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# Hydrogeochemical investigation and water quality assessment in the Sarough watershed, Takab mining district

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**ABSTRACT**

This study investigated the hydrogeochemistry and environmental water quality of rivers in Sarough watershed using the major ion chemistry and explored multivariate statistical methods for identification of processes which release the solutes in natural waters. Totally, 38 samples were collected along the main streams of the watershed. The mean concentrations of major cations (Na, K, Mg, Ca) and anions (Cl, $NO_3$, $CO_3$, $HCO_3$, $SO_4$) were measured about 15, 4.6, 10.5, 61, 30, 4.49, 89, 156 and 107 mg/l, respectively. The results indicated that the river waters in the Sarough watershed were neutral and fresh water in nature (mean values: pH=7.7 and TDS= 315.8 mg/l). Most of the water samples were categorized in hard and very hard water classes with mean value for TH=197 mg/l and were under-saturated regarding with major carbonates, sulfates and evaporate minerals in most of samples. The major water types were Ca–$HCO_3$–$SO_4$, Ca–Mg–$CO_3$ and Ca–$SO_4$–$HCO_3$. The Na, Cl and $NO_3$ concentration in all water samples fell within the accepted limit of national and international standards for drinking water. Nevertheless, Ca, Mg and $SO_4$ content in some samples were higher than the maximum desirable limits. Schuler diagram showed that majority of the water samples were good and acceptable for drinking. Evaluating the quality of river water for irrigation purposes using Wilcox diagram and SAR, EC and RSC indices indicated that majority of the water samples were suitable for irrigation. The results of multivariate statistical techniques such as correlation coefficient matrix, CA and PCA indicated the strong association between Na-K-Cl-$SO_4$ and Ca-Mg-$CO_3$-TH. It was assumed that weathering of carbonates (limestone/dolomite formations, calcareous marl formation and travertine) in the area were common source of Ca, Mg and $HCO_3$. Also, travertine springs were considered as active point sources which release these elements into the drainage system. Meanwhile, dissolution of halite and gypsum in red marl formations (lower part of Qom F. and Upper Red F.) were the main processes considered as the origin of Na, K, Cl and $SO_4$ in river water of study area.

## 1- Introduction

Rivers constitute the main inland water bodies for domestic, industrial and agricultural activities and often carry large waste water discharges from different sources (Hu et al., 2011). Numerous natural and anthropogenic factors such as climate, lithology, topography, vegetation and human activities influence the surface water quality (Berner and Berner, 1996). Deterioration of water quality not only has negative effects on aquatic organisms and agricultural activities but also threats public health in surrounding areas. Understanding of processes regulating river chemistry is a fundamental issue for both aquatic ecologists and water resources managers for its significance on aquatic environment management and protection (Meyer et al., 1988; Kimbadi et al., 1999). Monitoring the water quality of rivers is used to determine suitability of water for drinking, irrigation and industrial uses. Employing

integrated physicochemical approaches and multivariate statistical techniques provide an effective way for evaluation the effect of natural process and human activities on the overall water quality compared with standard values.

This study was carried out in Sarough watershed, North West of Iran, which has been affected by point and non-point pollution sources such as domestic waste, agricultural activities, mining and mineral processing runoff. So, monitoring the water quality throughout the watershed is necessary for appropriate water management. This study aimed to determine the physicochemical properties and quality of rivers water in the Sarough watershed for drinking and agricultural uses. It also investigated the origin of solutes from the hydrogeochemistry of main rivers in the area.

## 2- Study area

The Sarough watershed is located 10 km north of Takab, West Azerbaijan province, NW Iran. It covers an area about 913 km$^2$. The Sarough River (length 40 km, average annual flow 3.31 m$^3$s$^{-1}$) is the main permanent river which passes through the watershed. Zarshuran, Aq-Darreh and Ahmad Abad streams are the main tributaries of Sarouq River which supply the agriculture and drinking water for several populated areas. The catchment area of Sarouq River generally is covered by mountains, especially in the north parts.

Relatively sufficient water resources have caused widespread agriculture activities in this area. The average temperature varies from 30ºC in summer to about -9◦C in winter. Annual precipitation is about 400mm, falling mostly as snow and humidity is about 51%.

Figure1 presents the geological map of Sarough watershed. The oldest rock units are a series of metamorphic micaschist and quartzite of lower Precambrian age (P$\text{€}^{sh}_k$). These rocks underlie metamorphosed ultramafic rocks, including complexes of serpentinite and serpentine schist, metagabbro, and metamorphosed basaltic rocks of middle Precambrian (Sr). A thick bedded greyish crystalline dolomitic limestone and dolomite comprises the upper Precambrian sequence (P$\text{€}^l_j$). Cambrian deposits consist of dolomite of Soltanieh formation ($\text{€}^d_s$), shale and sandstone of Zagun formation ($\text{€}^{sh}_z$) and arkosic sandstone of Lalun formation ($\text{€}^s_l$). These units are followed by alternation of limestone and marly limestone of Ordovician age ($\text{€}^l_m$). Oligo-Miocene stratigraphic units are mainly composed of alternation of gypsiferous marl and sandstone (OM$^m_q$) and red marl and sandstone (M$^s$) which are equivalent to lower part of Qom formation and Upper Red formation, respectively.

These marl formations which are widespread through the watershed are rich in gypsum and evaporates such as halite, sylvite and anhydrite. Besides, outcrops of thick bedded to massive limestone (OM$^{l2}_q$) form high reliefs of northwestern parts of the area. The sedimentary formations of Olio-Miocene are associated with volcanic rocks such as pumecious tuff breccia (OM$^{tr}$), basalt (OM$^{vb}$), dacite and ignimbrite (OM$^{vd2}$) and porphyritic andesite (OM$^{va}$). The youngest rock units are loose clay-cemented polygenetic conglomerate (QP$^c$), travertine (Q$^{tr}$) and alluvium (Q$^l$). A number of intrusive rocks mainly granite (g), quartz porphyry microgranite (qp) and microdiorite-micromonzonite (Pl$^{md}$) are exposed in north and west of the study area (Babakhani and Ghalamghash, 1995). There is an abundance of hot springs notably near the travertine deposits. The travertine-forming springs are generated from fluids of an active hydrothermal system related to volcanic setting of the study area (Alavi et al., 1982).

