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An In-Depth Analysis of Water Quality Using GIS and Heavy Metal Pollution Index near a Gold Mining Area, Qorveh, Iran

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ABSTRACT

Introduction: Inappropriate management of mining activities may bring about water pollution and pose a heavy complication on aquatic ecosystem and humans. The study aimed to evaluate the effect of Qorveh gold mining activities on the quality of nearby groundwater.

Materials and Methods: The concentration of seven eco-toxic metals along with some general hydrochemical parameters were investigated for 27 sampling stations in the study area using Atomic Absorption Spectrometry (AAS) and conventional hydrochemical methods. The analysis results were further applied to compute pollution indices, namely heavy metal pollution index (HPI) for irrigation purposes.

Results: The main elements were within the World Health Organization (WHO) and Iranian National Water Standards (INWS) for irrigation water quality, except for NH_4^+ in some sampling points. The concentration of heavy metals followed the order Cu > Zn > Pb > Hg > Cd > As. The contents of Hg, As, Cd, and Cu in most sites were higher than the recommended values. Except for two stations, the value of HPI based on the mean concentration was found to be far beyond the critical pollution index value of 100, suggesting that the area is highly polluted with some heavy metals.

Conclusion: Elevated concentration of trace elements found in groundwater of this area represented the release of harmful elements from gold mining activities on surrounding environment.

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Introduction

Urbanization and industrial development over the last decade have brought about some grave concerns for the environment. Heavy metals contamination is one of the serious quality issues in many fast growing cities, due to the fact that the development of water quality maintenance and sanitation infrastructure have not complied with population and urbanization growth particularly for the developing countries [1, 2].

Heavy metals can pose a risk to human health. Eight common heavy metals are arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se), and silver (Ag).

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These are all naturally occurring substances which are often present in the environment at low levels; however, in high doses, they endanger human health [3-5]. Heavy metals enter groundwater from various sources; namely natural or anthropogenic [6]. Their natural sources include weathering of metal-bearing rocks and volcanic eruptions [7], while anthropogenic sources include agricultural and industrial activities, landfilling, mining, and transportation, which all introduce a great amount of heavy metals into groundwater [8]. Mining [9], disposal of untreated or incompletely treated effluents contain toxic metals [10], as well as metal chelates from assorted industries, [11] and undiscerning use of heavy metal-containing fertilizer and pesticides in agricultural fields [12] have been the subjects of many studies addressing the main sources of heavy metal water contamination.

One of the most impetuous environmental Issues related to metal mining activities is acid mine drainage (AMD), which is produced by oxidation of pyrite and other metallic sulphides [13]. Given precious metal found in small quantities, gold mining operations cover wide areas, and thus can cause environmental damage over a geographically wast area. The mining sites are often contaminated with various forms of heavy metals that come primarily from the processing of ores and disposal of tailings and wastewaters around mines [14-16]. Owing to the fact that the large amounts of ore have to be removed to get small part of gold, different hazardous chemicals are used as extractive materials. Gold mining can also have devastating effects on water resources in addition to its negative effects on nearby soil and air [17]. Toxic mine waste contains dangerous chemicals, including As, cadmium, lead, mercury, petroleum byproducts, acids, and cyanide [18]. The toxic effects of these metals, not only cause irreparable damages to ecosystem, but also lead to the devastating impacts on human body and its proper functioning [18].

Due to the use of dirty practices, such as open pit mining and cyanide heap leaching, mining companies generate roughly 20 tons of toxic waste for every 0.333-ounce gold ring. The waste, usually a gray liquid sludge, is laden with deadly cyanide and toxic heavy metals [19]. Many studies conducted on mining activities have focused on heavy metals and cyanide monitoring in the environment [20-22].

There are a large number of published studies [23-25] describing soil contamination of heavy metals near mining areas in Iran. Considering the possible release of noxious substances originating from Qorveh mining activity, potable water supply to the surrounding villages is provided by a water tanker, whilst groundwater is used for irrigation purposes. Limited empirical investigations have been conducted on large scale ground water quality monitoring in relation to Sarigoni gold mine activity located in Qorveh, Iran. The present study aimed to assess the physico-chemical properties of water sources (wells, Qanats, and river) in Qorveh area, west Iran, near a gold mining setting using the HPI approach and correlation analysis.

Materials and Methods

Study area

Qorveh is the capital of Qorveh County, Kurdistan Province, Iran (Figure 1). At the 2019 census, its population was 136961. It is restricted from the north to Bijar, from the east to Hamadan province from south to Hamadan and Kermanshah, and from west to Sanandaj. Its center is the city of Qorveh which is located in a large plain 93 km east of Sanandaj and northwest of Hamadan and has expanded in the direction of Sanandaj road towards Hamadan. Owing to its distinctive geological characteristics and mineral water springs, visitors and tourists are attracted to this city. Qorveh area is known as one of the major gold reservoirs in Iran. Sarigoni gold mine was commissioned in 2015 and works continuously, with eleven tons of gold being extracted each year. The climate of the region is semi-arid continental, very hot, and dry in summer, while cold and wet in winter. The average summer temperature varies from 35 °C in the coldest northern area to 40 °C in the southwest.

