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**Research Article**

# Natural Arsenic Pollution and Hydrochemistry of Drinking Water of an Urban Part of Iran

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Natural contamination of surface and groundwater resources with arsenic is a worldwide problem. The present study aimed to investigate and report on the quality of drinking water resources with special focus on arsenic presence in an urban part of Iran. Arsenic concentrations were measured by graphite furnace atomic absorption spectroscopy (GFAAS). In both surface and groundwater samples, arsenic concentrations ranged from 6 - 61 μg/L with an average value of 39 ± 20 μg/L. Concentration of arsenic, which was up to six times greater than guideline values (10 μg/L) indicates the presence of arsenic bearing materials in the geological structure of the region. It was found that the quality of treated surface water produced by the water treatment facility was good in respect to arsenic (9 μg/L) and solid content (EC = μs/cm). However, in drinking water samples of wells, total solids (mean EC = 1580 ± 150 μs/cm), total hardness (mean = 479 + 94 mg/L as CaCO3) and arsenic (mean = 42 + 16 μg/L) were significantly higher. Correspondingly, there was a significant correlation between arsenic concentration and EC, Na+, $K^+$ and $Cl^-$ values. The type of water in most of groundwater samples (70%) was determined as $HCO^{3-}$ $Na^+$. Considering the population of the city and probable health effects due to exposure to arsenic through drinking water, comprehensive measures as well as application of arsenic removal processes in water treatment facilities and replacement of contaminated wells with safe wells are required.

*Keywords:* Arsenic, Drinking Water; Groundwater; Exposure

## 1. Introduction

Preparing safe drinking water supply for both of rural and urban communities is an important task for governments. Having access to adequate and safe drinking water is a basic right of all individuals (1). The United Nations and World Health Organization (WHO) have declared the decade between 2005 and 2015 as an international decade for taking action about water supply, sanitation and hygiene (2). In terms of safety, presence of inorganic chemical contaminants such as lead (from water pipes) (3), arsenic (4, 5), fluoride (6, 7) and nitrate (from improper disposal of sewage and excess use of fertilizers) (8) can make water unsafe for human consumption and health. As a result, regular monitoring of the quality of drinking water especially for the presence of toxic materials is an important issue for water supply sectors. Today, natural contamination of groundwater with arsenic, used for drinking water purposes, is a significant problem and health concern in many countries (4, 9). This problem occurs when groundwater comes in contact with arsenic containing ore geomaterials. Thus contamination occurs as a result of arsenic dissolution and leaching from soil, sediments, ores and etc. (10, 11). There are more than 300 types of minerals containing arsenic at different concentrations in the earth crust. The total amount of arsenic in earth's upper crust is about 4.01 × 10 (12) kg with an average of 6 mg/kg (4) according to available estimations.

Consumption of arsenic-contaminated drinking water leads to adverse health effects associated with elevated exposure to inorganic arsenic via oral use (13). Accordingly, researchers have investigated health risks of exposure to arsenic via drinking water (14, 15). Chronic and acute health problems and outcomes due to the consumption of arsenic contaminated drinking water have been well documented in the literature (16, 17). The lethal dose (LD50) for inorganic arsenic species are much lower than organic species (4) and it has been considered that inorganic As (III) and As (V), which occur in drinking groundwater, are more toxic than organic arsenicals (18).

Natural contamination of drinking groundwater resources with arsenic has been reported from a number of countries such as USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan, India, Pakistan (13, 19, 20), Greece (21), Vietnam (22) and also more recently Turkey (23) and Cyprus (24). It has been reported that in Southeast Asia many people are at the risk of chronic arsenic poisoning; estimates show that 20-35 million people in Bangladesh, 5.6 million in China, five million in West Bengal and one million in Vietnam are at risk (25).

For the first time in Iran, drinking groundwater contaminated with arsenic in rural areas of Kurdistan province was reported for years 2003 (26) and 2008 (27). In the past decade, several studies have been conducted in Iran about arsenic contamination and related health effects (28). Keshavarzi et al. (2011) found a spatial coincidence between arsenic anomaly in groundwater and travertine springs distribution in groundwater resources of Kurdistan and west Azerbaijan provinces. They reported travertine springs to be the main source of arsenic contamination in groundwater resources (29).

In areas with naturally occurring high concentrations of arsenic, the situation becomes more critical when there is a limitation of safe drinking groundwater resources and when there is no other option for safe drinking water supply in the affected area. Therefore, it is of crucial importance to identify the extent of contamination of groundwater and to characterize the contamination sources and mechanisms in order to manage, solve and limit the problem through application of proper measures and mitigation strategies or application of treatment technologies for the removal of arsenic from water (30).

