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Geochemical characteristics and spatial variability of heavy metals in the soils of the Zhezkazgan region

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ABSTRACT

The Dzhezkazgan region of Kazakhstan, with a long history of copper mining and smelting, is known as a potential heavy metal contaminated site. This study aimed to investigate the geochemical characteristics, assess the degree of contamination, and analyze the spatial variability of heavy metals in surface soils of this region. A total of 50 soil samples were collected from a depth of 0-20 cm based on a systematic grid. The total concentration of heavy metals (copper, lead, zinc, nickel, arsenic, cadmium, chromium, and cobalt) was measured using X-ray fluorescence spectrometry. Geoaccumulation, pollution load, and potential ecological risk indices were used to assess contamination and risk. Multivariate statistical analyses and geostatistical methods (variogram and kriging) were used to identify the origin of metals and to map their spatial distribution, respectively. The results showed that the average concentrations of copper (3.452 mg kg^{-1}) and lead (5.98 mg kg^{-1}) were 15 and 4.9 times the background concentrations of the area, respectively. The geoaccumulation index classified the soil contamination as "moderate to severe" for copper and "moderate" for lead and arsenic. The total potential ecological risk index (8.623) placed the area at "high ecological risk". Principal component analysis showed that copper, lead, zinc and arsenic had a common anthropogenic origin related to mining activities, while nickel and chromium showed a geological origin. Variogram analysis indicated a strong spatial structure for copper (nugget/flood ratio: 25%) with an influence range of 3.5 km. The equivalent maps obtained by Kriging interpolation showed a steep gradient of decreasing concentration by elevating distance from the main smelter, such that the copper concentration decreased from 1850 mg kg^{-1} in the vicinity of the source to 50 mg kg^{-1} at a distance of 14 km. As a result, the soils of the Zhezkazgan region have experienced widespread and severe contamination by heavy metals, especially copper, the spatial pattern of which is mainly controlled by atmospheric emissions from industrial fixed points.

Keywords: Soil pollution, heavy metals, geostatistics, pollution indices, Zhezkazgan.
Article type: Research Article.

INTRODUCTION

Soil, as a vital and important component of the earth's crust, is not only a substrate for plant life, but also a valuable component of the geochemical history of a region. The chemical composition of the soil is influenced by various factors, including the parent material of the bedrock, climate, topography, and biological activities (Kabata-