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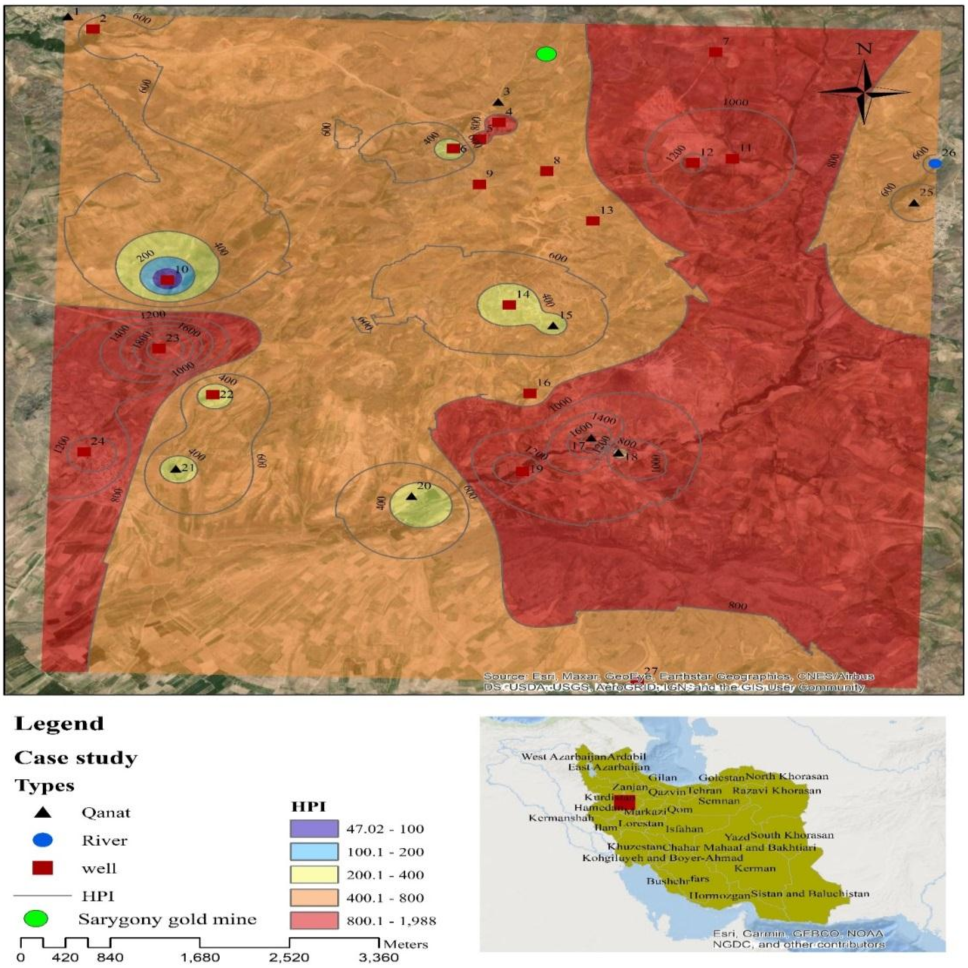

Figure 1: Map of the Sarigoni mining area with sampling stations and spatial distribution of HPI

Field sampling and analysis

In this study, 108 samples were collected from 27 ground water in different locations (Figure 1), including wells, qanats, and 1 surface water (river) in the vicinity of gold mine during four consecutive months (June, July, August, and September 2017-2018). River and qanats samples were taken in mid channel where the water was well-mixed at a depth of 10–20 cm. Groundwater samples were collected after 10 minutes of pumping. All the samples were placed into narrow-mouth pre-washed polyethylene bottles. The samples were preserved by adjusting the pH < 2 with 6 N ultrapure nitric acid to avoid metals precipitation, were kept in a cool place (below 4 °C), and were analyzed within 72 hours. Physical parameters, including pH, electrical conductivity (EC), and temperature were measured at field (Model: WA-2017SD, Taiwan). Concentrations of NO_3^-, NH_4^+, PO_4^{-3}, SO_4^{-2}, CN^-, and color values were determined by spectrophotometry method according to standards of water and wastewater analysis [26] using DR-5000 (Hach, Canada). Heavy metals concentrations were measured using Atomic Absorption Spectrometer (AAS) (Model: Analyst700**,** Perkin Elmer**,** USA). Several points were taken into account to perform the quality control and assurance of the obtained data as follows:

Bottle cleansing by nitric acid and washing with distilled water, twice sampling and reporting the mean values, checking accuracy by standard sample analysis, and drafting calibration curve and tripled repetition of the standard sample analysis for determining precision (RSD ± 5 % was taken acceptable).

Indexing approach

The heavy metal pollution index (HPI) is a ranking technique which provides the mixed effect of individual heavy metal on the overall quality of water. The ranking is a value between zero and one, presenting the relative significance individual quality considerations, which is assessed as inversely proposal to the recommended standard (Si) for each parameter [27]. The critical pollution index of HPI value for drinking water reported by Prasad and Bose is 100 [27]. Edet and Offiong classified HPI into three modified scale delimited as low, medium, and high for HPI values < 15, 15–30, and >30, respectively [28, 29].

The HPI was calculated using Equation 1.

$$HPI = \frac{\sum_{i=1}^{i=n}(Qi \times Wi)}{\sum_{i=1}^{i=n} Wi} \quad (1)$$

Where, Q_i is the sub-index of the i^{th} parameter. W_i is the unit weights of i^{th} parameter, and n is the number of parameters analyzed.

The unit weight W_i was calculated according to Equation 2.

$$W_i = \frac{K}{Si} \quad (2)$$

Where K and S_i represent the proportionality constant and highest permissible values of i^{th} parameter, respectively[28].

