

## Geochemical Characterization of Surface Waters and Groundwater Resources in the Gharye-Alarab Basin, Southeastern Iran

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### Abstract

This paper presents new information about the hydrogeochemistry of water resources in the Gharye-Alarab basin (south-eastern Iran) and determines the predominant hydrogeochemical processes in the basin. To study this basin, 31 water samples were sampled, including 11 samples from rivers and 20 samples from groundwater. These samples were analyzed for temperature, total dissolved solids, Eh, pH, electrical conductivity, major ions and 18 trace elements volumes. The most waters were grouped into Ca–Mg–HCO<sub>3</sub> type. Reaction of silicate minerals is the main factor of geochemical processes in the study area. Trace elements concentrations are low and Surface waters have lower trace element abundances compared to groundwater. Arsenic compared with other trace elements; shows a rather wide concentration range in the sampled waters, ranging between 0.6 to 502 µg/l and is not dependency with Eh and pH in surface water but are dependent on pH and Eh in groundwater.

**Keywords:** Hydro geochemical; Interaction; Water type; Arsenic.

### Introduction

The main water resources supply for industrial, domestic and agricultural use are groundwater and surface water. The chemical composition of groundwater and surface water is controlled by the composition of the rocks and sediments that pass through them. Standard and acceptable limits for elements in water are an important tool that can be used to assess water hydrochemistry and to plan for water quality monitoring [1, 2]. The geochemical characteristic of groundwater is a result of complex

interactions between different factors [3, 4]. They are highly dependent on the geological conditions of the environment, the hydrological and climatic conditions of the region, the groundwater recharge, the discharge and discharge, and the manner of human activities [5]. Hydrogeochemistry (including ground and surface water and stream sediments) has been applied successfully in mineral exploration and environmental studies [6-9]. Ground and surface waters are integral components of any hydrological system and the contamination or development of one has an effect on other [10]. Groundwater and surface water resources are closely

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related. For example Heavy pumping of groundwater, may drain adjacent streams, or surface water contamination may seep into the aquifers and lead to groundwater contamination [11]. Many methods can be used to understand the relationship between groundwater and surface water in a catchment. One approach, which has widely been used, is based on ion chemistry [12]. When hydrogeochemical information is analyzed based on the geological and hydrological environment of the region and using multivariate statistical methods can lead to comprehension water flow in complex aquifer systems and improve water quality monitoring and assessment [13-18].

Iran has a semi-arid climate with an average of 250mm annual rainfall, which is lower than one-third that of the world [19]. Therefore, water is a rare and

precious natural resource in Iran. Despite the shortage water resources especially in central and eastern parts of Iran, the ground and surface water hydrogeochemistry of these regions are poorly understood [20-22].

The aim of this study is to survey the quality of surface and groundwater, the relationship between them and determine the propriety of water for different applications and uses. The hydrochemical processes that control the chemistry of water in the Gharye-Alarab basin as an arid area in southeastern Iran are also assessed during 2012.

**Materials and Methods**

**Geological setting**

The study basin is located in the southeastern Iran in Kerman province and covers an area of 1176 km<sup>2</sup>. The

