	soft	Good
5	Sp 5	19.92	19.92	0	soft	Good
6	Sp 6	19.92	19.92	0	soft	Good
7	Sp 7	21.9	21.9	0	soft	Good
8	Sp 8	29.85	29.85	0	soft	Good
9	Sp 9	24.86	24.86	0	soft	Good
10	Sp 10	24.86	24.86	0	soft	Good
11	Sp 11	24.86	24.86	0	soft	Good
12	Sp 12	54.65	54.65	0	soft	Good
13	Sp 13	13.94	13.94	0	soft	Good
14	Sp 14	24.86	24.86	0	soft	Good
15	Sp 15	34.79	34.79	0	soft	Good
16	Sp 16	12.46	12.46	0	soft	Good
17	Sp 17	19.86	19.86	0	soft	Good
18	Sp 18	49.77	49.77	0	soft	Good
19	Sp 19	34.79	34.79	0	soft	Good
20	Sp 20	24.86	24.86	0	soft	Good
21	Sp 21	129.56	129.56	0	Moderately hard	Good
22	Sp 22	49.88	49.88	0	soft	Good
23	Sp 23	39.78	39.78	0	soft	Good
24	Sp 24	39.92	39.92	0	soft	Good
25	Sp 25	36.36	36.36	0	soft	Good
26	Sp 26	29.38	29.38	0	soft	Good
27	Sp 27	24.91	24.91	0	soft	Good

