



## Investigation of heavy metals contamination in agricultural soils of East Urmia based on contamination indicators

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### Article Info

**Article type:**  
Research Article

**Article history:**  
Received: April 2024  
Accepted: October 2024

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**Keywords:**  
Urmia Lake  
Soil Pollution  
Heavy Metals  
Pollution Index  
Agricultural Soil

### Abstract

Pollution and geo-accumulation of heavy metals in soil and agricultural products owing to human activities and natural factors pose significant environmental issues generating severe risks to human health and food security. To address these concerns, the concentrations of heavy metals, including As, Sb, Cu, Mo, Pb, and Zn, were measured using 20 randomly collected soil samples taken from depths of 0–30 cm in the eastern agricultural area of eastern Urmia. After preparation, the total concentrations of these elements in the soil samples were extracted using hydrochloric and nitric acids and then measured using ICP-OES. The results indicated that the mean concentrations of total As, Sb, Cu, Mo, Pb, and Zn in the study area were 7.04, 1.02, 21.57, 0.357, 7.60, and 57.19 mg/kg, respectively. These concentrations were lower than the limits set by the Iranian Environmental Protection Agency. The mean pollution factor and enrichment coefficient in the region were the highest for As, followed by Sb, Zn, Pb, Cu, and Mo. The average infection index was 13.46, which indicated a moderate degree of soil contamination. The Earth Repletion Index for Cu and Mo was between 0 and 1, suggesting a natural origin, whereas for As, Cu, Pb, and Mo it was greater than 5, indicating high pollution levels. Based on the Pearson coefficient, there was a high correlation between Pb, Sb, Cu, and Zn, suggesting a common origin or similar geochemical behavior.

**Cite this article:** Mehri Yari, Fatemeh; Pirkharrati, Hossein; Farhadi, Khalil; Soltananezhad, Noushin. 2024. Investigation of heavy metals contamination in agricultural soils of East Urmia based on contamination indicators. *Environmental Resources Research*, 12(1), 319-332.



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DOI: 10.22069/ijerr.2024.22368.1435

Publisher: Gorgan University of Agricultural Sciences and Natural Resources

## Introduction

With the increasing population and rapid technological progress, there is a growing concern about environmental pollution caused by heavy metals and the associated risks to both nature and humans. In this context, soil, as an integral part of the biochemical system, plays a crucial role in storing and purifying elements, as well as facilitating the transfer of components. Soil is a dynamic medium that serves as the primary source of contamination from land and manure sources (Qishlaqi et al., 2009).

The main sources of heavy metals include industrial, agricultural, and municipal wastewater (Chen et al., 2001). Soil contamination by potentially toxic elements is a significant environmental concern because of the instability of these elements, their long half-lives in the human body, and their tendency to accumulate in living tissues (Chen et al. 2008). Heavy metals are characterized by their relatively high density (specific volumetric mass greater than 5 g per cubic centimeter) and toxic nature, even at low concentrations (Adani et al., 2015; Järup, 2003).

The mobility of these metals in the soil is low, and they are typically not transferred to the underlying layers. Instead, they accumulate in the surface layers of the soil and are more prone to absorption and transfer to plants. Owing to their resistance to biological or chemical decomposition in nature, these metals persist in the soil and can be transported over long distances through water or air, thereby posing a threat to organisms as they enter the food chain. Consequently, it is crucial to investigate the dispersion of these metals in soil to facilitate effective environmental management. Urmia Lake, one of the most important and valuable ecosystems in Iran, has unfortunately experienced significant degradation in recent years due to human and natural interactions, making it one of the largest environmental crises. One of the negative consequences of Urmia Lake drying is the emergence of a significant amount of sediments and salt beneath the water level. These sediments have the