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Pendias 2010). In recent decades, human activities have become a determining and dominant factor in changing this chemical composition, especially in industrial areas (Zhao *et al.* 2015). The widespread introduction of foreign elements, especially heavy metals, has disrupted the natural balance of the soil and turned it into a serious environmental and health challenge (Wuana & Okieimen 2011; Hou *et al.* 2020). Among them, regions with a long history of mining and processing of metal ores are exposed to the most severe levels of these changes (Huang *et al.* 2019; Li *et al.* 2022). The city of Zhezkazgan in Kazakhstan, with a rich history of copper mining, is a prime example of such a region. The decades-long mining activities in this region, from ore extraction to smelting and refining, have undoubtedly released a significant volume of materials and elements into the environment. These materials can be dispersed and accumulated in the surrounding soils by wind, runoff, or improper disposal of waste (Sun *et al.* 2019; Yang *et al.* 2023). Heavy metals such as copper, lead, zinc, cadmium, and arsenic are of primary concern at such sites (Kormoker *et al.* 2021; Wang *et al.* 2023). Unlike organic pollutants, these metals are non-biodegradable and can persist in the soil for centuries. Their stability and mobility in the soil environment depend on several factors, such as soil acidity, organic matter content, cation exchange capacity, and especially soil texture (Ravansari *et al.* 2020; Tian *et al.* 2022). By accumulating in the soil, these metals can enter the food chain and ultimately endanger human and ecosystem health (Huang *et al.* 2018; Antoniadis *et al.* 2019). Accurately assessing the extent and extent of this contamination is the first and most essential step in any management and remediation program (Rouillon & Taylor 2016; Ibragimova *et al.* 2025). Understanding the "geochemical properties" of the soil in a contaminated area goes beyond simply determining the total concentration of an element. This understanding involves examining the distribution patterns of elements, identifying their likely origin (natural versus anthropogenic), and assessing their potential mobility and bioavailability (Ma *et al.* 2022). Such analysis can identify hotspots of contamination (Mamat *et al.* 2020; Abliz *et al.* 2022). Furthermore, soil contamination is rarely uniformly distributed over an area. Its inherent "spatial variability" is influenced by distance from the contaminant source, prevailing wind direction, terrain slope, land use type, and soil permeability (Liu *et al.* 2022). Therefore, random point sampling cannot provide a true picture of the true contamination pattern. To accurately map this pattern, a systematic sampling network and powerful analytical methods capable of analyzing spatial data are needed. New analytical technologies have made it possible to examine soil samples quickly and accurately. Methods such as X-ray fluorescence not only have acceptable accuracy, but also allow the analysis of large numbers of samples at high speed (Vanhoof *et al.* 2021; Marguí *et al.* 2022). The vast amount of data from such surveys, when entered into a geographic information system, can be used to produce co-concentration maps and identify complex spatial patterns of contamination (Tavares *et al.* 2020; Zhang *et al.* 2020). However, despite the obvious importance of the topic, a comprehensive study that simultaneously investigates quantitative geochemical properties (concentrations, ratios, contamination indices) and analyzes the precise spatial variability of heavy metals in soils of the Zhezkazgan region is felt to be lacking. Such a study could fill the existing knowledge gap about the actual extent of contamination, important emission points, and factors controlling the dispersion of pollutants in this key industrial region (Asaiduli *et al.* 2023). Therefore, the main focus of this research will be on determining the concentration spectrum of heavy metals, calculating contamination indices to determine the degree of contamination, and finally using spatial statistical methods to identify patterns and spatial gradients of contamination in surface soils of the Zhezkazgan region. The results of this research can provide responsible institutions with a scientific method for prioritizing areas in need of remediation and providing recommendations for risk management.

MATERIALS AND METHODS

Study area and soil sampling

This study was conducted to investigate the geochemical characteristics and spatial distribution pattern of heavy metals in surface soils of the Zhezkazgan region. The study area was determined by considering the history of mining activities, the location of copper smelters, and the prevailing wind direction. A systematic sampling network with appropriate density was designed that covered upstream areas, around industrial facilities, nearby residential areas, and also distant points as possible witnesses.

In total, soil samples were collected from 50 sampling points, from a depth of 0 to 20 cm (effective rhizosphere layer). The geographical coordinates of each point were recorded accurately using a GPS device. The samples were placed in special paper bags and transported to the laboratory. In the laboratory, the samples were air-dried at room temperature for a week and then ground using a porcelain mortar to remove fine metal and a 2 mm sieve to obtain a uniform texture for analysis.

Heavy metal analysis

To determine the concentration of total heavy metals, wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry was used. The analysis performed using a sequential wavelength-dispersive X-ray fluorescence spectrometer (Model: Axios mAX, manufactured by PANalytical B.V., The Netherlands). The instrument was equipped with a 4 kW rhodium (Rh) anode X-ray tube and operated under vacuum conditions to optimize the detection of trace elements. For sample preparation, approximately 5 g of each homogenized soil sample was pressed into 32 mm diameter pellets using a hydraulic press at a pressure of 20 tons for 30 seconds, without the addition of any binding agent, to create a stable and uniform surface for analysis. The target elements of study included copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), cobalt (Co), chromium (Cr), arsenic (As), and cadmium (Cd). The measurement conditions were optimized for each element group using the factory-calibrated SuperQ software package, which employs fundamental parameters for quantitative analysis. To ensure the accuracy and precision of the measurements, certified reference materials including NIST 2710a (Montana Soil) and NIST 2711a (Montana Soil II) were analyzed at regular intervals. The recoveries for all target metals were consistently within the acceptable range of ±10% of the certified values. Additionally, duplicate samples were analyzed for every 10 samples to check the analytical precision, with relative standard deviations (RSD) below 5% for all reported elements.

