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*Review*

# Geochemical assessment of groundwater around Razgah area, Sarab district, Northwest of Iran

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**The chemical analysis of 9 water wells in Razgah area, Azarbaijan province NW of Iran has been evaluated to determine the hydrogeochemical processes and ion, heavy and rare metal concentration background in the region. The dominated hydrochemical types are Na+Cl in area. The metals often concentrate in south and western part in study area. Due to geological conditions and water flow path in the region, probably due to increased metals in the western and southern parts of the area is Razgah intrusion. Based on the total hardness, the groundwater is very hard. According to EC and SAR the most dominant classes are C4-S4. The major ion concentrations are above the acceptable level for drinking water. The groundwater salinity hazard is very high and Na hazard is very high and in regard of irrigation water the quality is low. So the drainage system is necessary to avoid the increase of toxic salt concentrations.**

**Keywords**: groundwater quality, Major ion, Razgah, Metal.

## INTRODUCTION

As population grows, demands on ground and surface water resources are increasing worldwide in arid and semi-arid regions (Meigh et al., 1999). Water of adequate quantity and quality is required to meet growing household, industrial, and agricultural needs (Azaza et al., 2010). Iran is located in a semi-arid area with an average annual precipitation less than one third of that of the world (Baghvand et al., 2010). Furthermore, spatial and temporal distribution of the regional precipitation is not integrated. Iran is one of 27 countries that are likely to face increasing water shortage crises between now and 2025 unless action is taken to reduce current water consumption (Bidhendi et al., 2007). Intense agricultural have placed a high demand on groundwater resources in Razgah regions and also these resources at greater risk to contamination. The importance of water quality in human health has recently attracted a great deal of interest (Pazand et al., 2011). The evaluation and management of groundwater resources require an understanding of hydrogeological and hydrochemical properties of the aquifer. The importance of the groundwaters in the area is high because they are water resource for drinking and agricultural purposes. In Razgah area, agriculture is the most important economic activity, thus hydrogeochemical investigation was carried out to identify groundwater geochemistry and its suitability for irrigation and drinking purposes.

### Geographic and geologic description of the area

Study area is located within the boundaries of the district of Sarab in Azarbaijan province in northernwest Iran. It is situated about 12 km northwest of Sarab City (Figure 1) and covers approximately 122 km$^2$ with a mean altitude

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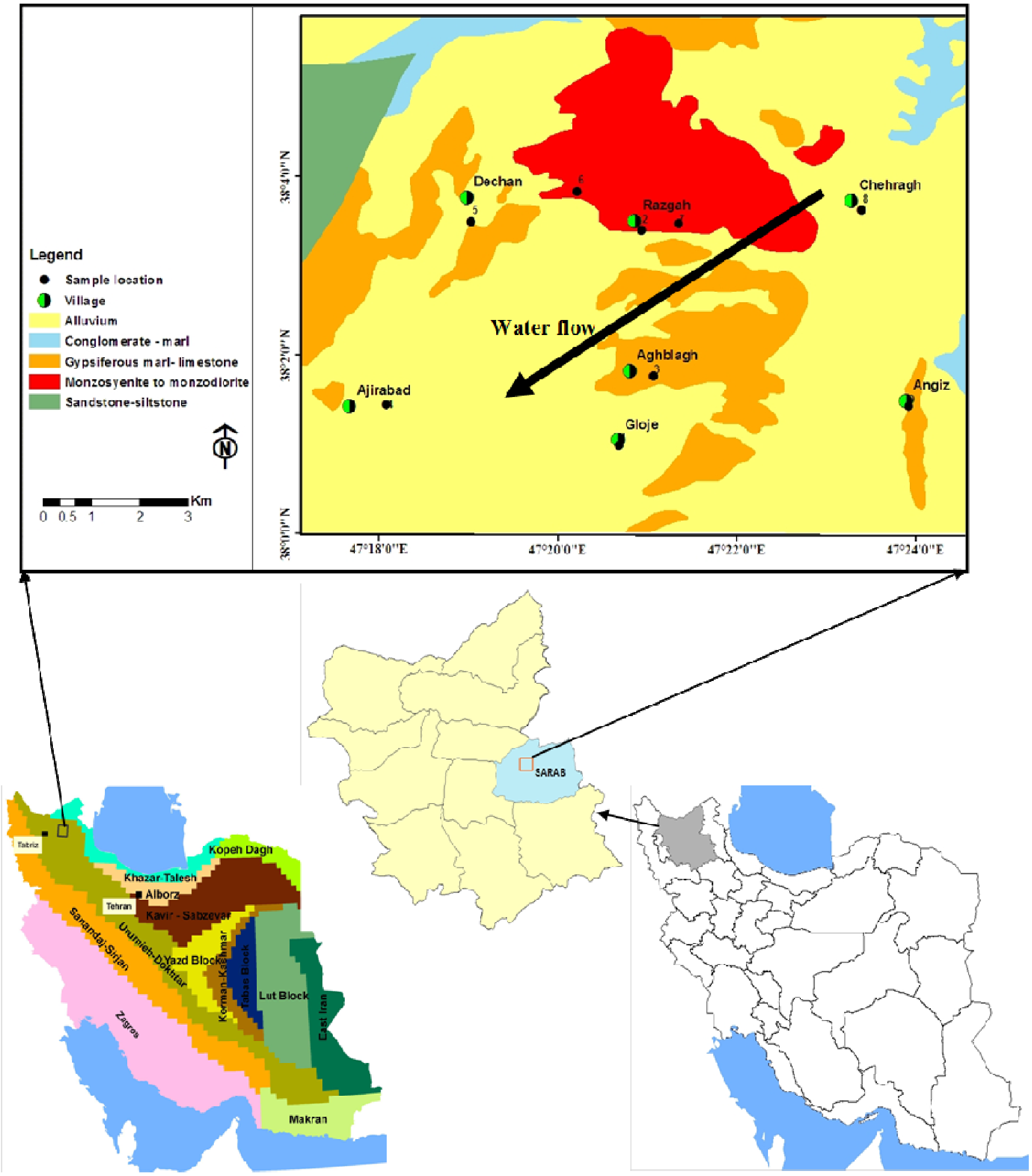