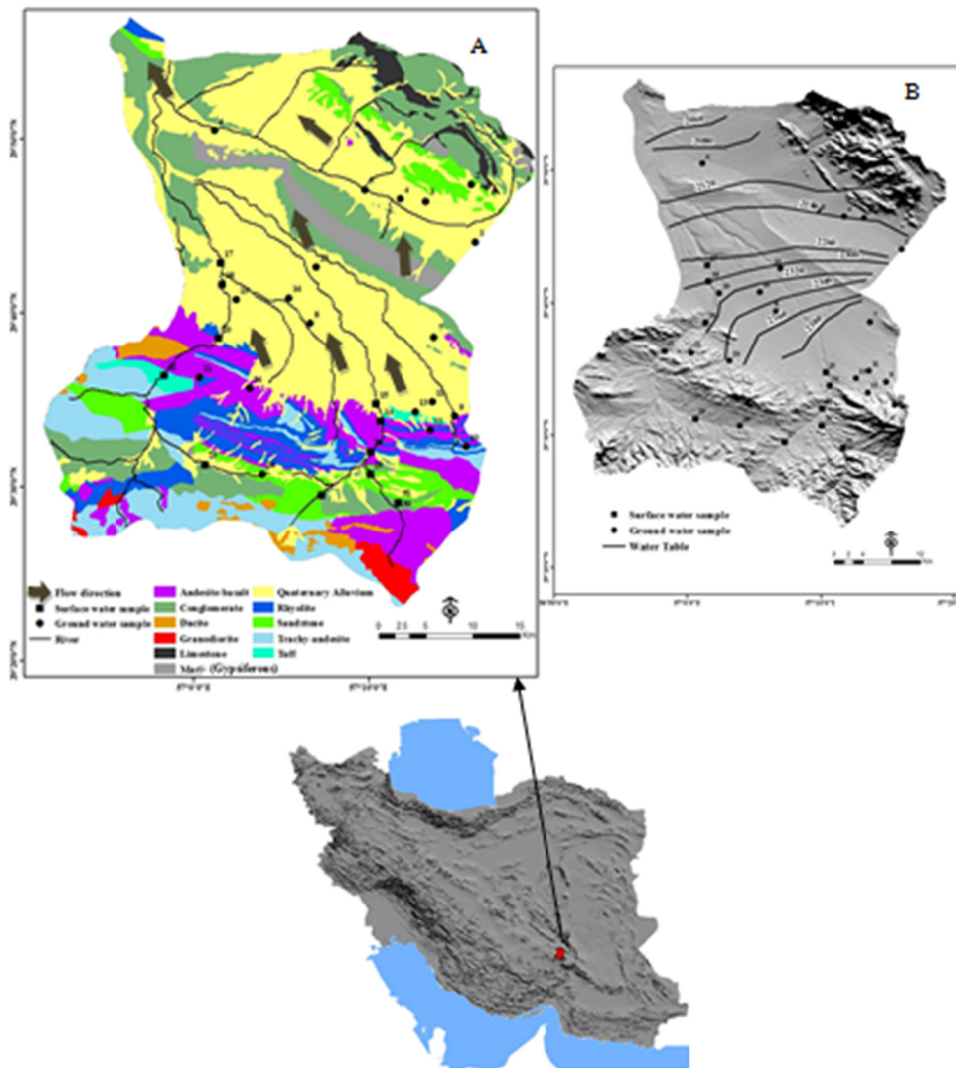


Figure 1. Map of the study areas showing: A) surface geological characteristics (after [23, 24]), B) sample

average height of its plain is 2295 meter above sea level and has unconfined aquifer. The average rate of depletion of groundwater (unbalance between extracted water and recharge) in Gharye-Alarab basin is approximately 30 million m<sup>3</sup> per year. Topographically, the study basin is a combination of flat plains and mountains (Fig. 1). The study basin is characterized by an arid climate, with minimum winter temperature of 15 °C and maximum summer temperature of about 45 °C. The annual rainfall is nearly 100 mm. Water table level of about 2400 m in the south reaches to about 2060 m to the north (Fig. 1). The depth of water in Gharye-Alarab aquifer of over 120 m in the south reaches to about 30 m in western plains. The amount of depth to the water in a large part of the central region of the aquifer is about 60 m. Average aquifer water table depletion in a 13-year period from 1995 to 2008 was approximate -0.31 m. Figure 1, which is a geological map of the area, shows that about 60 % of it is covered with recent alluvium, whereas document for the existence of older alluvium composed of various materials is found at depth [23, 24]. The basin consists of Quaternary alluviums which are compounded of coarse alluvial material, and confined by Paleocene and Neogene conglomerates, Cretaceous marl (with minor gypsum) and sandstone [23].

Volcanic rocks as trachyte, rhyolite, andesite, dacite and tuff of Eocene age are found mostly in the southern part of the region. Intrusive bodies with granodiorite composition crop out in southeastern and southwestern mountain ranges.