The present study was conducted to characterize the hydro-geochemical properties and arsenic anomaly of drinking water resources and mains in Ardabil, a city situated in the vicinity of Sabalan volcano, North-West of Iran.

## 2. Materials and Methods

### 2.1. The Area Setting of the Study

The studied city is located in the Northwestern part of Iran (Figure 1) with an area of about 17953 $km^2$ (1.09 % of total country area) and a population of over 537920, and with an average elevation of 1500 meters above sea level it is about 70 km far from the Caspian sea. The city is located east of Mount Sabalan (4,811 m), with cold spells occurring until late spring. Many hot springs exist around the city, attracting many tourists.

### 2.2. Sampling

Both groundwater and surface water resources are used to supply the drinking water of the studied city. There are a number of deep wells such as Zarnas and Piraqvam, located within the city. These wells provide a portion of the required drinking water after passing through the chlorination process. In order to cover the increasing demand for drinking water due to population increase during the recent years, Ardabil's Water Treatment Plant (WTP) (about 23.5 km far from the city) provides the main portion of water from the Yamchi dam through conventional treatment systems including coagulation, flocculation, sedimentation and chlorination.

There are 40 drinking water deep wells in three different locations of the studied city. Most of wells are in operation, and in each location, water of wells is mixed together in reservoirs then distributed through the water network. However in some parts of the city, mixing also occurs with WTP treated water.

Considering the current concerns about possible contamination of drinking water wells with arsenic, during a preliminary limited cross sectional study in 2012, eight deep wells were selected randomly from every part of the city. Two sampling points were also considered at the distribution network (center of the city) and WTP effluent. All water samples were collected in sterilized acid-washed polyethylene terephthalate (PET) containers and immediately transported to the laboratory. About 30-40 liters of water was flushed out for all samples before collection.

### 2.3. Analytical Procedure

All samples were collected and analyzed in accordance with procedures provided in the standard methods for the examination of water and wastewater, 20th edition (31). Physicochemical parameters such as electric conductance (EC), total and calcium hardness, alkalinity, pH, major cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$), major anions ($HCO^{3-}$, $SO_4^{2-}$, $Cl^-$), $NO^{3-}$ and arsenic concentration were measured in all samples. Electric conductance and pH were measured by an EC meter and pH meter, respectively. Titration and calculations were used for determination of hardness, alkalinity, $Ca^{2+}$, $Mg^{2+}$, $HCO^{3-}$ and $Cl^-$. A flame photometer was applied for measurement of $Na^+$ and $K^+$ after drawing a calibration curve for standard solutions, prepared using the dilution method. Sulfate and nitrate levels were determined with turbidimetry and spectrophotometry methods using a spectrometer after drawing a calibration curve, respectively. All materials, reagents and solutions were obtained from the Merck Company in analytical grade. Double distilled water was used in all experiments.

Graphite furnace atomic absorption spectroscopy (GFAAS) (Buck Scientific Model, Unites States of America) was used to measure arsenic concentrations with a detection limit equal to 0.5 μg/L. All experiments were performed in duplicates and averages were calculated. The device was calibrated with a blank and high quality arsenic standard solution (1, 5, 10, 50 μg/L) before analyzing the samples. A calibration curve was drawn with a correlation coefficient (r2) of 0.994, indicating acceptable precision and accuracy of the method (Figure 2). During the measurements, analysis of standard and blank samples and duplicate test samples was considered again in order to insure precision, accuracy and QC/QA.

### 2.4. Multivariate Statistical Analysis

Data are presented as means (SD) for quantitative variables. The linear regression model was used to estimate the calibration curve of GFAAS in analysis of arsenic. Correlation and ANOVA (analysis of variance) test were performed for the entire data set. Also, the principal component analysis (PCA) method (rotation method varimax, Kaiser normalization) and cluster analysis (CA) were applied in order to group related water quality parameters and to classify the sites (locations) of the water sources. Varimax rotation is the most widely employed orthogonal rotation in PCA for easier interpretation of the results (32). Data were analyzed using the SPSS software (12).

## 3. Results

### 3.1. General Quality of Water

The results obtained from the statistical analysis of all parameters of the sampled water are provided in Table 1. As shown in Table 1, the level of EC (1500 ± 287 µs/cm), hardness and major anions and cations are significantly in high concentration. High concentrations of nitrate can also be noted from Table 1. Table 2 presents results for the analysis of individual sources of water samples with all parameters except arsenic and nitrate. As this table shows, AW1 to AW8 refers to deep wells located within the city, AW9 is the sample from AWTP, and AW10 is related to the sample from the water distribution network. In comparison with samples from the well, it seems that the total dissolved solids (TDS) in the AWTP sample (AW9) are relatively low. This difference is also evident in the case of sulfate and calcium. The ANOVA test did not show a significant difference between analyzed parameters of water samples ($P > 0.05$). Figures 3 and 4 show the concentration of nitrate and arsenic, respectively. According to Figure 3, at the five sampled wells, nitrate concentrations were higher than maximum contaminant level (MCL = 50 mg/L as nitrate); in AW2, nitrate level was close to MCL.