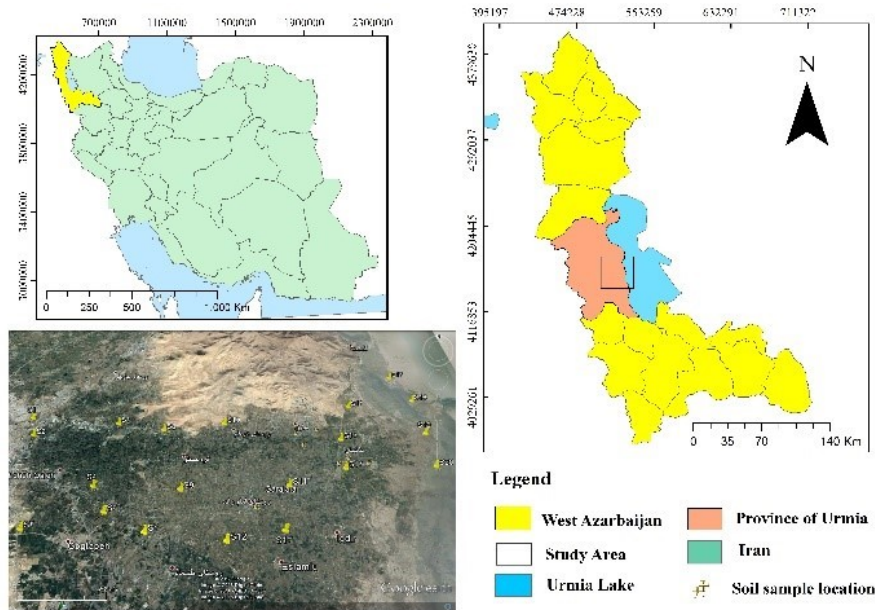
potential to transform into dust particles via wind erosion. Because of prevailing wind patterns and the region's morphology, these dust particles spread over large areas, particularly in urban regions. The harmful elements and compounds present in these dust particles are considered as potential dangers. Therefore, to assess the presence and impact of heavy metals, the concentrations of these elements were investigated in both Urmia Lake and agricultural land in eastern Urmia. Several studies have been conducted worldwide to investigate heavy metal contamination in agricultural and lake sediments. Some notable examples include research on the evaluation of heavy metals such as arsenic, cadmium, copper, nickel, lead, zinc, and sodium in agricultural soils near Urmia Lake (Mohammadi et al., 2017); the assessment of arsenic, cadmium, copper, nickel, zinc, and mercury in the sediments of lakes in China (Xu et al., 2017); the examination of cadmium, lead, copper, chromium, and zinc in the suburban areas of Tabriz in northwest Iran, which are adjacent to Urmia Lake (Taghipour et al., 2013); and the identification of high levels of arsenic, cadmium, copper, iron, nickel, sodium, and lead in the form of fine atmospheric particles on the northern and southern coasts of Urmia Lake (Gholampour et al., 2017). Collectively, these studies contribute to our understanding of heavy metal contamination in various environmental contexts. Therefore, the evaluation of heavy metals in agricultural soils at a local scale and the identification of their sources are essential. Considering the importance of this research, the aim of this study was to investigate the extent of heavy metal contamination (As-Fe-Cu-Pb-Zn) in the agricultural soil of eastern Urmia, northwest Iran. This investigation utilized Contamination factor (CF), enrichment coefficient (EF), geoaccumulation index (Igeo), degree of contamination (Cd), soil condition assessment.

**Materials and methods**

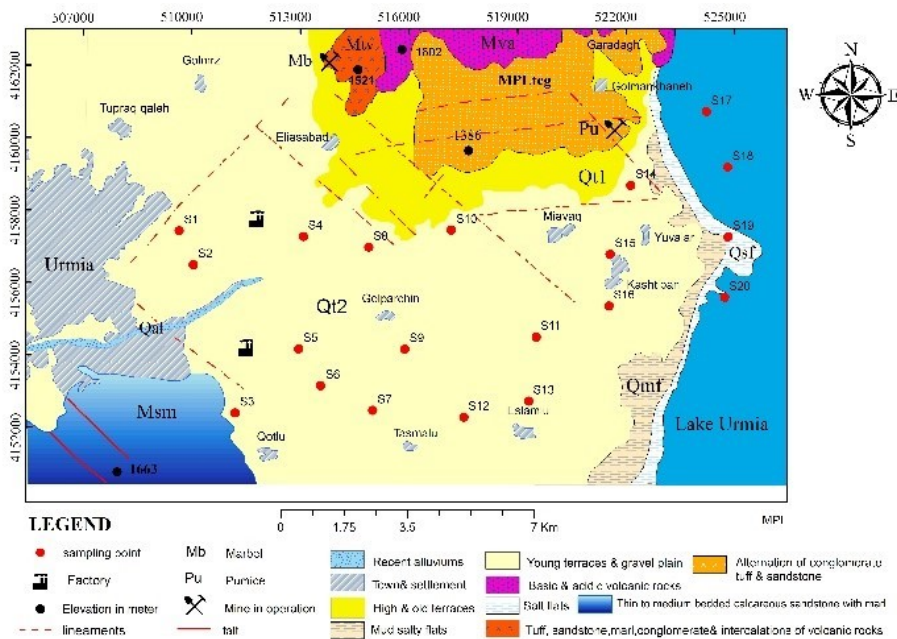
**location of study area**

The study area is located in West Azarbaijan Province, in the eastern part of Urmia city, between the geographical longitudes of 45° 16' 47.52" and 45° 6' 33.41", and geographical latitudes of 37° 32' 49.02" to 37° 33' 49.77". This study area is limited to the northern mountains of Hajiadaghi and Bizowdagh, eastwards to

Urmia Lake and westwards to Urmia city (refer to Figure 1). The climate of this area is primarily influenced by the rainy winds from the Atlantic and the Mediterranean regions. The average temperature ranges between 6 °C in winter and 30 °C in summer, with an average annual temperature of 12.6 degrees Celsius. The average annual precipitation is 22.7 mm, and there are 120 freezing days per year.