**Water sampling and analytical methods**

Thirty-one samples containing 20 groundwater samples pumped from wells and 11 river samples were collected during June 2012 (Fig. 1). Samples were stored in 100 ml polyethylene bottles. Field measurements of temperature, pH, dissolved oxygen concentration, electrical conductivity (EC) and Eh were carried out using a multiparameter portable meter (HACH, Germany). Water was pumped from well until the parameters measured in situ remained stable. In the each location, the pH electrode was calibrated by two buffers (4and8, Merck, Germany) that bracketed the measured pH and were thermally balanced with the water sample. Titration techniques were used to measure HCO<sub>3</sub><sup>-</sup> with CO<sub>3</sub><sup>2-</sup>, and ion chromatography for NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>. The cations, As and other trace elements were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) in the filtered (using a cellulose acetate membrane (0.45 μm)), and acidified (to pH< 2 with nitric acid) water samples within two week after sampling at the Amdel laboratory (Australia).

**Results and Discussion**

**Water chemistry**

The statistical summary of the analyzed samples is shown in Table 1. It indicates large variations in ground and surface water compositions. The pH changes range of groundwater in the study area is between 7.4 and 9.1, indicating that groundwater is slightly alkaline and

**Table 1.** Statistical summary of water compositions

Parameter	T	pH	Eh	EC	O2	TDS	Cl <sup>-</sup>	NO3 <sup>-</sup>	SO4 <sup>-</sup>	HCO3 <sup>-</sup>	F	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Al	Fe	S	
	°C		mv	μs/cm							mg/l								
<b>Detection Limits</b>							0.2	0.2	0.2	0.2	0.2	0.2	0.5	0.5	0.2	0.001	0.01	0.5	
<b>Min</b>	0.4	7.39	-114.5	289	6.94	138.1	14	6	30	150	<0.2	49.1	8.33	17.3	0.96	<0.001	<0.01	13	
<b>Max</b>	15.4	9.11	-27.9	747	10.26	365	82	31	123	250	0.6	76.1	22.9	146	8.64	0.032	0.02	70	
<b>Median</b>	4.3	7.71	-43	392	9.79	188.9	25	13	53	185	0.46	62.8	14.5	34.8	1.78	0.0125	0.02	31	
<b>SD</b>	4.53	0.52	25.99	177.08	0.98	87.67	28.62	7.65	37.86	35.81	0.12	8.52	5.16	55.00	3.13	0.01		22.47	
<b>Min</b>	5.2	6.81	-107.4	132.1	0.5	62.5	8	2	3	90	<0.2	32.8	2.81	7.26	0.62	0.002	<0.01	3	
<b>Max</b>	20.6	8.93	2.2	4640	11.51	2430	1338	93	1407	595	1.43	343	131	1280	5.05	0.024	<0.01	705	
<b>Median</b>	13.5	7.68	-43	390.5	7.08	187.75	22.5	8	40.5	170	0.385	63.15	12.05	34.15	1.935	0.01		23	
<b>SD</b>	4.66	0.57	29.60	1365.92	2.23	713.26	380.06	22.20	424.47	102.90	0.35	80.48	39.01	372.05	1.28	0.01		208.10	
<b>Parameter</b>		Si	Sr	As	B	Ba	Be	Co	Cr	Cu	Li	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
		mg/l										μg/l							
<b>Detection Limits</b>		0.01	1	0.5	0.5	1	0.05	0.02	0.001	0.1	1	0.01	0.1	0.2	0.1	0.1	0.5	0.2	0.5
<b>Min</b>		5270	0.27	1.9	<0.5	6.17	<0.05	0.06	<0.001	0.3	4.8	<0.01	0.4	0.6	<0.1	1.22	<0.5	<0.2	<0.5
<b>Max</b>		11400	1.14	502	3980	51.3	0.41	0.16	0.001	1.4	350	0.23	3.1	0.8	0.3	3.13	3	9.2	2.3
<b>Median</b>		7490	0.76	8.4	353	26.2	0.145	0.1	0.001	1	24.5	0.16	2.3	0.6	0.1	2.04	2.4	5.95	1.15
<b>SD</b>		2057.06	0.29	219.81	1699.55	13.86	0.12	0.04	0.00	0.35	148.37	0.07	0.84	0.08	0.12	0.61	0.90	3.74	0.51
<b>Min</b>		2490	0.34	0.6	<0.5	5.83	<0.05	<0.01	<0.001	<0.1	5.8	<0.01	0.3	<0.2	<0.1	1.55	<0.5	0.9	<0.5
<b>Max</b>		17600	17.8	15.9	4570	111	0.4	0.3	0.056	3.8	946	0.79	11.5	5.3	<0.1	2.51	22.6	17.1	2.3
<b>Median</b>		7000	0.905	4.2	368	23.9	0.2	0.1	0.001	0.65	27.05	0.115	1.85	0.85		2.05	2.2	4.65	1.5
<b>SD</b>		3104.88	4.03	3.52	1439.43	25.91	0.09	0.08	0.02	1.04	207.09	0.25	2.70	1.31		0.25	5.50	3.90	0.56