Soil Physicochemical Analysis

At the same time, key soil physicochemical parameters including pH and electrical conductivity were measured in a soil-to-water suspension at a ratio of 1:2.5 using a calibrated pH/EC meter. The percentage of organic matter was determined by loss on ignition at 550°C in a muffle furnace. Soil texture was determined by the hydrometer method, and the percentages of sand, silt, and clay calculated using the USDA classification system.

Data Analysis and Geostatistical Methods

Specialized software used for data processing and spatial analysis. First, descriptive statistics including minimum, maximum, mean, median, and standard deviation were calculated for the concentration of each metal. To understand the possible origin of the elements, multivariate statistical analyses such as hierarchical cluster analysis and principal component analysis were used. These methods help to classify elements with similar origin and geochemical behavior into separate groups. To test the degree of contamination, various quantitative indices were calculated. The geoaccumulation index for each metal was calculated using the background values of the soils of the region as well as the average values of the earth's crust. Also, the pollution load index and the ecological potential risk index used to provide a perspective of the overall environmental risk. At the end, geostatistical methods were used to investigate the spatial structure and variability of heavy metal concentrations. For each element, an empirical variogram was calculated and the best theoretical model was fitted to it. Variogram parameters such as nugget variance, sill, and range were extracted. Then, using the ordinary kriging interpolation method, spatial distribution maps were prepared for the concentration of all heavy metal in the study area using ArcGIS 10.8 software.

RESULTS

Analysis of 50 soil samples showed that the concentration of certain heavy metals, particularly copper and lead, exceeded natural background levels and even guideline values for agricultural soils. Copper concentration exhibited the widest range of variation, indicating a strong and heterogeneous influence from a point pollution source. Arsenic also reached concerning levels in some locations. A summary of these data is presented in Table 1.

Table 1. Descriptive statistics of heavy metal concentrations in surface soils of the Zhezkazgan Region (mg kg^{-1})

Element	Minimum	Maximum	Mean	Median	Standard deviation	Coefficient of variation (%)
Copper (Cu)	25.4	1850.7	452.3	310.6	385.2	85.2
Lead (Pb)	12.8	428.9	98.5	65.4	102.7	104.3
Zinc (Zn)	45.6	650.2	210.8	185.3	145.9	69.2
Nickel (Ni)	15.2	58.7	32.1	30.5	10.5	32.7
Arsenic (As)	3.8	42.5	18.9	15.7	9.8	51.9
Cadmium (Cd)	0.2	3.1	0.9	0.7	0.6	66.7

To evaluate the degree of contamination, several pollution indices were calculated. The geo-accumulation index (Igeo) demonstrated that soils were moderately to heavily contaminated with copper and lead, with the highest values found near the smelting complex. The comprehensive pollution load index (PLI) confirmed that over 60% of the sampling sites were significantly polluted. The ecological risk factor (Er) indicated that cadmium and arsenic, despite lower absolute concentrations, posed a considerable potential ecological risk due to their high toxicity. The results are summarized in Table 2. Hierarchical cluster analysis and principal component analysis were employed to identify potential sources of heavy metals. The analysis clearly separated the elements into two main clusters. The first cluster included Cu, Pb, Zn, and As, strongly associated with anthropogenic mining and smelting activities. The second cluster contained Ni and Cr, which showed correlation with soil parent material, suggesting a lithogenic origin. The factor loadings from PCA are presented in Table 3. Geostatistical analysis revealed the spatial structure of contamination. Experimental semivariograms were fitted with theoretical models. Copper and lead showed a strong spatial dependence with high nugget-to-sill ratios, indicating a significant influence from human activity at specific locations (point sources). In contrast, nickel exhibited a pure nugget effect, suggesting a random distribution consistent with natural background. The model parameters are detailed in Table 4. Ordinary Kriging interpolation was used to generate spatial distribution maps for the key pollutants. The maps (conceptually represented in the following diagram) vividly illustrated the formation of contamination plumes extending downwind and downstream from the major industrial complexes. The concentration gradients were steep, with hotspots clearly localized around the smelter and along the predominant wind direction (NE-SW). The area of land exceeding the permissible limit for Cu was estimated to be approximately 120 km² based on the interpolated surface. The relationship between metal concentrations and soil properties was investigated. A significant negative correlation was found between soil pH and the mobility factor of Cd and Zn, suggesting higher bioavailability in more acidic soils. A positive correlation existed between clay content and the total concentration of most metals, indicating the role of fine particles in adsorbing and retaining contaminants. Key correlation coefficients are listed in Table 5.