**Figure 1.** Major structural zones of Iran (after Nabavi, 1976) and the location of the Razgah area in these zones and a modified and simplified geologic map of it (after Mahdavi and Amini Fazl., 1988).

of 1800 m.a.s.l . The annual average precipitation being approximately 400 mm, of which about 37% occurs during winter. Another feature characterizing the precipitation in the study site is its irregular yearly distribution. The area has a cold temperate climate, with mean maximum summer temperatures (July) about 30 centigrade degree and minimum winter temperatures (January) of –10 centigrade degree. The area has complicated land use characteristics, mainly consisting of agricultural and residential areas. Groundwater use in instead of various purposes, such as drinking, agricultural and domestic needs. The most important economic activity of the area is agriculture. Continental collision between the Afro-Arabian continent and the Iranian microcontinent during closure of the Tethys ocean in the late Cretaceous resulted in the development of a volcanic arc in NW Iran (Mohajjel and Fergusson, 2000; Karimzadeh, 2005). In Iran, all known copper mineralization occurs in the Cenozoic Urumieh-Dokhtar orogenic belt (Figure 1). This belt was formed by

**Figure2 A,** B) Water sampling; C) Filtering; F) storing and D, E) field analysis

subdauction of the Arabian plate beneath central Iran during the Alpine orogeny (Berberian, And King, 1981; Pourhosseini, 1981). As seen from the geological map, five major formations are observed in the study area.

Figure1: Major structural zones of Iran (after Nabavi, 1976) and the location of the Razgah area in these zones and a modified and simplified geologic map of it (after Mahdavi and Amini Fazl., 1988).

The main lithology in study area is Oligocene-aged Razgah monzosyenite to monzodiorite that observed in the northern part of the study area that has copper mineralization as malachite. The northwestern parts of the study area are covered by the Miocene-Pliocene sandstone and siltstone. In east and northernwest of area there are conglomerate and marl with Miocene-Pliocene age. The gypsiferous marl and limestone area spread in all area. The quaternary alluviums cover often of study area (Mahdavi and Amini Fazl., 1988) (Figure1).

## Sampling and analytical methods

A total of 9 groundwater samples were collected from existing wells in the study areas in September-October 2010. Samples were stored in 100 ml polyethylene bottles after filtering through 0.45 µm membrane filters and divided into two groups: (i) filtered non-acidified for anion analysis, and (ii) filtered acidified (with few drops of 0.01 M $HNO_3$, Suprapur quality, Merck, Germany) for cation, heavy and trace element analysis. At each sampling site, Eh, pH, T, and electrical conductivity (EC) were measured using a pH multimeter.

Figure 2: A, B) Water sampling; C) Filtering; F) storing and D, E) field analysis

The Eh values reported in this study have not been corrected to the standard hydrogen electrode (SHE) but instead can be used as relative values. The major anions $Cl^-$, $F^-$, $NO_3^-$, $SO_4^{2-}$ and $PO_4^{3-}$ were analyzed with a Dionex DX-120 ion chromatography using IonPac As14 column. Alkalinity was measured in geological survey research center of Iran by a Radiometer Copenhagen PHM 82 Standard pH meter equipped with an ABU 80 autoburette following the standard method SS-EN ISO 9963-2. Concentrations of major cations ($Ca^{2+}$,$Mg^{2+}$,$K^+$ and $Na^+$) and heavy-trace elements (Al, As, Au, B, Ba, Br, Cd, Cr, Co, Cs, Cu, La, Li, Mn, Mo, Ni, P, Pb, Rb, Rh, Sb, Se, Si, Sn, Sr, V, Y, Zn, Fe) were determined by ICP-AES and ICP-MS, respectively in ACME Analytical

