



Evaluation of contamination by heavy metals around Urmia lake and Urmia city based on soil pollution indicators

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Article Info

Article type:
Research Article

Article history:

Received: September 2022

Accepted: July 2023

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Keywords:

Heavy metals
Soil contamination
Urmia Lake
Farming land

Abstract

The primary objective of this study is to evaluate the spatial distribution of heavy metals in the sediment of the western bed of Urmia Lake and its adjacent soil, utilizing pollution indicators. To achieve this goal, we collected twenty samples of soil and surface sediment from depths of 0-20 cm and determined the concentration of heavy metals through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The average total concentrations of nickel, manganese, cadmium, chromium, boron, and bismuth were found to be 19.97, 163.56, 0.39, 14.68, 68.38, and 0.76 mg kg⁻¹, respectively. The Geo-accumulation index categorizes nickel, manganese, chromium, cadmium, and boron as non-polluted, while bismuth falls into the moderate pollution category. Enrichment factor analysis reveals moderate to severe levels for manganese, severe levels for nickel, chromium, and boron, and enormous enrichment levels for cadmium and bismuth. Calculation of Contamination Factors in the region indicates that cadmium, boron, and bismuth fall into the middle pollution category. The Pearson correlation coefficient analysis demonstrates a negative correlation between the calcium carbonate content of the soil and all metals, suggesting that higher calcium carbonate content reduces mobility and diminishes heavy metal pollution. The study's findings highlight a significantly elevated total concentration of boron in the sediments of the Urmia Lake bed compared to the average crust. Additionally, the concentration of cadmium in agricultural land surpasses the earth's crust average, signaling the need for control measures to reduce the use of chemical fertilizers as a contributing factor to increased cadmium concentrations.

Cite this article: Naghshafkan, Fatemeh; Pirkharati, Hossein; Farhadi, Khalil; Soltananejad, Nooshin. 2023. Evaluation of contamination by heavy metals around Urmia lake and Urmia city based on soil pollution indicators. *Environmental Resources Research*, 11(2), 271-282.



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DOI: 10.22069/ijerr.2024.20569.1382

Publisher: Gorgan University of Agricultural Sciences and Natural Resources

Introduction

Urmia Lake stands as one of the world's three largest saline lakes, facing a substantial decrease in water levels over recent decades due to natural and human factors. Approximately 70% of its area has become saline, posing environmental challenges (Garousi et al., 2017; AghaKouchak et al., 2015). The exposed lake bed has led to wind erosion, potentially transforming sediment into saline dust. Salts containing heavy metals present a significant threat to the health of both human and agricultural communities in the region (Gholampour et al., 2015; Mardi et al., 2018). Moreover, the mud of Urmia Lake has long been recognized for its medicinal properties, making it crucial to understand the characteristics and elemental composition of these muds, particularly within the lake bed boundaries (Djamali et al., 2008). Given the limited solubility of heavy metals in water, lakes at the catchment base become key reservoirs for sediment. Consequently, these areas may experience significant concentrations of heavy metals (Suresh et al., 2012). It is an established fact that environmental and geological changes constantly impact human health, animals, and ecosystems (Bai et al., 2011). With a burgeoning population and growing demand for agricultural products, soil resources are under immense pressure, leading to the annual application of thousands of tons of chemical fertilizers and pesticides to enhance soil productivity (Teng et al., 2010; Wu et al., 2018).

Recent studies, such as that of Muhammad and Ullah (2022) on Sadpara Lake in Pakistan, underscore the contamination of sediments with heavy metals. Oura et al. (2022) explored the spatial distribution of heavy metals in the Ivorian coastal zone, revealing high contamination levels, particularly with Cadmium, Chromium, and Arsenic. Numerous studies consistently demonstrate that elevated concentrations of heavy metals in the environment, especially in soil, can accumulate in the food chain, resulting in severe poisoning in higher-level organisms (Doabi et al., 2018; Wu et al.,

2018; Jiang et al., 2021; Khan et al., 2022). The objective of this study is to assess the concentration of heavy metals in both agricultural land and the lake bed of Urmia, along with its coasts, utilizing soil pollution indicators such as the Geo-accumulation Index, Enrichment Factor, and Contamination Factor. Pearson correlation matrices are employed to identify correlations between heavy metals and the physical and chemical properties of the soil. These findings are essential for devising strategies to control and manage heavy-metal pollution in Urmia Lake.