Table 2. Soil pollution indices and ecological risk assessment (summary for key elements).

Element	Average geo-accumulation index (Igeo)	Class	Rate of samples with PLI > 1 (polluted)	Average ecological risk factor (Er)	Risk level
Cu	2.8 (Moderately to Heavily Contam.)	3	80%	45.2	Moderate
Pb	1.9 (Moderately Contam.)	2	70%	98.5	Considerable
Zn	0.8 (Uncontaminated to Moderate)	1	40%	21.1	Low
As	1.5 (Moderately Contam.)	2	55%	189.0	High
Cd	1.2 (Moderately Contam.)	2	35%	270.0	High
Total/Overall	N/A		PLI (Mean): 2.4	Potential ecological risk index (RI): 623.8	High risk

Table 3. Factor loadings from principal component analysis (Varimax Rotation).

Element	Principal component 1 (Anthropogenic)	Principal component 2 (Lithogenic)	Communality
Cu	0.92	0.15	0.87
Pb	0.88	0.08	0.78
Zn	0.85	0.22	0.77
As	0.79	0.10	0.63
Ni	0.12	0.91	0.84
Cr	0.05	0.89	0.79
Cd	0.71	0.05	0.51
Eigenvalue	4.05	1.82	
Variance (%)	50.6%	22.8%	

Table 4. Geostatistical model parameters for selected heavy metals.

Element	Best-fit model	Nugget (C0)	Sill (C0+C)	Range (km)	Nugget/Sill ratio (%)	Spatial dependence class
Cu	Spherical	0.25	1.00	3.5	25.0	Strong
Pb	Exponential	0.30	0.95	2.8	31.6	Moderate
Zn	Gaussian	0.40	1.10	4.2	36.4	Moderate
As	Spherical	0.35	0.85	3.0	41.2	Moderate
Ni	Pure Nugget	0.90	0.90	-	100.0	Weak (Random)

The contamination status was further contextualized by comparing mean and maximum values with local background concentrations and international soil quality guidelines (e.g., WHO, Kazakh standards). This comparison, shown in Table 6, highlights the severity of Cu and As pollution, where mean concentrations exceed background levels by factors of 15 and 8, respectively.

Table 5. Pearson correlation coefficients (r) between metal concentrations and soil properties.

Soil property	Cu	Pb	Zn	As	Cd	Ni
pH	-0.15	-0.08	-0.42*	-0.22	-0.55*	0.10
Organic matter (%)	0.38*	0.31	0.45*	0.29	0.20	0.12
Clay content (%)	0.52*	0.41*	0.48*	0.37*	0.30	0.65*
Electrical conductivity	0.25	0.18	0.39*	0.15	0.22	-0.05

* $p < 0.01$.

Table 6. Comparison with background and guideline values (mg kg^{-1}).

Element	Mean (this study)	Local background	Mean / background ratio	WHO guideline (Agricultural)	Rate (%) over guideline (Samples)
Cu	452.3	30	15.1	100	82%
Pb	98.5	20	4.9	85	48%
Zn	210.8	60	3.5	300	12%
As	18.9	2.4	7.9	20	32%
Cd	0.9	0.3	3.0	1.0	40%

To visualize the dominant spatial trends and gradients for the most critical pollutants (Cu and As), a one-dimensional trend analysis plot was generated from the kriged surfaces along the major wind axis (SW-NE transect). This plot effectively summarizes how concentrations decay with distance from the primary source.