### 3.2. Arsenic Presence

The mean concentration of arsenic was 39 ± 20 µg/L (Table 1), indicating the problem of arsenic contamination in some drinking groundwater resources of the studied city. As indicated by Figure 4, in all well samples except AW8, the arsenic concentration was much higher than the guideline value (GV) of 10 µg/L. interestingly, sample AW5 showed the highest arsenic concentration. However, the observed concentration of arsenic in AWTP was lower than GV. In contrast to the above findings, in samples taken from pipes (drinking water distribution network), the concentration of arsenic was significantly high, which indicates exposure of residents to arsenic via drinking water.

**Figure 1.** Location of the Studied Area on the Map of Iran

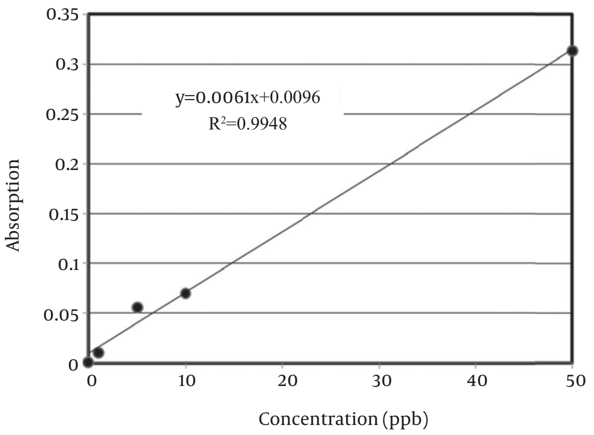

**Figure 2.** Calibration Curve of Graphite Furnace Atomic Absorption Spectroscopy in Analysis of Arsenic

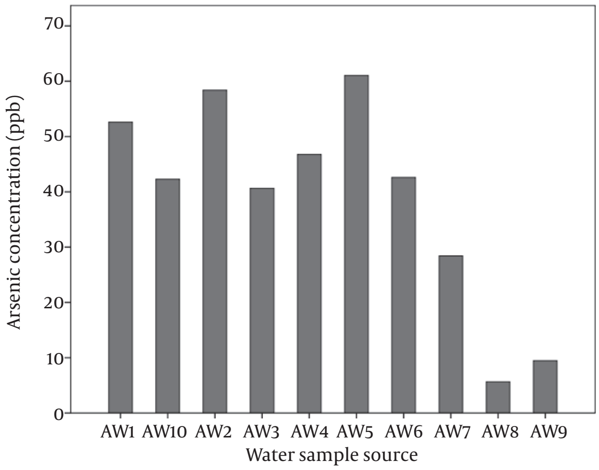

**Figure 3.** Concentration of Arsenic in Water Samples

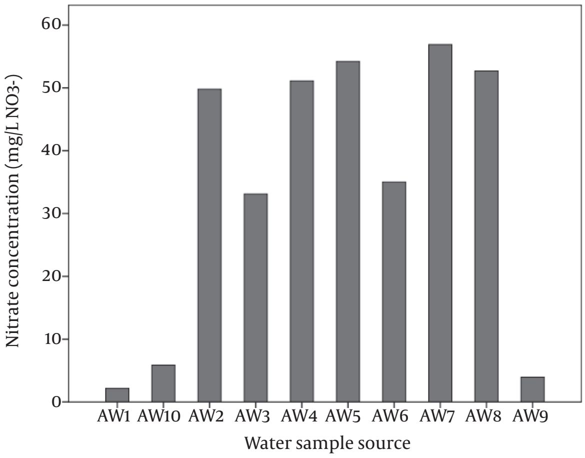

**Figure 4.** Variation of Nitrate Concentration in Water Samples

### 3.3. Hydrochemistry of Water Resources

Figure 5 (part A and B) illustrates classification of Piper diagram and the achieved diagram for analyzed water samples, respectively. As can be seen from this figure, most samples were from the border of zone 5 and 9 of the diagram and one sample was from zone 7. At zone 5, temporary hardness was more than 50%, and alkaline from the earth elements and weak acids were a dominant variety. General type of water from this zone was $HCO^{3-}$:$Ca^{2+}$, $Mg^{2+}$. Zone 9 had a mixture of elements, where none of the anion-cation pairs were more than 50%. In zone 7, noncarbonated alkaline was more than 50% and both alkaline and strong acids were dominant. The type of water at this zone was $Cl^-$, $SO_4^{2-}$: $Na^+$, $K^+$.