Materials and Methods

Study Area

The study area is located in Iran, west Azerbaijan Province in the east of Urmia City and the western coasts of Urmia Lake between the geographical latitudes $45^{\circ} 32' 4''$ and $45^{\circ} 14' 53''$, and the geographical longitude $37^{\circ} 34' 4''$ and $37^{\circ} 33' 44''$ (Figure 1). According to the data from the Meteorological Organization of West Azerbaijan Province, Urmia city has a semi-arid climate with a mean annual rainfall of 275 mm and the air temperature of 14 degrees Celsius (Vaheddost and Aksoy, 2017). The geology of the region is generally composed of alluvial deposits and quaternary strips, covering the entire area with fine-grained and sandy sediments (Figure 1).

Sampling and analysis

Plastic hoses were utilized for the extraction of soil samples from depths of 0–20 cm. A total of 20 surface soil samples were meticulously collected from both agricultural zones and the sediment areas surrounding the Urmia basin in West Azerbaijan province. The sampling process involved obtaining samples labeled 1 to 15 from agricultural land and 15 to 20 from the bed and margins of Lake Urmia. Geographical coordinates of the sampling points were accurately recorded using a portable GPS device (refer to Figure 1). To minimize the risk of potential contamination, all specimens were gathered using plastic hoses and deposited into plastic bags. Upon transportation to the laboratory, the samples

underwent a drying process at room temperature. Subsequently, the samples were sifted through a 2 mm sieve (mesh 10) to separate coarse grains, pebbles, and plant lesions. The soil's pH and electrical conductivity were determined in the extracted saturated mud, following the methods outlined by Thomas (1996) and Roades (1962). Additionally, the weight

percentage of organic matter was quantified using the Walkley and Blake method (1934), while the calcium carbonate percentage was calculated employing the neutral method with acid, as detailed by Roades (1962). Particle size distribution analysis was conducted according to Stokes' law utilizing the hydrometric method (Gee and Bauder, 1986).

