Heavy Metal Contamination in Drinking Water Supplies in the Villages of Divandarreh: The Use of Geographic Information System

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Abstract
One of the important aspects of drinking water pollution is the presence of heavy metals that can create hazards for consumer's health. This study was performed to find the concentration of heavy metals (arsenic, lead, iron, and zinc) in drinking water sources of Divandarreh in Kurdistan province and prepare its zoning map. A total of 99 wells, springs, and reservoirs were selected for sampling in 78 rural areas of Divandarreh County. Samples were collected from each source using grab sampling methods in two phases (rainy and dry seasons). To find the concentration of lead, the atomic absorption device (VARIAN 240 AA) was used, and Inductively Coupled Plasma (ICP: VARIAN 710) was used for determining the concentration of arsenic, iron, and zinc. Analysis of data was done using SPSS version 22.0 and the analysis of spatial variability and estimation of the concentration of heavy metals (preparation of zoning map) in the study area were carried out by ArcGIS software. The average concentrations of arsenic, lead, iron, and zinc in dry and rainy seasons were 1, 0.6, 62.9, 31.4, and 0.13, 2.16, 11.5, 19.8, respectively. Zinc, iron, and lead concentrations in sample No. 36 were higher than the standard level; therefore, it can be inferred that these three elements can create health problems in the future.

Keywords: Heavy metals, Divandarreh, Groundwater, Water supply, Geographic Information System (GIS)

1. Introduction
In recent years, the long-term use of groundwater resources and the discharge of industrial wastewater into the environment have caused an increase in groundwater contamination (1). One of the important dimensions of drinking water pollution is the presence of heavy metals that can be hazardous for consumer's health. Heavy metals are defined as a group of elements with a specific gravity greater than 6 g/cm3 or an atomic mass of 50 (2). Due to their toxicity, environmental persistence, and accumulation in the environment, heavy metals are classified as dangerous contamination; it mainly results from natural (i.e., weathering, erosion of bedrocks, and ore deposits) and anthropogenic (mining, smelting, industrial influx, agriculture, and wastewater irrigation processes) sources (3-5). Since heavy metals can enter water sources through environmental pollutants as well as the corrosion of pipe materials, the value of these elements in drinking water should be continuously monitored and controlled (6). To date, most of the developing countries face this challenge, usually due to their limited economic capacities to use advanced technologies for heavy metal removal. The greatest threat of toxic heavy metals was reported in the groundwater of several countries, including Mexico, Saudi Arabia, Bangladesh, India, China, Thailand, Chile, and Iran (7,8). For proper management of groundwater in every area, it is necessary to precisely evaluate its quality. Heavy metals exist as natural constituents of the earth's crust and are persistent environmental contaminants because they cannot be destroyed or degraded and most accumulate (9). However, their concentrations have increased as a result of human activities. Human exposure to heavy metals may occur by a variety of pathways, these species may enter the human body through inhalation of dust, direct ingestion of soil and water, dermal contact with contaminated soil and water, and consumption of vegetables grown in contaminated fields (10). The acute exposure to lead induces brain damage, kidney damage, and gastrointestinal diseases, while chronic exposure may cause adverse effects on the blood, cardiovascular
system, central nervous system, reproductive disorders, skin lesions blood pressure, kidneys, and vitamin D metabolism (11-15). Other heavy metals such as iron and zinc are essential and have physiological roles, but these elements can create toxic effects on living organisms when their concentration exceeds the maximum permissible level (16,17). Arsenic, lead, and zinc are considered most toxic and highly soluble in water that can be accumulated in aquatic organisms. The high concentration of these metals, especially lead and arsenic, may accumulate in the human body (18). Geographic information system (GIS) is a system which has been designed to capture, store, manipulate, analyze, manage, interpret and summarize data, and present all types of geographically referenced data needed for the use of land, the environmental changes, damages, wastes, and pollution. Therefore, the GIS can be considered as a bridge between databases, resources, and management (19, 20). Samani et al conducted a study on groundwater in the Marvdasht plains of Shiraz and reported that arsenic and lead concentrations were higher than the standard level in 7.5 and 2% of the samples (21).

Mebrahtu and Zerabruk investigated the heavy metal values in drinking water in urban areas of the Tigray Region, Northern Ethiopia. The results showed that arsenic (40.3%), iron (37.31%), and lead (29.85%) exceeded the maximum admissible and desirable limits recommended by the World Health Organization (WHO) (22).

It is vital to conduct studies to evaluate the level of contamination in drinking water resources in Iran. The results of such evaluation can be helpful for managers to provide drinking water with a good quality. Drinking water resources in the rural area of Divandarreh county include groundwater, and no sufficient study has been conducted on heavy metal contamination of drinking water in rural areas of Divandarreh so far. Therefore, this study was carried out to determine the concentration of heavy metals (arsenic, lead, iron, and zinc) in rural drinking water sources of Divandarreh in Kurdistan province during 2016-2017. These metals are considered the most toxic heavy metals which are highly soluble in water and can be accumulated in aquatic organisms.

