GROUNDWATER QUALITY ASSESSMENT IN A VOLCANIC REGION, IRAN

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ABSTRACT

Multiple factors can affect the quality of groundwater (e.g. geology, streams, human activities, agriculture, etc.). The present study aimed to characterize the hydro-geochemical properties, spatial variations, and arsenic anomaly of drinking groundwater resources in the north-east of Sarab County, situated in the vicinity of Sabalan Volcano, Iran, in which maximum area of the basin is covered with igneous rocks. In 20 out of 21 samples, electric conductivity was below 1000μs/cm. Arsenic concentration varied from non-detectable to 94ppb, the higher level of which was in the western part of the area. Origins of the water samples were recognized in 5 classes and most of the samples were in class 4, indicating the precipitation of rainfall and recharge to the aquifer origin. HCO_3^-–CO_3^{2-} and Ca^{2+}–Mg^{2+} were the dominant anions and cations, respectively. These indicate short residence time, contact with limestone, dolostone formations, or originating from recharge of rainfall and emergence from igneous rocks. The principal component consisted of Na, K, SO_4, pH, As, and SAR. High factor loading for SO_4 and As was notable and revealed that both of them could originate from chemical weathering in the oxidation condition of pyrite

Keywords: Arsenic, Contamination, Hydrogeochemistry, Multivariate Statistical Analysis

1. Introduction

Groundwater has a main role in water supply for communities across the world. In many residential areas, especially rural ones, more than 90% of the required water is supplied from wells (open, tube, or bore wells) and springs and there is an increasing stress on groundwater resources due to increasing demand and drought, depletion, and contamination of water resources (1) . Quality of drinking water should meet the recommended standard and guidelines in order to avoid possible health effects (2). World Health Organization (WHO) has published a guideline for drinking water quality (3) and countries also have their own national guidelines and standards.

A number of factors can affect the quality of groundwater (4) which includes precipitation, geological formation, soil-rock strata, weathering, acid rain, and human activities such as mining, agriculture, industrial discharges, and domestic wastewaters (5). Altered quality of water as contamination to microbiological agents (e.g. viruses, bacteria, and other pathogens) along with chemical contaminants (e.g. arsenic, fluoride, nitrate, and other elements) can create health-related problems. For example, natural contamination of groundwater to arsenic has been reported in many countries and (6) in communities which consume drinking water with the elevated concentration of arsenic, health problems such as different types of cancer (7) and skin lesions have been reported (8). There are also many examples related to adverse health effects such as fluorosis due to fluoride (9).

Monitoring the quality of drinking water resources (10) can provide useful information and tools for identifying possible contamination and also mitigating adverse health effects due to exposure to contaminants. Many studies have been conducted for assessing the quality of groundwater (11) and application of GIS as a leading tool in the field of groundwater researches

(12) alongside hydro-geochemical analysis (13) and application of factor analysis in the assessment of groundwater quality (14).

Studies have shown that, in areas with volcanic geological formations, the possibility of arsenic presence in groundwater is high (15). The present study was conducted to characterize the hydro-geochemical properties and arsenic anomaly of drinking groundwater resources in the north-east of Sarab situated in the vicinity of Sabalan Volcano, Iran. The main objective of the study was to recognize the major, trace, REE, and Sr-Nd isotopes characteristics of Sabalan Quaternary lavas and present a consistent tectonomagmatic model for the formation and evolution of Sabalan Volcano.

2. Study area

The studied area was located in the north-west of Iran near Sabalan Volcanic Mountain in Sarab County, East Azerbaijan province (Fig 1). Sabalan has geothermal capability and is the 29th highest mountain in the world and a Quaternary volcanic complex that rises to the height of 4811 m above sea level. Sabalan is an inactive stratovolcano in Ardabil province, Iran, and the third highest mountain in Iran with a permanent crater lake formed at its summit. Sabalan Volcano is among the youngest volcanic calderas in the eastern boundary of Turkish-Iranian Plateau, which consists of Miocene trachyandesites and Plio-Quaternary trachy-andesite, pumiceous andesites, and dacites with ultrapotassic-shoshonitic signatures (16). Elevation of the studied area (Fig 2) varied between 2668 and 1640 m above sea level. Fig 2 provides geological formation of the studied area.