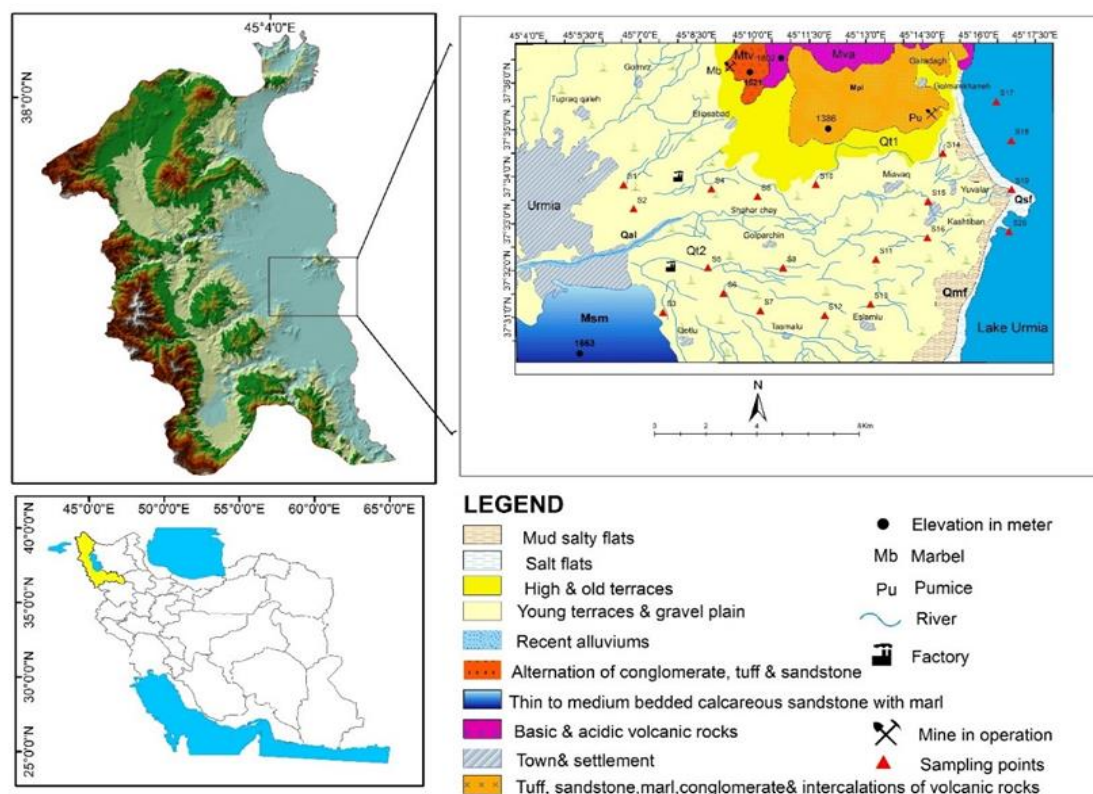


Figure 1. Position and Geology Map of the study area and the sampling points

Total heavy metal concentrations were determined through the digestion method (Rowell, 1994). This involved introducing 2 g of airborne dust into a 150 ml-capacity container, adding 10 ml of 65% nitric acid in a 1:1 ratio, and thorough mixing. To prevent content evaporation, the container was covered with glass and heated at 95 degrees inside a water bath for 15 minutes without agitation. Following cooling, 5 ml of concentrated nitric acid was added and heated to just below boiling point for 30 minutes, repeating this phase. Subsequently, 2 ml of distilled water and 3 ml of 95% hydrogen peroxide were added to initiate the reaction. After removing any foam, 1 ml of distilled water, 5 ml of

hydrochloric acid (37% HCl), and 10 ml of distilled water were sequentially introduced to the mixture over a 15-minute period. After cooling, the samples were filtered through a paper filter and distilled into distilled water. The total concentration of heavy metals in the resulting extracts was ultimately measured using ICP-MS-Perkin Elmer induction plasma spectroscopy.

Heavy Metals Pollution indicators

Heavy metals tend to accumulate predominantly in soil particles, particularly clay particles, where their persistence impedes decomposition and results in prolonged soil accumulation. However, relying solely on the concentration of heavy

metals may not provide a comprehensive measure for assessing soil contamination by these elements (Su and Yang, 2008). Therefore, to gauge the severity of soil pollution, indicators specific to heavy metals are employed. The Enrichment Factor (Ef) serves as a crucial tool for evaluating the enrichment of heavy metals in soil in comparison to bedrock or due to anthropogenic activities. Calculating the enrichment factor is a fitting method for discerning whether contamination is of natural origin or induced by human activities (Adamo et al., 2005). In determining the enrichment factor in a soil or sediment sample, the concentration of the element under consideration is measured relative to a reference element,

such as manganese, aluminum, iron, or cesium. In this study, aluminum (Al) has been chosen as the reference element due to its consistent distribution in the environment (normal Al distribution), and its concentration remains unaffected by human activities (Chabukdhara and Nema, 2012; Zoller et al., 1974).

The Geo-accumulation Index (I_{geo}), developed by Muller in 1969, stands out as a significant indicator in soil studies, aiding in the identification of heavy metal pollution levels. Additionally, the Contamination Factor (CF) is utilized as a determinant of environmental quality (Wojciechowska et al., 2019). The formulas and acceptable ranges for these indicators are presented in Table 1.

Table 1. Heavy Metals Pollution indicators and their Ranges

Factor	formulas	References	Ranges
Ef	$EF = \frac{C_n/C_{ref}}{B_n/B_{ref}}$	Li et al., 2013	50> Extremely severe enrichment, 25-<50 Very severe enrichment, 10-<25 Severe enrichment, 5-<10 Moderately severe enrichment, 3-<5 Moderate enrichment, 1-<3 Minor enrichment, <1 No enrichment
I _{geo}	$I_{geo} = \log_2 (C_n / 1.5 B_n)$	Chowdhury and Maiti, 2016	4<I _{geo} <5 Heavily to extremely contaminated, 3 < I _{geo} <4 Heavily contaminated, 2<I _{geo} <3 Moderately to heavily contaminated, 1<I _{geo} <2 Moderately contaminated, 0 < I _{geo} < 1 Uncontaminated to Moderately contaminated, I _{geo} ≤0 Practically uncontaminated
Cf	$CF = C_n / C_b$	Kabata-Pendias, 2011	6≤CF Very high contamination factor, 3≤CF<6 Considerable contamination factor, 1≤CF<3 Moderate contamination factor, CF<1 Low contamination factor

C_n, the concentration of the element in the sample, and C_{ref} is the concentration of the reference element (Al) in the study area, also B_n is content of the element in the reference medium (mean of earth crust) and B_{ref} is concentration of the reference element (Al) in the reference medium (average of earth crust), C_b is the natural concentration of the same element in question.

Results and Discussion

The physical and chemical properties of soil play a crucial role in influencing the behavior of elements within geochemical environments. Figure 2 and Figure 3 present the zoning maps and the physical and chemical properties of the studied soil, respectively. pH, in most cases, is considered the primary soil variable, significantly impacting chemical reactions and processes. Its measurement is essential for determining soil acidity or alkalinity. The soil pH values in the studied region

range from 7.1 to 8.1, with an average of 7.5. The highest acidity of saturated mud is found in Lake Urmia sediments, while the lowest is observed in the agricultural areas. Generally, acidity and alkalinity increase toward the lake, with agricultural land exhibiting a slightly alkaline pH that fluctuates.