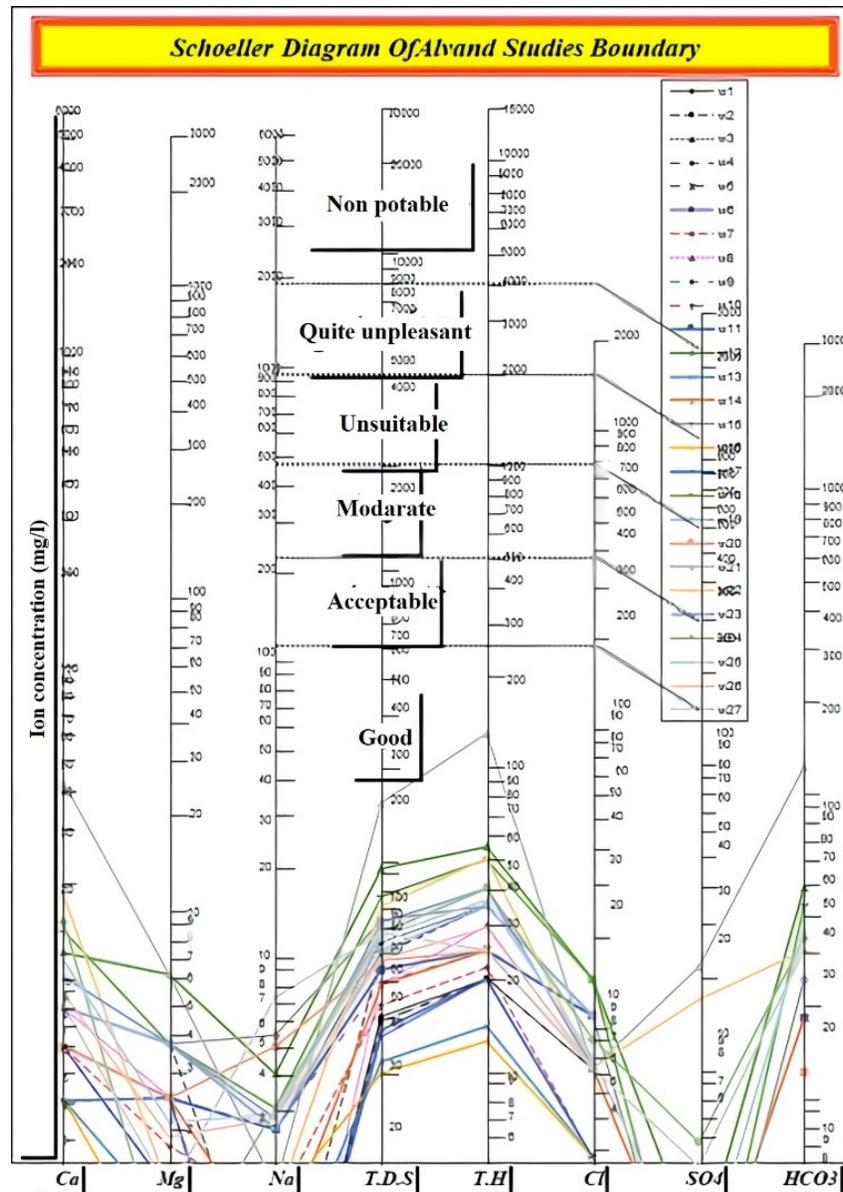


Figure 7. Schuler diagram for water samples taken from springs in the study area

#### Groundwater quality for agricultural use

From the agricultural point of view, using groundwater with high salt concentrations causes salinization of the soil and increases the percentage of exchangeable sodium. This process is even more severe in arid and desert areas due to lack of rainfall and proper soil leaching. In this study, the suitability of water from springs of the region for agriculture use was determined by studying the factors and parameters including sodium absorption ratio (SAR), electrical conductivity (EC), residual sodium carbonate (RSC), and dissolved sodium percentage ( $\text{Na}^+\%$ ). The higher the  $\text{Na}^+\%$ , the higher the sodium cation concentration is than the sum of other cations in the sample. Large amounts of sodium increase soil alkalinity and lead to the formation of sodium hydroxide, which burns and destroys plant root cells. As a result, it is not suitable for agriculture and soil structure sustainability and causes the loss of soil grains and soil erosion. The amount of SAR is directly related to ( $\text{Na}^+\%$ ). One of the most common classifications of irrigation water is the Wilcox diagram classification provided by the US Department of

Agriculture. The Wilcox classification method is the most practical technique for water classification in agriculture in hydrological studies. In this diagram, the horizontal axis shows EC water salinity (in microsiemens per centimeter;  $\mu\text{S}/\text{cm}$ ), and the vertical axis indicates SAR. In this classification, agricultural water is considered based on the two criteria of EC and SAR, each being divided into four parts, providing 16 groups of water quality. Each quality group is identified by combining letters C and S, representing CE and SAR, respectively (Mahdavi, 2007). The water used in irrigation is divided into excellent to unsuitable types based on EC and SAR. According to the diagram, C1S1 is the best water, and C4S4 is the worst water for irrigation. Table 4-shows the quality of water for agricultural use (Alizadeh, 2007).

In general, two important effects of sodium are reduced permeability and hardening of the soil. These two effects are due to the substitution of calcium and magnesium ions with sodium ions in soil loams and colloids. The degree of this substitution can be estimated by SAR, as follows:

$$SAR = \frac{Na^+}{\sqrt{0.5(Ca^{2+} + Mg^{2+})}} \quad (2)$$

In Eq. (2), the concentration of sodium, magnesium, and calcium ions is in meq/L.

Quality of groundwater samples for agricultural and irrigation and industrial use are presented in Table 5.

Sodium content in agricultural water causes reactions of  $Ca^{2+}$  and  $Mg^{2+}$  in soil clay particles, reducing soil permeability (Esmaili-Vardanjani et al., 2015). Sodium content is expressed as  $Na\%$  and is calculated as follows:

$$\%Na = \frac{(Na^+ + K^+)}{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)} \times 100 \quad (3)$$

In Eq. (3), the concentrations of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ , and  $K^+$  are all expressed in meq/l. The classification of groundwater samples is presented in Table 5. As can be seen, most of the specimens are in excellent condition in terms of quality for irrigation purposes (except Sp15, Sp20, and Sp27, which are in good condition).