## 3- Materials and methods

### 3- 1. Sampling and Sample preparation

Thirty – eight water samples were collected along the main river and streams of Sarough watershed such as Zarshuran, Agh Darreh, Ahmad Abad and Sarough streams in September 2015 (Fig. 2). A Garmin GPS instrument was used to record the location of sampling sites. Water samples were taken based on sampling guideline of EPA (2000). Samples were collected from mid-point at a depth of 30 cm beneath the river surface. Some of the physicochemical parameters of water such as temperature (T), pH, electrical conductivity (EC), oxidation-reduction potential (Eh), salinity and total dissolved solids (TDS) were measured in situ using Lovibond SensoDirect 150 portable instrument in the field. Water samples were collected in 250 ml polyethylene (metal free) bottles and then filtered with 0.45 microns filter papers. All samples were kept under 4°C and sent to the laboratory of Iran Mineral Processing Research Center (IMPRC). The concentration of major cations (Na, K, Mg, Ca) and anions (Cl, NO$_2$, NO$_3$, CO$_3$, HCO$_3$, SO$_4$, PO$_4$) were determined using an ion chromatography instrument (Metrohm 881 compact IC pro). The precision and accuracy of analytical results were estimated by analysis of 12 sample duplicates (30% of total samples) and house-made Certified Reference Material (CRM), respectively. The results showed the precision of analysis based on Thompson and Howarth (1976) error analysis procedure at the 95% confidence interval was less than 5% for all the elements and calculated accuracy was within the required range (better than ±10%).
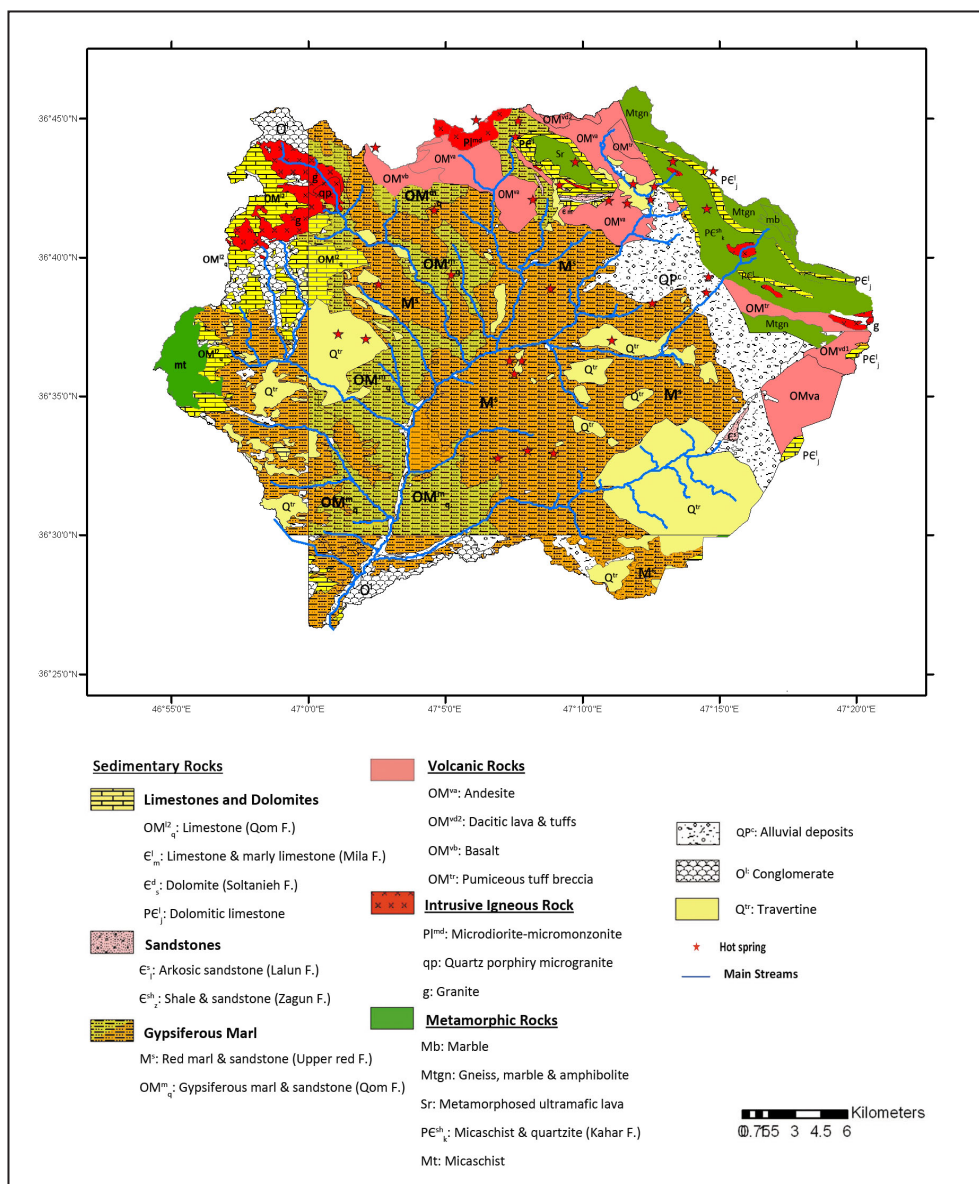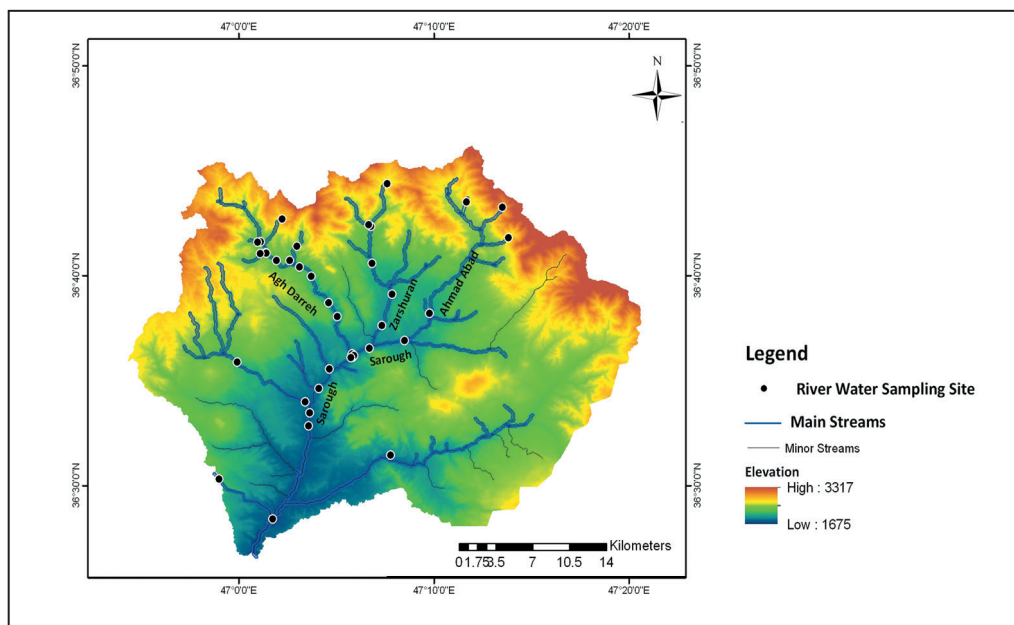
Fig. 1- Geological map of Sarough watershed.



Fig. 2- Location map of main streams (Zarshuran, Agh Darreh, Ahmad Abad and Sarough) in Sarough watershed and sampling sites.

## 4- Results and discussions

The statistical data processing and interpretation was employed using Microsoft Excel, SPSS and AquaChem softwares. The concentration of $PO_4$ and $NO_2$ in all collected water samples was lower than detection limit of 5 and 0.06 mg/l, respectively. The $NO_3$ content in 70% of samples was lower than detection limit (5 mg/l). So, the analytical data for $PO_4$, $NO_3$ and $NO_2$ were removed from the statistical calculations. The Descriptive statistical summary of physicochemical parameters measured in river water samples was presented in Table 1.

As indicated in the Table 1, the calcium content ranged from 9.28 to 121 mg/l with an average of 61 mg/l, while that of magnesium was from 0.6 to 32 mg/l. Similarly sodium and potassium content ranged from 1.17 to 64 mg/l and 1.3 to 14.8 mg/l, respectively. Regarding the anions, bicarbonate was the dominant anion in the surface water samples ranging from 11 to 440 mg/l with a mean value of 156 mg/l. This was followed by sulfate, with a range of 11 to 280 mg/l. The chloride concentration ranged from 3.7 to 182 mg/l with an average of 30 mg/l. The variation of major ion concentrations of water samples was illustrated in the Box and Whisker plots (Fig. 3).
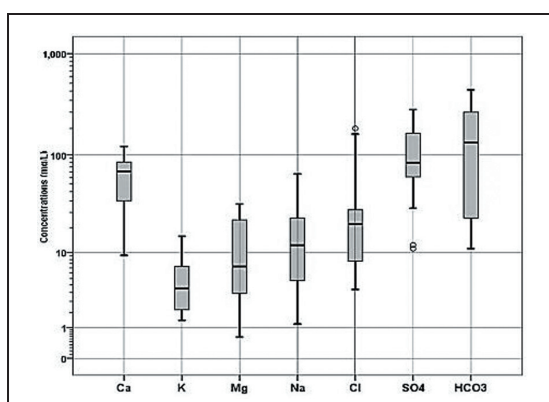


Fig. 3- Variation of major ions concentration in river water samples of study area on Box and Whisker plot.

The dominant cation and anion were Ca and $HCO_3$, respectively. Plotting major ions contents on Piper (Fig. 4- a) and Durov (Fig. 4- b) diagrams showed that bicarbonate water type is dominant and Ca is the major cation. Concentrations of cations and anions in water samples showed the order of Ca > Na > Mg > K for cations and $HCO_3$ > $SO_4$ > Cl for anions. The result of Stiff diagrams showed that the main water samples in this area belonged to Ca–$HCO_3$–$SO_4$ type, which included 13 water samples (35%). Ca–Mg–$CO_3$ (16%) and Ca–$SO_4$–$HCO_3$ (10%) water types fell in second and third places, respectively.

The total dissolved solids (TDS) ranged from 0.2 to 751 mg/l with a mean value of 315.83 mg/l. Electrical conductivity (EC) lied between 0.31 and 1502 μS/cm with an

average of 603μS/cm. The Eh values were in the range of -80 to 13.8 mV with the average value of about -51.6 mV. The pH range varied from 6.81 to 8.8 with a mean value of 7.73, which clearly showed the water to be circum-neutral. The maximum salinity was 0.7‰ with a mean value of 0.3 ‰. Total Hardness (TH) of water samples ranged from 29.23 to 421.47 mg/l with a mean value of 197 mg/l. The classification of water hardness in study area according to USGS hardness scale (Hem, 1991) showed that 60% of water samples were categorized in hard and very hard water classes (Table 2). The TDS versus TH plot (Fig. 5) showed that all water samples were classified in fresh water group. The water hardness varied from moderately soft (M.S), slightly hard (S.H) and moderately hard (M.H) to hard (H) classes. Only two water samples fell in soft and very hard water classes.