Figure 6 shows a Stiff diagram for water sampled from the distribution network of the city. Based on this figure, it can be concluded that this water sample originated from rhyolite (igneous) geological formation and the water type was $HCO^{3-}Na^+$. In other words, among the anions and cations, bicarbonate and sodium had the highest concentrations (meq/L), respectively. Of the studied water samples, 70% belonged to type $HCO^{3-}Na^+$. However for AW6, AW7 and AW8 samples, the type of water was $HCO^{3-}Ca^{2+}$, indicating that the water originated from the dolomite geological formation, and requires more investigations.

Table 3 provides a matrix of correlation coefficients between the measured parameters of water samples. Values in bold correspond to statistically significant correlation coefficients. According to the table, there was a significant correlation between arsenic and EC, $Na^+$, $K^+$ and $Cl^-$, which may point out that arsenic is dissolved from geological structure which contains Na, K and Cl. Correlation between $SO_4^{2-}$, alkalinity and $Na^+$ was also significant. Also, $Cl^-$ had a significant correlation with $Na^+$ and $K^+$. Correlation between $Ca^{2+}$ and pH was significantly negative.

Table 4 shows the rotated factor loadings. The first Principal Component (PC) included pH hardness (both total and calcium), calcium, alkalinity, nitrate, sulfate and bicarbonate. Furthermore, PC2 included electric conductance, magnesium, chloride, sodium, potassium and arsenic. These PCs in total explained 76.679% of variance. Figure 7 shows the dendrogram achieved by CA for water quality parameters. The figure indicates the relationship and similarity between water resources. From this figure, it can be observed that the analyzed sample from the distribution network (AW10) was similar to AW2, AW3 and AW4; these samples contained > 40 µg/L arsenic. In other words, site of sampling (AW10) may be close to the reservoir, which receives water from the mentioned wells. Besides, AW1 and AW6 were similar, indicating joint aquifers. AW7 was similar to the above-mentioned sources but AW8 had its own specific characteristics.