The sub index (Qi) of the parameter is calculated by Equation 3.

$$Q_i = \sum_{i=1}^{i=n} \frac{|Mi-I|}{Si-I} \times 100 \quad (3)$$

Where M_i is the tested value of heavy metal of i^{th} parameter, I is the ideal value (maximum desirable value for drinking or agricultural purposes) of the i^{th} parameter and S_i is the standard value (highest permissive value for drinking water) of the i^{th} parameter[28]. The sign (-) shows numerical difference of the two values, regardless of the algebraic sign.

In the current study, the concentration limits (highest permissive value) for agricultural purposes (S_i) and maximum desirable value (I_i) were taken from the Iran national standard (Standard No. 1053). The highest permissive values for irrigation (S_i) show the maximum allowable concentration in the absence of any substitute water source (Table 1).

The concentration of each tested parameter was converted into HPI. The higher HPI value indicates substantial damage to the environment and health.The critical HPI value is frequently considered 100 [27, 28].

Table 1: Desirable and permissible values for the tested heavy metals

Heavy metals	Maximum desirable value (I)(μg/L)	Highest permitted value for irrigation (Si)(μg/L)
Fe	300	5000
Hg	-	1
Zn	-	2000
Cu	50	200
Pb	-	5000
Cr	-	100
Cd	-	10
As	-	100
Se	-	20

Statistical evaluation and spatial distribution

Heavy metals data collected in this study were processed and exhibited on box plots using Graph Pad Prism version 8.0.2. Physiochemical data were summarized as mean, median, range, and standard deviation for each tested parameters. Statistical analyses were performed with Graph Pad Prism version 8.0.2. Considering the distribution of data, nonparametric spearman correlation was used to assess correlations among the concentrations of several heavy metals in water samples. The significant difference was considered 0.05. Spatial analysis (IDW interpolation) was performed using ArcGIS 10.2 ESRI software. IDW relies mainly on the inverse of the distance raised to a mathematical power. Since its power of parameter controls the significance of known points on the interpolated values, power of 5 was chosen for densely sampling points [29, 30].

Results

General Hydrochemistry

The concentrations of total dissolved solids (TDS) and electrical conductivity (EC) in water samples ranged widely from 112-180 mg/L and 234-1790 µS/cm and exhibited distinct variation between sampling points (Table 2). However, these values all fall within the limit standards of Iranian National Water Standards (INWS). High values of EC shows moderate mineralization of water, indicating long term contact of ground water with basement. The electrical conductivity of surface water (river) was relatively low for four consecutive months. The pH values varied from 5.18 to 8.13 with a mean value of 7.26 ± 0.57, revealing fluctuation from acidic to basic characteristic (Table 2). Except for sites Nos. 11 and 23 other samples were basic. Nitrate concentration was highly variable between sampling points ranging from 4.4 to 44 mg/L and it lies within the maximum permissible value of 50 mg/L. Sulfate values varied significantly between sampling points and ranged from 0.7-112 mg/L. However, phosphate concentration varied slightly ranging from 0 to 1.2 mg/L. Considering Se concentration in water samples, no sampling point was recorded beyond the Iranian irrigation water guidelines of 5 µg/L. Water samples from all sites near the mining area were not dominated by cyanide.

Table 2: Results of groundwater physicochemical analysis in the study area

Parameters	Unit	Min	Max	Ave	Med	SD	INWS
EC	µS/cm	234	1790	604.6	495.5	322.7	-
Color	Pt-Co	0	11	1.583	1	2.18	15
pH	-	5.18	8.13	7.26	7.42	0.57	6.5-9
NO_3^{-2}	mg/L	4.4	46	18.37	16	9.38	50
SO_4^{-2}	mg/L	0.7	112	28.51	22.5	21.31	400
NH_4^+	mg/L	0.07	2.14	0.59	0.35	0.53	1
TDS	mg/L	112	880	290.9	231	161.5	1500
CN^-	mg/L	0.001	0.011	0.004	0.005	0.0026	0.07
PO_4^{-3}	mg/L	0	1.2	0.23	0.2	0.19	5
Se	µg/L	< DL	5	0.76	0	1.17	10

DL: Detection Limit

Heavy metals contamination status

The box plots of heavy metals are provided in Figure 2 (a-h). The samples were taken from 1 river, 7 Qanats and 19 wells. Arsenic, cadmium, copper, iron, selenium, zinc, chromium, and lead were all detected in water samples.

Regarding irrigation purposes, the values of Hg, As, and Cd in almost 100%, 41%, and 85% of the sampling points exceeded the limit of Iranian water guidelines. It is noteworthy that the concentration of lead in none of sampling points was beyond the Iranian water standards for irrigation as the maximum permissible value of Pb is set 5000 µg/L. In general, the concentrations of Hg, Pb, As, and Cd ranged 0.2-45 µg/L (SD ± 10.19), 15-193 µg/L (SD ± 41.45), 2-682 µg/L (SD ± 130.7), and 1-551 µg/L (SD ± 95.73), respectively. Cr concentration was determined between 3-80 µg/L (SD ± 12.76). Cr concentrations were far below the Iranian water standards for irrigation purposes (it's the maximum permissible value is 100 µg/L). The concentrations of Se, Fe, Zn, and Cu were all within the Iranian water quality standards for irrigation purposes. The concentration of these parameters ranged 0-5 (SD ± 1.17), 38-850 (SD ± 163.7), 1-512 (SD ± 91.76), and 1-489 (SD ±