Increasing the total content of  $CO_3^{2-}$  and  $HCO_3^-$  in groundwater compared to the total content of  $Ca^{2+}$ ,  $Mg^{2+}$  makes water suitable for agriculture and irrigation, which is expressed as RSC. Its high content in irrigation water leads to increased sodium uptake by the soil (Eaton, 1995). The RSC value is calculated using the following equation:

$$RSC = (HCO_3 + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (4)$$

In Eq. (4), all ion concentrations are expressed in meq/l. According to the USDA Classification (1954), water containing more than 2.5 meq/l of the RSC is not suitable for agricultural and irrigation purposes

#### Investigating water quality in terms of industrial use

Hardness, alkalinity, total dissolved salts (TDS), silica content, turbidity, and amount of dissolved gases are the most important factors determining water quality for industrial use. Water analysis parameters such as alkalinity and pH can be used to determine the state of water in terms of corrosion and scaling. The main indicator for this purpose is the saturation coefficient presented by Langelier (1964) (Eq. 5).

$$l_e = pH_a + pH_s \quad (5)$$

$$pH_s = P_{alk} + P_c$$

Where  $l_e$  is Langelier index,  $pH_a$  is measured acidity or actual pH of water,  $pH_s$  is acidity measured under conditions of calcium carbonate saturation or calculated water pH,  $P_{alk}$  is a function of total alkalinity,  $P_c$  is a function of calcium hardness, and  $C$  is a function of temperature and TDS. The pHs can be calculated from the following equation.

**Table 4.** Water quality classification based on Wilcox diagram groups (Alizadeh, 2007)

Water quality for agriculture	Classification group
Very good	C <sub>1</sub> S <sub>1</sub>
Good	C <sub>2</sub> S <sub>2</sub> -C <sub>2</sub> S <sub>1</sub> - C <sub>1</sub> S <sub>2</sub>
Average	C <sub>3</sub> S <sub>3</sub> -C <sub>1</sub> S <sub>3</sub> -C <sub>2</sub> S <sub>3</sub> -C <sub>3</sub> S <sub>2</sub> - C <sub>3</sub> S <sub>1</sub>
Inappropriate	C <sub>1</sub> S <sub>4</sub> -C <sub>2</sub> S <sub>4</sub> -C <sub>3</sub> S <sub>4</sub> -C <sub>4</sub> S <sub>4</sub> -C <sub>4</sub> S <sub>3</sub> -C <sub>4</sub> S <sub>2</sub> - C <sub>4</sub> S <sub>1</sub>

