

Determination of arsenic concentration and physiochemical characteristics of water samples from Babagorgor fountain

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ABSTRACT

Since Babagorgor fountain in the Ghorveh city of Kurdistan province is located in the arsenic belt of Iran, to raise awareness about the quality of drinking water from this fountain the concentration of arsenic and other heavy metals as well as other physicochemical parameters were investigated to protect the public health. In this study, water samples were collected from Babagorgor fountain. Arsenic in the water was measured by field and laboratory methods. Its concentration was estimated to be more than 500 ppb in a field method and 596 ppb in a SDDC method with absorbance measurements at 520 nm. The SDDC method can measure arsenic species separately and the concentration of arsenite and arsenate were found to be 239 and 357 ppb, respectively. Other physiochemical parameters and heavy metals in the fountain water were evaluated according to standard methods. According to the World Health Organization guidelines the maximum safe level of arsenic in drinking water is 10 ppb. The concentration of arsenic in this fountain's water is estimated at 60 times the limit and therefore its use is very dangerous for public health.

Keywords: Total arsenic, Arsenic species, Babagorgor fountain, Water, ICP-AES, SDDC

Introduction

The population of the world is rapidly increasing. However, globalization has helped to increase emissions and other destructive environmental activities. Arsenic is one of the most important environmental pollutants, especially in groundwater. Since arsenic is mobile in water and aquifers (for example due to hydraulic fracturing), contamination by arsenic can spread through aquatic systems. Therefore, water pollution can affect a large population of people.¹ The arsenic concentration found in water has been reported in numerous articles, with a range of 0.5 to 5000 ppb of natural arsenic contamination in more than 70

countries.² Standard acceptable levels of arsenic in water resources are 10 ppb in most countries and up to 50 ppb in others.

Arsenic contamination is a widespread phenomenon and in many parts of the world those who use water contaminated with arsenic for prolonged periods suffer from serious health problems. The World Health Organization (WHO) and the Institute of Standards and Industrial Research of Iran both recommend that the maximum safe limit for arsenic in drinking water is 10 ppb, which is determined by a dye-based measurement. However, there are practical problems with removing arsenic from drinking water. In countries that find it difficult to comply with the above guidelines, they can set higher acceptable concentrations, according to local conditions.

Arsenic is the third element in the fifth group of the periodic table. Its atomic number is 33 and its atomic mass is 75. It can be found with different valences and in inorganic/organic forms. Arsenic is an element that naturally exists in the environment. It ranks 20th in the list of the

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more abundant elements in Earth's shell and is usually found in places that also contain sulfur and/or many metals, e.g., Cu, Co, Pb, and Zn.³ Widespread and natural pollution of many water resources of the world with arsenic and continuous consumption of such water by humans can result in diverse diseases, including liver, kidney, and skin disease, and even cancer and death in the cases of severe contaminations.⁴

Arsenic compounds can spread through the environment in the form of different chemical species with various mobility and hazard levels. Many As-containing chemicals can alter biological activities or cause environmental changes such as changes in redox potential and pH. Water soluble inorganic forms of As are highly toxic, whereas its organic forms, which are often found in sea food, are less hazardous.⁵ Most natural As species are the inorganic As(III) (arsenite) and As(V) (arsenate).⁶ Important measures of As toxicity include its bioavailability and mobility in the environment, which is highly dependent on its valence.^{7,8} Generally, the mobility of As(III) species is greater than As(V) species, and therefore, As(III) complexes are more toxic.⁹ Bioavailability, namely the amount of As that can be absorbed by living organisms, is an important measure in understanding the environmental risk of As. On the other hand, the presence of some cations and anions in the environment can directly influence mobility and/or fixation of As species.¹⁰ Consequently, environmental samples should be analyzed to determine the potency of changes and As hazards in environmental management. The analysis should be comprised of identification and measurement of all physiochemical parameters in addition to determination of total As concentration and detecting its specific chemical forms.^{11,12}

Materials and Methods

In this section, the sampling site and methods used are illustrated. Also, an extended description of the analysis procedures is provided.