**Table1.** Result of physicochemical analysis of deep groundwater samples

| Sample | EC ms/cm | pH | Eh mv | T $^{0}$C | $F^-$ mg/l | $Br^-$ mg/l | $NO_3^-$ mg/l | $Cl^-$ mg/l | $SO_4^{2-}$ mg/l | $HCO_3^-$ mg/l | $Ca^{2+}$ mg/l | $K^+$ mg/l | $Mg^{2+}$ mg/l | $Na^+$ mg/l | TDS mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.79 | 7.34 | 153.00 | 12.30 | 0.54 | 0.91 | 23.01 | 192.70 | 1079.83 | 267.17 | 265.80 | 16.74 | 147.96 | 259.98 | 2272.5 |
| 2 | 2.38 | 6.34 | 128.00 | 12.00 | 0.68 | 1.82 | 16.33 | 208.45 | 382.21 | 615.66 | 194.60 | 24.52 | 40.29 | 310.94 | 1814.7 |
| 3 | 3.95 | 7.04 | 160.00 | 7.60 | 0.44 | 0.89 | 47.80 | 168.54 | 2013.60 | 202.04 | 453.09 | 8.69 | 176.71 | 401.19 | 3503.69 |
| 4 | 9.06 | 6.72 | 154.50 | 9.60 | 0.73 | 13.17 | 34.87 | 1451.89 | 2358.75 | 1219.87 | 273.00 | 49.33 | 320.89 | 1750.37 | 7482.5 |
| 5 | 5.60 | 6.65 | 156.60 | 12.00 | 0.45 | 11.34 | 23.39 | 1075.27 | 393.59 | 1050.50 | 331.69 | 55.16 | 69.16 | 948.46 | 3972.48 |
| 6 | 4.64 | 6.57 | 133.40 | 11.20 | 0.82 | 8.41 | 3.93 | 791.79 | 429.39 | 1089.07 | 156.54 | 40.50 | 55.83 | 772.34 | 3359.10 |
| 7 | 2.72 | 6.87 | 192.60 | 8.00 | 0.64 | 2.36 | 9.23 | 257.34 | 408.00 | 771.69 | 273.53 | 26.39 | 51.75 | 379.79 | 2198.39 |
| 8 | 1.72 | 7.17 | 95.00 | 11.00 | 1.77 | 0.22 | 23.17 | 24.60 | 644.80 | 404.86 | 254.87 | 14.48 | 61.86 | 105.13 | 1555.3 |
| 9 | 0.89 | 7.60 | 188.80 | 0.00 | 0.58 | 0.13 | 36.14 | 9.17 | 194.73 | 259.43 | 68.88 | 4.03 | 16.58 | 115.72 | 715.42 |
| Max | 9.06 | 7.60 | 192.60 | 12.30 | 1.77 | 13.17 | 47.80 | 1451.89 | 2358.75 | 1219.87 | 453.09 | 55.16 | 320.89 | 1750.37 | 7482.5 |
| Min | 0.89 | 6.34 | 95.00 | 0.00 | 0.44 | 0.13 | 3.93 | 9.17 | 194.73 | 202.04 | 68.88 | 4.03 | 16.58 | 105.13 | 715.42 |
| Mean | 3.75 | 6.92 | 151.32 | 9.30 | 0.74 | 4.36 | 24.21 | 464.42 | 878.32 | 653.36 | 252.44 | 26.65 | 104.56 | 560.43 | 2986.02 |
| Median | 2.79 | 6.87 | 154.50 | 11.00 | 0.64 | 1.82 | 23.17 | 208.45 | 429.39 | 615.66 | 265.80 | 24.52 | 61.86 | 379.79 | 2272.55 |
| Std | 2.47 | 0.40 | 30.13 | 3.89 | 0.41 | 5.15 | 13.75 | 515.49 | 786.35 | 395.87 | 108.30 | 18.04 | 96.18 | 527.61 | 1978.09 |

Laboratories (Canada).

## Groundwater chemistry

The results of physicochemical and metal analysis of groundwater samples are given in Table 1 and 2.

Table 1. Result of physicochemical analysis of deep groundwater samples

The distribution pattern of the concentration of main cation and anions is shown as contour maps (Figures 3, 4). The spatial variation of chemical parameters in the groundwater reflects the natural and human activity variation. The relative content of a cation or an anion is defined as the percentage of the relative amount of that ion to the total cations or anions, respectively. The concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ represent on average 26.74, 11.08, 59.36 and 2.82% of all the cations, respectively. Among the anions, the concentrations of $HCO^{3-}$, $Cl^-$, $SO_4^{2-}$, and $NO_3^-$ represent on average 32.33, 22.99, 43.47 and 1.21%, respectively. Thus, the order of cation and anion abundance is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $SO_4^{2-} > HCO^{3-} > Cl^- > NO_3^-$, respectively.

Table 2. Concentration of elements in groundwater.

Comparing the relative concentration of major ions in the waters from Razgah, Na is always higher than K, since Na is more abundant than K in the host rocks, and K-minerals in primary volcanic parageneses are more resistant to weathering than Na-minerals (i.e. plagioclase is more alterable than K-feldspar); moreover K is easily stabilized in neo-formation minerals (clay minerals). Mg is lower in concentration than Ca, probably due to the low abundance of Mg in the outcropping rocks. The agricultural application of fertilizer may be a possible source of $Cl^-$ concentration in groundwater Thus, the agricultural application of fertilizer may be a possible source of $Cl^-$ concentration in groundwater. On the other hand, the Groundwater pH is predominantly near neutral to slightly alkaline (6.34–7.6). TDS ranges from 715.4 to 7482.5 with an average of 2896 mg $l^{-1}$.

Figure 3: Spatial distributions of $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$ in the groundwater in the study area

Figure 4: Spatial distributions of $Cl^-$, $NO_3^-$, $HCO_3^-$ and $SO_4^{2-}$ in the groundwater in the study area.

The high correlations between $Cl^-$ and $HCO_3^-$ (R= 0.89), $Cl^-$ and $K^+$ (R=0.92), $Cl^-$ and $Na^+$ (R=0.97), $SO_4^{2-}$ and $Mg^{2+}$ (R=0.95), $K^+$ and $HCO_3^-$ (R= 0.95), $Na^+$ and $K^+$ (R=0.83) and between $Na^+$ and $HCO_3^-$ (R= 0.83) indicating that they most likely derive from the same source of water (Table 3). The EC values ranges from 890 to 9060 with a mean of 3750 µs $cm^{-1}$. Salinity has long been a constraint