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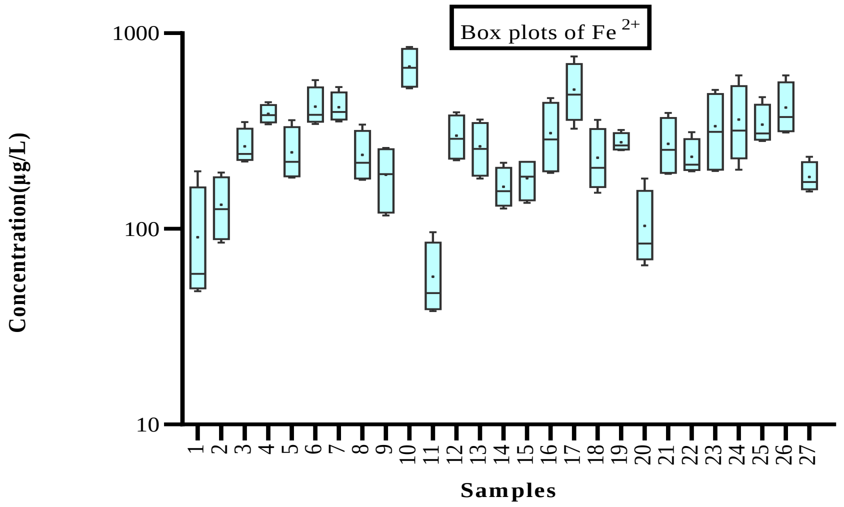
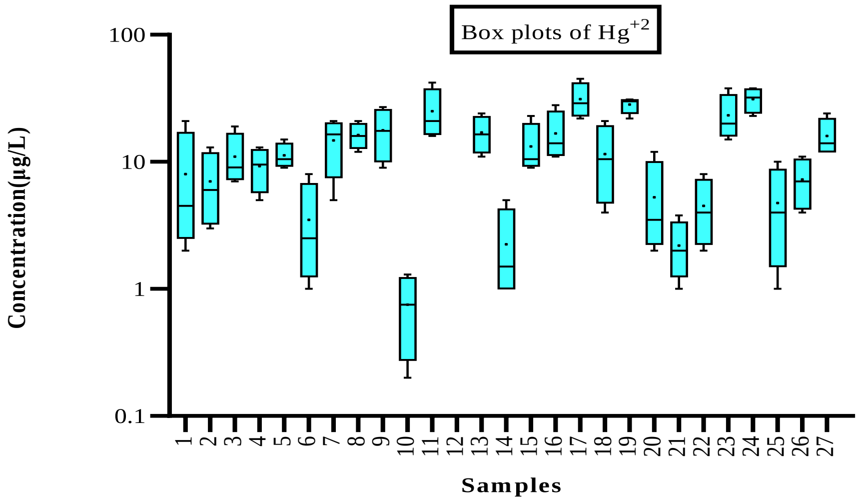
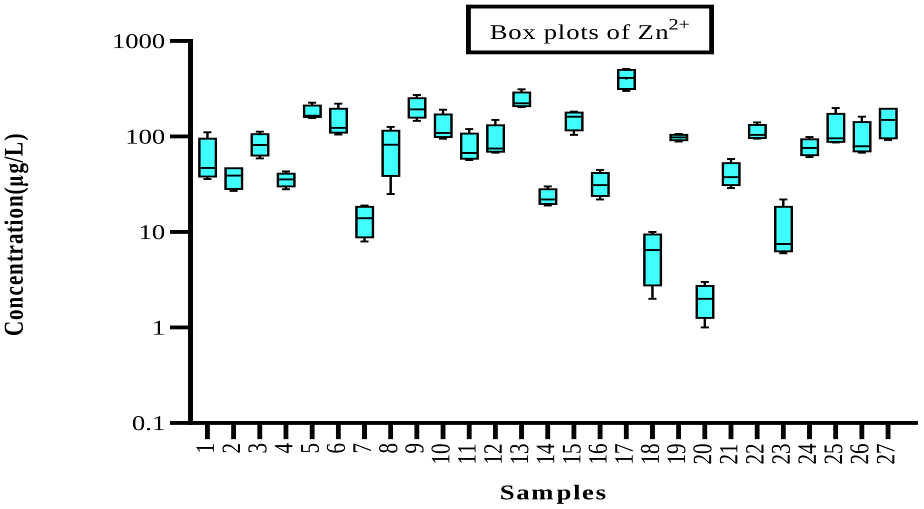
126.8). Surprisingly, the concentration of Cu in almost 41% of sampling sites was much higher than the critical value of 200 μg/L set for irrigation purposes.







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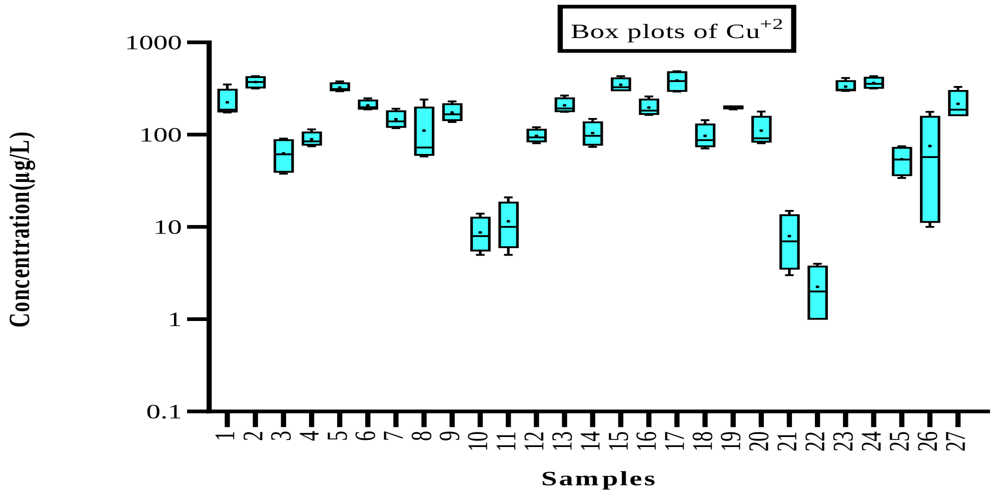