Given the high salt content in Lake Urmia's bed, Sample No. 17 demonstrates the highest electrical conductivity at 2480 micro-Siemens per cm, while the minimum conductivity of 53.5 micro-Siemens is

recorded for Sample No. 4. Electrical conductivity increases from Urmia city's margin to the lake, indicating higher conductivity in sediment and marginal soils due to elevated salt levels. In agricultural soils, electrical conductivity fluctuates within the normal range, suggesting variations in organic matter, clay content, or chemical fertilizers. The calcium carbonate content in the studied samples ranges from 4.75% to 40.37%, exhibiting an increasing trend from west to east and the bed of Lake Urmia. Lake Urmia samples show the highest calcium carbonate content, with a mean of 16.34%, classifying the soils as relatively

calcareous. The mean percentages of clay, silt, and sand are 10.45%, 45.09%, and 44.48%, respectively. In comparison to sand and silt particles, the clay content is negligible. According to the Soil Classification Triangle (USDA, 1993), the studied soils from agricultural areas fall within the sandy loam and loamy silt texture class. These soils are characterized by a mixture of sand, silt, and clay. The organic matter content, highest in the agricultural area at 2.61%, results from agricultural activities and the use of animal manures for soil fertilization. Organic carbon content varies between 0.98% and 3.45%.

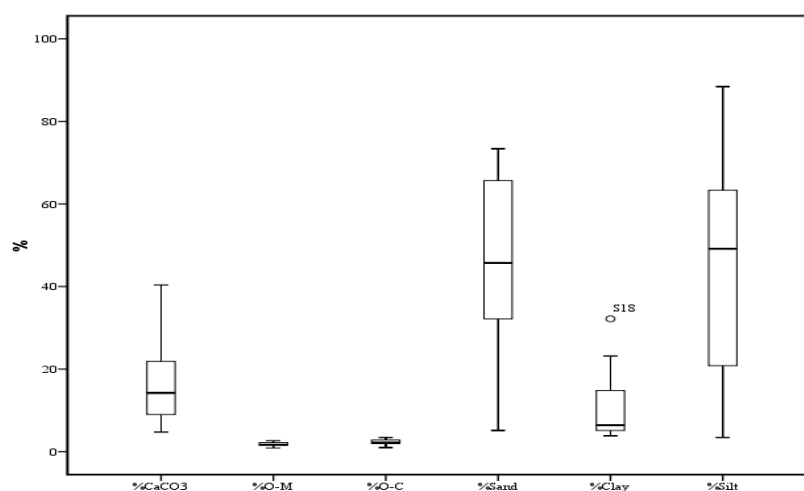


Figure 2. General properties of soils in the study area

Table 2 provides an overview of general descriptive information regarding heavy metals in the study area, while Figure 4 depicts zoning maps illustrating the total concentration of heavy metals in soil samples. The minimum and maximum concentrations of manganese in samples were 69.83 and 270.25 mg/kg, respectively, with a regional mean of 163.56 mg/kg. Manganese exhibits a negative skew, and its concentration distribution reveals higher values in samples from urban marginal areas designated for agricultural use. Nickel levels vary from 7.55 to 39.08 mg/kg, with a regional mean of 19.80 mg/kg, and the highest nickel concentration occurs in marginal city samples. Chromium distribution is uniform across the region,

with levels ranging from 5.12 to 28.63 mg/kg and a mean chromium concentration of 14.68 mg/kg. Cadmium content in samples ranges from 0.19 to 0.47 mg/kg, with a mean of 0.39 mg/kg. Notably, areas with agricultural use show significant proportions of cadmium. The results highlight that boron concentrations span from 38.10 to 283.50 mg/kg, with a mean value of 87.31 mg/kg. The maximum boron concentration is reported in samples from the Urmia Lake bed. Bismuth levels range from 0.03 to 1.65 mg/kg, with an average of 0.76 mg/kg. Similar to cadmium, the distribution of bismuth significantly exceeds the average values found in the Earth's crust (Kabata-Pendias and Mukherjee, 2007).