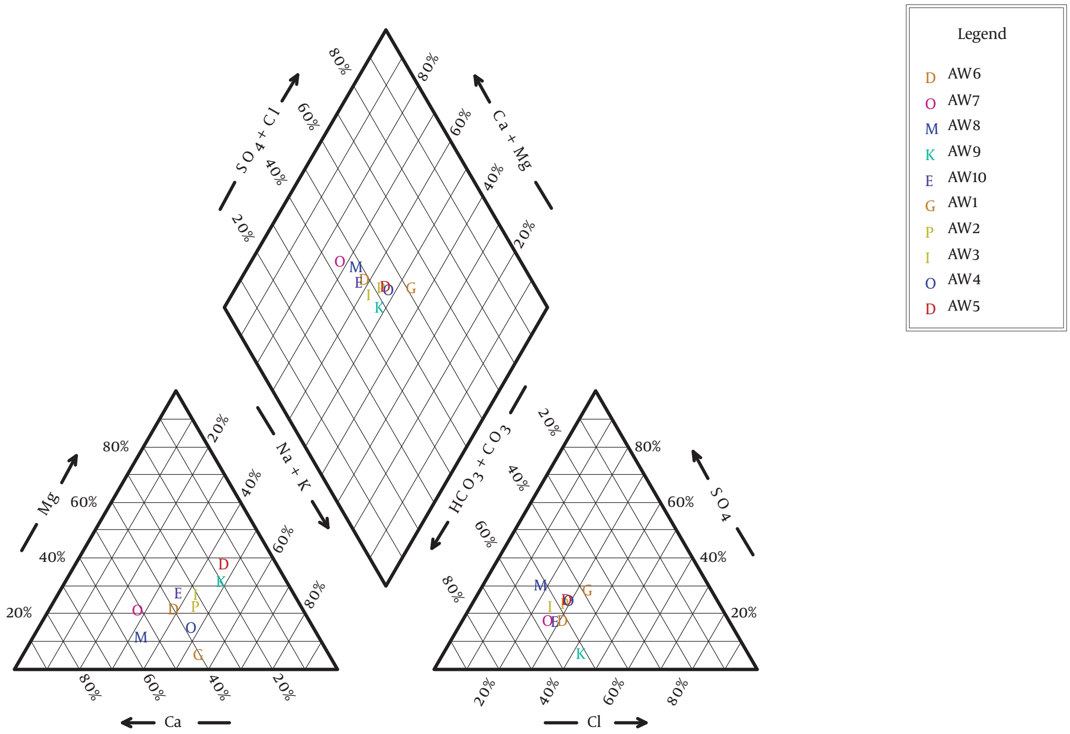

**Figure 5.** Piper Diagram For All Water Samples

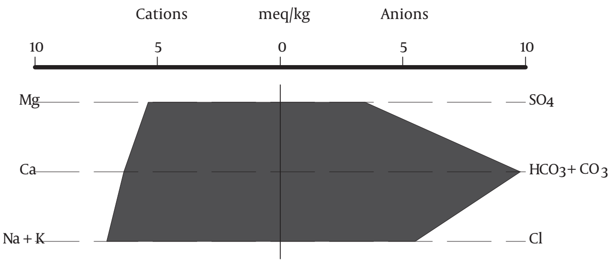

**Figure 6.** Stiff Diagram of the Water Distribution Network Sample

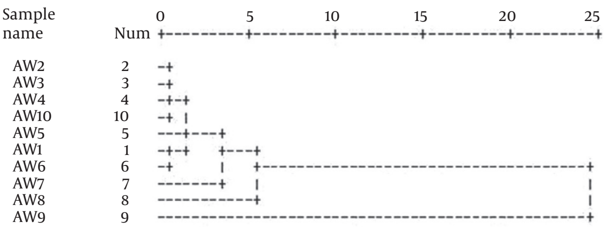

**Figure 7.** Dendrogram Achieved by Cluster Analysis Applied to Data of the Analyzed Samples

**Table 1.** Descriptive Statistics for Quality of Analyzed Water Samples

| Parameter | Minimum | Maximum | Mean | Standard Deviation |
|---|---|---|---|---|
| **Electric Conductance, µs/cm** | 789 | 1720 | 1500.9 | 287.4 |
| **Total Hardness, mg/L, $CaCO_3$** | 220 | 640 | 453.9 | 121.1 |
| **Calcium Hardness, mg/L $CaCO_3$** | 80 | 440 | 272.0 | 104.6 |
| **Alkalinity, mg/L $CaCO_3$** | 196 | 488 | 377.6 | 74.1 |
| **pH** | 6.95 | 7.54 | 7.19 | 0.18 |
| **Calcium, mg/L** | 32 | 176 | 108.8 | 41.86 |
| **Magnesium, mg/L** | 11 | 77 | 44.1 | 20.56 |
| **Sodium, mg/L** | 87 | 180 | 140.4 | 35.47 |
| **Potassium, mg/L** | 10 | 26 | 17.0 | 4.94 |
| **Bicarbonate, mg/L** | 239.1 | 595.4 | 460.67 | 90.44 |
| **Sulfate, mg/L** | 26 | 225 | 180.4 | 60.5 |
| **Chloride, mg/L** | 85 | 195 | 168.5 | 35.44 |
| **Nitrate, mg/L** | 2.2 | 56.9 | 34.47 | 22.44 |
| **Arsenic, ppb** | 5.65 | 61.05 | 38.78 | 18.95 |

**Table 2.** Quality of Analyzed Water Samples From the Studied City

| Sample code | Electric Conductivity | Total Hardness | Ca Hardness | Alkalinity | pH | Ca$^{2+}$ | Mg$^{2+}$ | Na$^{+}$ | K$^{+}$ | HCO$^{3-}$ | SO$_4^{2-}$ | Cl$^{-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AW1** | 1495 | 327 | 280 | 400 | 7.20 | 112 | 11 | 170 | 18 | 488.0 | 220 | 185 |
| **AW2** | 1660 | 460 | 260 | 380 | 7.36 | 104 | 48 | 160 | 26 | 463.6 | 215 | 190 |
| **AW3** | 1682 | 520 | 260 | 380 | 7.26 | 104 | 62 | 175 | 15 | 463.6 | 207 | 170 |
| **AW4** | 1653 | 460 | 320 | 420 | 7.19 | 128 | 34 | 180 | 18 | 512.4 | 225 | 190 |
| **AW5** | 1600 | 420 | 120 | 400 | 7.26 | 48 | 77 | 160 | 20 | 488.0 | 220 | 180 |
| **AW6** | 1473 | 480 | 300 | 352 | 7.15 | 120 | 43 | 127 | 17 | 429.4 | 148 | 185 |
| **AW7** | 1686 | 640 | 440 | 488 | 6.95 | 176 | 48 | 105 | 12 | 595.4 | 170 | 180 |
| **AW8** | 1251 | 420 | 340 | 360 | 7.00 | 136 | 19 | 90 | 10 | 439.2 | 207 | 85 |
| **AW9** | 789 | 220 | 80 | 196 | 7.54 | 32 | 34 | 87 | 12 | 239.1 | 26 | 125 |
| **AW10** | 1720 | 592 | 320 | 400 | 7.00 | 128 | 65 | 150 | 22 | 488.0 | 166 | 195 |