Sampling description

Water samples were collected from the great Babagorgor fountain, which is 18 km away from Ghorveh county in Kurdistan province,

west of Iran. Geographical coordinates of this fountain are between 35° 17' 22" geographical latitude and 47° 54' 14" geographical longitude. Water samples were collected in 1 L polyethylene bottles washed previously with 5% nitric acid and double-distilled water. Samples were stored at 4 °C and transferred to a laboratory after adding 1 ml of concentrated nitric acid. Temperature, pH, and electrical conductivity (EC) were measured by a portable Orion multiparameter device and the total amount of arsenic was measured using the Quantofix field kit at the sampling site. In laboratory experiments, total As and other heavy metals were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Also, As species were determined through the silver diethyldithiocarbamate (SDDC) method. The other principal anions and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^-) were evaluated using a HACH DR 6000 spectrophotometer. All above physiochemical parameters were studied according to the Handbook of Standard Methods for the Experimentation of Water and Wastewater.¹³ The sampling site is shown in Figure 1.



Fig. 1. Location of Kurdistan province on a map of Iran and the sampling site

Measuring the Arsenic Species by the SDDC Method

In most developing countries, to determine the arsenic concentration in water, because of the simplicity of equipment the method of silver diethyldithiocarbamate (SDDC) is widely used.¹⁴ In this method, As (III) is selectively reduced to arsine (AsH_3) by a sodium borohydride solution and in an aqueous environment at pH 6. The produced arsine gas is removed in oxygen-free nitrogen gas, and after

passing through a regenerative tube containing glass or cotton wool, is impregnated with lead acetate solution (to prevent sulfide hydrogen interference) and injected into a silver diethyldithiocarbamate absorbent solution containing chloroform-soluble morpholine. The intensity of the redness produced is measured by a spectrophotometer at 520 nm, which is equivalent to the As (III) value.

To measure total inorganic arsenic in the absence of methyl arsenic compounds, the sample is adjusted to pH 1. A sample from which arsenite has been removed (as described above) is used to measure As (V). The sample is first acidified with hydrochloric acid and then a sodium borohydride solution is added to it. Arsine composed of As (V) is injected into the silver diethyldithiocarbamate absorbent solution and chloroform-soluble morpholine. The intensity of the redness produced is measured by spectrophotometer at 520 nm, which is equivalent to the As (V) value.

To calibrate the spectrophotometer, synthetic samples of 70 ml water with an arsenic content of 0, 1, 2, 5, 10, 15, and 20 µg were prepared and the operation of arsenic extraction was performed. Then an absorption chart was plotted based on absorption values against chloroform and the absorption equation was obtained (Figure 2). The accuracy and precision of the analytical method were determined with different concentrations of arsenic in water (50, 250, 500, and 1000 µg).

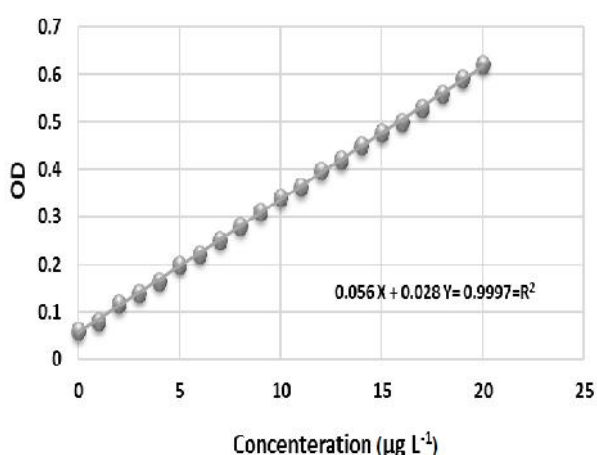


Fig. 2. Absorption rate of arsenic concentrations against chloroform based on the SDDC method

Results and Discussion

Physicochemical characteristics of the samples

The results of the physicochemical analysis showed that the temperature, pH, EC, and

arsenic concentration were 23 °C, 7.5, 2700 µmohs/cm, and <500 ppb, respectively. The measurement results of heavy metals and other physicochemical parameters of the water sample taken from the fountain are shown in Tables 1 and 2. After transferring samples to the laboratory, the arsenic concentration was determined to be 614 ppb and 596 ppb using the ICP-AES and SDDS method, respectively. Also, the concentration of arsenic species (arsenite and arsenate) in the sample were measured at 239 and 357 ppb, respectively, by the SDDS method. However, according to the WHO and also the Institute for Standardization and Industrial Research of Iran, the permitted level of arsenic concentration in drinking water is 10 µg/L. In addition, the concentration of iron and manganese, which play an important role in the movement and formation of arsenic species,¹⁵ were also higher than the WHO standard. Arsenic is strongly associated with the distribution of iron, manganese, and aluminum.¹⁶ Hydrous manganese and iron and aluminum oxides are considered to be the main components of the solid phase controller of arsenic absorption in the soil. It seems that the iron, manganese, and aluminum oxides present in these soils can increase arsenic mobility.¹⁷