**Table 5** Quality of groundwater samples for agricultural and industrial uses

Sampling site	SAR	EC	Water class based on Wilcox	Na%	Water quality based on Na%	RSC	Water quality based on RSC	Alkalinity based on CaO	Ca (mg/l)	C coefficient	pHs	pH	pHs-pH	Water quality for industry use
Sp1	0.02	45	C1-S1	2.44	Excellent	-0.2	Suitable	0.23	6	11.23	11.1	7.74	3.36	Corrosive
Sp 2	0.03	75	C1-S1	2.78	Excellent	-0.3	Suitable	0.46	8	11.24	10.7	7.95	2.75	Corrosive
Sp 3	0.19	84	C1-S1	13.58	Excellent	-0.2	Suitable	2.53	8	11.24	9.9	7.9	2	Corrosive
Sp 4	0.02	46	C1-S1	2.44	Excellent	-0.1	Suitable	0.23	4	11.23	11.3	7.85	3.45	Corrosive
Sp 5	0.02	46	C1-S1	2.44	Excellent	-0.2	Suitable	0.23	6	11.23	11.1	8.07	3.03	Corrosive
Sp 6	0.02	41	C1-S1	2.44	Excellent	-0.1	Suitable	0.23	6	11.22	11.1	7.7	3.4	Corrosive
Sp 7	0.13	52	C1-S1	12	Excellent	-0.05	Suitable	1.38	6	11.23	10.3	8.5	1.8	Corrosive
Sp 8	0.02	61	C1-S1	1.64	Excellent	-0.2	Suitable	0.23	8	11.23	11	8.61	2.39	Corrosive
Sp 9	0.22	68	C1-S1	18.03	Excellent	-0.1	Suitable	2.53	6	11.23	10	7.21	2.79	Corrosive
Sp 10	0.22	62	C1-S1	18.03	Excellent	-0.2	Suitable	2.53	6	11.23	10	7.56	2.44	Corrosive
Sp 11	0.22	68	C1-S1	18.03	Excellent	-0.2	Suitable	2.53	6	11.23	10	7.55	2.45	Corrosive
Sp 12	0.23	147	C1-S1	13.39	Excellent	-0.3	Suitable	3.91	12	11.25	9.6	7.94	1.66	Corrosive
Sp 13	0.08	34	C1-S1	9.68	Excellent	-0.08	Suitable	0.69	4	11.22	10.8	7.4	3.4	Corrosive
Sp 14	0.08	61	C1-S1	7.41	Excellent	-0.2	Suitable	0.92	6	11.23	10.5	8.01	2.49	Corrosive
Good	0.39	99	C1-S1	24.73	Good	-0.1	Suitable	5.29	8	11.24	9.6	9.1	0.5	Corrosive
Sp 16	0.17	31	C1-S1	19.35	Excellent	-0.05	Suitable	1.38	4	11.22	10.5	7.73	2.77	Corrosive
Sp 17	0.02	43	C1-S1	2.44	Excellent	-0.1	Suitable	0.23	4	11.22	11.3	7.66	3.64	Corrosive
Sp 18	0.18	119	C1-S1	11.5	Excellent	-0.3	Suitable	2.99	14	11.25	9.6	7.96	1.64	Corrosive
Sp 19	0.19	79	C1-S1	13.58	Excellent	-0.2	Suitable	2.53	8	11.24	9.9	8.32	1.58	Corrosive
Sp 20	0.42	73	C1-S1	29.58	Good	0	Suitable	4.83	6	11.24	9.8	9.38	0.42	Corrosive
Sp 21	0.06	242	C1-S1	2.99	Excellent	-0.6	Suitable	2	42	11.26	9.3	7.52	1.78	Corrosive
Sp 22	0.08	110	C1-S1	5.66	Excellent	-0.5	Suitable	1.38	18	11.25	9.9	7.21	2.69	Corrosive
Sp 23	0.19	97.8	C1-S1	13.04	Excellent	-0.1	Suitable	2.76	10	11.24	9.8	7.73	2.07	Corrosive
Sp 24	0.21	90.6	C1-S1	13.98	Excellent	-0.25	Suitable	2.99	15	11.24	9.6	8.15	1.45	Corrosive
Sp 25	0.2	87.3 333	C1-S1	14.45	Excellent	-0.15	Suitable	2.83667	11.267	11.24	9.7	7.75	1.95	Corrosive
Sp 26	0.22	73.6	C1-S1	16.9	Excellent	-0.09	Suitable	2.76	8.8	11.24	9.9	7.37	2.53	Corrosive
Sp 27	0.62	90.2	C1-S1	38.27	Good	0	Suitable	7.13	8	11.24	9.5	7.97	1.53	Corrosive

If the saturation index is positive, it indicates that the water is supersaturated with calcium carbonate and is in a deposition state. Also, if this index is negative, it indicates that the water is saturated with calcium carbonate and is corrosive. The Langelier Index is a tool for measuring water quality and only indicates the tendency of water to cause sediment or dissolution.