2. Materials and Methods
2.1. Study Area
In this cross-sectional study, the concentration of heavy metals (arsenic, zinc, iron, and lead) in drinking water supplies of rural areas of Divandarreh city was investigated. Divandarreh is located at 34°N latitude and 46°32'E longitude, and it is one of the main towns in Kurdistan, Iran (Fig. 1). It includes 170 villages, of 117 villages are covered by Kurdistan Rural Water and Wastewater Company. The locations of sampling stations were recorded using geological positioning system (GPS, Garmin 62S).

Fig. 1. Location of the Study, Divandarreh County, Kurdistan Province, Iran.

2.2. Sample Collection and Analysis
In this project, according to the request of the Rural Water and Sewerage Company of Kurdistan province, 99 wells, springs and reservoirs were selected for sampling in 78 villages of Divandarreh city. Samples were collected from each source using grab sampling methods in two phases (rainy and dry seasons) during 2016-2017 according to standard methods for the examination of water and wastewater (23). The concentration of heavy metals (arsenic, zinc, iron, and lead) in drinking water was investigated and the results were compared with national standards and WHO guidelines. The containers were washed and rinsed with double distilled water before sampling and the bottles were rinsed twice with the water being sampled prior to filling. Then, 2 mL of concentrated nitric acid was added to each sample until the pH was reduced to less than 2, and it was kept at 4°C for further analysis. To determine the lead concentration, the atomic absorption device (Varian 240 AA), and for determining the concentration of arsenic, iron, and zinc, Inductively Coupled Plasma (ICP, Varian 710) was used. Statistical analysis of data was done using SPSS version 22.0 and the analysis of spatial variability and estimation of the concentration of heavy metals (preparation of zoning map) in the study area were done by ArcGIS software version 10.2.

3. Results and Discussion
Concentrations of the studied heavy metals (arsenic, iron, lead, and zinc) are presented in Tables 1 and 2. The results showed that the average concentration of heavy metals (arsenic, lead, iron, and zinc) in most of the samples of this project is lower than the maximum allowed in the national and the WHO standards.

3.1. Arsenic
Tables 1 and 2 showed that concentrations of arsenic in the water samples collected from Divandarreh villages ranged from 0.01 to 16.9 and 0.1 to 0.2 µg/L in dry and rainy seasons, respectively. The results for arsenic show that in Sample No. 84, the arsenic value was higher than...
the standard level. In other cases, the arsenic level was less than 10 ppb (24). However, in the second stage, the amount of arsenic reached below the standard level. Mean concentration values of arsenic were 1.0 and 0.13 µg/L in dry and rainy seasons, respectively. In a study conducted in Nangodi, arsenic concentrations ranged from 0 to 0.120 mg/L (25), and in Datuku, they ranged from 0.002 mg/L to 0.004 mg/L (26).

3.2. Lead
The lead concentrations in samples ranged from 1.1 to 46.4 µg/L and 0.1 to 9.9 µg/L in rainy and dry seasons, respectively, with a mean concentration of 1.38 µg/L (Tables 1 and 2). It is observed that in most of the villages surveyed in the first (low rain) and second (high rain) stages, the amount of lead in drinking water did not exceed the standard level. In all cases, the concentration of lead was reported to be below 10 µg/L. However, Sample No. 36 was an exception. In the second stage, the concentration of lead in the well water of this village was reported to be 0.046 mg/L, which was higher than the standard level. The high concentration of lead in the stream could be due to weathering and leaching of lead from waste rock dumps (27).

3.3. Iron
The iron concentrations in samples ranged from 83.4 to 912.2 µg/L and 1.8 to 292.9 µg/L in dry and rainy seasons, respectively, with a mean concentration of 1.38 µg/L (Tables 1 and 2). In the studied villages, Sample No. 92 and Sample No. 36 had unacceptable concentrations of iron.

3.4. Zinc
The zinc concentrations recorded in samples from Divandarreh villages ranged from 0.3 to 268 µg/L and 0.3 to 785 µg/L in dry and rainy seasons, respectively. In this study, the concentration of Sample No. 36 was higher than the standard concentrations of zinc.

Figs. 2 to 5 show zoning maps of the heavy metals studied in the villages of Divanderreh in dry and rainy seasons. Considering the maps, it can be seen that in most cases, the heavy metal values were lower in the second stage than in the first stage, which is normal. Because in the rainy season, due to the infiltration of water into the lower layers, pollutants and elements are diluted, and as a result, the amount of different parameters is relatively low. Of the parameters examined, only total lead concentration increased compared to the first stage in the dry season, while most of the parameters decreased. Some parameters also had minor changes. Chronic exposure to high levels of arsenic in drinking water may cause skin disorders, internal cancers (bladder, kidney, lung, etc), and neurological disorders in humans and animals (28). The sources of contamination of lead in the ecosystem are paint, pesticides, smoking, automobile emissions, burning of coal, and mining. In this study, the most important sources of lead contamination in groundwater are pesticides (29). Iron and zinc are important trace elements that play a