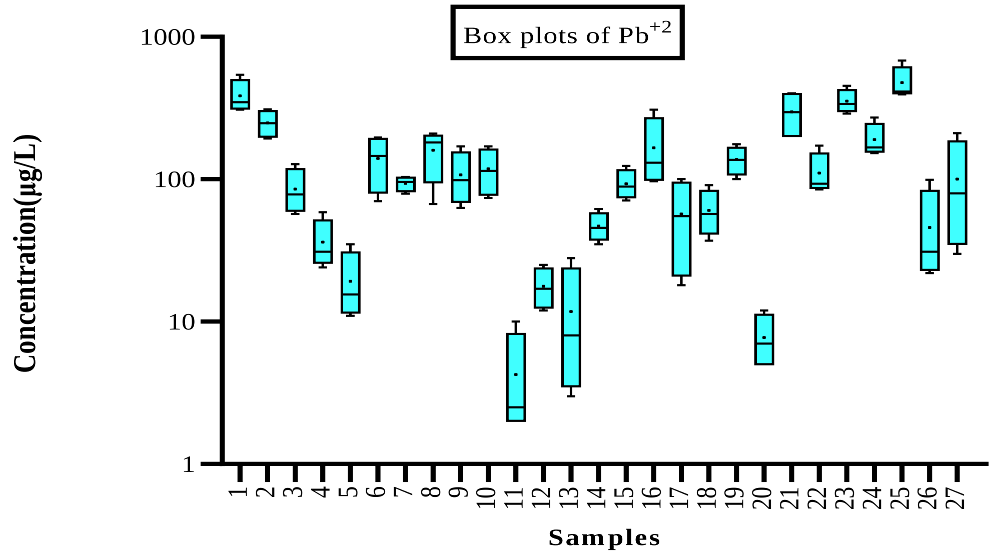

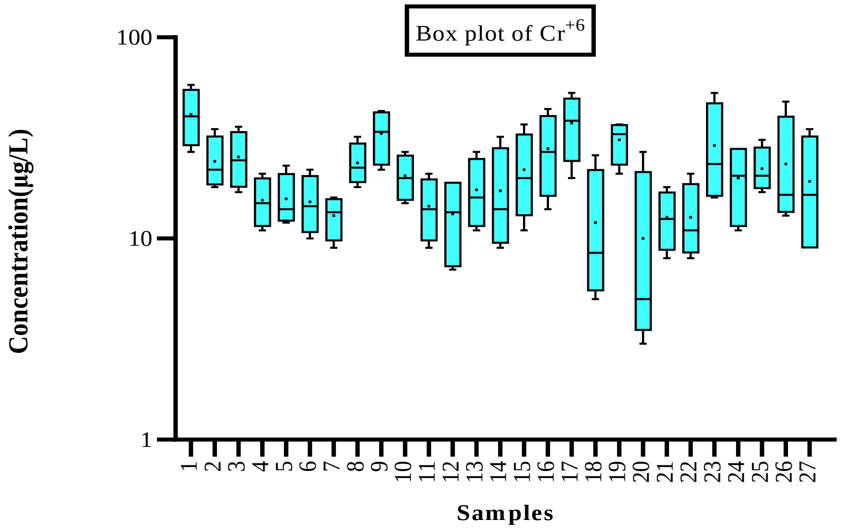

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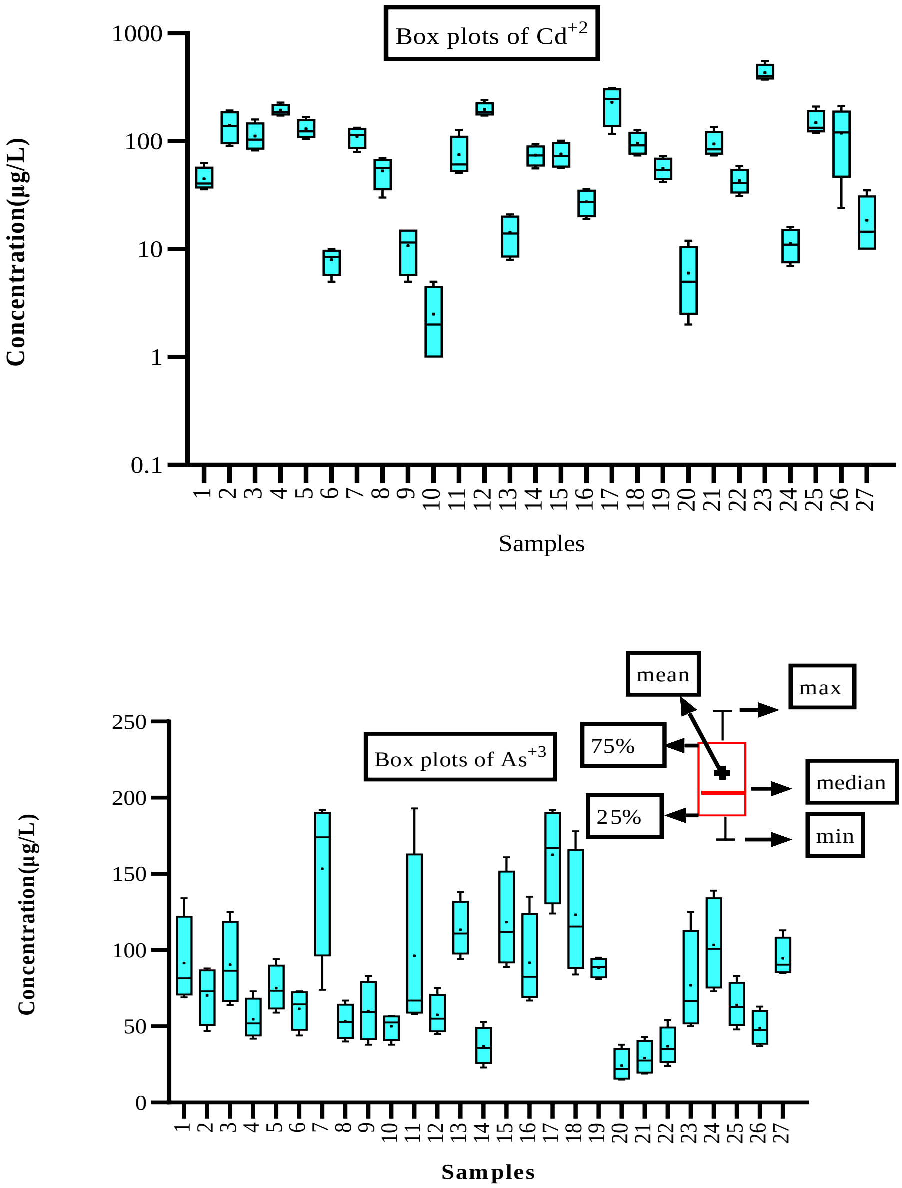

Figure 2: Box plots showing the distribution of metals' concentration in the groundwater samples

Spatial pattern of HPI

In order to calculate the HPI of the ground water, the mean concentration value of the selected metals was taken into account. The analysis results of HPI for the study area and corresponding spatial distribution are presented in Figures 3 and 1, respectively. The mean HPI values were obtained 898.23, 595.36, and 698.52 for wells, river, and Qanats, respectively. The maximum value of HPI was (1989.60) found at the sampling location No 23 (Figure 1). However, the lowest HPI value was observed in well No 10 which is located completely