**Table 2**. Concentration of elements in groundwater.

| Sample | Ag µg/l | Al µg/l | As µg/l | Au µg/l | B µg/l | Ba µg/l | Br µg/l | Cd µg/l | Co µg/l | Cr µg/l | Cs µg/l | Cu µg/l | Fe µg/l | La µg/l | Li µg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | <0.05 | 9 | 18.4 | 0.18 | 783 | 21.35 | 1114 | <0.05 | <0.02 | 3.6 | 0.18 | 3.1 | <10 | 0.02 | 75.6 |
| **2** | <0.05 | 9 | 25.1 | <0.05 | 1411 | 62.97 | 2291 | <0.05 | <0.02 | 7.0 | 0.16 | 2.6 | 197 | 0.06 | 63 |
| **3** | <0.05 | 8 | 30.3 | 0.08 | 2378 | 11.09 | 1163 | 0.10 | <0.02 | 6.6 | 0.08 | 6.5 | <10 | 0.02 | 71.8 |
| **4** | <0.05 | 8 | 36.5 | 0.11 | 8026 | 27.62 | 17133 | <0.05 | 0.21 | 5.3 | 0.2 | 7.8 | <10 | 0.04 | 607.1 |
| **5** | <0.05 | 3 | 63.1 | 0.11 | 5013 | 55.41 | 16143 | <0.05 | <0.02 | 2.3 | 0.08 | 3.4 | <10 | 0.02 | 171 |
| **6** | <0.05 | 2 | 4.6 | 0.34 | 3387 | 38.57 | 10970 | <0.05 | <0.02 | 38.6 | 0.26 | 3.5 | <10 | <0.01 | 137.8 |
| **7** | <0.05 | 10 | 5.4 | 0.08 | 1977 | 67.48 | 3235 | 0.06 | <0.02 | 0.8 | 0.27 | 4.6 | <10 | 0.01 | 88.1 |
| **8** | <0.05 | 3 | 4.1 | <0.05 | 916 | 20.89 | 267 | <0.05 | <0.02 | <0.5 | 0.02 | 4.5 | <10 | <0.01 | 40.7 |
| **9** | <0.05 | 3 | 3.2 | <0.05 | 371 | 23.38 | 155 | 0.40 | <0.02 | 1.1 | 0.02 | 8.1 | <10 | <0.01 | 10.7 |

| Sample | Mn µg/l | Mo µg/l | Ni µg/l | P µg/l | Pb µg/l | Rb µg/l | Rh µg/l | Sb µg/l | Se µg/l | Si µg/l | Sn µg/l | Sr µg/l | V µg/l | Y µg/l | Zn µg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.36 | 23.3 | <0.2 | 137 | 0.3 | 2.82 | 0.18 | 2.66 | 20 | 19362 | 0.63 | 9164.39 | 34.5 | 0.03 | 7.1 |
| **2** | 7.84 | 6.3 | <0.2 | 135 | <0.1 | 17.14 | 0.05 | 1.9 | 4.9 | 21707 | 0.19 | 3003.09 | 10.3 | 0.2 | 3.3 |
| **3** | 1.12 | 18.8 | <0.2 | 21 | <0.1 | 1.95 | 0.13 | 2.85 | 18 | 32039 | 0.29 | 8477.55 | 54.6 | 0.06 | 11.3 |
| **4** | 259.1 | 5.5 | 3.0 | 388 | 6.1 | 16.23 | 0.49 | 1.92 | 48 | 23554 | 0.17 | 21148.7 | 45.8 | 0.17 | 15.6 |
| **5** | 11.74 | 6.1 | <0.2 | 183 | <0.1 | 79.16 | 0.17 | 4.09 | 28.1 | 25264 | 0.69 | 8632.98 | 21.4 | 0.03 | 10 |
| **6** | 0.15 | 6.3 | <0.2 | 24 | 0.1 | 45.63 | 0.23 | 2.58 | 30.7 | 19712 | 0.2 | 4684.01 | 8.7 | 0.02 | 5 |
| **7** | 29.61 | 8.9 | <0.2 | 54 | 0.3 | 16.61 | 0.1 | 3.02 | 10.6 | 20678 | 0.23 | 4111.23 | 7.2 | 0.11 | 13.9 |
| **8** | 3.9 | 10.1 | <0.2 | 34 | 0.2 | 0.93 | 0.14 | 2.79 | 3.7 | 21543 | 0.28 | 4512.48 | 15.5 | 0.03 | 176.5 |
| **9** | 0.7 | 5.6 | <0.2 | 27 | 0.3 | 1.38 | 0.03 | 2.06 | 1 | 10761 | 0.34 | 1039.13 | 8.7 | 0 | 6.4 |

