

SEQUENTIAL EXTRACTION-BASED SPECIATION OF HEAVY METALS IN CONTAMINATED MINING SOILS**Shukurov Nosir Egamovich**

H.M. Abdullayev Institute of Geology and Geophysics

E-mail: nosirsh@yahoo.com**Makhammatov Anzor Bobir ugli**

PhD Candidate at the National University of Uzbekistan named after Mirzo Ulugbek

E-mail: anzormakhammatov@gmail.com**Abstract.**

Mining and metallurgical activities lead to the emission of heavy metals and subsequent soil contamination. This study investigates the distribution and chemical speciation of heavy metals in soils from mining-affected areas. Sequential extraction (Tessier method) and atomic absorption spectroscopy (AAS) were applied to determine metal fractions. The results indicate that Cu, Pb, Zn, and Cd are mainly present in mobile and bioavailable forms, while Ni and Cr are predominantly associated with lithogenic fractions. These findings confirm the technogenic nature of soil pollution. The results are important for environmental monitoring, risk assessment, and sustainable land management.

Keywords:

Mining industry, technogenic pollution, heavy metals, soil geochemistry, sequential extraction, chemical fractionation, metal migration, environmental monitoring.

INTRODUCTION. Mining and metallurgical activities are recognized as major sources of technogenic heavy metal contamination in the environment. The processes of ore extraction, beneficiation, and smelting generate significant emissions of dust and particulate matter, which subsequently lead to the accumulation of heavy metals in surrounding soils. As a result, soil ecosystems in mining-impacted regions undergo considerable geochemical alteration, including changes in elemental composition, reduction of soil fertility, and disturbance of microbial and structural properties.

The environmental impact of heavy metals is governed not only by their total concentrations but also by their chemical speciation, including their distribution among different geochemical fractions. The mobility, bioavailability, and toxicity of elements such as Cu, Zn, Pb, Cd, Ni, and Cr depend strongly on their binding forms in soil matrices. Therefore, detailed fractionation studies are essential for a reliable assessment of contamination risks in technogenic landscapes.

The present study is focused on soils affected by mining and metallurgical activities, where heavy metal contamination exhibits a clear technogenic origin and spatial variability. The investigation is based on sequential extraction (Tessier method) combined with atomic absorption spectroscopy (AAS), which enables the determination of metal partitioning among exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, and residual fractions.

The study is motivated by the need to better understand the behavior, migration, and environmental availability of heavy metals in contaminated soils. The novelty of this work lies in the integrated evaluation of both total concentrations and chemical forms of metals, providing a more comprehensive geochemical characterization of polluted soils. The results are expected to

support environmental monitoring, risk assessment, and the development of scientifically grounded remediation strategies in mining-affected regions.

LITERATURE REVIEW. Heavy metal contamination of soils in mining and metallurgical regions is a widely recognized environmental problem caused by anthropogenic activities such as ore extraction, beneficiation, and smelting. These processes lead to the accumulation of potentially toxic elements in surrounding soils, resulting in long-term geochemical disturbances of natural ecosystems. It is well established that the total concentration of heavy metals alone is insufficient for environmental assessment, since their toxicity, mobility, and bioavailability depend strongly on their chemical forms in soils[1].

Biogeochemistry provides the theoretical basis for understanding the migration and transformation of chemical elements in the biosphere under the influence of living matter. The foundational works of Vernadsky (1924) and Vinogradov (1957) established that living organisms play a key role in the cycling and distribution of chemical elements within natural systems[2], [3]. In soils, heavy metals may exist in different geochemical fractions, including exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, and residual forms, each characterized by different levels of mobility and ecological availability.

Sequential extraction techniques, first systematically developed by Tessier et al. (1979), are widely used to determine the speciation of heavy metals in soils and sediments[4]. This method allows the operational separation of metals into different fractions using selective chemical reagents. Despite certain limitations, such as possible redistribution of metals during extraction, sequential extraction remains one of the most effective approaches for studying metal fractionation in contaminated environments.