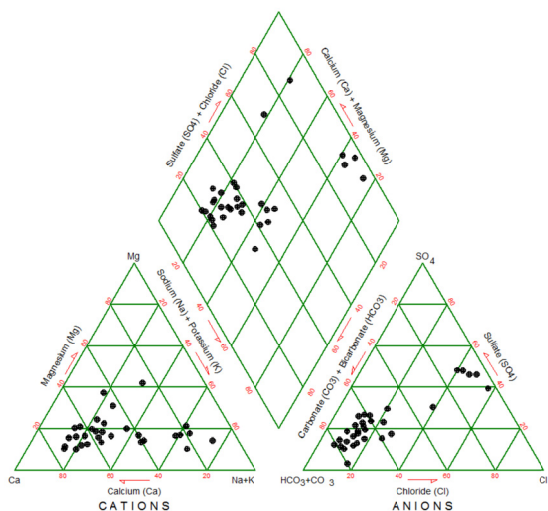


Figure 2. Piper diagram for the water samples in the studied area

surface samples are alkaline. The amount of dissolved CO<sub>2</sub>, carbonate and bicarbonate concentrations control the pH of water samples [5]. The high pH may be due to a decrease in the dissolved salts. Groundwater samples show large variation in conductivity values (EC; 132.1-4640 μS/cm); whereas, samples of surface water have low EC values (289-747 μS/cm). Total dissolved salts (TDS) are an important criteria that can be used to observe the influence of major components in groundwater quality. The TDS values, as a function of mineralization characteristics, of water range from 138.1 to 365 mg/l in surface waters, while TDS values in groundwater samples display a large variation, ranging from 62.5 to 2430 mg/l.

Compared with groundwater, dissolved oxygen (DO) is high in the surface water as they are close to chemical equilibrium with the atmosphere (Table 1). By determining the type of water, the composition of the dominant cations and anions of water is characterized (Fig. 2). The prominent hydrogeochemical type is Ca-Mg-HCO<sub>3</sub> (Fig. 3).

In deep aquifer, Na-Cl and Ca-SO<sub>4</sub> water types are dominant (Figs. 1 and 3). Hydrolysis of aluminosilicate minerals will increase by infiltration of meteoric water (which contains considerable CO<sub>2</sub>), resulting in production of HCO<sub>3</sub><sup>-</sup> in the water and usually controls the chemistry of waters in the recharge area (Fig. 3) [25].

In arid regions, dissolved species is the main controller of groundwater salinity and water chemistry in the discharge area.

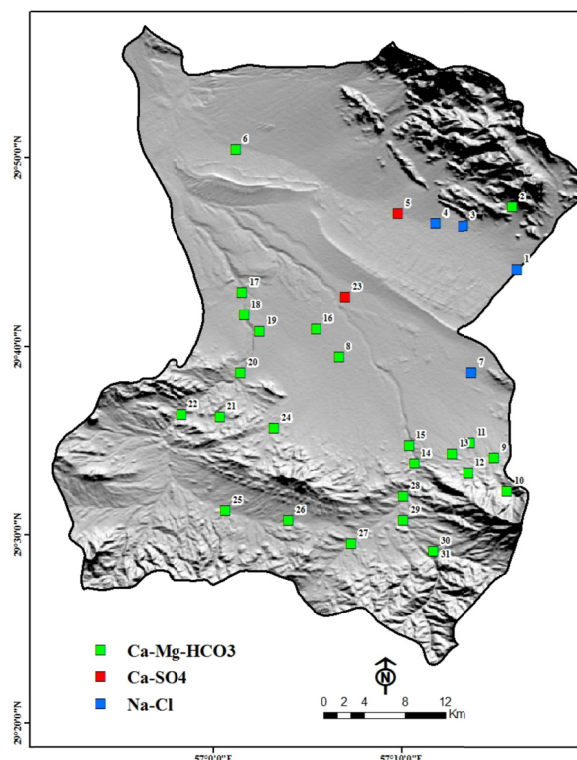
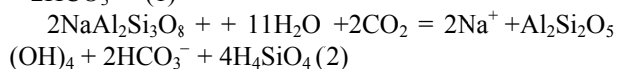
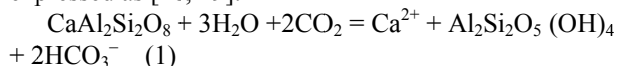