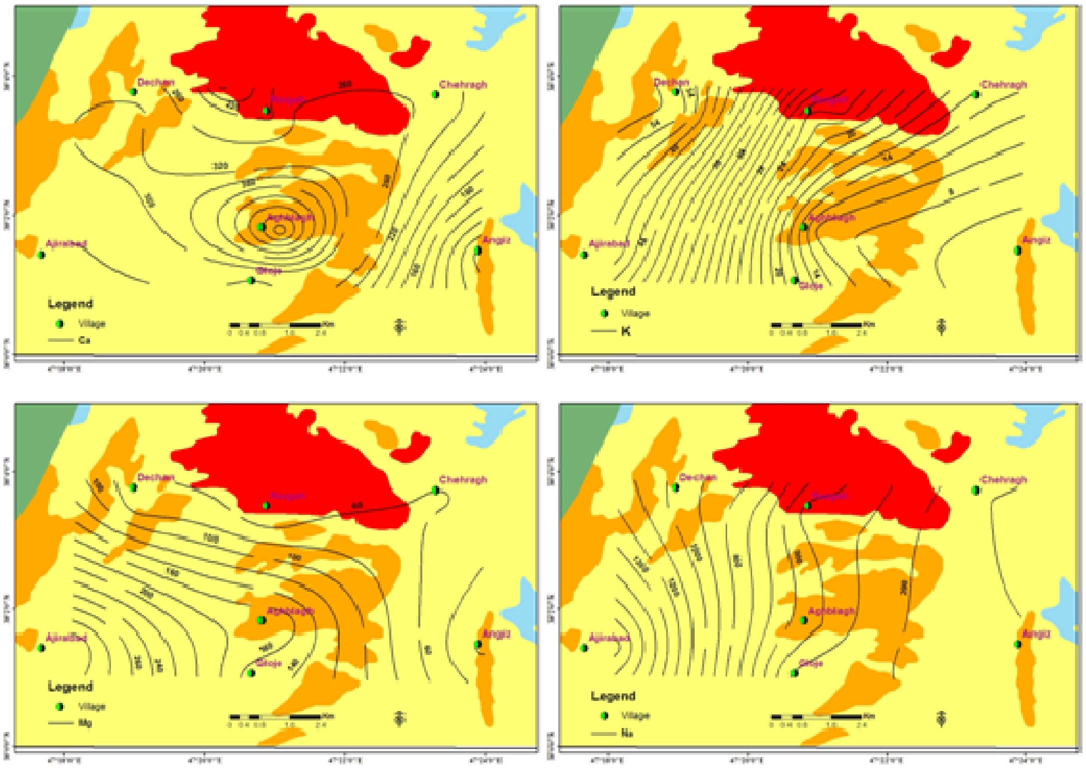

**Figure 3 A, B**) Water sampling; C) Filtering; F) storing and D, E) field analysis

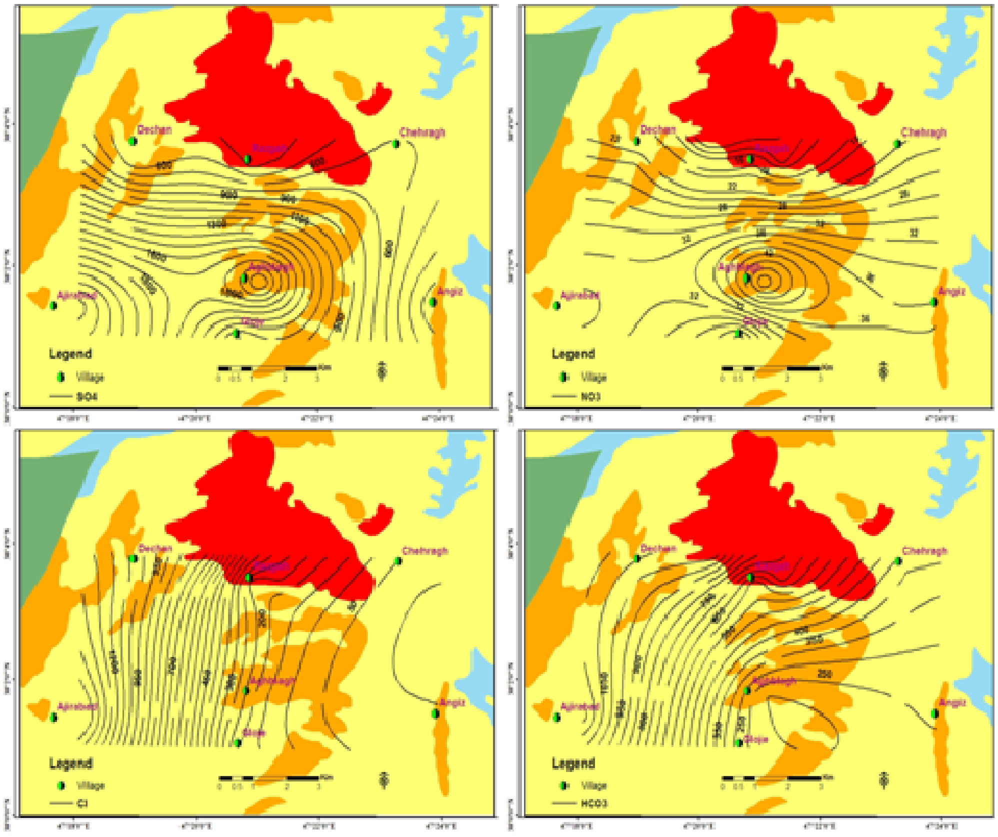

**Figure 4.** Spatial distributions of $Cl^-$, $NO_3^-$, $HCO_3^-$ and $SO_4^{2-}$ in the groundwater in the study area

for groundwater development for drinking and irrigation purposes in the study area. A good correlation of EC with sodium ($Na^+$) (R=0.98) and chloride ($Cl^-$) (R=0.95) implies that the increase in EC is directly related to salinity. The molar ratio of $Na^+/Cl^-$ close to unity usually suggested halite dissolution and $Na^+/Cl^- > 1$ is typically interpreted as reflecting $Na^+$ released from silicate weathering reactions (Pazand et al ., 2011).

Table 3. Correlation of physicochemical and trace-heavy metal for water sample data

The $Na^+$ /$Cl^-$ molar ratio in most of ground waters samples of the study area (except sample 5, 6) is more than 1 (Figure 5a), indicating that silicate dissolution can be a probable source for $Na^+$ in groundwater of the Miocene aquifer and thus $Na^+$ release from silicate weathering is important in this area. In the case of weathering of carbonates, the molar ratio of $Ca^{2+}+Mg^{2+}/HCO_3^-$ reaches close to unity. The plots of ($Ca^{2+}+Mg^{2+}/HCO_3^-$) (Figure 5b) show that samples except two wells (1 and 3) have ratio less than 1 and suggesting carbonate weathering is not a dominant process and the source of high $HCO_3^-$ is different.