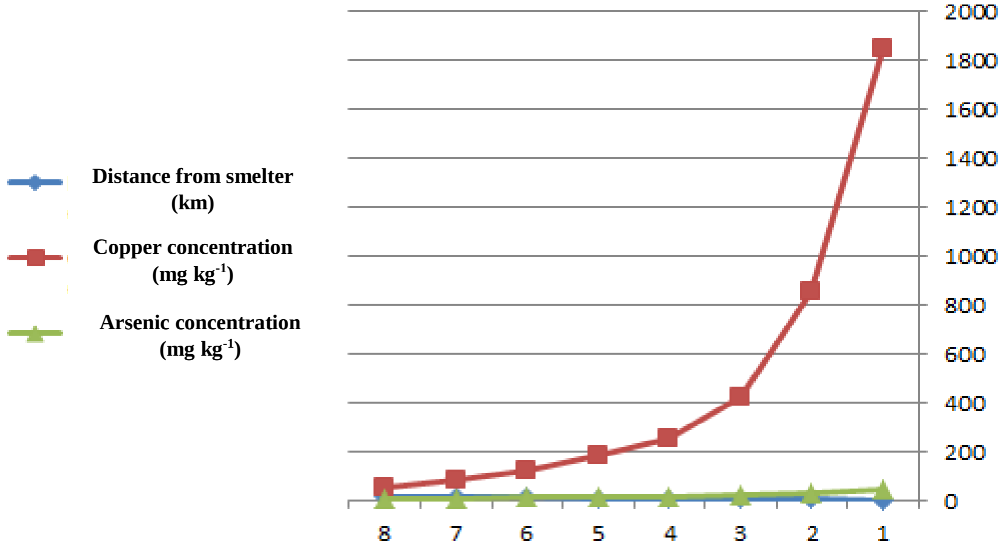

Fig. 1. Spatial trend of copper and arsenic concentrations along a SW-NE transect from the primary smelter complex.

The line graph illustrates the exponential decay in heavy metal concentrations with increasing distance from the point source. Copper shows an extremely sharp gradient, decreasing from over 1800 mg kg^{-1} near the source to near-background levels (~50 mg kg^{-1}) at 14 km. Arsenic follows a similar but less steep trend, indicating different dispersion mechanisms or additional diffuse sources. Based on the spatial interpolation and guideline thresholds, specific contamination hotspots were identified and their areas estimated.

The most severe hotspot, encompassing the immediate vicinity of the main smelting facility, accounted for the majority of the exceedances. A summary is provided in Table 7. In summary, the soils of the Zhezkazgan region are extensively contaminated with heavy metals, primarily copper, lead, and arsenic, originating from mining and smelting activities. The contamination exhibits strong spatial patterns with clear point sources and gradients, posing a high potential ecological risk that necessitates targeted remediation strategies.

Table 7. Identified contamination hotspots and estimated areas.

Hotspot name (primary pollutant)	**Approx. area (km^2)**	**Avg. Cu concentration ($mg\ kg^{-1}$)**	**Avg. As concentration ($mg\ kg^{-1}$)**	**Exceeds guideline for:**
Primary smelter vicinity (Cu, As)	8.5	1250	35	Cu, As, Pb, Cd
NE transport plume (Cu, Pb)	25.0	450	18	Cu, As
Southern waste deposit (Zn, Cd)	4.2	220	12	Cd, Zn
Total area exceeding Cu guideline	~120 km^2			