#### *Investigating the origin of soluble ions in groundwater*

Ion ratios are effective indicators for the chemistry of groundwater resources, and their use is an efficient method to determine the source of salts. Using ion ratios, we can determine the minerals that are the source of anions and water-soluble cations (Hounslow, 1995). In the evolution of groundwater chemical composition, these ratios are affected by the chemical composition of water-soluble minerals, and the amount of dissolved minerals is of secondary importance (Howard et al., 1996). The dissolution action varies according to the type of mineral. Potassium feldspars are highly soluble in freshwater, while calcium and sodium feldspars are relatively soluble. In general, the strength of alkaline ions is effective in releasing them. For example, sodium ions leave the mineral faster than potassium ions, and potassium ions leave the mineral faster than calcium ions. Table 6 presents the ratio between some ions studied in this research.

**Table 6.** Results of ion ratios of water samples in the study area

	PH	TDS	Ca/(Ca+SO4)	Na/(Na+Cl)	Mg/(Mg+Ca)	Cl/Sum Anion	(Na+K-Cl)/(Na+K+Ca-Cl)
1	7.74	30.15	1.00	0.05	0.25	0.50	-1.73
2	7.95	48	1.00	0.06	0.43	0.43	-2.33
3	7.9	52.92	1.00	0.27	0.43	0.38	-0.90
4	7.85	28.98	1.00	0.09	0.50	0.25	-0.82
5	8.07	28.98	1.00	0.05	0.25	0.50	-1.73
6	7.7	25.83	1.00	0.00	0.25	0.25	-0.50
7	8.5	32.76	1.00	0.38	0.32	0.20	-0.15
8	8.61	38.43	1.00	0.05	0.33	0.33	-0.90
9	7.21	42.84	1.00	0.35	0.40	0.33	-0.43
10	7.56	39.06	1.00	0.27	0.40	0.50	-1.73
11	7.55	42.84	1.00	0.27	0.40	0.50	-1.73
12	7.94	92.61	0.92	0.30	0.45	0.32	-0.62
13	7.4	21.42	1.00	0.23	0.29	0.33	-0.54
14	8.01	38.43	0.91	0.17	0.40	0.38	-1.14
15	9.1	62.37	0.95	0.43	0.43	0.33	-0.21
16	7.73	19.53	1.00	0.38	0.20	0.33	-0.25
17	7.66	27.09	1.00	0.09	0.50	0.25	-0.82
18	7.96	74.97	0.97	0.25	0.30	0.36	-0.63
19	8.32	49.77	1.00	0.27	0.43	0.38	-0.90
20	9.38	45.99	1.00	0.51	0.40	0.29	0.03
21	7.52	152.46	0.82	0.26	0.19	0.08	-0.06
22	7.21	69.3	0.72	0.23	0.10	0.19	-0.18
23	7.73	61.614	1.00	0.38	0.38	0.22	-0.19
24	8.15	57.078	0.86	0.34	0.06	0.27	-0.19
25	7.75	55.02	0.93	0.36	0.23	0.26	-0.20
26	7.37	46.368	1.00	0.38	0.25	0.29	-0.22
27	7.97	56.826	0.80	0.61	0.20	0.25	0.22

## Results and discussion

From the water sample's location in the piper diagram, it is inferred that the groundwater of the study area is mostly high in bicarbonate, calcium, and chlorine and has a temporary hardness. Examining triangular diagrams shows that the predominant type of groundwater in the region is calcium bicarbonate. According to these diagrams, in the water samples of the study area, the amount of soil alkaline elements (calcium and magnesium) are more than alkali elements (sodium and potassium), and weak acids (carbonate and bicarbonate) have a higher frequency than strong acids (sulfate and chloride).

In sample 22 (Sp 22), which falls in region 4 of the piper diagram, the strong acids are more than the weak acids. Most specimens are located in region 5 of the piper diagram, except for Sp22 in region 9. In this region, the carbonate hardness exceeds 50%. As a result, alkalines and weak acids are dominant in the studied samples.

According to Durov diagram (Fig. 6), the predominant type in the study area is calcium bicarbonate. The dominant anions and cations in the samples are bicarbonate and calcium. In other words, Stiff diagrams show that the water type of the springs is calcium bicarbonate, and the amount of chlorine is high.