Figure 3. Distribution of water types in the study area

**Hydrogeochemical Evaluation**

Stoichiometric relationships between soluble species were studied to identify the predominant geochemical processes occurring in the aquifer, such as ion exchange processes.

In this study, most samples had Na<sup>+</sup>/Cl<sup>-</sup> ratio larger than 1 (Fig. 4), therefore, silicate weathering was the one of the presumptive source of sodium excess [26]. The reaction of silicate minerals with groundwater is also an important process that produces high pH groundwater. South part of the study area (recharge zone) includes volcanic rocks that contain silicate minerals such as plagioclase. Plagioclase minerals compose a complete solid-solution series with Ca<sup>2+</sup> and Na<sup>+</sup> end-members. The Ca<sup>2+</sup> end-member is privilegedly weathered compared with Na<sup>+</sup> and, hence the Na<sup>+</sup>/Ca<sup>2+</sup> ratio in plagioclase growth as the reaction proceeds [27]. As a result, the concentration of Ca in groundwaters increment along the regional flow path (Fig. 4). Reaction of albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) with water to produce kaolinite, can be expressed as [28, 29]:



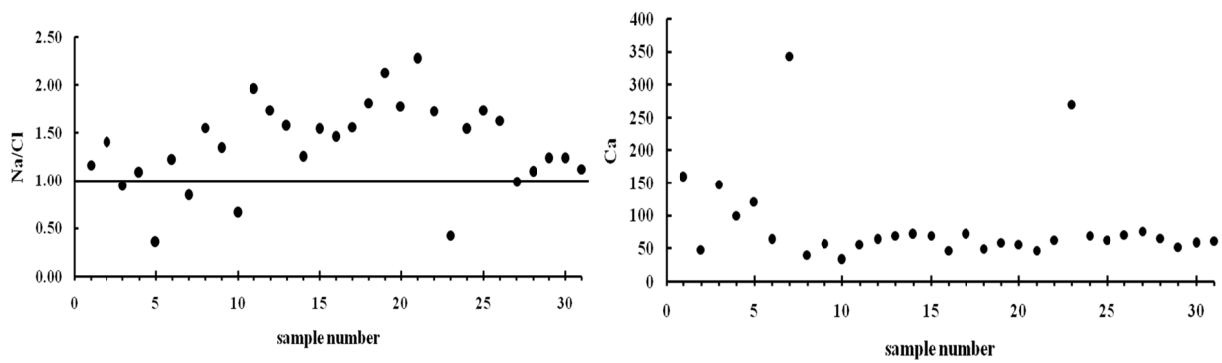
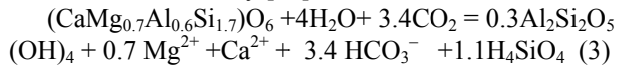


Figure 4. Na/Cl ratio and Ca concentrations in water samples of study area

Clinopyroxene, as a Ca–Mg aluminosilicate, could be dissolved incongruently pursuant to the following idealized stoichiometry [27].