Figure 5: Correlation of (a) $Na^+/Cl^-$ along samples; (b) ($Ca^{2+}$ + $Mg^{2+}$)/$HCO_3^-$ along samples

Piper plots for water samples from the study site are presented in Figure 6. Based on dominant cations and anions, three water types were found for the water samples: (1) Na-Cl (2) Ca-Mg-Cl-$SO_4$, (3) Ca-Mg–$HCO_3$–Cl that each represents 67, 22and 11% of the total number of water samples.

Figure 6: The piper diagram for the groundwater samples of the study area

## Distribution of rare and heavy metal

Concentration of metals in groundwater including As, Fe, Mn, Pb and others is presented in Table 2. Most metal concentrations in water depending on the mineral solubility, and pH, Eh and salinity of the solution (Caron et al., 2008). The content of As in some groundwater (sample: 1, 2, 3, 4, 5) is above the WHO guideline for dirking water (<10µg/l) (WHO, 2004). Concentration of Fe above WHO permissible limit (<10µg/l) only in sample 2 is seen. Mn concentration is relatively low and vary from 0.15 to 259.1 µg/l in the area, and below WHO guideline for drinking water (<500µg/l). Concentration of Cu in groundwater is observed between 2.6 and 8.1 µg/l in the study area. Fluorine occurrence is associated with the presence of silicic rocks and their weathering products. The fluoride concentration in natural waters is inversely related to Ca. This permits free mobility of the fluoride ion into the solution at lower Ca content. Such conditions are sometimes recorded in aquifers constituted by volcanic rocks (Ashely and Burley 1994). In study area correlation between $Ca^{2+}$ and $F^-$ is negative (R=-0.57) that confirm this mechanism in area (Table 3). The maximum Pb concentration is approximately 6.1 µg/l and the minimum is below detection limit (<0.1 µg/l). Concentration of Sr in groundwater varies from 1.04 to 21.14 mg/l with a mean value of 7.2 mg/l. Concentrations of dissolved Ba (11.09–67.48 µg/l), Zn(3.3–176.5 µg/l), Ni (<0.2–3 µg/l), Mo (5.5–23.3 µg/l) and Se (1 to 48 µg/l) also vary in groundwater of the study area. The content of Se in some groundwater (sample: 1, 3, 4, 5, 6, 7) is above the WHO guideline for dirking water (<10µg/l) (WHO, 2004). In figure 7 concentration of As, Se, V, Mo and Cu metal in samples are showed.

Figure 7: concentration of As, Se, V, Mo, Cu metal in sample of area

These metals often concentrate in south and western part in study area. Due to geological conditions and water flow path in the region, probably due to increased metals in the western and southern parts of the area is Razgah intrusion.

## Groundwater quality

Natural chemical composition of groundwater results from two main processes: the first is the atmospheric salts that coming from marine aerosols, dust and concentration by evaporation of dissolved salts in precipitation, and the second are the interaction of groundwater with the formation minerals (Jordana and Batista 2004). A hydrogeological environment is a conceptual model of morphological, geological and climatic parameters that determine the main groundwater flow features in given area (Toth 1970). Understanding the quality of groundwater is as important as its quantity because it is the main factor determining its suitability for drinking, domestic, agricultural, industrial and touristic purposes. The analytical results of physical and chemical parameters of groundwater were compared with the standard guideline values as recommended by the World Health Organisation for drinking and public health purposes (WHO 2004). Concerning the taste, there is a relationship between the quality of the taste and the total amount of solids in solution: Very good (<300 mg $l^{-1}$), good (300–600 mg $l^{-1}$), acceptable (600–900 mg $l^{-1}$), poor (900–1,200 mg $l^{-1}$) and unacceptable (>1,200 mg $l^{-1}$) (WHO 2004). Except for sample 9, TDS concentration was unacceptable (Table 1). All groundwater samples have lower $K^+$ content than the acceptable limits (200 mg $l^{-1}$) for drinking water (WHO, 2004). The low levels of $K^+$ in natural waters are a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals (Pazand et al., 2011). In water sample 4 the amount of sodium equal to 1750.37 mg/l and is larger than the maximum acceptable level for drinking water (1538 mg/l). Also in both sample (3 and 4) $SO_4^{2-}$ are higher than the maximum acceptable level limit (1492 mg/l). In sample 3 amount of $Ca^{2+}$ and in samples number 1,3 and 4 the concentrations of $Mg^{2+}$ are above