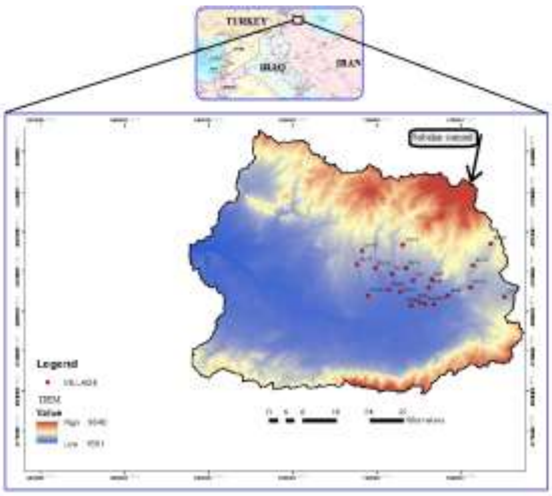

Figure 1: Position of samples in their watershed

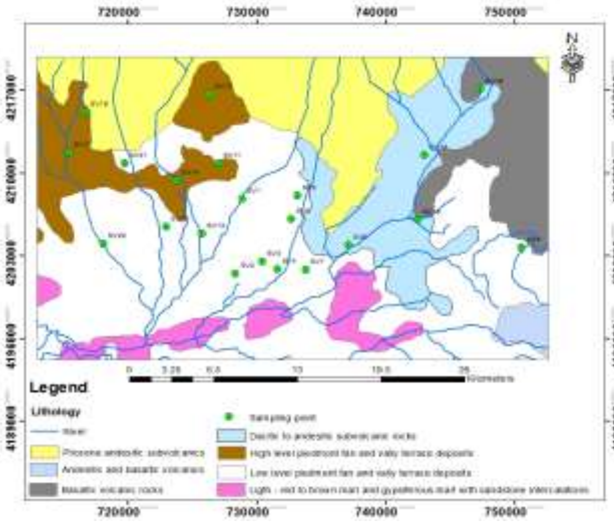

Figure 2: Lithology of the study area

3. Sampling and analysis

Groundwater resources including wells and springs were used to supply the drinking water of studied 21 villages. During a cross-sectional study, samples of drinking water resources were collected and analyzed in accordance with the procedures provided in the standard methods for the examination of water and wastewater, 20th Edition (17). Statistical characteristics of water quality data presented in Table 1.

3.1. Results and discussion

For examining the relationships among the variables, factor analysis was used. For decreasing the number of variables in the data matrix and also choosing the most discriminating parameters and investigating the overall data variation, principal component extraction was used. Table 2 indicates the loading of Varimax-rotated component matrix for two resulted components and cumulative eigenvalue percentage. With regard to the predefined values of

KMO test by McNeil *et al*. (Table 2), data of this study showed the mediocre level of explanation (18). For this investigation, KMO value was 0.603, which indicated the mediocre ability of data for applying this method to this data. So, care should be taken in applying this method for this study. Based on PFA, two factors for these data were obtained, which had eigenvalues of greater than one that were described together as 84.16% for all variances of data (Table 2).

Table 1: Descriptive statistics of quality of analyzed groundwater samples

Parameter	Min	Max	Mean	SD	Parameter	Min	Max	Mean	SD
EC (µs/cm)	230	1690	519	319	Na (mg/L)	6	95	33	26
Hardness(as mg/L $CaCO_3$)	88	780	199	145	K (mg/L)	0.5	13	3	2.6
TDS (as mg/L)	181	1513	435	287	HCO_3^- (mg/L)	107	951	243	177
Alkalinity (as mg/L $CaCO_3$)	76	240	161	45	SO_4^{2-}(mg/L)	2	150	59	49
pH	6.5	8.2	7.5	0.5	Cl (mg/L)	8	82	25	19
Ca (mg/L)	20	200	55	37	NO_3^- (mg/L)	1	50	12	13
Mg (mg/L)	0	67	15	15	As (ppb)	0	93.6	12.7	24

Table 2: Rotated factor loadings of PCA application for water quality parameters

Rotated Component Matrix[a]		
	Component	
	1	2
Ca^{2+}	**0.908**	0.084
Mg^{2+}	**0.910**	-0.092
Na^+	0.670	**0.706**
K^+	0.098	**0.907**
HCO^{3-}	**0.987**	0.016
SO_4^{2-}	0.433	**0.824**
Cl^-	**0.782**	0.472
EC	**0.951**	0.289
pH	0.358	**-0.611**
Hardness	**0.987**	0.016
NO_3^-	**0.727**	0.020
As^{4-}	-0.086	**0.891**
TDS	**0.957**	0.266