These reactions also account for the origin of high

$Mg^{2+}$ ,  $Na^+$ ,  $Ca^{2+}$  and  $HCO_3^-$  concentrations in the groundwater, resulting in formation of Ca–Mg– $HCO_3$  type waters. To comprehension the spatial control on major ions concentration, the correlation between TDS and major ions are shown in Figure 5. The  $Cl^-$  and  $Na^+$  concentration increases with increasing TDS in all of

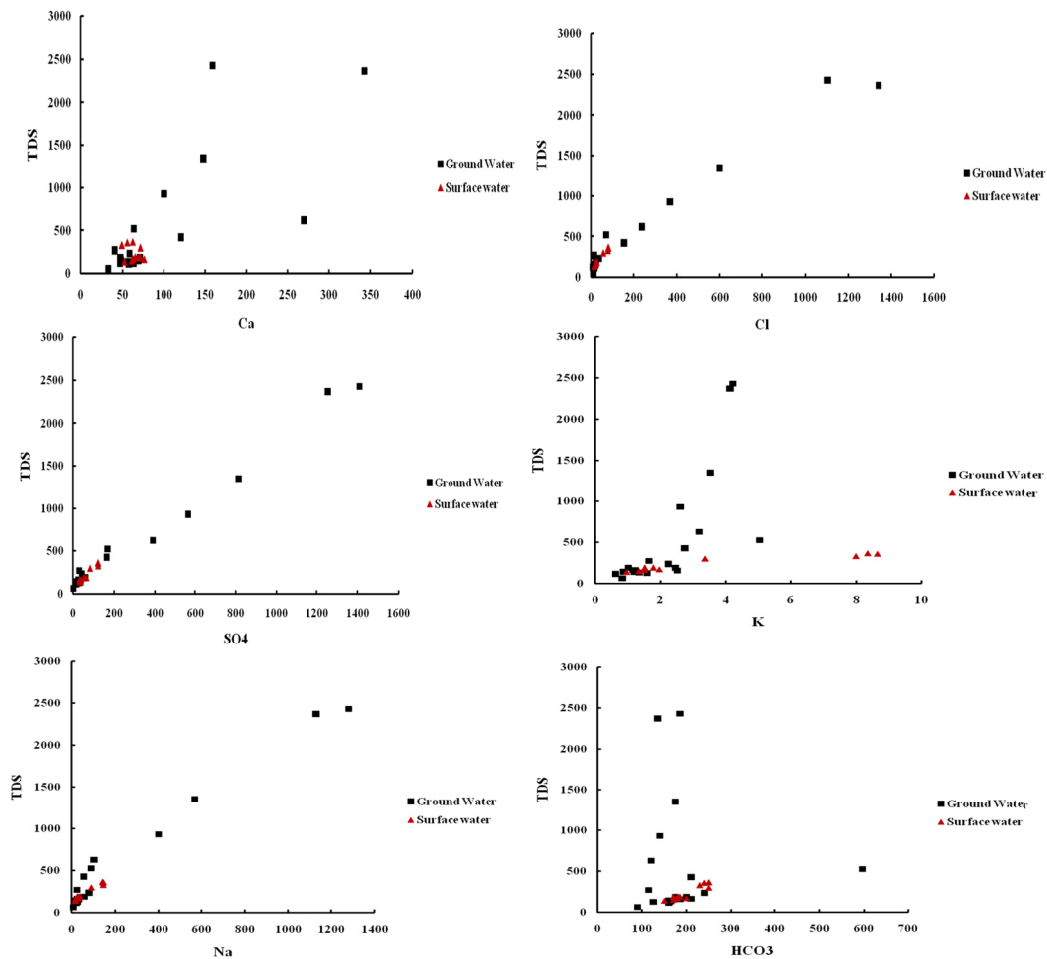


Figure 5. Relationships between ion concentrations for  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $HCO_3^-$  with TDS