**Table 3.** Correlation of physicochemical and trace-heavy metal for water sample data.

| | EC | pH | Eh | $Br^-$ | $F^-$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | As | B | Ba | Cu | Mn | Mo | P | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EC | 1 | | | | | | | | | | | | | | | | | | | | |
| pH | -0.49 | 1 | | | | | | | | | | | | | | | | | | | |
| Eh | 0.01 | 0.30 | 1 | | | | | | | | | | | | | | | | | | |
| $Br^-$ | 0.91 | -0.56 | 0.01 | 1 | | | | | | | | | | | | | | | | | |
| $F^-$ | -0.23 | 0.09 | -0.74 | -0.20 | 1 | | | | | | | | | | | | | | | | |
| $Cl^-$ | 0.95 | -0.54 | 0.02 | 0.99 | -0.21 | 1 | | | | | | | | | | | | | | | |
| $NO_3^-$ | 0.14 | 0.47 | 0.20 | -0.12 | -0.21 | -0.05 | 1 | | | | | | | | | | | | | | |
| $SO_4^{2-}$ | 0.66 | 0.00 | 0.00 | 0.29 | -0.13 | 0.39 | 0.63 | 1 | | | | | | | | | | | | | |
| $HCO_3^-$ | 0.77 | -0.71 | -0.04 | 0.92 | -0.06 | 0.89 | -0.44 | 0.06 | 1 | | | | | | | | | | | | |
| $K^+$ | 0.80 | -0.70 | -0.07 | 0.95 | -0.15 | 0.92 | -0.36 | 0.09 | 0.95 | 1 | | | | | | | | | | | |
| $Na^+$ | 0.98 | -0.49 | 0.06 | 0.94 | -0.21 | 0.97 | 0.08 | 0.56 | 0.83 | 0.83 | 1 | | | | | | | | | | |
| $Ca^{2+}$ | 0.53 | -0.07 | 0.38 | 0.33 | -0.57 | 0.33 | 0.32 | 0.48 | 0.00 | 0.28 | 0.48 | 1 | | | | | | | | | |
| $Mg^{2+}$ | 0.79 | -0.07 | 0.02 | 0.47 | -0.15 | 0.58 | 0.50 | 0.95 | 0.26 | 0.30 | 0.72 | 0.67 | 1 | | | | | | | | |
| As | 0.62 | -0.41 | 0.04 | 0.61 | -0.44 | 0.62 | 0.31 | 0.33 | 0.38 | 0.62 | 0.57 | 0.73 | 0.39 | 1 | | | | | | | |
| B | 0.98 | -0.51 | 0.04 | 0.94 | -0.19 | 0.97 | 0.11 | 0.56 | 0.82 | 0.84 | 0.99 | 0.52 | 0.70 | 0.62 | 1 | | | | | | |
| Ba | 0.00 | -0.65 | 0.17 | 0.23 | -0.20 | 0.17 | -0.68 | -0.54 | 0.50 | 0.47 | 0.08 | -0.07 | -0.42 | 0.17 | 0.09 | 1 | | | | | |
| Cu | 0.21 | 0.48 | 0.44 | 0.05 | -0.09 | 0.10 | 0.71 | 0.48 | -0.11 | -0.23 | 0.26 | 0.03 | 0.43 | -0.09 | 0.25 | -0.52 | 1 | | | | |
| Mn | 0.81 | -0.22 | 0.09 | 0.65 | -0.02 | 0.72 | 0.24 | 0.68 | 0.57 | 0.50 | 0.85 | 0.50 | 0.82 | 0.29 | 0.82 | -0.08 | 0.51 | 1 | | | |
| Mo | -0.21 | 0.44 | 0.00 | -0.48 | -0.15 | -0.42 | 0.30 | 0.36 | -0.64 | -0.48 | -0.37 | 0.28 | 0.25 | -0.05 | -0.38 | -0.51 | -0.16 | -0.29 | 1 | | |
| P | 0.81 | -0.34 | 0.01 | 0.72 | -0.18 | 0.78 | 0.17 | 0.54 | 0.59 | 0.65 | 0.83 | 0.22 | 0.74 | 0.60 | 0.80 | 0.09 | 0.18 | 0.87 | -0.21 | 1 | |
| Zn | -0.27 | 0.23 | -0.67 | -0.27 | 0.95 | -0.29 | 0.00 | -0.07 | -0.21 | -0.23 | -0.28 | 0.53 | -0.12 | -0.30 | -0.23 | -0.29 | -0.04 | -0.09 | 0.00 | -0.21 | 1 |