**Figure 1:** Location of study area and distribution of sampling points



**Figure 2:** Geological map of the studied area

The study area is characterized by young Quaternary alluvial arches and deposits, which have facilitated the expansion of agricultural land and gardens at the same sediment level. The oldest exposed rocks in the region consist of a series of thin-to medium-sized limestone sandstones from the Miocene, primarily found in the southwestern part of the area. Lakeside strips surround the lake in the eastern part of the region. In the northeastern part of the study area, andesitic volcanic rocks are widely distributed, along with dacitic rocks, tectonized rubble, sandstone, tuff, marl, limestone, and conglomerate. These formations extend from the old Miocene to the Miopliocene period (refer to Fig. 2 and geological map 1:100,000 Urmia).

#### Soil sampling and chemical analysis

The research was carried out by randomly collecting 20 surface soil samples (at a depth of 0-30 cm) and placing them in plastic bags for transportation to the laboratory. Out of these samples, 16 were collected from agricultural soils, including gardens and agricultural land, while four samples were obtained from the dry bed of the western margin of Urmia Lake. The locations of these samples are depicted in Figure 1. Once the samples arrived at the laboratory, they were dried at room temperature. Pebbles were removed, and the plant waste was sieved using a 2 mm (20 mesh) sieve, followed by a subsequent sieving through a 63-micron (230 mesh) sieve. Extraction using HCl and HNO<sub>3</sub>, as described by Black et al. (1965), was employed to determine the total concentration of heavy metals in the soil. The measurement of total metal concentrations was performed using inductively coupled plasma spectroscopy (ICP-OES) with a Perkin Elmer Optima 7300DV instrument. Soil texture was determined using the stocks and hydrometric method, as outlined by Gee et al. (1986). Organic matter content was assessed through wet oxidation following the methodology established by Walkley et al. (1934). The calcium carbonate equivalent was determined using the acid neutralization method described by Roades et al. (1962).

The electrical conductivity and pH of the soil samples were determined using a saturated flower extract and a mixture of 1–5 water and soil, as specified by Chapman et al. (1965).

#### Determination of soil contamination

##### *Enrichment Factor*

The enrichment factor (EF) is a useful method for evaluating both natural and human-induced pollution sources as well as their impact on soil contamination and human health. It was calculated individually for each element using the following equation:

$$EF = \frac{(C_n/C_{fe})_{sample}}{(C_n/C_{fe})_{background}} \quad (1)$$

The enrichment factor (EF) was calculated using the equation proposed by Taylor (1964), where  $C_n$  (sample) represents the concentration of a specific element in the studied soil sample and  $C_{fe}$  (sample) denotes the concentration of iron (the reference element) in the same soil sample. Similarly,  $C_n$  (background) and  $C_{fe}$  (background) refer to the concentrations of the element and reference element in the background or reference sample, respectively.

In environmental studies, elements such as aluminum, scandium, zirconium, titanium, and iron are commonly used as reference elements because of their relatively low variability (Abraham and Parker, 2008). These elements serve as suitable references for calculating the enrichment factors. In the study area, the element iron (Fe) was chosen as the reference element to calculate the enrichment factor. This selection was based on the geochemical characteristics of Fe, which exhibited modest changes and low mobility within the geochemical environment (Cevik et al., 2009). Using Fe as the reference element, the enrichment factor can effectively assess the contamination and enrichment levels of other elements in the study area. The enrichment factor calculation provides valuable insights into the origin of elements in environmental samples, whether they

stem from natural sources or human activities (Atiemo et al., 2011). When the enrichment factor is low, it suggests that the observed pollution is not significant. Low enrichment values may be attributed to slight differences in the composition of the local soils or the choice of reference elements used in the calculation (Lu et al., 2009). On the other hand, an enrichment factor greater than 1.5 indicates a human-induced source, whereas a value between 0.5 and 1.5 typically represents a natural origin (Zhang and Liu, 2002). These thresholds served as indicators to distinguish between natural and anthropogenic influences on element concentrations in the study area. Based on the enrichment factor (EF) values obtained from the soil samples, the contamination levels of metals were classified into five categories according to the Sutherland classification: no enrichment to low enrichment ( $EF < 2$ ), medium enrichment ( $2 < EF < 5$ ), significant enrichment ( $5 < EF < 20$ ), very high enrichment ( $20 < EF < 40$ ), and Infinity high enrichment ( $EF > 40$ ) (Sutherland, 2000).