**Table 3.** Correlation Matrix of Quality Parameters of Analyzed Water Samples From the Studied City

| Parameter | EC | Total Hardness | Calcium hardness | Alkalinity | pH | Ca$^{2+}$ | Mg$^{2+}$ | Na$^{+}$ | K$^{+}$ | HCO$^{3-}$ | SO$_4^{2-}$ | Cl- | NO$^{3-}$ | Arsenic |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **EC** | 1 | | | | | | | | | | | | | |
| **Total Hardness** | 0.799$^{a}$ | 1 | | | | | | | | | | | | |
| **Calcium hardness** | 0.549 | 0.743$^{b}$ | 1 | | | | | | | | | | | |
| **Alkalinity** | 0.882$^{a}$ | 0.778$^{a}$ | 0.735$^{b}$ | 1 | | | | | | | | | | |
| **pH** | -0.515 | -0.740$^{b}$ | -0.849$^{a}$ | -0.728$^{b}$ | 1 | | | | | | | | | |
| **Ca2+** | 0.549 | 0.743$^{b}$ | 1.000$^{a}$ | 0.735$^{b}$ | -0.849$^{a}$ | 1 | | | | | | | | |
| **Mg2+** | 0.467 | 0.498 | -0.209 | 0.210 | 0.002 | -0.209 | 1 | | | | | | | |
| **Na+** | 0.694$^{b}$ | 0.176 | -0.016 | 0.429 | 0.096 | -0.016 | 0.282 | 1 | | | | | | |
| **K+** | 0.547 | 0.161 | -0.129 | 0.224 | 0.179 | -0.129 | 0.400 | 0.684$^{b}$ | 1 | | | | | |
| **HCO3-** | 0.882$^{a}$ | 0.778$^{a}$ | 0.735$^{b}$ | 1.000$^{a}$ | -0.728$^{b}$ | 0.735$^{b}$ | 0.210 | 0.429 | 0.224 | 1 | | | | |
| **SO42-** | 0.766$^{a}$ | 0.399 | 0.418 | 0.762$^{b}$ | -0.424 | 0.418 | 0.070 | 0.667$^{b}$ | 0.381 | 0.762$^{b}$ | 1 | | | |
| **Cl-** | 0.734$^{b}$ | 0.443 | 0.164 | 0.525 | -0.054 | 0.164 | 0.434 | 0.724$^{b}$ | 0.723$^{b}$ | 0.525 | .327 | 1 | | |
| **NO3-** | 0.378 | 0.421 | 0.326 | 0.501 | -0.290 | 0.326 | 0.221 | -0.003 | -0.04 6 | 0.501 | 0.499 | -0.043 | 1 | |
| **Arsenic** | 0.708$^{b}$ | 0.214 | -0.069 | 0.470 | 0.093 | -0.069 | 0.417 | 0.859$^{a}$ | 0.841$^{a}$ | 0.470 | 0.591 | 0.854$^{a}$ | 0.101 | 1 |

[a] Correlation was significant at the 0.01 level (2-tailed).
[b] Correlation was significant at the 0.05 level (2-tailed).

**Table 4.** Rotated Factor Loadings of Principal Component Analysis For Water Quality Parameters

| Parameter | PC1 | PC2 |
|---|---|---|
| **pH** | -0.906 | 0.152 |
| **EC** | 0.688 | 0.714 |
| **Total Hardness** | 0.834 | 0.253 |
| **Calcium Hardness** | 0.939 | -0.136 |
| **Ca$^{2+}$** | 0.939 | -0.136 |
| **Mg$^{2+}$** | 0.016 | 0.553 |
| **Alkalinity** | 0.880 | 0.411 |
| **Cl$^{-}$** | 0.203 | 0.849 |
| **Na$^{+}$** | 0.074 | 0.888 |
| **K$^{+}$** | -0.089 | 0.870 |
| **NO$^{3-}$** | 0.516 | .062 |
| **SO$_4^{2-}$** | 0.582 | 0.532 |
| **Arsenic** | 0.059 | 0.970 |
| **HCO$^{3-}$** | 0.880 | 0.411 |