far from mining site. Considering the classes of HPI, 2 locations were under the critical HPI value of 100 (Nos 26 and 10), while remaining stations were in high class. In general, HPI values indicated that almost all groundwater were critically polluted with heavy metals; since most of sampling points exhibited HPI values far beyond 100. It was also found that the far from the gold mine the less the value of HPI (Figure 1). A significant increase in the value

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of HPI was observed at the sampling points (11, 17, 19, 23, and 24) compared to other sampling locations, which could be attributed to superbly values of As, Cd, and Hg; their corresponding spatial concentrations are depicted in Figure 2.

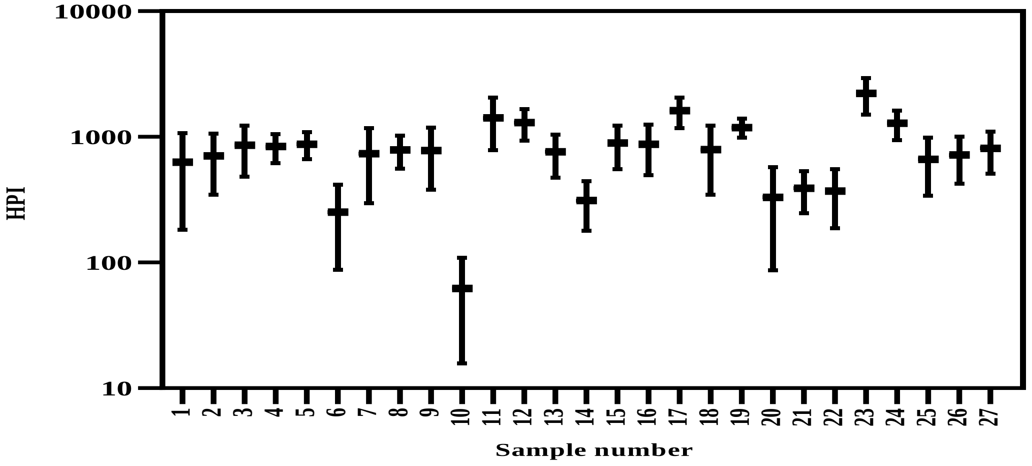
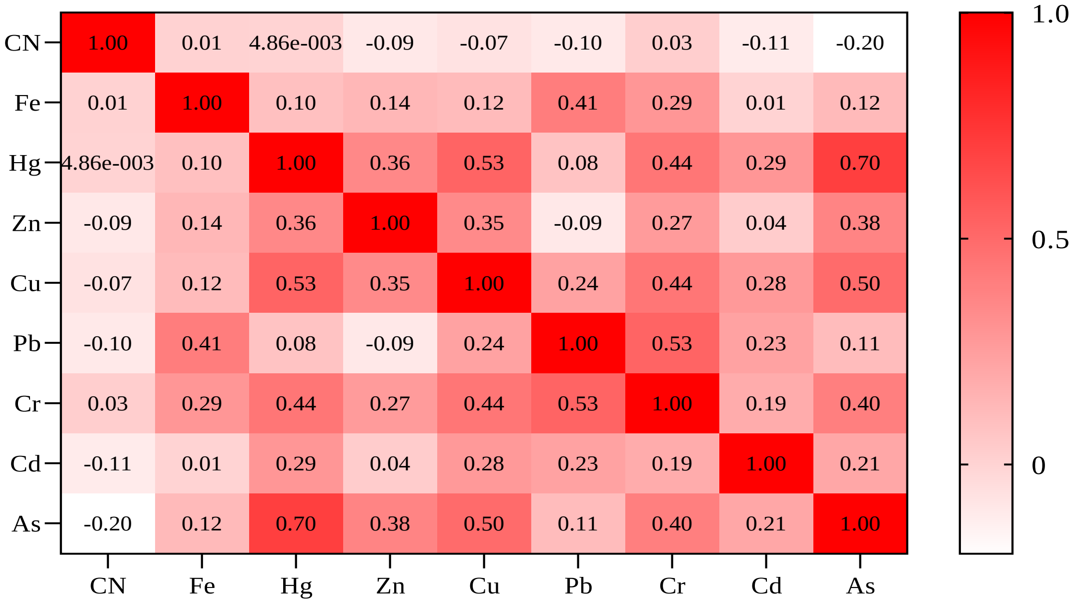