Table 1. The results of metals and heavy metals measurement by the ICP-AES technique of the collected water sample

Sample	Result (ppb)	Sample	Result (ppb)
Al	36.238	Mn	> 3126.83
As	614.177	Mo	< 1.666
B	> 3971.36	Ni	24.71
Ba	18.817	P	215.087
Be	0.178	Pb	< 2.166
Ca	> 89256.3	Sb	< 0.462
Cd	< 0.049	Se	< 1.153
Co	9.147	Si	> 72830.2
Cr	< 0.096	Sn	< 0.161
Cu	3.854	Sr	603.336
Fe	> 11790.8	Tl	< 1.147
Hg	< 0.4	V	< 0.064
K	1416.11	Zn	19.193
Li	114.573	Ag	< 0.3
Mg	45426.2		

Water quality depends on the composition of the feed water, its mineral composition, reactivity of geological components of its watershed, human activities, and environmental factors that affect mobility of its geochemical constituents.¹⁸ One of the most important parameters in evaluating underground water

quality is determining the level of rare elements, such as arsenic, since water quality affects its possible applications. Specifically, pollution of

underground water with As is a concern due to it being highly toxic and distributed widely by underground water.¹⁹

Table 2. The results of the physicochemical parameters of the collected water sample

Physicochemical agents	Result	Anions	Result (mg/L)	Cations	Result (mg/L)
Turbidity (NTU)	5	Fluoride (F ⁻)	0.22	Calcium (Ca ²⁺)	168
Temp (°C)	25	Chloride (Cl ⁻)	260	Magnesium (Mg ²⁺)	86.57
pH	7.56	Sulphate (SO ₄ ²⁻)	280	sodium (Na ⁺)	260
EC (µmohs/cm)	2720	Carbonate (CO ₃ ²⁻)	0.00	Potassium (K ⁺)	35
TDS at 180 °C	1620	Bicarbonate (HCO ₃ ⁻)	1,049.20		
Total hardness (mg/l CaCO ₃)	776	Nitrate (NO ₃ ⁻)	7.48		
Temporary hardness (mg/l CaCO ₃)	776	Nitrite (NO ₂ ⁻)	0.036		
Alk (mg/l CaCO ₃)	860	Phosphate (PO ₄ ³⁻)	0.74		
Ammonia (NH ₃)	0				

High levels of arsenic are reported in Chile, Mexico, China, Argentina, the United States, Hungary, India, Bangladesh, and Vietnam,^{19,20} as well as in some regions of Iran.²¹ Arsenic concentrations in contaminated water have been reported from 100 to 2,000 µg/L in many countries of the world, including Argentina, Bangladesh, India, Mexico, Thailand, and Taiwan.²² Studies in Iran show that the amount of arsenic is 42 to 652 µg/L, 37 to 356 µg/L, and up to 1460 µg/L in areas of Khorasan province, 56 km north of Kashmar, and the villages around Kermanshah province, respectively.²³ However, the permitted concentration of arsenic in drinking water has been decreased to 10 µg/L by the WHO and from 50 to 10 µg/L in the national standard of Iran.²⁴

The arsenic zone is located in Iran and between Sanandaj-Sirjan. The region mainly has semi-active volcanoes that extend from the northwest to the southeast of the country.²⁵ Most of the water resources in this area have excess arsenic concentrations for groundwater. Kurdistan province is facing serious challenges regarding water pollution. Babagorgor fountain is one of the water resources of this province, which is rich in minerals and heavy metals. In this fountain, the existence of hydrogen sulfide gas that originated from a volcanic resource is a source of sulfide minerals, which can be accompanied by As.

The contamination of this fountain with As means its uses are faced with severe problems. Many studies have been conducted about the pollution of Iran's water resources with As and some chemical removal approaches have been proposed.^{21,26} However, employing any removal

methods requires detailed information about the water's chemical composition and recognition of its dissolved cations and anions. The findings of this study might be useful in selecting an appropriate method for removing As from the water of Babagorgor fountain.

Conclusion

This study presents findings obtained through measurement of total arsenic, arsenic species, heavy metals, and other physiochemical parameters of water samples from Babagorgor fountain. We found that the concentration of As and some heavy metals in the water are much higher than the determined universal standard values for drinking water. Since local residents are not aware of the presence of arsenic in the fountain's water and they are not familiar with health issues associated with swimming in and drinking such waters, we recommend they be informed via health centers located in that zone. Furthermore, the SDDC method can be developed in reference labs for more precise evaluations, because it can identify different arsenic species and does not require advanced equipment.

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