Previous studies have shown that elements such as Cu, Zn, Pb, and Cd are generally associated with more mobile and bioavailable fractions, while Ni and Cr tend to occur in more stable lithogenic or residual phases. These differences reflect both the geochemical properties of the elements and the nature of their sources in mining-affected areas.

Thus, understanding heavy metal speciation is essential for accurate assessment of environmental risk and pollution behavior in technogenic soils.

MATERIALS AND METHODS. The study of heavy metal speciation in contaminated mining soils was carried out in order to determine the distribution, mobility, and geochemical association of trace elements in technogenic environments. Soil contamination in mining regions is mainly associated with ore processing activities, including smelting, beneficiation, and waste disposal, which lead to the accumulation of heavy metals in surrounding soils.

Soil samples were collected from areas influenced by mining and metallurgical activities. The sampling strategy was designed to capture spatial variability of contamination, including proximity to emission sources such as tailings, waste dumps, and industrial zones. Samples were air-dried, homogenized, and sieved to obtain a uniform particle size prior to chemical analysis.

Chemical fractionation of heavy metals was performed using the sequential extraction method proposed by Tessier et al. (1979). This method allows operational separation of metals into seven geochemical fractions reflecting different binding forms and mobility levels in soils. The extraction procedure was carried out on 1–2 g of dry soil placed in polypropylene centrifuge tubes. Each fraction was extracted stepwise using specific reagents under controlled shaking and centrifugation conditions.

The sequential extraction scheme included the following fractions: (F1) exchangeable and water-soluble metals, extracted using 1M NH_4NO_3 ; (F2) weakly adsorbed metals extracted with 1M ammonium acetate (pH 4.6); (F3) metals bound to Mn oxides using $\text{NH}_2\text{OH}\cdot\text{HCl}$ in ammonium acetate buffer; (F4) organically bound metals extracted with EDTA solution; (F5) metals associated with amorphous Fe oxides using ammonium oxalate (pH 3.25); (F6) metals bound to crystalline Fe oxides using ascorbic acid in ammonium oxalate medium; and (F7) residual fraction associated with silicate minerals, extracted using a mixture of concentrated nitric and perchloric acids.

After sequential extraction, the obtained solutions were analyzed to determine heavy metal concentrations. The total number of analyzed subsamples was standardized through replicate measurements to ensure statistical reliability. The analytical determination of metal concentrations (including Cu, Pb, Zn, Ni, Cr, Cd and others) was performed using atomic absorption spectroscopy (AAS), which provides high sensitivity and accuracy for trace metal analysis in environmental samples.

In addition, geochemical interpretation was supported by comparison of obtained concentrations with background element abundances and calculation of concentration coefficients. This approach enabled identification of anthropogenic enrichment and differentiation between lithogenic and technogenic sources of contamination.

The methodological approach applied in this study integrates sequential chemical extraction and instrumental analysis, allowing detailed assessment of heavy metal behavior in contaminated soils and providing a reliable basis for environmental risk evaluation in mining-affected areas.

RESULTS AND DISCUSSION. As is well known, the extraction, beneficiation, and smelting of metals from ores lead to the emission of heavy metals, which subsequently accumulate in the vicinity of mining and metallurgical enterprises. Soil contamination by heavy metals, in turn, results in a reduction of soil fertility by altering the specific composition of microbial communities as well as the overall soil structure. High concentrations of heavy metals present in technogenic landscapes and within the food chain pose a significant risk to human health. However, the “toxicity” of metals largely depends on their mode of occurrence, including particle size distribution, structural form, and the emission characteristics of individual elements.

Chemical forms of heavy metals were investigated using the sequential extraction method (Tessier et al., 1982). According to this procedure, 1–2 g of dry, sieved soil sample is placed in a polypropylene centrifuge tube. Heavy metals are then extracted from the solid matrix into different fractions through a stepwise sequential extraction scheme. The obtained data provide information on the distribution of heavy metals among various geochemical forms.