Water hardness is mainly caused by contribution of Ca and Mg ions. The source of these ions is typically sedimentary rocks, the most common being limestone ($CaCO_3$) and dolomite [Ca Mg ($CO_3)_2$] (Hounslow, 1995). As it is obvious in geological map of the study area (Fig. 1), thick bedded to massive limestone and dolomite of Precambrian ($PЄ^l_j$), Cambrian ($Є^d_s$), Ordovician ($Є^l_m$) and Olio-Miocene ($OM^{l2}_q$) form high reliefs in north and northwestern parts of the watershed. Travertine deposits of Quaternary ($Q^{tr}$) are relatively widespread through the study area. These yellowish-white, porous, flat lying deposits are mainly exposed along main faults and around active hot springs. Meanwhile, calcareous marls of Qom formation ($OM^m_q$) and Upper Red formation ($M^s$) cover much of the drainage area. It seems that weathering of above mentioned rocks produce large amount of Ca, Mg and bicarbonate due to high reactivity and solubility of carbonate minerals. Also, travertine spring water is reported to be characterized by domination of Ca and $HCO_3$ ions. It is notable that water samples located close to the hot springs displayed high Ca and $HCO_3$ content. This result slightly highlighted the mixing of surface water with thermal springs and dissolution of travertine deposits. These results were completely in agreement with the dominant water type (calcium-bicarbonate) in Sarough watershed.

## 5- Processes influencing the hydrogeochemistry of Sarough watershed

A variety of physical and chemical processes in a drainage basin control the geochemical composition of solutes in river water. The main sources which release the elements into river water system include (Berner and Berner 1996; Chen et al., 2002 and 2005) (1) sea salt carried inland in the atmosphere and deposited on land (cyclic salts);

Table 1- Descriptive statistical parameters of major ions in river water samples of study area.

| | EC μs/cm | TDS mg/l | pH | TH mg/l | Eh mv | Sal ‰ | Ca mg/l | Mg mg/l | Na mg/l | K mg/l | CO₃ mg/l | HCO₃ mg/l | Cl mg/l | SO₄ mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Min** | 0.31 | 0.2 | 6.81 | 29.23 | -80 | 0 | 9.28 | 0.6 | 1.17 | 1.36 | 0 | 11 | 3.7 | 11 |
| **Max** | 1502 | 751 | 8.8 | 421.47 | 13.8 | 0.7 | 121 | 32 | 64 | 14.8 | 356 | 440 | 182 | 280 |
| **Mean** | 603.18 | 315.83 | 7.73 | 197.09 | -51.63 | 0.30 | 61 | 10.5 | 15 | 4.6 | 89 | 156 | 30 | 107 |
| **Median** | 569 | 316 | 7.59 | 203.01 | -56.7 | 0.3 | 67 | 6 | 11.5 | 3.8 | 0 | 132 | 20 | 83 |
| **Std. Deviation** | 362.52 | 183.88 | 0.58 | 109.64 | 20.29 | 0.20 | 29 | 10.26 | 14.6 | 3.14 | 125 | 134 | 40 | 75 |
| **Skewness** | 0.60 | 0.38 | 0.54 | 0.17 | 1.06 | 0.26 | -0.12 | 0.92 | 1.89 | 1.21 | 0.8 | 0.53 | 2.68 | 1.06 |
| **Kurtosis** | 0.37 | 0.05 | -0.99 | -0.98 | 1.42 | -0.47 | -0.95 | -0.75 | 4.03 | 1.46 | -1.19 | -0.94 | 7.45 | 0.08 |

Table 2- Classification of water hardness

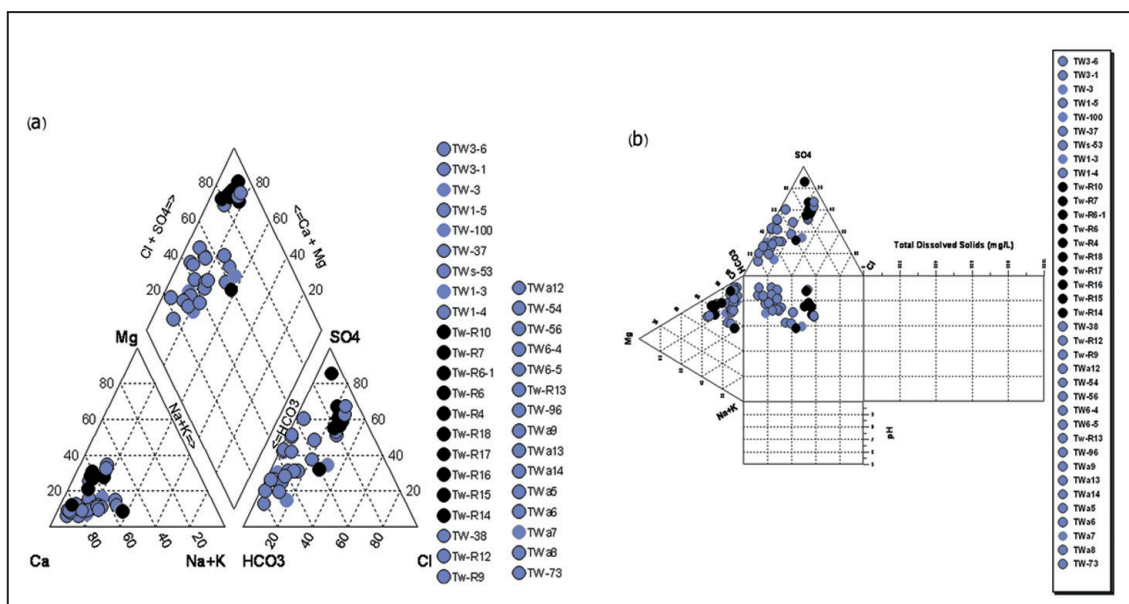| Classification | TH (mg/l) | Number of samples | % |
|---|---|---|---|
| **Very hard** | >180 | 10 | 26.31 |
| **Hard** | 121-180 | 13 | 34.21 |
| **Moderately hard** | 61-120 | 9 | 23.68 |
| **Soft** | 0-60 | 6 | 15.78 |



Fig. 4- a)Piper diagram and b) Durov diagram showing major ion composition of water samples in the study area.
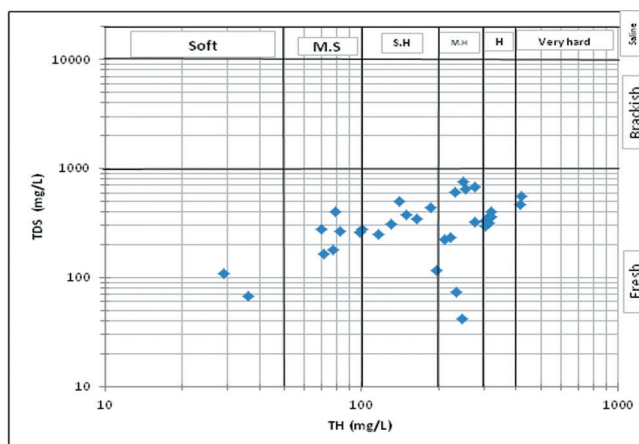


Fig. 5- Classification of river water samples based on TH and TDS.

(2) weathering of silicate, carbonate, evaporate and sulfide minerals; (3) anthropogenic inputs. Among above mentioned processes, the variability in the chemical composition of rivers is mainly control by rock weathering in the drainage area (Holland, 1978; Livingston, 1963). The major ion chemistry is an appropriate tool for identification of solute sources and for describing water evolution as a result of water-rock interaction (Elliot et al., 1999; Edmunds and Smedley, 2000; Jeelani and Shah, 2006). In order to understand the source of the solutes, the hydrochemical data were plotted in the Langelier-Ludwig diagram (Langelier and Ludwig, 1942) in Figure 6a. The plot showed that most of water samples were characterized by two main trends i.e., carbonate weathering and gypsum/anhydrite dissolution. Figure 6b showed the Mg/Na versus Mg/Ca molar ratios of water samples. All of samples had low Mg/Ca ratios and variable Mg/Na ratios which emphasized on rock interaction as dominant process controlling the water chemistry. The soil-salt leaching, especially Ca-salts, was assumed to be the other source of solutes in the watershed. The high ratio of $(Ca+Mg)/TZ^+$ (about 1.04) and the low ratio of $(Na+K)/TZ^+$ (about 0.13), in addition to a high average ratio of $(Ca+Mg)/(Na+K)$ (about 6.86), indicated the dominance of carbonate weathering over silicate weathering in Sarough watershed.