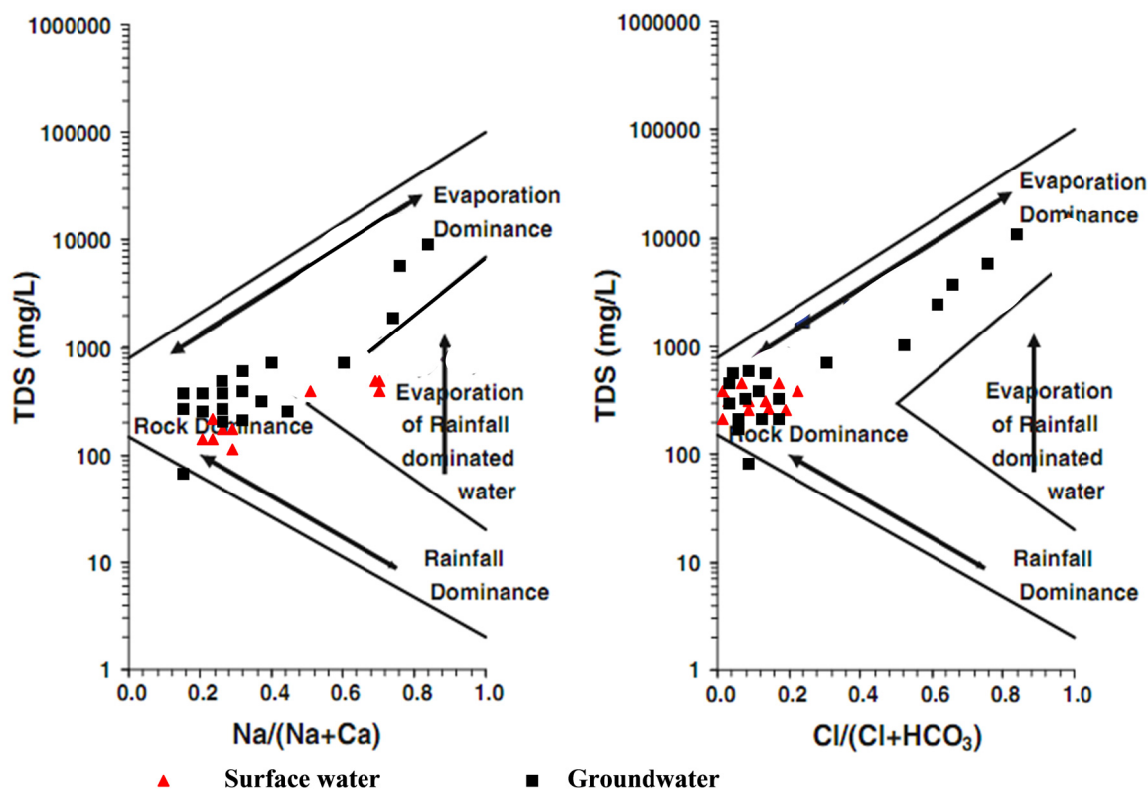


Figure 6. Scatter of water samples in Gibbs's diagram

the groundwater samples. The TDS and  $\text{SO}_4^{2-}$  amounts were severely correlated, suggesting that dissolution of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) occurred in the area (Fig. 5). Potassium shows poor association with TDS in groundwater and no correlation in surface water. To determine the functional sources of dissolved chemical constituents. Figure 6 show that rock-water interaction is the major process in the chemical compound evolution of water (Fig. 6).

#### Minor and trace elements

Concentration of trace elements in the water samples collected from the Gharye-Alarab basin show variation. The maximum-minimum range for the elements (Table 1) is documentary of various rock-water interplay regimes and/or abundance of source processes. Surface waters are distinguished by lower trace element plenty than groundwater (except for As), it illustrate that atmospheric deposition is a lesser source of trace elements [30]. Arsenic compared with other trace elements; show a rather wide concentration range in the sampled waters, ranging between 1.9 to 502  $\mu\text{g/l}$  in surface water and 0.6 to 15.9  $\mu\text{g/l}$  in groundwater. The copper (Cu), zinc (Zn) and lead (Pb) concentrations are

low. Zn concentrations are generally less than 2.3  $\mu\text{g/l}$ , While Pb concentrations are commonly under the detection limit. Elements such as Fe, Mn, Cr, Be, Se and B are mostly below detection limits in the sampled waters. Dissolved Mo and V speciation are a function of pH and Eh in the area (Fig. 7). Arsenic concentrations are not related with Eh and pH in surface water but are a subordinate of Eh and pH in groundwater.