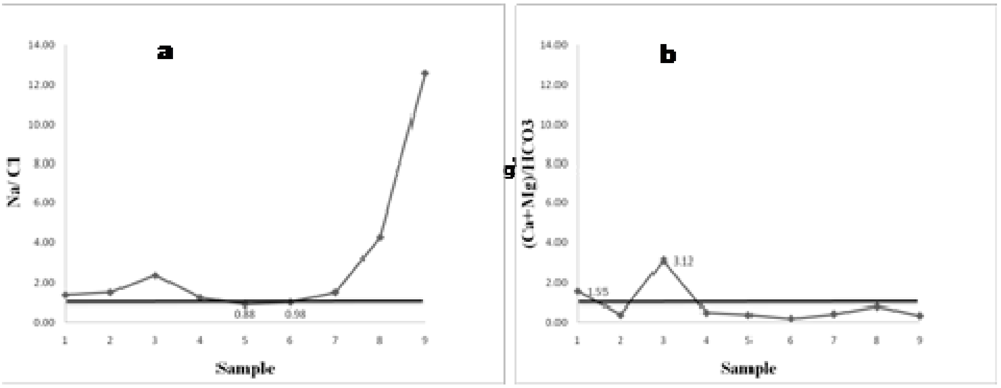

**Figure 5.** Correlation of (a) Na+/Cl- along samples; (b) (Ca2+ + Mg2+)/HCO3- along samples

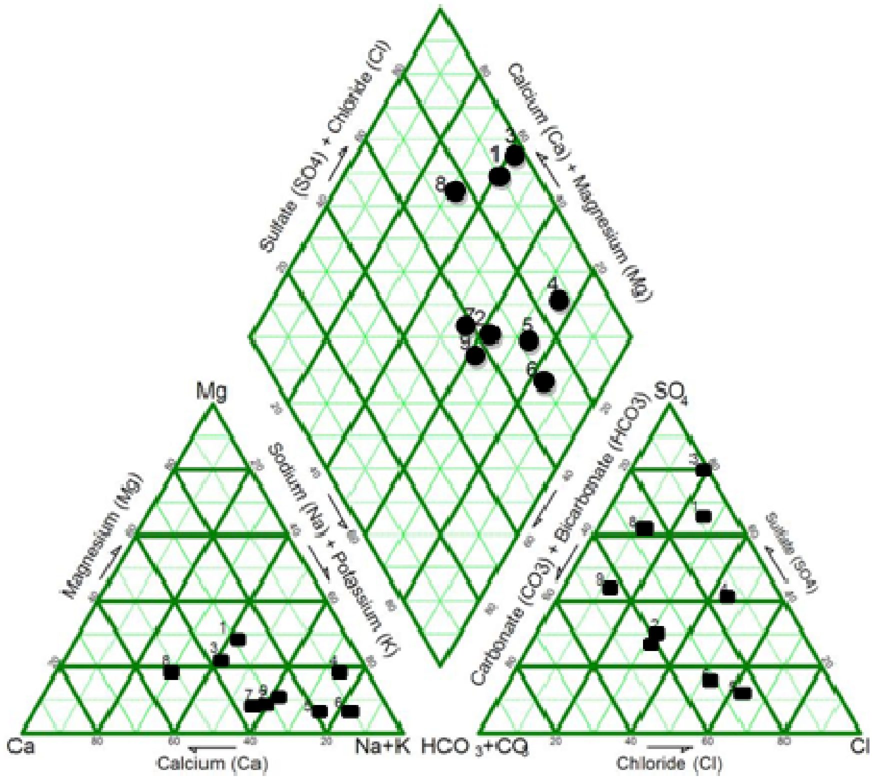

**Figure 6**. The piper diagram for the groundwater samples of the study area

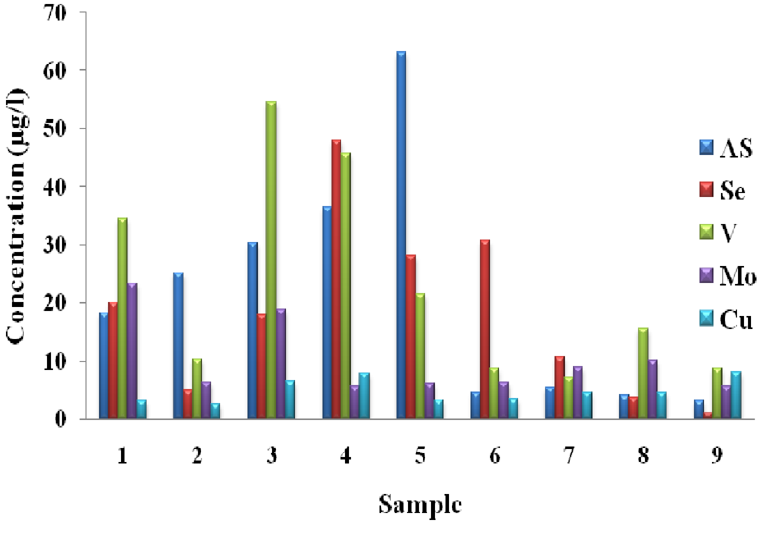

**Figure 7.** concentration of As, Se, V, Mo, Cu metal in sample of area

the limit (349 and 133 mg/l, respectively)(WHO, 2004). All these examples are in the South and South-West region. Hardness of water depends mainly upon the amounts of divalent metallic cations, of which $Ca^{2+}$ and $Mg^{2+}$ are the more abundant in groundwater. Hardness ($H_T$) of groundwater was calculated using following equation (Pazand et al., 2011):

$$H_T = 2.5Ca^{2+} + 4.1Mg^{2+}$$

The degree of hardness in water is commonly based on the classification (0–75) soft, (75–150) moderately hard, (150–300) hard, (>300) very hard and hence groundwaters are soft (Todd and Mays 2005). The hardness values in water samples range from 240 to 1998, the average being 1059 mg/l. In all of samples, $H_T$

concentration was very hard (except sample 9 that it is hard). The suitability of water for irrigation purpose depends on the sodium ion and total salt content of the water. Plants intake water from soil by osmosis and osmotic pressure is proportional to the salt content, which affects the growth of plants, soil structure and permeability (Gupta et al., 2009). Sodium concentration is important when evaluating the suitability of groundwater for irrigation. High concentrations of $Na^+$ are undesirable in water because $Na^+$ is adsorbed onto the soil cation exchange sites, causing soil aggregates to disperse, reducing its permeability (Jalali, 2009). The sodium adsorption ratio (SAR), which indicates the effect of relative cation concentration on $Na^+$ accumulation in the soil, is used for evaluating the sodicity of irrigation water. The sodicity hazard of water is generally described by the SAR (Pazand et al., 2011):

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

The ionic symbols indicate concentrations of the ions in the water in milliequivalents per liter. The calculated SAR ranged from 8.35 to 101.57. In order to identify the availability of waters for irrigation use, the Wilcox classification diagram has been used (Figure 8). According to this graph, water classes of water samples are mainly C4–S4and only one sample are C3–S2 (sample 8), and one sample is C3–S2 (sample 9). Therefore groundwater samples in study area indicating very high salinity and median to very high sodium water type which unsuitable for irrigation purposes.

Figure 8: Diagram of sodium adsorption ratio and salinity for the calssification of groundwater for irrigation purposes

## CONCLUSIONS

The major cations in the studied groundwater is in the decreasing order as $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. The anions are also arranged in decreasing order as $SO_4^{2-} > HCO^{3-} > Cl^- > NO_3^-$, respectively. Based on the major constituents, in general, groundwaters from the studied area the main hydrochemical facies for the groundwaters is Na+Cl. Heavy metals often concentrate in south and western part in study area. Due to geological conditions and water flow path in the region, probably due to increased metals in the western and southern parts of the area is Razgah intrusion. Amounts of anions in the groundwater, particularly in South and South-Western area in shows that are higher than the maximum acceptable level limit for dirking water, and $H_T$ and TDS are high. The water types are unsuitable for irrigation purposes. Thus due to the rural population in the region, water management and provide the necessary guidelines for its use is essential.

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