The bicarbonate mainly originates from carbonate weathering in the catchment areas. Ca and Mg ions are particularly derived from dissolution of carbonates (limestone, dolomite), sulfates (gypsum and anhydrite) (Hounslow, 1995) and cation exchange process (Garrels, 1976). Weathering of gypsum-bearing sedimentary rocks is the main source of sulfate in the river water (Jeevanandam et al., 2006).

The $Ca/(Ca+SO_4)$ molar ratio in 80% of water samples was equal to greater than 0.5 which indicated gypsum and carbonate as possible sources of Ca. The molar ratio lower than 0.5 along with the neutral to alkaline nature in 20% of samples was attributed to calcium removal by ion exchange or calcite precipitation (Hounslow, 1995). The $Ca+Mg$ vs. $HCO_3$ scatter diagram (Fig.7- a) showed two possible sources for Ca and Mg. Samples plotted close to the 1:1 line showed carbonate dissolution as the predominant source of these two ions whereas samples fell above the line indicated that the excess Ca and Mg may be provided by the other processes beside carbonate weathering such as dissolution of gypsum or weathering of Ca and Mg bearing-clay minerals. The $Ca+Mg$ vs. $SO_4$ scatter diagram (Fig. 7- b) indicated that both carbonate and sulfate weathering play a role for supplying these ions to the surface water.

The $Ca/(Ca+Mg)$ molar ratio of 0.5 and 1 correspond to the dissolution of stoichiometric dolomite and pure calcite, respectively (Frondini, 2008). This molar ratio in the water samples averaged ~0.82 (0.59–0.93) which was attributed to the weathering of calcite. In $Ca/(Ca+Mg)$ vs. $SO_4/(SO_4+HCO_3)$ plot (Fig. 7- c) most of the water samples were characterized by high $Ca/(Ca+Mg)$ molar ratio indicating that the water reacted mainly with calcite.

The possible sources of Na concentrations in natural waters are attributed to the atmospheric precipitation, dissolution of evaporate, weathering of silicate minerals and ion exchange process (Stallard and Edmond, 1983; Meybeck, 2004). Cl is mainly derived from dissolution of halite (Hounslow, 1995). According to Na vs. Cl plot (Fig. 8- a), Na concentrations in most water samples scattered above the seawater line (0.8). Consequently, Na and Cl in river water cannot be originated from atmospheric deposition of sea salt. The Na/Na+Cl molar ratio values indicated the involvement of salts dissolution in contribution of Na and K ions to the surface water in 65% of samples, where the values of this ratio were close to 0.5. The molar ratio greater than 0.5 corresponded to ion exchange process or weathering of silicate minerals which may be the source of Na and K in 33% of water samples (Hounslow, 1995). Although, the samples plotted above the 1:1 line in Na vs. Cl diagram (Fig. 8- a) proposed the ion exchange of clay minerals as an additional source for Na rather halite. The significant positive correlation between Na and Cl ($R^2= 0.87$) as well as Na+K and $SO_4+Cl$ ($R^2= 0.8$) (Fig. 8- a and b), confirmed halite dissolution as a prevalent process.

The molar ratio of Na/Cl against EC plot was used to understand ion exchange process in the watershed. The molar ratio of Na/Cl is approximately close to 1.0 in the case of halite dissolution, whereas greater and lower ratios are attributed to ion exchange and reverse ion exchange processes, respectively (Marie and Vengosh, 2001). Figure 8- c showed that the majority of samples had molar ratio close to 1 indicating halite dissolution as the major process. Moreover, locating of some samples above the horizontal line proposed the cation exchange as the subdominant process which releases Na and K into surface water. Plotting the data on $Ca+Mg$ vs. $SO_4+HCO_3$ plot (Fig.8- d) showed that the dissolutions of calcite and gypsum were the dominant process for samples were close to the 1:1 line. Samples clustered below the 1:1 line represented excess of $SO_4+HCO_3$ (ion exchange) while the samples clustered above the equiline showed a large excess of calcium and magnesium (reverse ion exchange) (Cerling et al. 1989; Fisher and Mulican 1997).
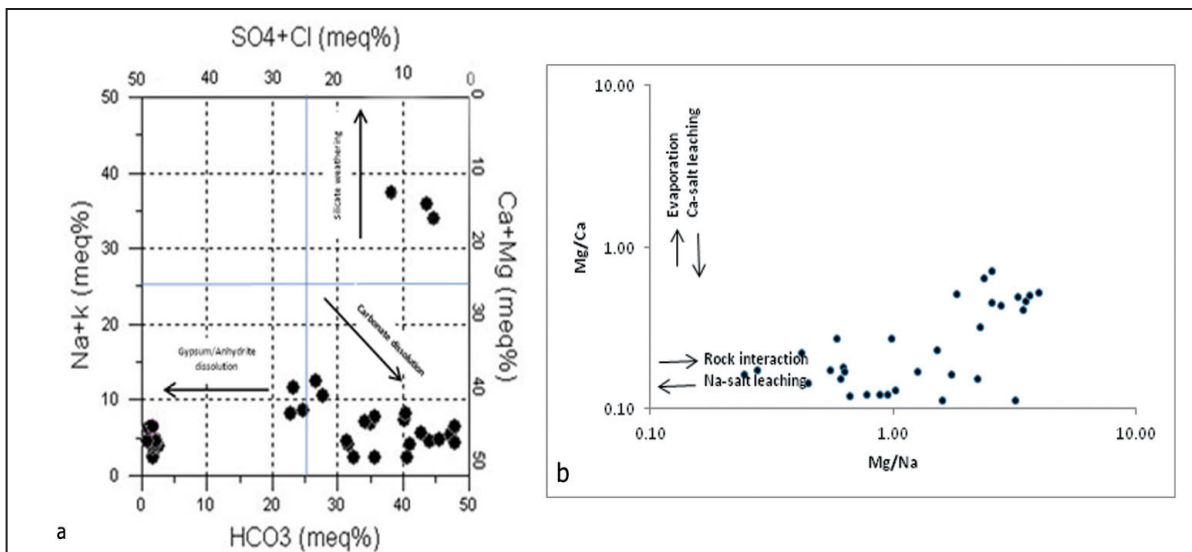
Fig. 6- a) Langelier –Ludwig plot and b) Mg/Ca vs. Mg/Na plot show the possible geochemical trends in the watershed.
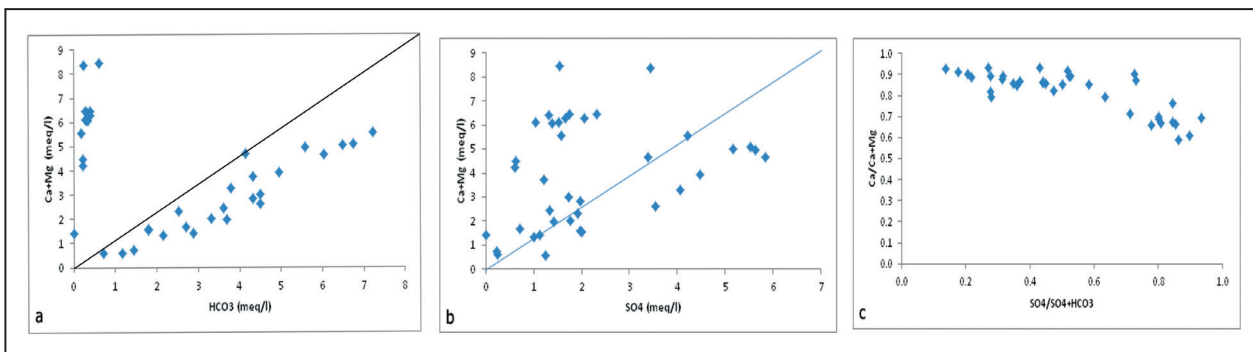