#### **Index of Geo-accumulation**

The geo-accumulation index was used to evaluate the degree of metal pollution in the soil. It was calculated using the following equation proposed by Muller (1969):

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n} \quad (2)$$

where  $I_{geo}$  is the geo-accumulation index,  $\log_2$  is the logarithm of base 2,  $C_n$  is the concentration of a specific element in the soil sample, and  $B_n$  is the background concentration of the studied element, typically represented by the average shale composition. To account for natural fluctuations, low human impact, and local variations compared to the background, a correction coefficient of 1.5 is often used (Ji et al., 2008). Based on  $I_{geo}$  values, soils can be classified into seven groups according to the degree of contamination: no contamination ( $I_{geo} < 0$ ), no pollution to moderate contamination ( $0 < I_{geo} < 1$ ), moderate contamination ( $1 < I_{geo} < 2$ ), moderate to severe contamination ( $2 < I_{geo} < 3$ ), severe contamination ( $3 < I_{geo} < 4$ ),

severe infections ( $4 < I_{geo} < 5$ ), highly contaminated contamination (extremely contaminated) ( $I_{geo} > 5$ ) (Muller, 1969).

#### **Contamination Factor (CF)**

Contamination factor (CF) is a method used to assess soil pollution caused by heavy elements. This involves comparing the concentrations of elements in the soil to their natural background levels and determining the degree of contamination. The contamination factors for the studied elements were calculated using the equation proposed by Hakanson (1980):

$$CF = \frac{C_{sample}}{C_{background}} \quad (3)$$

In this equation, CF is the contaminant factor, C is the concentration of the specific element in the studied soil sample, and C background is the concentration of the element in the background sample, which is typically derived from the combination of the mean crust. According to the Hakanson classification, the contamination factor is categorized into four groups: low contamination factor ( $CF < 1$ ), moderate contamination factor ( $1 \leq CF < 3$ ), significant contamination factor ( $3 \leq CF < 6$ ), and very high contamination factor ( $CF \geq 6$ ).

The degree of soil contamination ( $C_d$ ) was calculated based on the total contamination factor of the studied metals. The soil was classified into four groups according to the degree of contamination: low degree of contamination ( $C_d < 8$ ), average degree of pollution ( $8 \leq C_d < 16$ ), significant degree of contamination ( $16 \leq C_d < 32$ ), and high degree of contamination ( $C_d \geq 32$ ) (Hakanson, 1980).

#### **The zoning of heavy metals in the soil**

Creating an equivalent map of heavy metal distribution using ArcGIS 10.4 software through the Inverse Distance Weighting (IDW) interpolation method is a commonly used approach to evaluate the concentration of heavy metals in a study area. Colorimetric methods are often applied to maps to enhance the understanding of contamination risk. Darker colors typically represent high concentrations of heavy metals, whereas brighter colors indicate

lower concentrations. This color-coded map allows for easy identification of areas with different levels of contamination. By utilizing these maps, important information can be obtained for the selection and identification of suitable areas for various land uses or soil remediation. Contaminated or potentially contaminated areas can be identified, helping to make informed decisions regarding land management, site remediation, and other land-use planning activities.

**Statistical ways of Data Analysis**

To study the statistical relationship between the elements and determine the potential sources of metals in the soil, the results were analyzed statistically. Descriptive statistics, Pearson correlation coefficients, and cluster analyses were calculated using the SPSS 16 software.

**Results and Discussion**

**Statistical description of the data**

The statistical analysis of the physical and

chemical properties of the soil in the samples taken from the study area is shown in Table 1. The coefficient of equivalent calcium carbonate, electrical conductivity, and clay at the measured points is higher than 50%, which indicates that there is a significant change in the concentration of these variables in the soil of the study area. Among the physical and chemical properties, the pH had the lowest coefficient of variation. The data skidding index shows that the organic carbon histogram and sand have negative skewness, while the rest of the soil properties are skewed positively. High variations in electrical conductivity and silt percentage indicated a high variety of soil samples in terms of chemical and physical properties. Based on the experimental results, the range of soil texture variations in the lime-sandy to loamy-silt regions is significant. The distribution of parameters such as silt, sand, organic carbon, organic matter, and pH, based on the Shapiro-Wilk test, follows the normal function. The soil was neutral-to-alkaline.