Copper, zinc, lead, and cadmium are predominantly present in soils in “bioavailable” forms, including exchangeable, adsorbed, and organically bound fractions. In contrast, chromium and nickel behave as lithogenic elements, with their highest concentrations observed in the residual (poorly soluble) fraction.

A significant proportion of zinc and lead is associated with iron and manganese oxides/hydroxides and sulfide phases, accounting for 56.4% and 53%, respectively. A markedly higher proportion of copper (60.4%), compared to zinc (16.6%), lead (10.2%), and cadmium (13.9%), is bound to organic matter, while the remaining 39.6% is associated with iron and manganese oxides/hydroxides and sulfides. The exchangeable fraction is generally very low for zinc, lead, copper, and chromium (<1%), for nickel it is 1.2%, and for cadmium 3%.

The highest proportion of carbonate-bound heavy metals was observed for cadmium (38.7%), followed by lead (22.8%), zinc (18%), and copper (13.2%). Chromium and nickel showed very low levels in the carbonate fraction, with 1% and 7.1%, respectively. These results reflect differences in the geochemical behavior of metals, which are also influenced by their sources of input. In particular, 53.6% of zinc and 33.2% of chromium are associated with silicate minerals or other resistant primary mineral phases.

The results of ecogeochemical studies of heavy metal contents in soils using the sequential extraction technique allow for a more detailed understanding of metal behavior in contaminated environments and provide a scientific basis for environmentally sound management practices.

In this study, 2 g of dry, sieved soil sample was used (in polypropylene tubes), and after centrifugation, heavy metals were extracted into different fractions according to the sequential extraction scheme presented in Table 1.

Table 1.

Scheme of chemical fractionation (sequential extraction) of heavy metals in soil samples

No	Fraction	Extractant and Method	Form of Heavy Metal Occurrence
1.	Easily soluble (F1)	1M NH ₄ NO ₃ ; shaking 24 h; centrifugation 15 min	Highly mobile (ionic form)
2.	Adsorbed and weakly bound in soil microparticles (F2)	1M NH ₄ -acetate (pH 4.6); shaking 24 h; centrifugation 15 min	Mobile (ionic form)
3.	Bound to Mn oxides (F3)	0.1M NH ₂ OH·HCl + 1M NH ₄ -acetate (pH 6.0); shaking 30 min; centrifugation 15 min	Sorbed on Mn oxides (nano-mineral fraction)
4.	Bound to organic matter (F4)	0.025M NH ₄ -EDTA* (pH 4.6); shaking 90 min; centrifugation 15 min	Organically bound (nanomineral fraction)
5.	Associated with amorphous and partially crystalline Fe oxides (F5)	0.2M ammonium oxalate (pH 3.25); shaking 4 h; centrifugation 15 min	Reductive/Fe-oxide bound (mineral fraction)
6.	Bound to crystalline Fe oxides (F6)	0.1M ascorbic acid in 0.2M ammonium oxalate (pH 3.25); heating in water bath 30 min, shaking 10 min; centrifugation 15 min	Oxide-bound (mineral fraction)
7.	Residual fraction (F7)	Mixture of concentrated HNO ₃ (4 parts) and HClO ₄ (1 part)	Lithogenic (silicate-bound mineral fraction)

* EDTA (ethylenediaminetetraacetic acid)

After fractionation into 7 described fractions from 8 soil samples (for accuracy and averaging, the samples were analyzed in duplicates), a total of 112 samples were obtained. All these samples were analyzed using atomic absorption spectroscopy (AAS). Based on the statistical processing of the obtained data, the following conclusions were drawn:

1. The concentrations of heavy metals consistently increase with proximity to the pollution source and decrease with increasing distance from it. The main sources of soil and vegetation contamination are dust and gas emissions from mining and processing enterprises, as well as the dispersion of ore material during transportation and the deflation of tailings and waste dumps.

2. The total percentage content of heavy metals in soil samples follows the order Cu > Zn > Pb > Ni > Cr > Cd (Fig. 2). Comparison of this sequence with the natural abundance of elements in soils [6], based on the calculation of concentration coefficients (Table 2), yields the following order: Cu > Pb > Cd > Zn > Ni > Cr. This can be explained by the specific influence of copper and lead–zinc production at the Almalyk Mining and Metallurgical Complex (AMMC) and the composition of the processed ores.