Fig. 7- a) Ca + Mg vs. HCO$_3$, b) Ca + Mg vs. SO$_4$ and c) Ca/(Ca + Mg) vs. SO$_4$/(SO$_4$+HCO$_3$) plots.
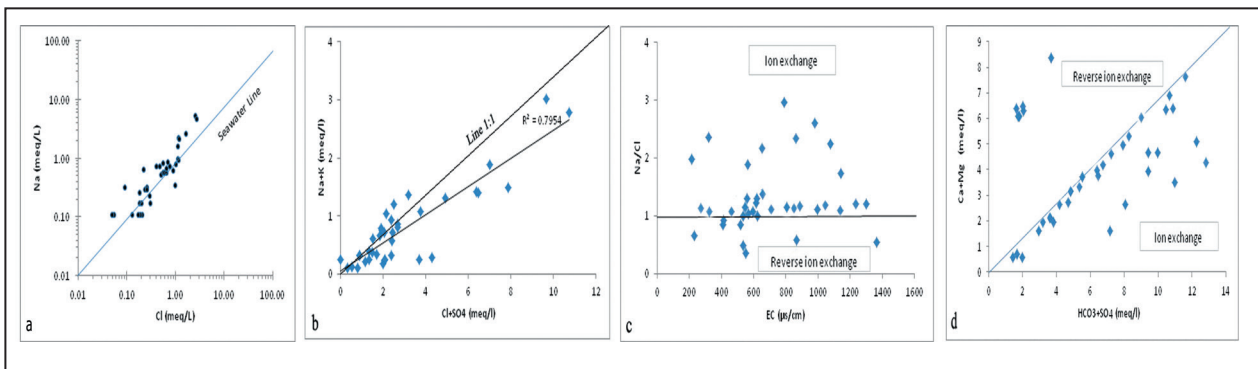


Fig. 8- a) Na vs. Cl, b) Na + K vs. Cl +SO$_4$, c) Na/Cl vs. EC and d) Ca + Mg vs. HCO$_3$+SO$_4$ plots.

saturation indices (SI) of some common mineral phases of water samples were estimated using the USGS hydro-geochemical model PHREEQC (Parkhurst and Appelo, 1999). Calculation was conducted by setting a CO$_2$ partial pressure of 10-2 atm for all water samples which is typical for wetland soil in an arid environment (Humphries et al., 2011). To replicate field conditions, temperature was set to 20◦C. The summary statistics of saturation indices (Table 3) indicated that most

of the minerals, except calcite and aragonite, remained unsaturated in river waters of study area. A plot of calcite saturation indices versus dolomite saturation indices (Fig. 9) showed that 18 water samples (50%) of total 38 studied samples were unsaturated with respect to both calcite and dolomite. In return, 13 water samples (34.21%) showed super–saturation regarding these minerals. Only 6 samples (15.78%) were supersaturated in terms of calcite and unsaturated regarding dolomite.
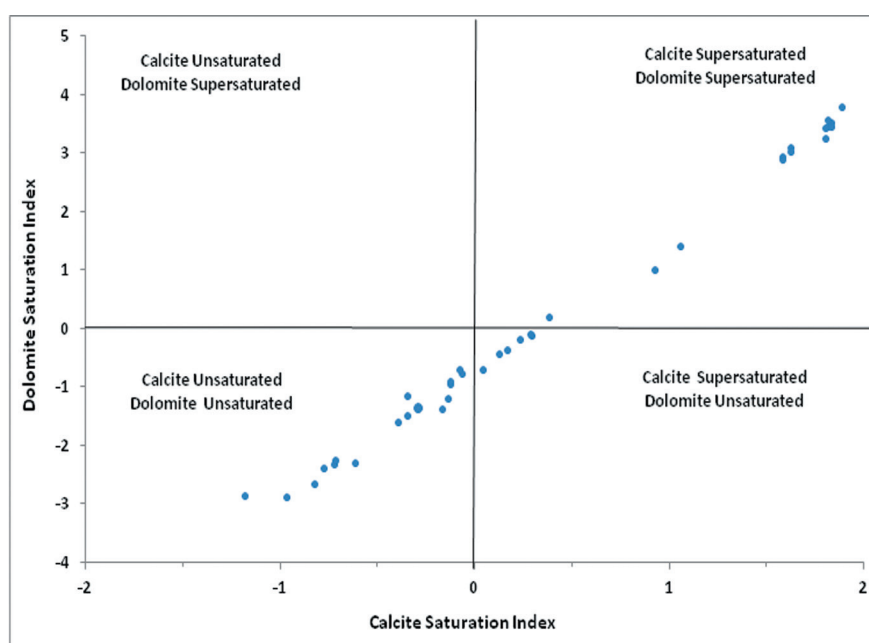
Fig. 9- Relationship between calcite and dolomite saturation indices for water samples in study area.

Table 3- Saturation indices (SI) of mineral phases for river waters in study area

| Minerals | Formula | Min | Max | Mean | SD |
|----------|---------|-----|-----|------|-----|
| Anhydrite | $CaSO_4$ | -3.32 | -1.46 | -2.09 | 0.44 |
| Aragonite | $CaCO_3$ | -1.37 | 1.70 | 0.21 | 1.00 |
| Calcite | $CaCO_3$ | -1.18 | 1.89 | 0.41 | 1.00 |
| Dolomite | $CaMg(CO_3)_2$ | -3.47 | 3.19 | -0.38 | 2.25 |
| Gypsum | $CaSO_4:2H_2O$ | -3.05 | -1.19 | -1.82 | 0.44 |
| Halite | NaCl | -9.92 | -6.58 | -8.36 | 0.84 |

## 6- Identification of the sources of chemical compounds in river water

Multivariate statistical techniques such as cluster analysis (CA), principal component analysis (PCA) and correlation coefficient, are widely used in water quality assessment and identification of possible sources or factors that influence water system (Wunderlin et al., 2001; Reghunath et al., 2002, Simeonova et al., 2003). In this study, the data sets were subjected to following multivariate statistical techniques:

Cluster analysis (CA) is a common method for classifying large number of data into smaller homogenous groups based on their correlation structure (Boyaciaglu, 2007). The result of cluster analysis of analytical data was presented as a dendogram in Fig. 10. The results depicted a strong association between Ca, Mg, $CO_3$ and TH indicating the same origin for these ions. TDS, EC and salinity fell in the same cluster. The association between Na, Cl, SAR with $SO_4$ and K proposed a common source for releasing of these

elements into the natural waters in this area.

A correlation analysis on values of measured parameters (Table 4) indicated the strong correlation between Na with Cl and $SO_4$ (0.9 and 0.7, respectively) as well as Cl and $SO_4$ (r=0.7, p<0.01) which was attributed to their common origin. Also, the positive correlation between Ca with Mg and $CO_3$ (0.7 and 0.6, respectively) and carbonate with Mg (r=0.9, p<0.01) confirmed the common source of these ions. Bicarbonate was weakly correlated with the K (r= 0.44, p< 0.01) and Na (r= 0.44, p< 0.01) in samples.

Principle component analysis (PCA) tendered three components with total variance of 85.16% (Table 5). The result of PCA analysis of variables in water samples in the study area was illustrated in Table 6. The first factor with 42.35% of the total variance had a strong loading on K, Na, Cl, $SO_4$ and SAR which signified the same origin of these compounds. The F2 had Ca, Mg, $CO_3$, TH and pH which had strong loading describing 26.77% of the total variance.
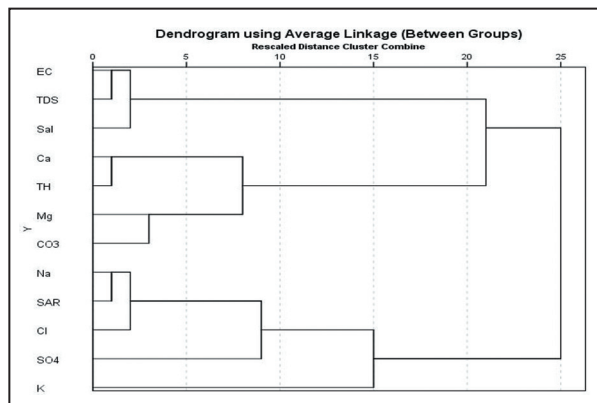
Fig. 10- Dendogram showing the clusters of chemical parameters in water samples .