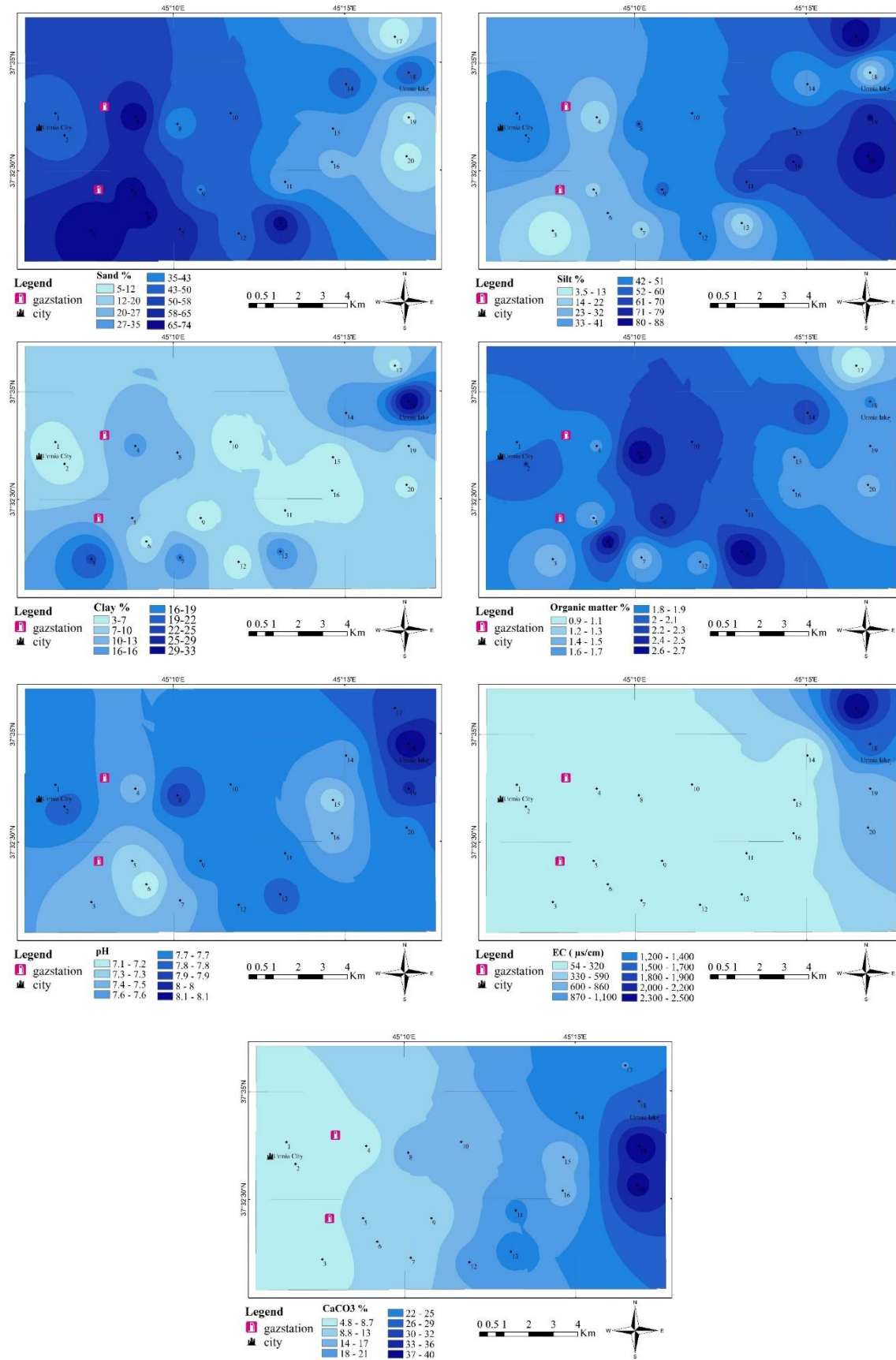
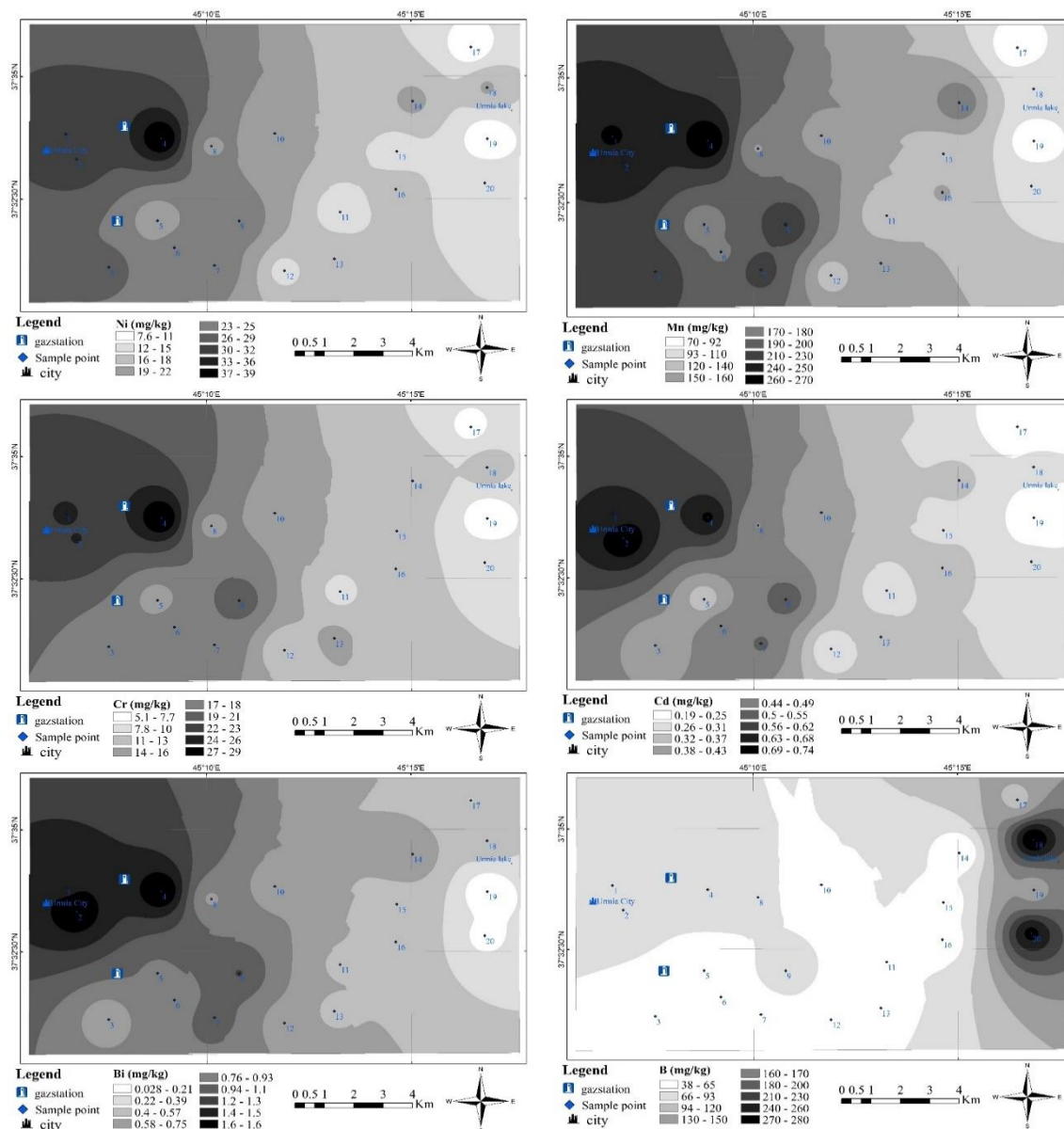