3. The obtained data allow assessment of heavy metals in different chemical forms. Copper, zinc, lead, and cadmium in soils are mainly present in bioavailable forms, either in adsorbed states or in organic compounds (fractions F1–F4). Chromium and nickel behave as lithogenic elements, with their highest contents observed in the poorly soluble fractions (F5–F7) (Fig.1, Table 1).

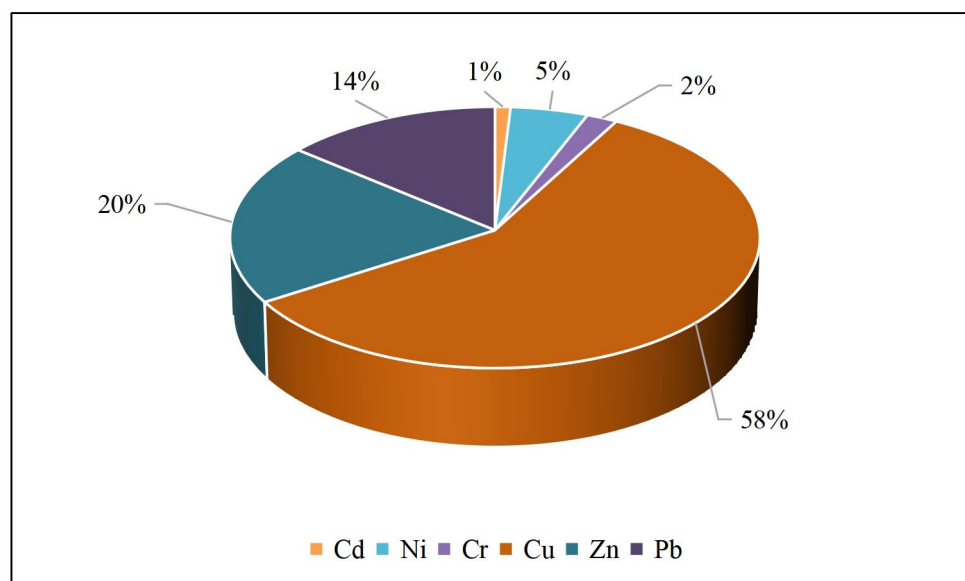
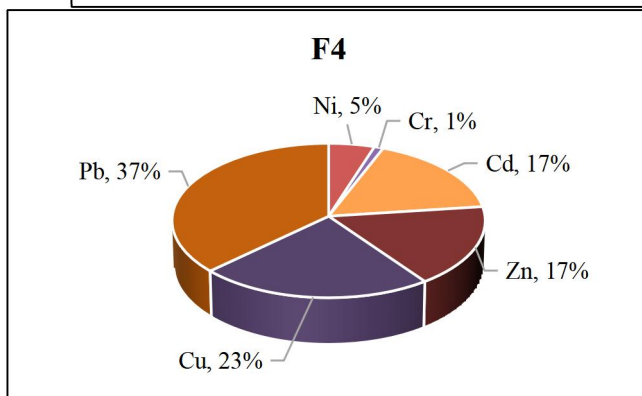
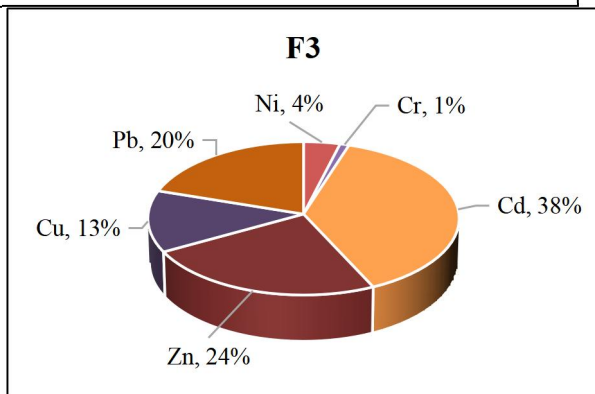
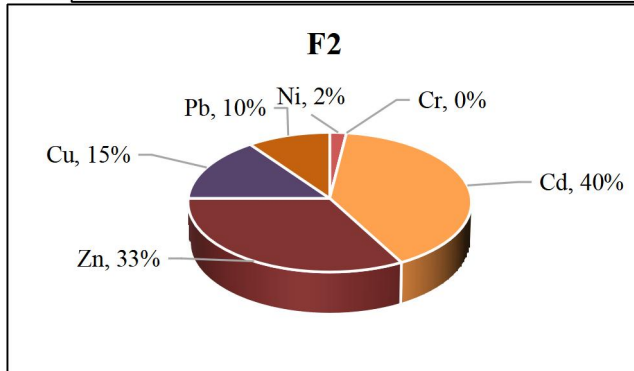
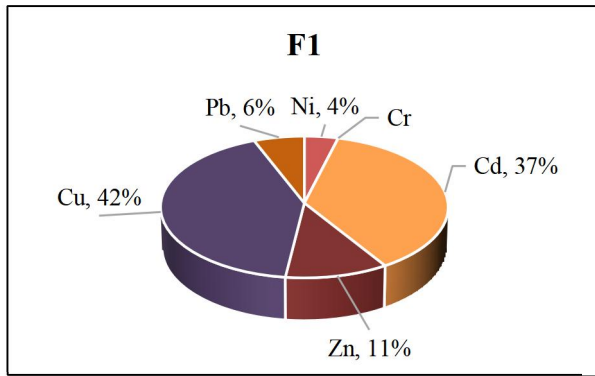