Table 1. The Amount of Heavy Metals in the Water Resources of Divandarreh Villages and the Relevant Standard Levels in the Rainy Season

| Sampling Season | Metal | Number of Samples | Minimum (ppb) | Average (ppb) | Maximum (ppb) | SD | WHO Limit (ppb) | National Standards (1053) | Total Number of Unacceptable Samples |
|-----------------|-------|------------------|---------------|--------------|---------------|----|----------------|--------------------------|-------------------------------------|
| Rainy season (spring) | Arsenic | 99 | 0.1 | 0.13 | 0.2 | 0.05 | 10 | 10 | 0 |
| | Lead | 99 | 1.1 | 2.16 | 46.4 | 5.04 | 10 | 10 | 1 (1.01%) |
| | Iron | 99 | 1.8 | 11.5 | 292.9* | 40.83 | 300 | 300 | 1 (1.01%) |
| | Zinc | 99 | 0.3 | 19.8 | 18283 | 28.34 | 3000 | 3000 | 1 (1.01%) |

*The maximum value was 1662, but it was deleted due to high standard deviation

Table 2. The Amount of Heavy Metals in the Water Resources of Divandarreh Villages and the Relevant Standard Levels in the Dry Season

| Sampling Season | Metal | Number of samples | Minimum (ppb) | Average (ppb) | Maximum (ppb) | SD | WHO Limit (ppb) | Total Number of Unacceptable Samples |
|-----------------|-------|------------------|---------------|--------------|---------------|----|----------------|-------------------------------------|
| Low rain season (autumn) | Arsenic | 99 | 0.1 | 1.0 | 16.9 | 2.0 | 10 | 1 (1.01%) |
| | Lead | 99 | 0.1 | 0.6 | 9.9 | 1.5 | 10 | 1 (1.01%) |
| | Iron | 99 | 83.4 | 62.9 | 912.2 | 98 | 300 | 0 |
| | Zinc | 99 | 0.3 | 31.4 | 785 | 97.13 | 3000 | 0 |

Fig. 2. Zoning Map of Arsenic Concentration in the Villages of Divandarreh.
vital role in the physiological and metabolic processes of many organisms. Nevertheless, higher concentrations of them can be toxic to organisms. An excessive amount of zinc causes prominent health problems, such as nausea, skin irritations, cramps, vomiting, and anemia (30). In the studied villages, Sample No. 92 and sample No. 36 had unacceptable concentrations of iron, and the concentration of zinc in Sample No. 36 was higher than the standard level. The accumulation of zinc in the body, especially in liver tissue, is among the side effects of zinc. However, the problems caused by iron are more aesthetic than environmental. Thus, by oxidizing iron (Fe\(^{2+}\)) to iron (Fe\(^{3+}\)) in groundwater and sediment, it causes color in the water and may lead to customer protest. (26,30).

The average concentration of heavy metals studied in this study was lower than the average concentration of these elements in Lorestani et al (31).
The concentration of zinc and iron in this study was lower than that found by Eldaw et al and higher than that found by Alinejad et al (6, 32). Moreover, the mean concentration of lead and arsenic in groundwater in the study areas was lower than the mean concentration of these elements in the study conducted by Cobbina et al but the mean concentration of zinc was higher (33). There was a significant difference between the measured concentrations of iron (\(P<0.001\)) and zinc (\(P<0.046\)) in the dry and rainy seasons. Camaraee et al reported that the mean concentration of lead, arsenic, and barium in the wells was 5, 0, 322 µg/L, respectively, which was higher than the results of this study (34).

Several studies have evaluated the level of toxic metals in drinking water and reported that the concentrations of these metals reported from Germany, the United States, Jordan, Malaysia, and Turkey were below permissible limits, which are similar to the results of this study (35,36).

4. Conclusion
Heavy metal contamination in drinking water in the rural area of Divandarreh county was relatively low and lower than the standard level in most cases. However, it should be continuously monitored in the areas where the amount of heavy metals approached the standard level. Finally, the water quality of western and southwestern areas of Divandereh was better than other places, so if there are plans to supply drinking water for rural areas of Divanderreh, the water sources of these areas are desirable options. Zinc, iron, and lead values in sample No. 36 were higher than standard levels. As a result, the adverse effects of each of these parameters and their cumulative effect on consumers can cause serious problems in the future. It is suggested that the water resources of the villages be reconsidered as much as possible. Only 1% of the samples were unacceptable. Although the use of pesticides, geological texture, and mining were the main reasons for the high concentration of heavy metals in some surveyed areas, we could not trace the origin or the specific route through which the metals entered the groundwater. Despite having this limitation, we believe that our research demonstrated which part of the groundwater was better or worse in terms of quality. The groundwater of the southern regions of Divandarreh was suitable and desirable in terms of heavy metal concentration.

Conflict of Interests
The authors declare that they have no conflict of interest.

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