Table 4- Spearman correlation matrix between chemical parameters of the water samples in Sarough watershed

| | Ca | K | Mg | Na | Cl | SO$_4$ | HCO$_3$ | pH | Eh | EC | TDS | Sal | TH | SAR | CO$_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 1 | | | | | | | | | | | | | | |
| K | .572** | 1 | | | | | | | | | | | | | |
| Mg | .745** | .273 | 1 | | | | | | | | | | | | |
| Na | .566** | .597** | .300 | 1 | | | | | | | | | | | |
| Cl | .401* | .553** | .051 | .935** | 1 | | | | | | | | | | |
| SO$_4$ | .419** | .538** | .006 | .746** | .720** | 1 | | | | | | | | | |
| HCO$_3$ | -.028 | .443** | -.509** | .448** | .556** | .681** | 1 | | | | | | | | |
| pH | .483** | .077 | .859** | .045 | -.192 | -.239 | -.735** | 1 | | | | | | | |
| Eh | -.066 | -.142 | -.381* | -.065 | .067 | -.004 | .260 | -.630** | 1 | | | | | | |
| EC | .477** | .446** | .229 | .339* | .206 | .324 | .401* | -.035 | .184 | 1 | | | | | |
| TDS | .545** | .444** | .329* | .344* | .186 | .299 | .315 | .066 | .144 | .991** | 1 | | | | |
| Sal | .604** | .398* | .403* | .315 | .141 | .230 | .199 | .149 | .159 | .946** | .969** | 1 | | | |
| TH | .966** | .494** | .891** | .500** | .293 | .287 | -.216 | .659** | -.192 | .412* | .497** | .566** | 1 | | |
| SAR | .414** | .551** | .144 | .979** | .945** | .743** | .526** | -.081 | -.038 | .282 | .269 | .227 | .337* | 1 | |
| CO$_3$ | .662** | .036 | .904** | .044 | -.161 | -.261 | -.736** | .869** | -.217 | .070 | .179 | .296 | .800** | -.113 | 1 |
| **. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed). | | | | | | | | | | | | | | | |

Table 5- Principle component analysis of measured chemicals in water samples

| Component | Initial Eigenvalues | | | Extraction Sums of Squared Loadings | | | Rotation Sums of Squared Loadings | | |
|---|---|---|---|---|---|---|---|---|---|
| | Total | % of Variance | Cumulative % | Total | % of Variance | Cumulative % | Total | % of Variance | Cumulative % |
| **1** | 5.930 | 42.356 | 42.356 | 5.930 | 42.356 | 42.356 | 4.302 | 30.728 | 30.728 |
| **2** | 3.749 | 26.779 | 69.135 | 3.749 | 26.779 | 69.135 | 4.181 | 29.866 | 60.595 |
| **3** | 2.244 | 16.032 | 85.167 | 2.244 | 16.032 | 85.167 | 3.440 | 24.572 | 85.167 |
| 4 | .959 | 6.849 | 92.016 | | | | | | |
| 5 | .548 | 3.918 | 95.934 | | | | | | |
| 6 | .367 | 2.622 | 98.556 | | | | | | |
| 7 | .073 | .524 | 99.080 | | | | | | |
| 8 | .054 | .383 | 99.464 | | | | | | |
| 9 | .032 | .228 | 99.691 | | | | | | |
| 10 | .028 | .199 | 99.890 | | | | | | |
| 11 | .009 | .067 | 99.957 | | | | | | |
| 12 | .004 | .028 | 99.985 | | | | | | |
| 13 | .002 | .015 | 100.000 | | | | | | |
| 14 | 3.238E-10 | 2.313E-09 | 100.000 | | | | | | |

Table 6- The results of varimax rotated factor analysis in water samples

|  | Component | | |
|---|---|---|---|
|  | 1 | 2 | 3 |
| **Ca** | .443 | .667 | .460 |
| **K** | .640 | .157 | .326 |
| **Mg** | .099 | .960 | .156 |
| **Na** | .953 | .152 | .134 |
| **Cl** | .956 | -.066 | .033 |
| **SO$_4$** | .835 | -.127 | .174 |
| **CO$_3$** | -.160 | .939 | .117 |
| **pH** | -.150 | .949 | -.143 |
| **Eh** | .046 | -.443 | .470 |
| **EC** | .192 | .045 | .943 |
| **TDS** | .177 | .153 | .940 |
| **Sal** | .123 | .240 | .937 |
| **TH** | .339 | .828 | .372 |
| **SAR** | .958 | .002 | .067 |

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization

This factor appeared to be associated to water–rock interaction processes mainly carbonates dissolution. The $F_3$ consisted of Eh, EC, TDS and Sal having strong loading with 16.03% of the total variance. For better indication of extracted factors, the component loading plots were illustrated in Fig. 11.

The occurrence of highly reactive minerals, such as evaporate minerals and calcite, even in low proportions in a given rock, determine the chemical character of stream water (Drever, 1988).

Comparing the results of multivariate analysis of hydrogeochemical data with geological map of study area suggested two types of rocks as the main sources of two groups of ions (Na-K-Cl-SO$_4$ and Ca-Mg-CO$_3$) in the catchment area:
- Carbonate formations: Ca, Mg and CO$_3$ which showed strong correlation in surface water samples are mainly derived from weathering of carbonate rocks in the study area. These carbonate formations which outcrops in north and northwestern parts of the watershed belong to Precambrian (P$\text{C}^l_j$), Cambrian ($\text{C}^d_s$), Ordovician ($\text{C}^l_m$) and Olio-Miocene (OM$^{l2}_q$). Dissolution of carbonate minerals, increases the concentration of Ca and HCO3 in river water of study area via following formula:

$$CaCO_3 + (CO_2 + H_2O) \longrightarrow Ca^{2+} + 2\ HCO^{3-}$$

- **Evaporate– bearing sedimentary formations:** One of the most notable geological features of the Sarough drainage basin is the dominance of Oligo-Miocene marl deposits, which are composed of two formations; The lower layer of Qom formation (OM$^m_q$) which includes salt, gypsum

and anhydrite with alternating layers of silt and clay and Upper Red formation (M$^s$) which is characterized by gypsiferrous marl and alternation of red-yellow sandy marl. These formations contain abundant layers of gypsum, halite and other salt deposits especially in the basal beds of the continental deposits which are exploited as small mines in local scale (Alavi et al., 1982). The higher solution rate of gypsum and halite compared with other associated layers, has ended to development of karstification and formation of sinkholes and caves in gypsum member of these formations. The results of drilling data in this area demonstrated the high extent of evaporate dissolution and karstification process in Qom formation (Nassery and Nick ghojough, 2012). Development of faults and fractures resulting from dynamic tectonics of the area has increased the intensity of this process. Dissolution of evaporate minerals releases large amounts of Na, K, Cl and SO$_4$ into the surface water system which can produce high ionic contents in drainage waters.

## 7- Comparison the chemistry of water in Sarough watershed with world average data

The average of major solute concentrations in the main tributaries of studied watershed including Zarshuran, Agh Darreh, Ahmad Abad streams and Sarough River were shown together with the world spatial median values (WSM) (Meybeck, 2004) in Table 7 and Fig. 12. The average distribution patterns of major ion concentration in river waters of study area were mainly similar to global rivers values but showed a relatively higher range of concentration for all major solutes. The average concentrations of main solutes in river waters of Sarough watershed were in the order of Sarough > Agh Darreh > Ahmad Abad > Zarshuran. In all of the four rivers of studied watershed the concentration of major ions was higher than the world spatial median value (WSM). The average TDS concentrations in Zarshuran, Agh Darreh, Ahmad Abad and Sarough were 345, 330, 231 and 305 mg/l, respectively which were 2.7, 2.5, 1.8 and 2.4 times higher than that of the world spatial median (127 mg/l), respectively.

## 8- Water quality assessment

The water quality for drinking and irrigation uses in Sarough watershed was assessed based on the recommended standards of the World Health Organization (WHO, 2011), Iranian national water standard (ISIRI 1053, 2009) and Food and Agriculture Organization (Ayers and Westcot, 1994). Total hardness (TH), total dissolved solids (TDS) and the concentrations of Na, Cl and NO$_3$ in all water samples were below the limits of the WHO (2011) and ISIRI 1053.
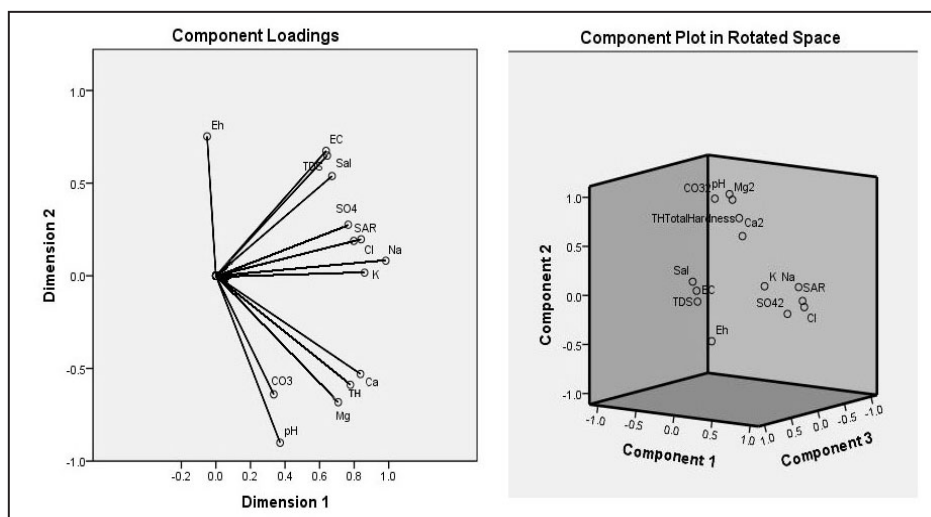
Fig. 11- Component loading plots in the factor analysis.