#### Conclusions

Our research showed that the control of groundwater hydrogeochemistry in the Gharye-Alarab basin is the reaction between water and rock in the basin. Waters in the Gharye-Alarab basin are alkaline. Groundwaters are mostly Ca-Mg- $\text{HCO}_3$  type. The TDS value in sampled groundwater is higher than surface water. The reaction of silicate minerals in the recharge area is the main and important factors of hydrogeochemical processes in the study area. Surface waters have lower trace element abundances compared to groundwater. Arsenic concentrations are not correlated with pH and Eh in surface water. The recent Eh-pH conditions controlled dissolved Mo and V in waters and Zn, Cu and Pb ions are not mobile.

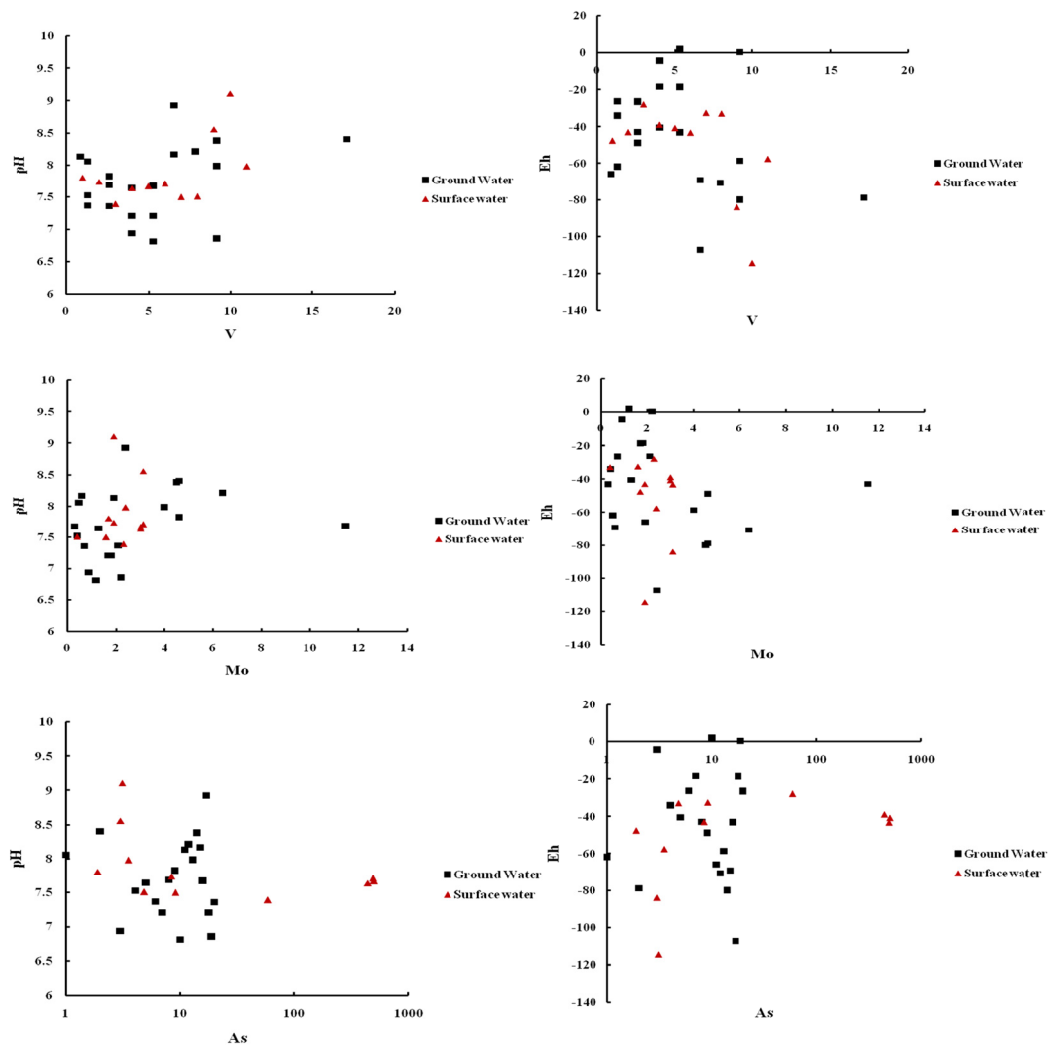


Figure 7. Plot of V, Mo and As versus Eh and pH in waters of study area

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