**Table 1:** Statistical summary of physical and chemical properties of soil in the study area

Soil parameters	Minimum	Maximum	Mean	Std. Deviation	CV(%)	Skewness	Kurtosis	Shapiro-wilk
pH	7.11	8.14	7.62	.2537	3	.099	-.182	0.95
EC (µS/cm)	53.50	2480.00	94.25	627.50	665	2.67	7.09	0
Calcium carbonate equivalent (%)	4.75	40.38	14.25	10.06	70	1.11	.880	0.02
Organic matter (%)	.90	2.67	1.68	.4839	28	.283	-.576	0.28
Organic carbon (%)	.99	3.45	2.17	.6870	31	-.022	-.401	0.43
Sand (%)	5.15	73.38	45.70	20.89	45	-.412	-.649	0.17
Clay (%)	3.86	32.18	6.43	7.42	115	1.643	2.718	0.00
Silt (%)	3.45	88.42	49.14	25.24	51	.114	-.017	0.39

The descriptive statistics of heavy metal concentrations in the soil samples of the study area are summarized in Table 2. Among the measured heavy metals, the highest mean concentration of metals in the studied soil was related to zinc (57.19), whereas the lowest mean concentration was molybdenum metal (0.357). The average concentration of metals in the soils of the study area decreased in the following order: zinc > copper > lead > arsenic > antimony > molybdenum. The coefficient of variation (CV) indicates the degree of variation in the

concentration of metals in the soil.  $CV \leq 20\%$  indicates slight variability,  $21\% \leq CV < 50\%$  indicates moderate variability, and  $50\% < CV \leq 100\%$  indicates high variability and change coefficients above 100% indicates infinite variability (Karimi Nezhad et al. 2015). The coefficients of change in the concentrations of metals in the studied soils were molybdenum (84.76) > lead (52.96) > copper (38.52) > antimony (36.63) > zinc (33.15) > arsenic (29.97). High values of the coefficient of variation for molybdenum

and lead metals show significant changes in the concentration of these metals at different sampling locations and also indicate their heterogeneous distribution due to human activities. In other words, the distance from the contamination source can affect the increase or decrease in pollutant concentrations. The coefficients of variation of arsenic, copper, antimony and zinc showed moderate variation, which reflects the relatively non-homogeneous distribution of these elements in the soil of the study area. The standard deviation of the concentration of metals in the soil decreased in the order zinc>copper> lead>arsenic> antimony> molybdenum. High levels of standard deviation reflect a wide range of metal changes in the periphery of the city, which was observed for zinc, copper, lead and antimony. The densities of

all the metals were positive, indicating a positive tendency toward lower concentrations. The elongation rates of all elements except lead and molybdenum were negative, which indicates a slope of the distribution diagram of these elements relative to the normal distribution curve.

The average concentrations of heavy metals in the study area for copper, molybdenum, lead and zinc were lower than the average concentration in the Earth's crust. The concentrations of arsenic and antimony are higher than those of these metals in the Earth's crust. The high concentrations of these metals determine the role of human resources and industrial plants in soil contamination. In this study, the lead, zinc and copper concentrations were affected more by human resources.

**Table 2:** Statistical summary of the concentration of heavy metals in soil samples (number: 20) in the eastern part of Urmia city (mg/kg)

Statistical Analysis	As	Cu	Mo	Pb	Sb	Zn
Minimum	4.18	10.96	.02	3.68	.57	33.90
Maximum	10.67	38.18	1.32	18.15	1.69	94.32
Mean	7.04	21.57	.357	7.60	1.02	57.19
Std. Deviation	2.11	8.31	.302	4.025	.373	18.96
CV (%)	29.97	38.52	84.76	52.96	36.63	33.15
Skewness	.493	.749	2.48	1.611	.249	.666
Kurtosis	-1.02	-.586	6.903	2.396	-1.217	-.671
Shapiro-wilk	0	0.29	0	0.003	0.07	0.56
Dried bed of Urmia Lake	24.57	8.24	0.37	3.26	0.53	26.38
Average Shale <sup>a</sup>	13	45	2.6	20	1.5	95
Iran-EPA guidelines <sup>b</sup>	18	100	10	50	10	200
Canadian soil quality guidelines	12	63	5	70	20	200
Earth's soil <sup>d</sup>	5	26		29		60
Earth's crust <sup>c</sup>	1.5	50	1.5	14	0.2	75