## 4. Discussion

The amount of EC indicates high content of dissolved solids in comparison with desired levels, which may be undesirable for consumers because of taste. In term of hardness, according to the literature, water is classified as soft water (0-75 mg/L CaCO3), medium hard (75-150 mg/L CaCO$^3$), hard (150-300 mg/L CaCO3) and very hard (> 300 mg/L CaCO$^3$). The average value of total hardness in sampled water of 454 ± 121 mg/L indicates that the studied water samples can be grouped as very hard water. Mean concentration of nitrate was equal to 34 ± 22 mg/L, indicating that the presence of this compound should be considered adverse, with consequent health problems (33). High concentrations of nitrate in groundwater can be attributed mainly to improper disposal of domestic wastewater and leakage from sewers (36); excess application of fertilizer on agricultural lands (34) and uncontrolled disposal and dumping of animal wastes on the soil (35). There is no sewer system in some parts of the studied city, and accordingly application of absorption wells for disposal of household sewage and probable leakage from sewers can be considered as the main cause of the nitrate contamination in groundwater resources. Correspondingly, development of municipal wastewater collection and treatment facilities is the best solution for nitrate level control in groundwater. As well as, application of nitrate removal technologies from drinking water e.g. biological processes (36, 37), absorbents (41), electro dialysis (38, 39), electrocoagulation (40, 41) and other methods (46) can be considered as other approaches. Also for identification of nitrate sources in groundwater, application of nitrate and Oxygen (42) isotopes has been studied by Khayat et al. 2006 (43).

Most researches performed in Iran on the presence of arsenic in drinking water have been conducted in rural areas. A study in Hashtrood county during 2007 indicated that 50 villages out of 200 monitored villages, had arsenic in their drinking water at a concentration above the national MCL, 10 µg/L (44), and in total 11087 people (22% of the population of rural areas) were exposed to different levels of arsenic via drinking water. In the study of Charoymagh county, neighboring Hashtrood, it was determined that out of 210 studied villages, arsenic was present in the drinking water of 41 villages (20%) (45). However, there is no published paper about arsenic contamination of urban drinking water resources in Iran. New monitoring programs indicate an increasing trend in the number of drinking water resources, which are contaminated by naturally occurring high concentrations of arsenic. The present study showed that contamination of the studied city's drinking groundwater resources with arsenic (mean concentration 39 ± 20 mg/L) must be considered as an important health concern for the responsible organizations e.g. Urban Water and Wastewater Engineering Company (UWWEC) and also the health sector of the province. In the water sample from the distribution network, concentration of arsenic was four times higher than GV (46). Also, concentrations six-fold higher than GV were observed in some wells, indicating the presence of arsenic in geological structure of the city. The observed range of arsenic in the present study was similar to the study of Christodoulidou et al. in Cyprus (24), in which groundwater concentrations ranged from < 0.3 to 41 µg/L and the maximum total arsenic concentration was six times higher than the WHO guideline limit. In Vietnam, arsenic concentrations in groundwater of Mekong River delta was reported at < 0.1 to 1351 µg/L (22). In the study of Kouras et al. (21) in Northern Greece, in 65% of examined wells, arsenic levels exceeded GV for human consumption and there was high spatial variation in the concentration of arsenic (1 to 1840 µg/L). In our study, 87.5% of examined wells had arsenic concentrations above the WHO guideline limit. Results of this study indicated that there was a significant difference between arsenic levels of surface and groundwater resources. Thus, the treated water from the water treatment plant in the studied city, which is supplied from surface water, was safe with respect to arsenic, considering GV. In addition, the arsenic concentration was much lower than GV in a sample of one of the wells, showing the presence of arsenic at different levels in different parts of the city. This is an important issue and should be considered for the management of contamination issues. For example as a simple solution, water exploration could be increased from safe wells where discharge is appropriate to decrease the use of water from polluted wells.

For practical management of the contamination problem, information regarding water hydrochemistry can be useful. Spatial distribution of arsenic levels in the city, on one hand, and its water distribution network map, using GIS (Geographic Information System), on the other can provide an appropriate perspective for decision making and treatment strategies, especially for the point of entry (POE) methods (47). Undoubtedly, the application of different treatment methods that have been well discussed in the literature (30) should be considered as an approach after pilot studies, using real water samples for the co-removal of arsenic and nitrate. Among the new methods for arsenic removal, filters based on zero-valent iron (48, 49), SONO arsenic filters, electrochemical coagulation (50) and modified granular activated carbon (51, 52) can also be considered. Universally, there are two sources for arsenic contamination in groundwater. These include geogenic sources, which are sometimes called background or natural and anthropogenic sources (4, 11). When water flow passes through arsenic rich deposits and stones, the toxic material can make a way into the water. Chemical degradation of stones also leads to dissolution and mobility of arsenic in the form of acidic salts. Generally, arsenic concentration in regions, with the geothermal phenomenon, is high. The studied city is located near the Sabalan volcano. The presence of volcanic deposits in geological formations of the city is probable. Also, there are hot springs in the region, which are used for recreation and beneficial medical treatment purposes. It is expected that in the studied areas, high concentration of arsenic in water can be attributed to regional geologic formations, especially volcanic and geothermal activities (53, 54). Volcanic activities can be considered as the main source of natural contamination with arsenic that is very effective in widespread spreading of arsenic. It seems that volcanic activities and related processes release considerable amounts of arsenic to the environment in different ways i.e. geothermal activities.