Fig. 1. Relative percentage contents of heavy metals in soil samples

Table 2.

Elemental abundance and concentration coefficients of heavy metals in soils of the AMMC

Element s	Average content in soil samples (g/t)	Element abundance in soils (according to A.P. Vinogradov) (g/t)	Concentration coefficient in soils
Cu	857.5	20	42.8
Zn	312.2	50	6.2
Pb	204.4	10	20.4
Ni	71.3	40	1.7
Cr	36.8	200	0.2
Cd	7.1	0.5	14.2



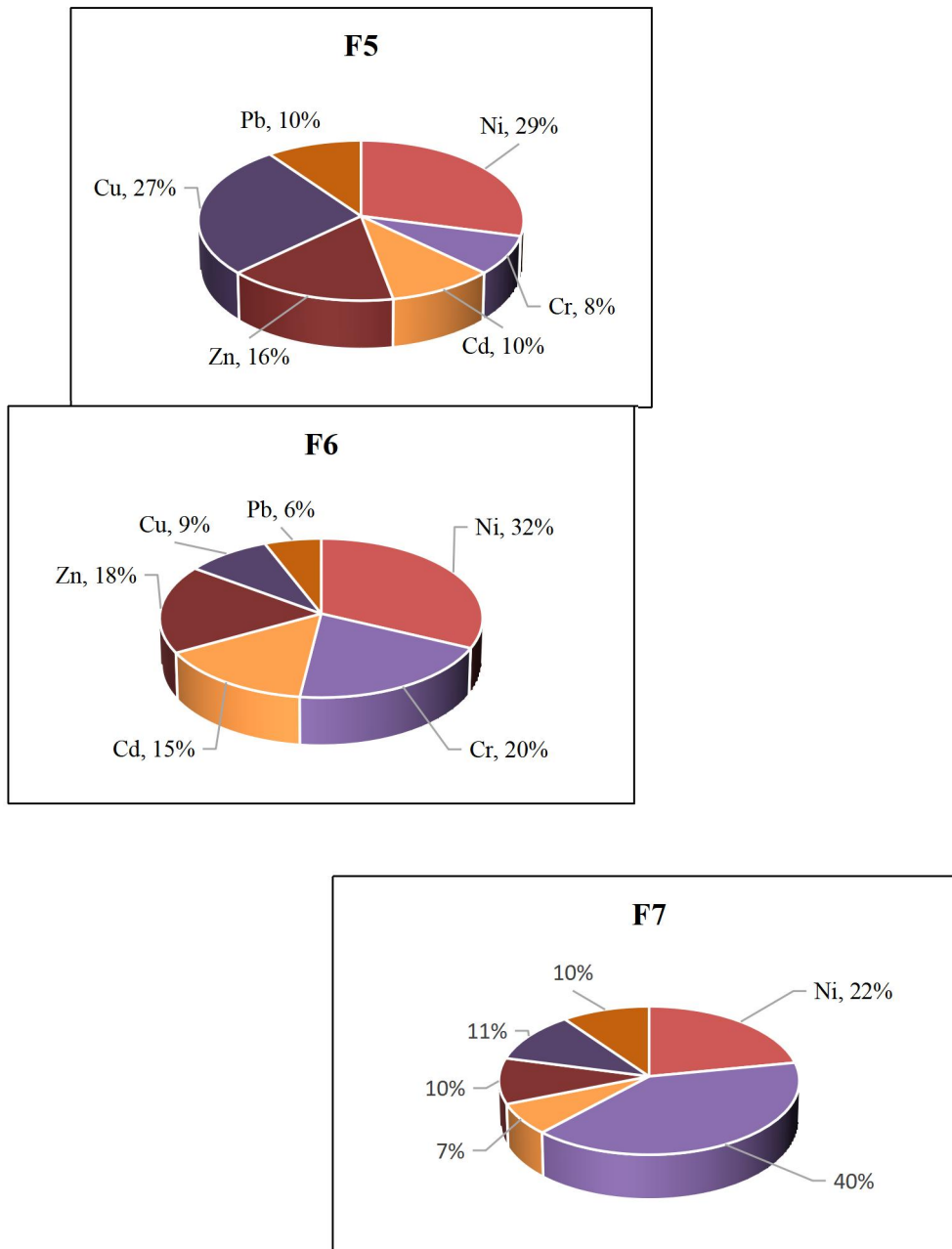


Fig. 2. Percentage distribution of heavy metals in different fractions

CONCLUSION. Therefore, the above allows us to draw the following conclusions:

1. The distribution of hazardous elements, particularly lead, zinc, copper, arsenic, and cadmium, across the study area exhibits a clearly technogenic (anthropogenic) character.
2. There is a distinct spatial confinement of anomaly halos of these elements to specific technogenic sources, as well as a consistent decrease in contamination intensity with depth.

The practice of environmental monitoring of pollution in environmental components—such as the atmosphere, hydrosphere, soil, and vegetation cover—by specific elements classified as toxic in industrial and urban areas is based on geochemical assessment of the object. The quantitative criterion in this case is the ratio of the concentration of a given element in a particular environmental subsystem to a calculated value known as the maximum permissible concentration (MPC).

The MPC values, which are mainly obtained empirically through the analysis of impacts on living organisms and human health, also serve as a basis for developing industrial and urban development programs and implementing environmental protection measures.

From the above, it is evident that as new data accumulate, the MPC values themselves must also be revised in order to more accurately reflect the actual environmental conditions [5].

REFERENCES

1. Fergusson, J.E. (1990). *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*. Pergamon Press, Oxford.
2. Vernadsky, V.I. (1924). *La Géochimie*. Paris.
3. Vinogradov, A.P. (1957). *Geochemistry of Rare and Dispersed Chemical Elements in Soils*. Moscow.
4. Tessier, A., Campbell, P.G.C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844–851.
5. Shukurov, N. E., 2024. Heavy metals in soils of mining industry waste dumps: occurrence, migration patterns, effects on soil microorganisms, soil fertility, bioindication and bioremediation aspects (Final report on fundamental research results). Tashkent.
6. Bagdasaryan, A. S. (2005). *Biotesting of soils in technogenic zones of urban territories using plant organisms* (PhD dissertation in Biology: 03.00.16). Stavropol, 159 pp.