Figure 3. Spatial dispersion patterns for general properties of surface soils.

Table 2. Descriptive statistics of heavy metals in mg.kg-1 in the studied soils

	Minimum	Maximum	Mean	Std.deviation	Skewness	Kurtosis
Ni	7.55	39.08	19.79	7.92	0.67	0.43
Mn	69.83	270.25	163.56	58.33	0.24	-0.81
Cr	5.12	28.63	14.68	5.93	0.69	0.28
Cd	0.19	0.74	0.39	0.15	0.90	0.05
B	38.10	283.50	87.31	68.38	2.28	4.46
Bi	0.03	1.65	0.76	0.43	0.70	0.30



Statistical characteristics, including First Quartile Mean, Third Quartile, and irregular samples, of the soil pollution indicators are succinctly summarized in Figures 5 and Table 3. The assessment of soil contamination using the enrichment factor reveals a sequence of $Bi > Cd > B > Cr > Ni > Mn$, with the highest

enrichment observed for bismuth (mean of 42.50), cadmium (mean of 39.80), and boron (mean of 36.12), categorizing them as highly enriched. In Figure 5A, element boron exhibits significant enrichment in specimens 18 and 20 related to the Urmia basin, while samples 5 and 4 contain enriched bismuth

elements. Chromium demonstrates an average enrichment factor of 16.41, placing it in the strong enrichment category, whereas nickel's average enrichment factor is 10.85, with the city margin displaying the highest enrichment, and other areas showing moderate to severe enrichment. The mean Mn enrichment factor is 5.81, ranging from moderate to severe enrichment.