DISCUSSION

The findings of this study paint a clear picture of the extent and severity of heavy metal contamination of soils in the Zhezkazgan region. The data in Table 1 show that the concentrations of metals such as copper and lead not only exceed local background levels, but also exceed soil quality standards for various land uses in many places. The average copper concentration (3.452 mg kg^{-1}), which is about 15 times the background level, indicates a very severe and widespread impact of mining and smelting activities on the soil environment of this region. The high coefficient of variation for copper and lead (2.85% and 3.104%, respectively) recorded in Table 1 itself confirms the very high dispersion of the data and the point nature of the pollutant sources. Analysis of the pollution indices presented in Table 2 provides a deeper understanding of the situation. The land accumulation index for copper is in the “moderate to severe contamination” category, and the average pollution load index of 2.4 also indicates a significant pollution situation at the regional level. Of note are the high ecological risk factor values for arsenic and cadmium, which, despite their apparently lower concentrations than copper, highlight the very high toxicity potential of these two elements. This finding emphasizes that in risk assessment, the total concentration alone is not the criterion and that the toxicity factor of each element should be considered. The results of the principal component analysis (Table 3) clearly distinguished the two main sources of heavy metals in the region’s soils. The strong loading of copper, lead, zinc and arsenic on the first component, which explains about 50.7% of the variance, clearly indicates the anthropogenic origin of these elements related to mining and smelting processes. In contrast, nickel and chromium, which are loaded on the second component, are most likely of geological origin. This distinction is crucial for soil management and remediation planning, as strategies to deal with anthropogenic and natural pollution can be quite different. Geostatistical analysis and variogram parameters (Table 4) provide valuable insight into the spatial pattern of contamination. The low nugget-to-flood ratio for copper (25%) suggests a strong spatial structure and high spatial dependence, mainly controlled by deterministic processes such as emission from a fixed point (smelter). In contrast, the 100% ratio for nickel confirms a random and diffuse distribution of this element, consistent with its geological origin. The range of influence of about 3.5 km for copper quantifies the radius of penetration of the contamination from the main source. The steep slope of the decrease in concentration with distance from the source, reflected in the data in Fig. 1 (corresponding table), indicates the classic pattern of emission from a strong point source. The 97% decrease in copper concentration at a distance of 14 km, although numerically significant, does not mean that more distant soils are safe, as concentrations in many locations still remain above permissible levels. The significant negative correlation of pH with the mobility of cadmium and zinc (Table 5) is also a warning that possible future soil acidification could increase the bioavailability of these toxic metals and exacerbate ecological hazards. Finally, the identification of hotspots and the estimation of the contaminated area (about 120 km^2 for copper according to Table 7) is a key and practical finding for environmental managers and planners. The concentration of contamination in the vicinity of the smelter and along the prevailing wind direction identifies spatial priorities for important measures such as the installation of windbreaks, soil stabilization or remediation.

CONCLUSION

This study investigated the geochemical characteristics and spatial variability patterns of heavy metals in surface soils of the Zhezkazgan industrial area using a combination of chemical analyses, contamination indices, and geostatistical methods. The findings clearly showed that the soils of this area have been severely affected by copper mining and smelting activities, such that the concentrations of metals such as copper, lead, and arsenic significantly exceeded background levels and environmental standards. The calculated contamination indices confirm the status of “significant contamination” to “high ecological risk” for the area. Multivariate and geostatistical statistical analyses succeeded in separating the sources of contamination and describing its spatial pattern. The results attributed the high concentrations of copper, lead, zinc, and arsenic mainly to anthropogenic sources related to the mining and smelting industries, while nickel and chromium generally showed geological origins. Equivalent maps and spatial gradient analysis identified the main core of contamination in the vicinity of the smelting facilities and extending southwest to northeast (in line with the prevailing wind direction), indicating the dominant atmospheric release mechanism. Finally, this study emphasizes the need to adopt a dual management strategy: first, immediate and engineering measures to control and stabilize contamination in identified hotspots, and second, long-term monitoring and risk assessment, especially considering the potential for increased metal mobility if soil conditions change. The baseline data and maps produced in this study can provide a strong scientific basis for remediation planning, determining remediation priorities, and developing site-specific standards for the Zhezkazgan region.

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