References: <sup>a</sup> (Turekian and Wedepoh 1961); <sup>b</sup> (Department of Environmental Protection 2017); <sup>c</sup> (CCME 2007); <sup>d</sup> (Mirsal 2008); <sup>e</sup> (Alloway, 1995)

Table 3 lists the statistical characteristics of the enrichment factor, contamination factor, and geoaccumulation coefficient. The average enrichment factor decreased as follows: arsenic> antimony> zinc> lead> copper> molybdenum. It can be stated that the highest soil enrichment with metals based on the EF index is related to arsenic and the lowest is related to molybdenum. The average CF content also decreased in the order arsenic> antimony> zinc> lead> copper> molybdenum. The average  $I_{geo}$  exhibited a downward trend for zinc>

copper> lead> arsenic> molybdenum> antimony. In other words, the average of the two CF and EF indices showed a similar decrease for the studied metals. The amount of contamination factor in the study area for arsenic metal showed that 65.54% of the samples had very high pollution, 32.47% had significant pollution, and 1.98% of them were in the middle class. In addition, 39.48% and 43.22% of the samples also had very high and significant contamination with antimony, respectively. For zinc and lead metals, 66.94% and 75.41% of the

samples had low pollution, and 33.05% and 24.58% of them had mean contamination, respectively. In addition, according to the contamination factor classification, 100% of the soil samples had low pollution for copper and molybdenum elements.

Based on the results of calculating the geo-accumulation indexes, arsenic, copper, and zinc elements in all samples were in the infinite pollution class ( $I_{geo} > 5$ ), and for lead element 96.10% of the samples had infinite

pollution. Of the soil samples, 29.43% were moderate in terms of antimony anti-pollution contamination, whereas no trace of contamination with this element was observed in 70.56%. In addition, 5.10% of the samples had moderate contamination with molybdenum, and in the other samples, no contamination was observed. Figure 3 shows the distribution of  $I_{geo}$  and CF indices for each heavy metal in the box diagram.

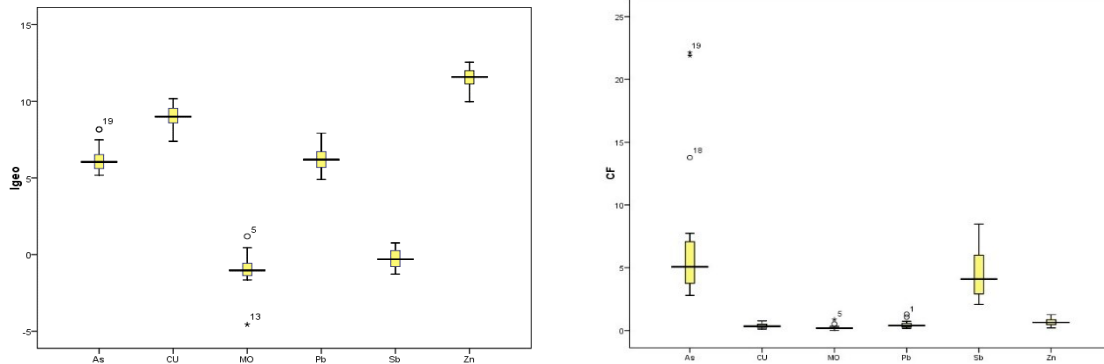


Figure 3: Box diagram of  $I_{geo}$  and CF values of heavy metals studied

The enrichment factor classification results showed that 62.13% and 20.85% of arsenic and antimony caused infinite enrichment rates, respectively. In addition, 36/18 and 79/14 percent of the samples showed high levels of enrichment for these elements. Copper, molybdenum, and lead were 11.76% and 43.56%, respectively, and 2.48%, lacking enrichment and low enrichment, respectively.

The percentage enrichment factor of arsenic (57.24%) was higher than that of other heavy metals. This is probably due to environmental changes associated with

human activity. The lower percentages of enrichment factors for molybdenum (1.71%), Copper (2.49%), lead (3.11%), and zinc (4.57%) may also be attributed to the natural origin of these metals. According to the EF and CF indices, in the present study, arsenic is highly enriched in soil and has a very high potential for contamination. As an enriched pollutant in the soil, arsenic is an unnecessary metal for the human body, and excessive absorption of this metal can lead to pulmonary, metastatic, and cancerous diseases; nervous system problems; and liver damage (Fujihara, 2009).