There are several possible explanations for the release of arsenic into groundwater resources. Effective parameters can generally be cited to show the role of anions e.g. bicarbonate, nitrate, phosphate and fluoride, role of pH, organic matter, iron, and water detention in geo-formation. A high significant correlation between arsenic, EC, Na, K and Cl in our study indicates that arsenic is co-entered into water with mentioned solids through dissolution.

Also, arsenic bearing formations seem to be highly soluble and have high content of salinity agents e.g. Na and $Cl^-$. Kim et al. reported that bicarbonate causes the release of arsenic from sulfate ores in the groundwater (55). Kouras et al. reported a high correlation between arsenic concentrations and potassium, boron, bicarbonate, sodium, manganese and iron (21). In our study, the correlation between arsenic and bicarbonate was not significant ($r = 0.47$). This may indicate the ineffectiveness of bicarbonate ions in the dissolution of arsenic into the water of the studied area. According to the literature, oxy-hydroxides, redox potential, iron and organic matter are responsible for arsenic release and mobility of arsenic (11, 56, 57). In our study, a correlation was observed between arsenic and alkalinity, bicarbonate, magnesium and sulfate but not at significant levels. However, a more complete analysis is required for better judgment of aquifer conditions of the studied areas and effective mechanisms should be established to stop the release of arsenic into the water.

Adsorption and the release of arsenic to oxides is pH dependent and the dominancy of arsenic species and their distribution between solid and liquid phases are associated with pH and redox conditions (56). In water samples of the studied region, no correlation was observed between arsenic and pH; more investigations are required to confirm the validity of this finding. Behavior of nitrate in analyzed water samples was different from arsenic and there was no correlation between nitrate and arsenic. Calcium had a positive significant correlation with total hardness and alkalinity and negative significant correlation with pH. Thus, the results were different from the study of Baig et al. (19).

Physicochemical parameters and arsenic presence in surface and groundwater and geochemistry of water have been studied in many parts of the world (19, 42, 57). The present study aimed to investigate the quality of drinking surface water, groundwater and tap water in central part of the Ardabil province. The results indicated the presence of arsenic contamination in most groundwater resources of the city. It was determined that dissolved solid content, hardness, salinity, nitrate and arsenic of drinking water were high. The findings of this study indicate that there is a highest correlation between arsenic, sodium, potassium, chloride and solid content. Taken together, at the studied region arsenic anomaly in water is generally due to the regional geologic formations and volcanic activities, which in turn are considered as the main source of natural contamination of arsenic.

There are some limitations associated with the present study such as number of analyzed samples. Considering the consequences of exposure to arsenic through drinking water, it is recommended to conduct a more extensive study for better determination of contamination ranges, to understand the release mechanisms, and distribution and periodic fluctuations of arsenic in the aquifers. The quality of the water produced at water treatment facility (WTF) of the city was good with respect to solid content and arsenic. Increasing the portion of WTF for providing more drinking water can be useful to decrease the arsenic levels in the distribution system.

## 5. Concluding Remarks

Evaluation of physico-chemical parameters and arsenic presence in surface and groundwater and geochemistry of water have been studied in many parts of the world. Present study aims to investigate the quality of drinking surface water, groundwater and tap water in center of Ardabil province. The results indicated the presence of arsenic contamination in most of groundwater resources of the city. It was determined that dissolved solid content, hardness, salinity; nitrate and arsenic of drinking water were high. The findings of this study indicate that there is a highest correlation between arsenic, sodium, potassium, chloride and solid content. At the studied region arsenic anomaly in water is generally due to the regional geologic formations and volcanic activities, which in turn are considered as the main source of natural contamination of arsenic.

There are some limitations for the present study such as number of analyzed samples. Considering the consequences of exposure to arsenic through drinking water, it is recommended to conduct a more extensive study for the better determination of contamination range, to understand the release mechanisms, distribution and periodic fluctuations of arsenic in the aquifers; and to think about health risk assessment. The quality of the water produced at water treatment facility (WTF) of the city was good with respect to solid content and arsenic. Increasing the portion of WTF for providing more drinking water can be useful to decrease the arsenic levels in distribution system.

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