Table 7- Mean concentration of major solutes (meq/L) and TDS (mg/l) in river waters of study area compared with the world spatial median values (Meybeck, 2004).

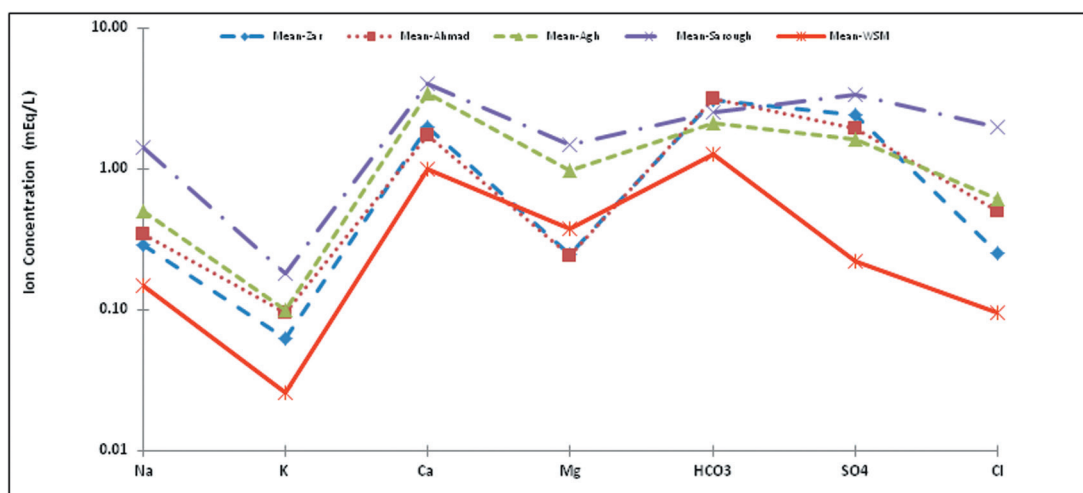| Rivers | Na | K | Ca | Mg | HCO$_3$ | SO$_4$ | Cl | TDS |
|---|---|---|---|---|---|---|---|---|
| Zarshuran | 0.29 | 0.06 | 1.96 | 0.25 | 3.07 | 2.43 | 0.25 | 345 |
| Ahmad Abad | 0.34 | 0.10 | 1.73 | 0.24 | 3.17 | 1.94 | 0.50 | 231 |
| Agh Darreh | 0.50 | 0.10 | 3.46 | 0.98 | 2.12 | 1.61 | 0.61 | 330 |
| Sarough | 1.40 | 0.18 | 4.03 | 1.49 | 2.53 | 3.39 | 1.99 | 305 |
| world spatial median | 0.148 | 0.026 | 1.000 | 0.375 | 1.260 | 0.219 | 0.096 | 127 |



Fig. 12- Diagram showing the average of major solute concentrations in the main rivers of the Sarough watershed (Zarshuran, Agh Darreh, Ahmad Abad and Sarough) and WSM values (Meybeck, 2004).

The concentrations of Ca (47%), Mg (5%) and SO$_4$ (8%) were higher than the maximum desirable limits of 75, 30 and 250 mg/l respectively, prescribed for drinking purpose by WHO (2011) and ISIRI 1053. The pH values ranged from 6.8 to 8.8, which shows that 15% of samples exceeded the desirable limit of 8.5 (WHO, 2011). Determination of the percentage of non-potable water from ion content using Schuler graph showed that most of the water samples were good and acceptable for drinking (Fig. 13- a).

To determine the quality of river water samples for irrigation purposes, the SAR vs. EC values of water samples were plotted in Wilcox diagram (Fig. 13- b). In this diagram, majority (54%) of the water samples fell in the C2-S1 (medium salinity with low sodium) category and they were suitable for irrigation. 27% of samples were in the C3-S1 (high salinity with low sodium) category, which can be used for irrigation. This type of water may be suitable for plants with acceptable salt tolerance, but its application for

irrigation is restricted, especially in soils with restricted drainage (Alobaidy et al., 2010). 0nly 18% of samples were in the C1-S1 category (fresh and harmless) and qualitatively were the best water for irrigation. The quality of water samples for agricultural usage was determined in terms of SAR, EC and residual sodium carbonate (RSC) index which indicates the alkalinity hazard for soil. The computed SAR values for water samples ranged from 0.06 to 1.77, with an average value of 0.45. The RSC index was used to find the suitability of the water for irrigation in clay soils which had a high cation exchange capacity. When dissolved sodium in water is higher in comparison with dissolved calcium and magnesium, clay soil swells or undergoes dispersion which drastically reduces its infiltration capacity (Hopkins et al., 2007). Accordingly, 18% of water samples were unsuitable for irrigation, the rest of samples were classified in suitable and acceptable categories.

## 9- Conclusions

This study aimed to evaluate the applicability of using major ion chemistry for identification of hydrogeochemistry and water quality in Sarough watershed. It also demonstrated the efficiency of using multivariate statistical techniques for interpretation of analytical data in water quality assessment, identification of solute sources and understanding spatial variations in water quality.

The results indicated that the water in the Sarough watershed was circum-neutral and fresh in nature. The water hardness varied from moderately soft to hard water with a mean value of 197 mg/l. The major water types identified using the Piper diagram were $Ca–HCO_3–SO_4$, $Ca–Mg–CO_3$ and $Ca–SO_4–HCO_3$. This result showed that the water type of Sarough watershed was similar to the majority of the typical carbonate rivers of the world which is alkaline in nature (Meybeck, 1987). Except for calcite and dolomite, all natural waters were under saturated regarding the major sulfates and evaporate.

Analyses of the waters of the Sarough Watershed tributaries demonstrated the strong control of bedrock lithology on stream water chemistry.

Using different ionic ratios indicated that the water–rock interaction mainly carbonate weathering and evaporate

dissolution along with the ion exchange processes were the multi-chemical processes which affected the surface water chemistry in the study area. The results obtained by correlation coefficient, CA and PCA, confirmed the common origin for two groups of ions: 1) Na, K, Cl, $SO_4$ and 2) Ca, Mg, $HCO_3$. Weathering of carbonates (limestone and dolomite formations, calcareous marl formation and travertine deposits) in the area may be attributed as common source of Ca, Mg and $HCO_3$. Also, travertine springs were considered as active point sources which release these elements into the drainage system. This result was completely consistent with the major water types ($Ca–HCO_3–SO_4$ and $Ca–Mg–CO_3$) in the watershed. Meanwhile, dissolution of halite and gypsum in red marl formations (lower part of Qom F. and Upper Red F.) along with the cation exchange were the main processes considered as the origin of Na, K, Cl and $SO_4$ in river water of study area.

The suitability of river water in Sarough watershed for drinking and an irrigation purpose was evaluated compared with recommended standards of WHO, ISIRI and FAO. Total hardness (TH), total dissolved solids (TDS) and concentration of Na, Cl and $NO_3$ in all water samples fell within the accepted limit for drinking. Nevertheless, Ca, Mg and $SO_4$ content in some collected samples were higher than the maximum desirable limits. Plotting the ion contents on Schuler graph showed that majority of water samples were good and acceptable for drinking. Evaluating the quality of river water for irrigation purposed using Wilcox diagram, SAR, EC and RSC index results indicated that majority of the water samples were suitable for irrigation.