Figure 3: Statistical analysis results of HPI for the study area

Correlation analysis

The matrix correlation was analyzed in the case of heavy metals and CN-. According to Figure 4, a nonparametric spearman correlation analysis was performed on the concentrations of eight heavy metals and CN^{-}. Significantly positive relationships ($p < 0.05$) existed between Hg - As ($r = 0.7$), Cr - Pb ($r = 0.53$), and Hg - Cu ($r = 0.53$). Besides, relatively weak positive relationships with high significance ($p < 0.05$) were observed between As - Cu ($r = 0.5$), possibly indicating similarity in their sources in water.



	CN	Fe	Hg	Zn	Cu	Pb	Cr	Cd	As
CN	1.00	0.01	4.86e-003	-0.09	-0.07	-0.10	0.03	-0.11	-0.20
Fe	0.01	1.00	0.10	0.14	0.12	0.41	0.29	0.01	0.12
Hg	4.86e-003	0.10	1.00	0.36	0.53	0.08	0.44	0.29	0.70
Zn	-0.09	0.14	0.36	1.00	0.35	-0.09	0.27	0.04	0.38
Cu	-0.07	0.12	0.53	0.35	1.00	0.24	0.44	0.28	0.50
Pb	-0.10	0.41	0.08	-0.09	0.24	1.00	0.53	0.23	0.11
Cr	0.03	0.29	0.44	0.27	0.44	0.53	1.00	0.19	0.40
Cd	-0.11	0.01	0.29	0.04	0.28	0.23	0.19	1.00	0.21
As	-0.20	0.12	0.70	0.38	0.50	0.11	0.40	0.21	1.00

Figure 4: Correlation matrix of tested parameters in groundwater samples of Sarigoni mining areas

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Discussion

The pH values observed in Qorveh were generally higher than those observed in another study by Mitileni et al. [33] who reported pH values of 3.25- 6.28 in the vicinity of gold mine in South Africa. Numerous authors have documented highly acidic pH values in AMD emerging from gold mine activities [34, 35]. However, Rafiei et al. (2010) demonstrated mean pH value of 7.35 in gold mine tailings in Iran [23]. With respect to the maximum permissible limits, none of the samples demonstrated excessive values of color, nitrate, sulfate, and phosphate. These basic pH values could be attributed to oil spills or leakages from excavation machinery and transportation vehicles [31, 32]. It is claimed that low SO_4^{2-} contents in groundwater indicates sulfate reduction process in the aquifer system [36, 37]. Moreover, this result support previous research, linking enhanced sulfate values with lower pH. It is assumed that gold mine tailings comprises of up to 6% pyrite and this high sulphides content leads to high acidity in groundwater near the gold mines [38]. pH values obtained in the current study (5.40–8.84) did not elevate oxidation of metal sulphides, such as arsenopyrite (FeAsS), pyrite (FeS_2), which are mostly shaped at pH 3.6-5.7 [39]. Moreover, 25% of the samples had excessive concentration concerning NH_4^+. Some evidence has demonstrated high ammonium concentration in the vicinity of gold mine activities; since solutions containing ammonia are particularly effective for extracting gold from refractory ores [39, 40]. In fact, the CN^- concentration in the study area was within the permissible values and may be directly linked to artisanal small-scale mining (semi-mechanized manner) from gold processing (Cyanidation process), which comprises of leaching gold from ore as a gold-cyanide complex and recovering gold by precipitation [41]. A sodium cyanide solution is commonly used to selectively leach gold. It easily combines with many metals like gold and aids in its separation from ore [42]. Similarly, Osamn et al. (2010) found low concentration of CN^- below the detection limit of 5 ppb in groundwater near Yanqul mine of Oman. They concluded volatilization of CN^- (converted to HCN), lined dam structure, high evapotranspiration rate and deeper water table, contributed to the absence of cyanide in groundwater [43]. The CN^- concentration in the present study is low and may be also attributed to intermittent release from gold mining activities. The observations in Qorveh reflected the effect of various land uses, especially mining activities, which are associated with the inflow of both mine drainage and sewage from mining areas.