Table 3: Statistical Characteristics of Enrichment Factor, Contamination Factor, and Land massification Coefficient of Heavy Metals in the Soil of the Study Area

Indicator	Values	As	Cu	Mo	Pb	Sb	Zn
EF	Minimum	19.44	1.37	0.11	1.56	20.24	2.60
	Maximum	271.24	4.91	5.77	6.50	46.14	9.79
	Mean	57.62	2.51	1.73	3.13	31.05	4.60
CF	Minimum	2.79	0.11	0.02	0.16	2.07	0.21
	Maximum	22.13	0.76	0.88	1.30	8.47	1.26
	Mean	7.03	0.37	0.24	0.48	4.64	0.68
$I_{geo}$	Minimum	5.18	7.39	-4.56	4.90	-1.27	9.98
	Maximum	8.17	10.16	1.19	7.92	0.76	12.54
	Mean	6.22	8.97	-1.00	6.28	-0.22	11.53

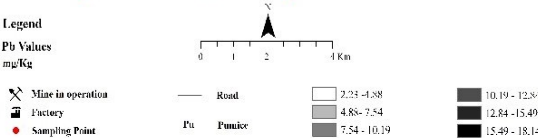
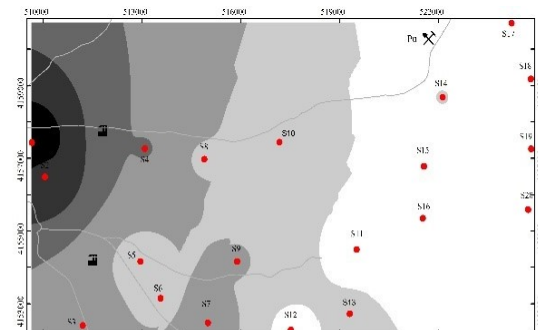
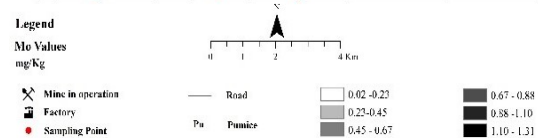
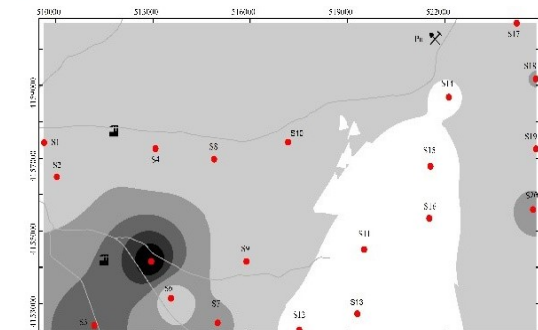
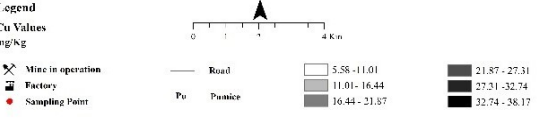
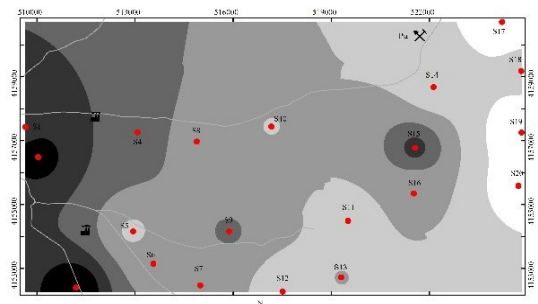
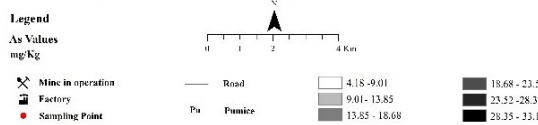
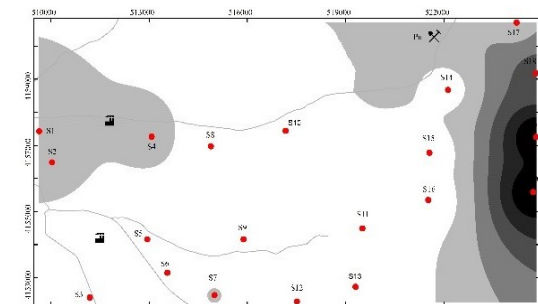