The spatial variation of physicochemical parameters such as TDS, TH and salinity as well as Wilcox classes in sampling stations of study area was illustrated as gradient and symbol maps using GIS software (Fig.14). The gradient maps were compiled within a 100m-wide buffer zone from the streamline using kriging interpolation method. The spatial distribution of TDS, TH and salinity in river water indicated that the tributaries which flow over sedimentary rocks such as carbonate formations, travertine and calcareous marl formations, have higher amount of TDS, TH and salinity compared with the branches which draining the areas with silicate rocks (metamorphosed rocks, volcanics and igneous intrusive rocks).
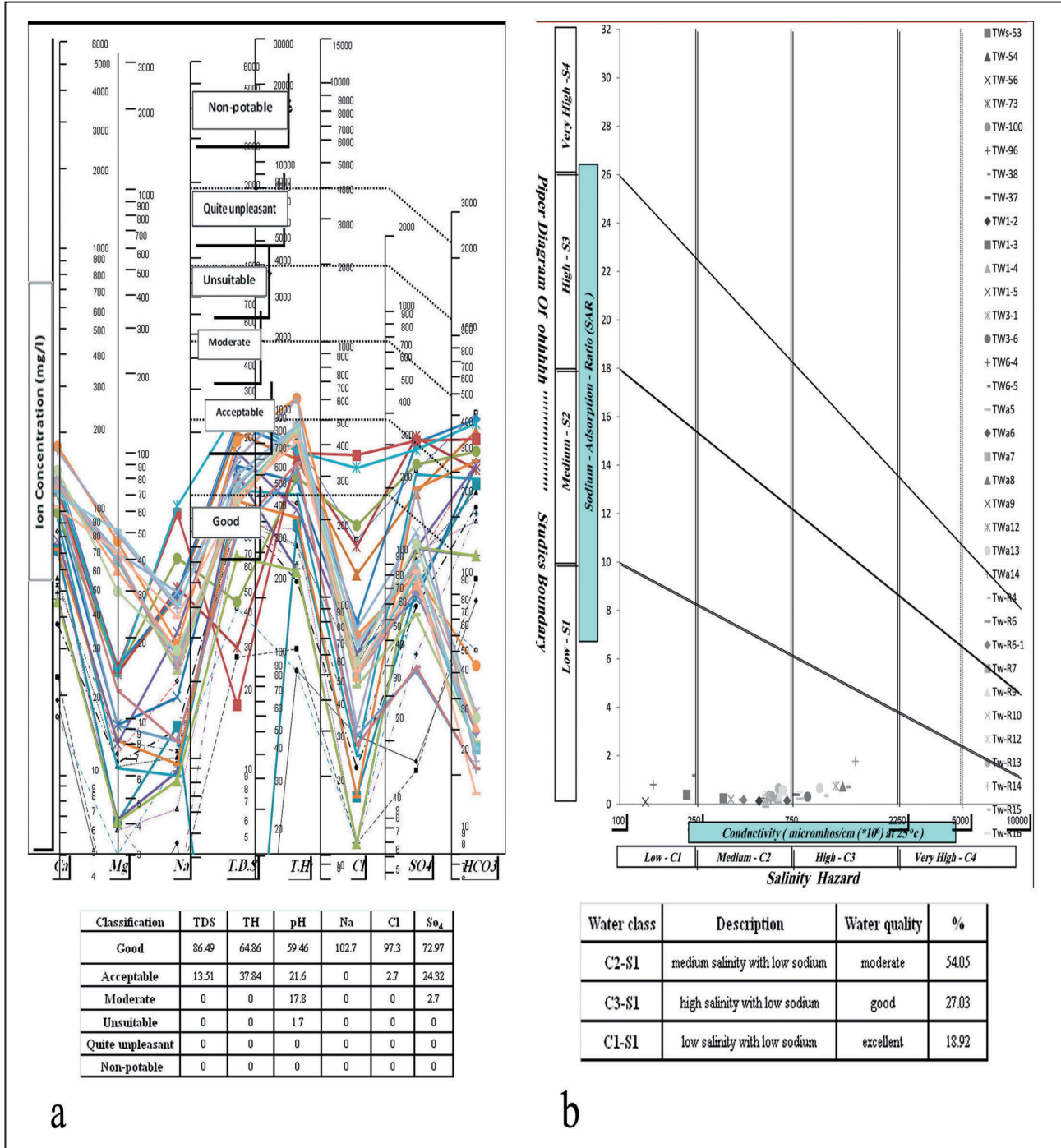
| Classification | TDS | TH | pH | Na | Cl | So₄ |
|---|---|---|---|---|---|---|
| Good | 86.49 | 64.86 | 59.46 | 102.7 | 97.3 | 72.97 |
| Acceptable | 13.51 | 37.84 | 21.6 | 0 | 2.7 | 24.32 |
| Moderate | 0 | 0 | 17.8 | 0 | 0 | 2.7 |
| Unsuitable | 0 | 0 | 1.7 | 0 | 0 | 0 |
| Quite unpleasant | 0 | 0 | 0 | 0 | 0 | 0 |
| Non-potable | 0 | 0 | 0 | 0 | 0 | 0 |

| Water class | Description | Water quality | % |
|---|---|---|---|
| C2-S1 | medium salinity with low sodium | moderate | 54.05 |
| C3-S1 | high salinity with low sodium | good | 27.03 |
| C1-S1 | low salinity with low sodium | excellent | 18.92 |

a

b

Fig. 13- a) Schuler diagram classification of water samples for drinking uses; b) Wilcox water diagram classification of water samples for irrigation uses.
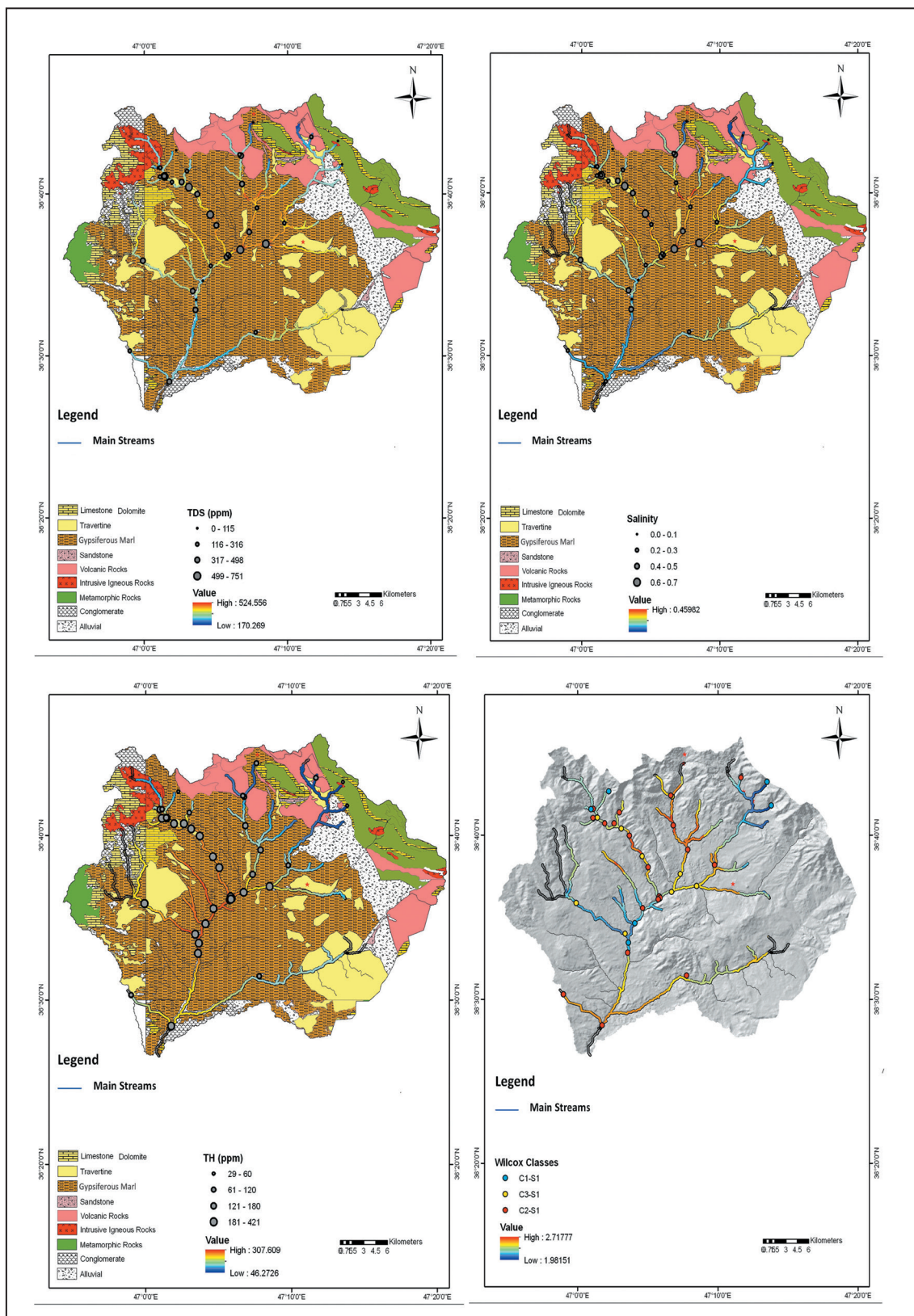
Fig. 14- Maps showing the spatial variation in concentrations of TDS, TH and salinity and Wilcox classes in the river water samples of Sarough watershed.

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