PC1

According to Table 2, principal component 1 (Ca, Mg, HCO_3, Cl, EC, hardness, NO_3, and TDS) was responsible for the largest part (38.52%) of the total variance of the data set. Result of PC1 showed that strong correlation of Ca, Mg, Na, HCO_3, Cl, hardness, NO_3, and TDS with EC can be explained by controlling groundwater EC with Ca, Mg, Na, HCO_3, Cl, EC, hardness, NO_3, and TDS contents. Very high positive factor loading of HCO_3 and high positive factor loading of NO_3 demonstrated the influence of rainfall and somewhat agricultural wastewater and their return water to the aquifer recharge. This component was characterized by very high positive factor loading (>0.9) for Mg, HCO_3, EC, Hardness, and Ca, high positive correlation with (>0.7) with Cl and $NO_{3,}$ and moderate positive correlation (0.4-0.7) with Na. It was also characterized by alkaline earth elements, implying special lithology like basalt and rocks with mafic properties. High factor loading for Mg and Ca reflected weathering and alteration processes of basaltic rocks with minerals like olivine, pyroxenes, amphiboles, biotites, and so on and implied the dissolution of these ions from these minerals. Main sources of Ca and Mg in groundwater were olivine, pyroxene, amphiboles, feldspars, gypsyferouse, aragonite, calcite, dolomite, and clay minerals (19). Also, main sources of HCO_3 in groundwaters were water compounds with CO_2 rain water, soils, and dissolution of carbonate rocks. With regard to the lack of carbonate rocks and the existing igneous (basaltic rocks), it can be concluded that sources of Ca and Mg in the groundwater of the area were because of chemical weathering and alteration of mafic minerals like olivine, pyroxenes, and amphiboles in the studied area. High factor loading of HCO_3 implied the recharge area and effect of rainfall water. High factor loading of NO_3 can be resulted from agricultural drainages and returned water from farms. Quality of water originated from igneous formations is always suitable due to low solubility of rocks. Among the sampled waters, EC was below 500 µs/cm for 12 samples, below 1000 µs/cm for 8 samples, and only over 1000 µs/cm (1690 µs/cm) for one sample. High positive factor loadings of EC and TDS can be interpreted by high concentration for major ions in PC1 relative to PC2. Therefore, factor loading of Na in both components was considerable; in PC2, it was greater than PC1, which may be due to reverse ion exchange with Mg.

PC2

Principal component 2 (Na, K, SO_4, pH and As) explained 38.52% of the total variance (Table2). In this component, the K has very high positive correlation (>0.9), high factor loading (>0.7) for Na, SO_4, pH, As, and for pH is intermediate (0.4-0.7) negative factor loading. PC2 was characterized by Na and K which was most likely related to weathering of silicate minerals. Sabalan area has hydro-thermal potential (Ardabil province, in eastern hillside of Sabalan, has the maximum number of hydro-thermal springs in Iran); thus, the existence of arsenic may be related to the hydro-thermal properties of this area. As related with geothermal waters has been reported in several regions of the world, which have hot springs from parts of the USA, Japan, New Zealand, Chile, Iceland, Kamchatka, France, and Dominica (e.g. White *et al*., 1963; Welch *et al*., 1988; Criaud and Fouillac, 1989)(20-22). Volcanic rocks and ashes of this volcano may be impressed by the vicinity of this mountain in terms of As concentration in the water. Despite the absence of exceptional concentrations of As, volcanic rocks, especially ashes, are often associated with the production of high-As waters (23, 24). In the present study, the relationship between pH and As was negative, which was in contrast to the results of previous studies. In the study by Robertson and Smedley (24, 25), a positive correlation was observed between pH and As concentration.

Several studies have been conducted in order to examine the aqueous speciation of arsenic and its conservative or nonconservative behavior in geothermal systems. However extensive efforts have been directed to the removal of arsenic from water bodies. Technologies such as coagulation and precipitation with iron and aluminum salts(26), adsorption onto activated alumina and activated carbon, ion exchange and reverse osmosis are the common methods for arsenic removal(27). Konstantina Tyrovola *et al* (2009) have used Zero-valent iron (ZVI) as an inexpensive, nontoxic material for the removal of arsenic from geothermal waters located in agricultural regions(28). Therefore, a comprehensive study is required about the case of available removal technologies and the existing condition in the study area to adopt the best removal technology in contaminated areas.

3.2. Conclusion

Contamination of groundwater of the surroundings of Sabalan Volcano with arsenic can be considered a problem for the water quality of this area. Out of the sampled resources, three samples related to wells had high As concentration (over 50 ppb). However, considering the characteristics of calc-alkaline volcanic of Sabalan and presence of arsenic in the margins of the volcano, this issue was expected. PCA recognized two main factors which explained 84.17% of total variances. First components explained 53.03% of total variances related to alkaline earth elements and NO_3 with HCO_3. Main causes of the first component were effects of special lithology (domain with mafic minerals) of rainfall and somewhat influence of agricultural drainages. Main cause of the second component is special lithology (domain felsic minerals). With direct and indirect signs, and nature of area, the weathering and breaking up of sulfide minerals could be main reason of arsenic in study area.

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