Table 3 shows the classification of groundwater in the study area based on the degree of hardness. According to data in Table 3, except for the Sp21 sample, which is moderately hard, all samples are soft and have a temporary hardness.

According to the drawn Schuler diagram for the studied water samples, the concentration of the soluble elements in the groundwater of the study area is good in most samples (Fig. 7; Table 3). In general, good quality for drinking use (in the absence of pollution) is a prominent feature of calcareous aquifers and hard formations.

SAR was less than 10 meq/l for all samples, indicating excellent water quality for agricultural purposes (Table 5). According to the Wilcox (1955) diagram, in terms of sodium hazard and

salinity, all samples are in the S1 range and C1 range, respectively, meaning that the water quality of the springs is excellent to good for agriculture and irrigation purposes (Fig. 8).

Table 5 presents the groundwater of Alvand heights classified according to RSC. As shown in the table, all samples are in the “appropriate” range in terms of irrigation and agricultural uses. Negative RSC values indicate that the amount of dissolved  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  ions are less than calcium and magnesium ions. Table 5 also shows the status of groundwater samples in the study area for industrial use. As observed, all groundwater samples are corrosive.

In the following, the obtained results from table 6 that presents the ratio between some ions studied in this research are interpreted.

1)  $\text{Ca}/(\text{Ca} + \text{SO}_4)$ : This ratio is more than 0.5 in all samples, suggesting a source of calcium other than gypsums such as carbonate and silicate.

2)  $\text{Na}^+/(\text{Na}^+ + \text{Cl}^-)$ : This ratio is used to investigate the origin of sodium ions in water sources. As shown in Table 6, it is less than 0.5 in all samples except for Sp20 and Sp27. In these samples, when the TDS is less than 50, according to Table 4, the source of sodium ion is rainwater (all samples except Sp12, Sp15, Sp18, Sp20, Sp21, Sp22, Sp23, Sp24, Sp25, and Sp27).

When this ratio is less than 0.5 and the TDS values are between 50 and 500, these conditions indicate errors in the analysis (Sp2, Sp12, Sp15, Sp18, Sp21, Sp22, Sp23, Sp24, Sp25, and Sp27).