These results are similar to those reported by Dorleku et al. who performed a similar series of experiments and found high values of the mentioned heavy metals in groundwater of small scale gold mine[44]. Hg release from gold mining activities has caused great damage to the environment. In line with the present study, previous studies have demonstrated Hg as one of the threat to environment from gold mining activities [45]. It is proposed that for almost every gram of gold produced, two grams of inorganic Hg are released into the environment, which are further converted into organic forms [46]. Hg is extremely harmful to human health. The amount of vapor released by mining activities has been proven to damage the kidneys, liver, brain, heart, lungs, colon, and immune system. Chronic exposure to Hg may conclude in fatigue, losing weight, tremors, and shifts in behavior. In children and developing fetuses, Hg can impair neurological development [45]. There have been a number of longitudinal studies involving groundwater contamination with As in gold mining areas [47]. It can be seen in forms of arsenopyrite (FeSAs), orpimrnt (As_2S_3), and realgar (As_2S_2) in gold bearing rock [47]. Previous research has established high values of As in Obuasi region originated from arsenopyrite in the gold-bearing ore [48]. Predominant configuration of As in mine tailings are arsenite [48] and arsenate [49] which both exhibit the highest toxicity. Background concentration of Cd in unpolluted soil is roughly 1 mg/kg; however, in gold mine tailings, concentration of up to 11.7 mg/kg has been reported [49, 50]. The isometric form of Cd is observed in gold bearing orebodies in sphalerite which controls its concentration in the ore body [50, 51]. Copper is amply found in sulphides, arsenites, chloride, and carbonates forms in gold ores [52]. Despite the natural background level of 5-70 mg/Kg in unpolluted soil samples, elevated concentration of Cu has been observed in gold mine tailings. Copper tends to bind to particles of organic matter and clay minerals upon its release to the environment [53]. Utterly, Hg and Cd were the predominant compounds with the highest values in water samples; whereas Se accounted for a minor concentration compared to all the detected heavy metals and in many sites its values were below the limit of detection. Except for Se, concentration of heavy metals displayed fundamental variations in various months especially for lead (Pb), chromium (Cr), and cadmium (Cd). Changes in most heavy metals concentrations were also observed among sampling points; sites Nos, 6, 10, and 20 exhibited lower heavy metals contents compared to others. The high level of heavy metals in ground water is consistent with a previous study that considerable concentration of metals were detected in water samples near mines [54-56]. The outermost concentration of Hg, As, and Cd were observed at sampling sites 11, 17, and 23. Likewise, exceptionally high detected levels of Cu were observed in sampling sites 2, 5, 15, and 17, which outlined against the Iranian high permissible values. The detected concentrations in this study were higher than or similar to those previously reported in published studies [57-59].

Despite the great distance of sampling points 23 and 24 from the mine site, high HPI values were observed, which may be related to other anthropogenic factors like agricultural activities and wastewater discharge [1, 60, 61]. Compared to other environmental samples, the levels of heavy metals in this study were one to two orders of magnitude higher than those found in water from citizens well, soils or vegetables in the vicinity of gold mines [59], implying that the level of heavy metals in groundwater samples of Qorveh was relatively high. In this study, the exceptionally high amounts of heavy metals in groundwater raised concern; since they are the major source of irrigation water in Qorveh province.

Although some of these elements can be derived from geological units, their high concentration can be attributed to the contribution of anthropogenic activities. The correlation among metals can provide information on the source and pathways of metals [62-64]. Generally, the tailings from gold extraction and chemical products used during gold separation are the predominant source of heavy metals in water [65,66]. No significant correlation was observed between CN^- and other heavy metals, probably reflecting different sources and consumption practices of these heavy metals in Qorveh.

Conclusion

The present study aimed to monitor some of heavy metals and general physico-chemical parameters in the surface and groundwater of Sarigoni gold mine, Qorveh province, using HPI and GIS techniques. Out of the seven heavy metals analyzed in 27 sampling sites, the concentrations of As, Hg, Cd, and Cu were above the maximum permissible levels for irrigation. The high concentration of these noxious elements was probably due to the erosion of mining waste (tailings) and the release of wastewater from gold washing into the surrounding environment. The physical parameters (pH, EC, and color) as well as the concentrations of major chemicals in water were all within the INWS for irrigation purposes. HPI was calculated for each sampling site and also mean HPI by taking values for each station during 4 consecutive months in order to compare the heavy metal pollution spatial distribution and assess the quality of water for irrigation purposes. According to the result, it can be concluded that the pollution load at 2 sampling sites was below the critical index limit of 100 and other samples were found to be high and hence unacceptable. For future research, it is imperative that further work be set out to examine the accumulation of the mentioned heavy metals in agricultural crops and to evaluate their possible health risks for human health. Additionally, the result of this study also

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cause for alarm due to the resulting adverse health effects of gold mining activities on human health via soil and air transportation of heavy metals. Thus, urgent action by policymakers is required to combat the devastating impacts of the mining activities. Importantly, environmental and health studies should be carried out on the gold mining activities even in other regions of Iran.

Abbreviations

HPI: Heavy metals pollution index
WHO: World Health Organization
AMD: Acid mine drainage
IDW: Inverse distance weighted
TDS: Total dissolved solids
EC: Electrical conductivity
AAS: Atomic absorption spectrometry

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Conflict of interest

No conflict of interest.

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