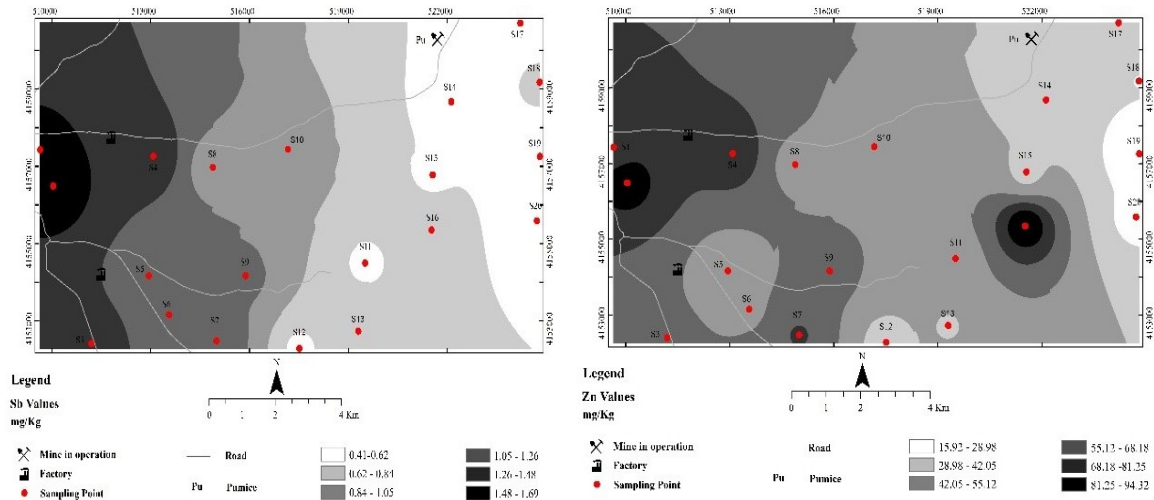
Figure 4 shows the spatial distribution map of the total concentrations of the elements studied using the interpolation method. According to the shape, the western part of the area has higher levels of copper, lead, antimony, and zinc, where the industrial complexes are located. Industrial activities, atmospheric subsidence, traffic, and smoke from fossil fuels can increase the concentration of elements in the area. Environmental conditions, such as atmospheric conditions and annual rainfall, slope, geographic location, type of materials used in factories, production levels, factory age, and dominant winds affect the distribution of atmospheric deposition (Tiller et al., 1976). As shown in Figure 4, the highest concentration of molybdenum was observed around the factory in the southwestern part of the region. The southwestern part consists of alleys and alluvial deposits of young, thin to moderate limestone sandstones with marl. The average concentration of

molybdenum calculated in the region shows the lower limit of contamination, and only at this high concentration point was observed.

According to the spatial distribution map, copper, lead, antimony, and zinc elements exhibit similar spatial variations and are more affected by human activities of the same origin. On the other hand, the spatial distribution pattern of arsenic is inversely proportional to previous metals and from the west to the east of the region, reducing the distance from the dry bed of Urmia Lake. The increase in arsenic in the periphery of the city was probably due to the atmospheric deposition of particles caused by industrial emissions.

Mohammadi et al. (2018) pointed to the different distribution of arsenic compared to other heavy metals in the northeastern, southern, and southwestern parts of the lake in the evaluation of heavy metals in the soil of agricultural areas around the Urmia Lake.





**Figure 4:** Spatial Distribution Map of Heavy Metals Concentration in the Study Area

Arsenic sources in the northeast of the local industrial areas, southern regions, roads, and southwestern parts, as well as cement plant publishing, have been reported to increase arsenic concentrations (Mohammadi et al., 2018).

**Correlation analysis of heavy metals**

The correlation coefficients of heavy metals in the soil of the study area are presented in Table 4. According to the correlation coefficient matrix, copper showed a positive and significant correlation with lead ( $r = 0.75$ ), antimony ( $r = 0.81$ ), and

zinc ( $r = 0.67$ ) at a confidence level of 0.01. Therefore, copper, lead, antimony and zinc may have similar origins in the samples. Arsenic has a negative and significant correlation with zinc ( $r = - .47$ ,  $P < 0.05$ ) which can be due to different geochemical behaviors of these two elements in the soil. Molybdenum has a low correlation with all the elements, and it can be deduced that the concentration of metals is not dependent on molybdenum. According to the results in this table, no correlation was found between the other parameters.

**Table 4:** Pearson Correlation Coefficients of the Investigated Elements

	As	Cu	MO	Pb	Sb	Zn
As	1					
Cu	-0.433	1				
MO	0.077	0.104	1			
Pb	-0.191	.758**	0.077	1		
Sb	-0.276	.819**	0.311	.883**	1	
Zn	-.470*	.678**	-0.071	.673**	.723**	1

\*. Correlation is significant at the 0.05 level.

\*\* . Correlation is significant at the 0.01 level.

According to the cluster diagram in Fig. 5, the elements are located in five clusters: the first cluster, MO; the second cluster, As; the third cluster, Pb; the fourth cluster, Zn; and

the fifth cluster, Sb and Cu. The presence of Sb and Cu in a cluster and their relationship with the cluster represent the same origins of these elements.



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