The geo-accumulation index categorizes nickel, magnesium, chromium, and cadmium as practically uncontaminated, while the geo-accumulation index for bismuth falls within the uncontaminated to moderately contaminated range (see Figure 5B). The contamination factor for the studied elements follows a similar trend to the enrichment factor, with $Bi > Cd > B > Cr > Ni > Mn$. The average pollution factor for bismuth is 1.90, placing it in the middle

class. Stations 1, 2, 4, 5, 6, 7, and 9 exhibit higher pollution rates, falling within the medium to high contamination levels. An examination of the element boron contamination factor indicates that most samples are uncontaminated to moderately contaminated, except for samples from Urmia Lake, which show significant contamination. Cadmium contamination factor identifies stations 19 and 17 as uncontaminated, while other stations exhibit moderate contamination. The chromogenic coefficient places stations 1, 2, 4, 7, and 9 in the moderate contamination class (between 1 to 3), while the remaining stations are categorized as uncontaminated. The contamination factor for nickel and manganese elements is less than one, indicating uncontaminated samples (refer to Table 4 and Figure 5).

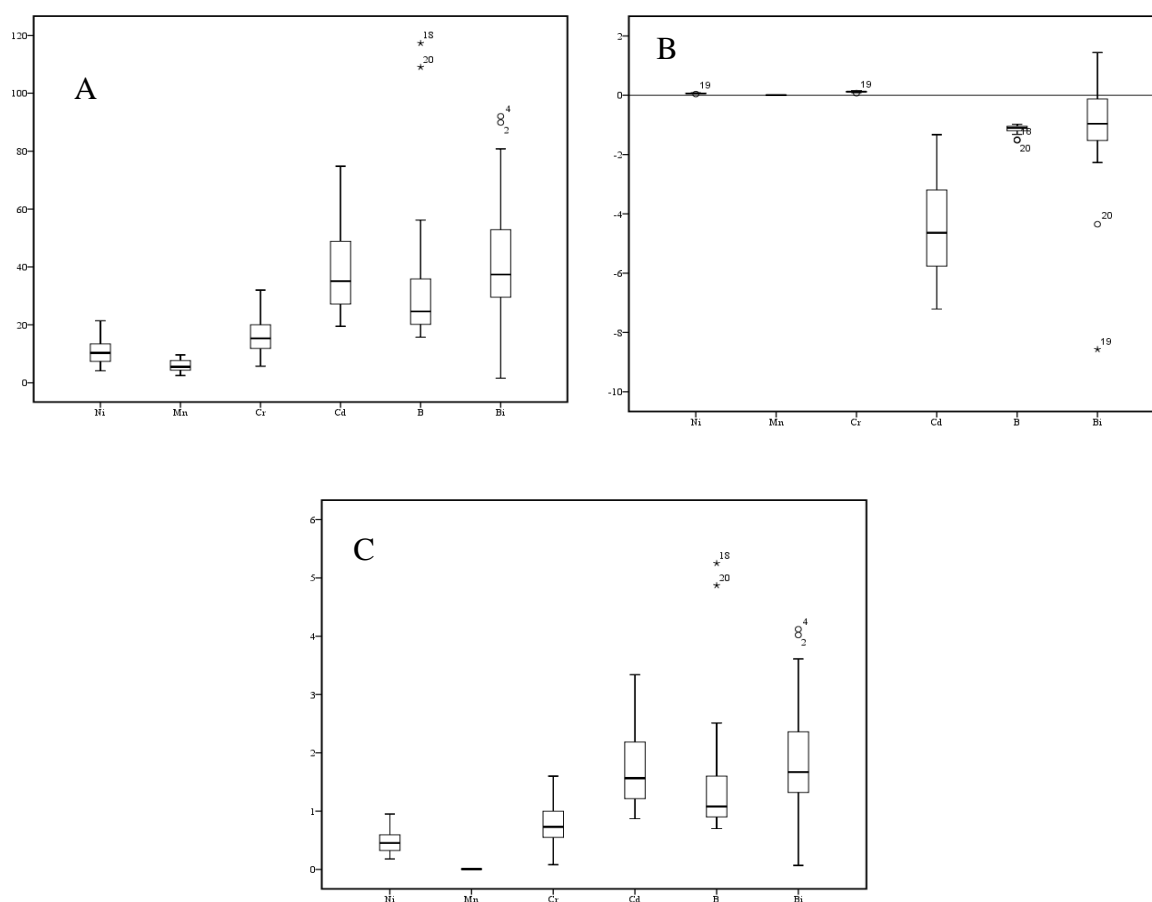


Figure 5. Average of the first and third quartiles of soil contamination indices in the study area, enrichment factor A, geo-accumulation index B, contamination factor C