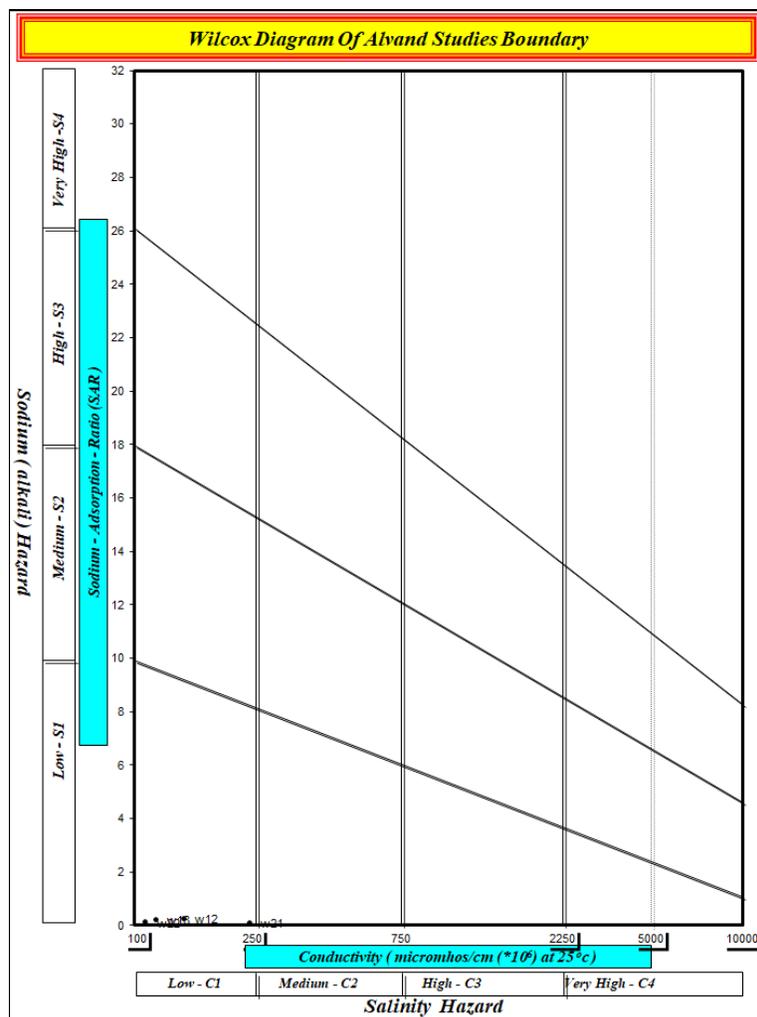


Figure 8. Wilcox diagram for groundwater samples in the study area

Since the TDS values of these samples are slightly larger than the threshold (i.e., 50), the small error that occurred in the analysis can be ignored, and the source of sodium ions in them can be considered rainwater. Sp20 and Sp27 have ratios greater than 0.5, indicating ion exchange and non-halite origin for sodium, such as albite or cation exchange in the range.

3)  $Mg^{2+}/(Mg^{2+} + Ca^{2+})$ : This ratio is less than 0.5 for most samples, indicating that the effective carbonate in the water chemistry of these samples is dolomite and limestone. When this ratio is 0.5 (Sp4 and Sp17), it indicates the weathering of dolomite. Regarding the lack of limestone and dolomite expansion in the study area, the origin of these ions can be weathering of silicate ores containing calcium and magnesium in igneous rocks and metamorphic rocks in the region.

4)  $(Na^+ + K^+ - Cl^-)/(Na^+ + K^+ + Ca^{2+} - Cl^-)$ : This ratio is used to determine the weathering effect of plagioclase on water quality (Drever & Hurcomb, 1986). This ratio is 0.2-0.8 in about 40% of the samples (Sp2, Sp6, Sp9, Sp12, Sp13, Sp15, Sp16, Sp18, Sp25, Sp26, and Sp27), suggesting the effect of plagioclase weathering on water chemistry.

## Conclusions

EC variations in different neighborhoods of the study area show that the lowest (i.e., 31  $\mu\text{m}/\text{cm}$ ) and highest EC (i.e., 242  $\mu\text{m}/\text{cm}$ ) belong to the Sp16 and Sp21 sampling points, respectively. In addition, pH variations in water samples do not follow a specific trend and range from 7.21 to 9.38. Overall, the pH of water samples of Alvand heights is in the category of almost neutral waters.

The groundwater quality of the samples is suitable for drinking and agriculture, which is the predominant hydrochemical property of hard water resources. Based on the obtained results, most groundwater samples are corrosive for industrial use, which should be considered in the metal industry.

Based on Piper, Durov, and Stiff diagrams, the predominant facies of water resources obtained from the analysis of samples is the bicarbonate-calcium. The bicarbonate content of water indicates that the water is young and enters the aquifer quickly due to rainwater feeding. Igneous formations and magmatic minerals in the study area, including quartz, plagioclase, orthoclase, biotite, and muscovite (with  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Al^{3+}$ , and  $Si^{4+}$  dominant in these minerals), play a positive role in groundwater quality. However, some of the rocks and minerals in these formations (magmatic minerals such as many silicates, especially feldspars) have been weathered by various agents over the years and converted to other compounds such as clay minerals. Thus, they can have a more destructive effect on groundwater quality in the region.

The springs of the region are mostly fault-type and drain-free aquifers. This study shows that the springs created where the fractures are denser have more EC and TDS. In these places, the weathering has acted more intensely and increased the springs' water-soluble materials. Therefore, it can be concluded that due to the low solubility of crystalline rocks in the region, faults and fractures are the most important factor controlling the hydrochemical quality of groundwater in the active tectonic zone.

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