Table 3. Average of contamination factors for the studied metals

	EF	Igeo	CF
Ni	10.84	0.064	0.481
Mn	5.80	0.007	0.006
Cr	16.39	0.119	0.781
Cd	39.79	-4.39	1.777
B	36.12	-1.15	1.61
Bi	42.50	-1.21	1.89

According to the Pearson correlation matrix provided in Table 4, nickel, cadmium, manganese, chromium, and bismuth metals exhibit a strong positive correlation of 95%, suggesting similar geochemical behaviors and likely indicating a common origin for these metals (Çevik et al., 2009). Conversely, the pseudo-metal does not show a significant correlation with any of the metals. The lime content in the soil and bed of Lake Urmia demonstrates a notable increase. These chemical properties of the soil show a negative correlation of 99% and 95% with all metals, highlighting their significance in reducing mobility and mitigating heavy metal pollution. The augmentation of lime content contributes to

a decreased risk of heavy metal presence. None of the investigated elements display a correlation with clay, but they do exhibit a significant correlation with the amounts of sand and soil silt. This aligns with findings from Zhang et al. (2009), where particles with average sizes demonstrated the highest correlation with heavy metals. This diminishes the adsorption of metals in the clay, reduces soil cation exchange, increases metal leaching, and enhances plant bioavailability. Boron shows a significant and positive correlation with pH, electrical conductivity (EC), and calcium carbonate at a 99% confidence level, indicating higher concentrations in both acidic and alkaline conditions.

Table 4. Pearson correlation between heavy metals and the general soils properties.

Items	Cr	Cd	Mn	Ni	B	Bi	PH	EC	CaCO ₃	OM	Sand	Clay	Silt
Cr	1												
Cd	.96**	1											
Mn	.95**	.92**	1										
Ni	.98**	.92**	.95**	1									
B	-.22	-.24	-.36	-.16	1								
Bi	.94**	.93**	.90**	.90**	-.31	1							
PH	-.28	-.22	-.37	-.25	.58**	-.24	1						
EC	-.46*	-.47*	-.57**	-.43	.62**	-.41	.51*	1					
CaCO ₃	-.76**	-.73**	-.79**	-.72**	.61**	-.79**	.52*	.45*	1				
O-M	.25	.28	.23	.21	-.23	.20	.06	-.51*	-.10	1			
Sand	.63**	.48*	.67**	.65**	-.37	.55*	-.42	-.53*	-.63**	.30	1		
Clay	.068	-.06	.081	.20	.36	-.05	.27	.20	.06	-.07	.46*	1	
Silt	-.54*	-.38	-.58**	-.60**	.20	-.05	.27	.38	.50*	-.22	-.96**	-.68**	1

* Significant Correlation at the 0.05 level

** Significant Correlation at the 0.01 level

Conclusion

Cadmium holds particular significance among heavy metals, exhibiting an absorption rate in plants that is 20 times higher than that of other heavy metals. Given its high enrichment factor and alarmingly elevated levels in agricultural areas, the primary contributing factors

include intensified agricultural activities, indiscriminate use of pesticides and fertilizers on agricultural land, and, in certain instances, the utilization of contaminated water for irrigation. Furthermore, the concentrations of boron and its compounds in Urmia Lake bed samples surpassed the average levels found

in the upper crust. Borax, a salt of boric acid, plays a pivotal role as one of the principal boron compounds. Its formation in lake environments, as observed in Urmia Lake, can be attributed to various factors outlined in this study. Notably, borax possesses antiseptic and anti-fungal properties, leading to its historical utilization in Urmia Lake for alleviating skin ailments and providing pain relief. Given the substantial concentrations of bismuth and boron in Lake Urmia sediments, further investigations in the medical domain, encompassing therapeutic applications and the potential respiratory risks associated with saltwater storms emanating from the lake bed containing

these elements, appear imperative.

The elevated levels of active mineral solvents and the abundance of calcium carbonate have resulted in the formation of complexes and insoluble compounds with heavy metals, diminishing their soluble form concentrations. It is pertinent to highlight that the concentrations of nickel, manganese, and chromium were reported as environmentally normal, posing no potential hazards.

Acknowledgments

The authors are very thankful to the Urmia Lake Research Institute for their support, cooperation, and sponsorship of this research.

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