

ASSESSMENT OF HEAVY METAL CONTENTS IN BIO-ORE DERIVED FROM AGRICULTURAL LANDSCAPES OF EASTERN KAZAKHSTAN

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ABSTRACT

This study investigated the contents of heavy non-ferrous metals in soil and plant biomass (bio-ore) using an experimental agricultural site located 10 km northeast of a non-ferrous metallurgical enterprise producing heavy metals, including Pb, Zn, Cu, and others. The total contents of the studied heavy metals in the ash product were determined, and their potential quantities in the ash residue generated from 1 ha of agricultural land after thermal treatment were estimated. The obtained results indicate the feasibility and potential of developing an alternative metallurgical technology for the recovery of non-ferrous metals from bio-ore.

INTRODUCTION

Eastern Kazakhstan is one of the major centers of the country's mining and metallurgical industry. The processing of polymetallic raw materials is accompanied by the generation of dust and gaseous emissions, slags, beneficiation tailings, and wastewater. Metals entering the soil do not undergo degradation and may persist in the upper soil horizon for long periods, transition into mobile forms, and become incorporated into biogeochemical cycles. For agricultural landscapes, the transfer of elements into crops is of particular importance, as it links soil conditions with the quality of feed and food raw materials (Gupta et al., 2019; Vanisree et al., 2022). The soils of Ust-Kamenogorsk are characterized by a spatially heterogeneous distribution of Zn, Cd, Pb, and Cu. A study of the fractionation of urban and industrially impacted soils demonstrated that environmental assessment should consider not only total metal concentrations but also their chemical forms, soil acidity, and sorption properties (Woszczyk, Spychalski, & Boluspaeva, 2018). A more recent study conducted in the northern industrial zone of the city revealed a high degree of contamination by acid-soluble metal forms and a zinc-cadmium specialization of the technogenic impact (Boluspayeva et al., 2023). A comparative study of private vegetable gardens located near an industrial site and in the suburban village of Akhmirovo revealed substantially higher concentrations of Cu, Cd, Pb, and Zn in soils from the industrial zone. The authors also demonstrated differences in metal accumulation by vegetable crops and emphasized the need for joint analysis of soil and plant materials (Boluspayeva et al., 2024).

One potential approach to addressing this problem is the development and implementation of alternative methods for the recovery of non-ferrous metals from the environment using plants, i.e., phytomining. Phytomining, also referred to as agromining, is an environmentally oriented technology for recovering metals from soils using specialized plants workings,



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known as hyperaccumulators. Instead of conventional open-pit mines and underground this approach involves cultivating a «metal crop» on low-grade ores, industrial wastes, or contaminated sites. In the work of Brooks et al. (1998), phytomining was described as the production of a metal «crop» by cultivating plants with high biomass that accumulate elevated concentrations of metals. Some of these plants are natural hyperaccumulators, whereas in others this property can be induced. Pioneering experiments in this field may contribute to the development of a «green» alternative to existing environmentally disruptive mining practices. Phytomining of a range of metals represents a viable possibility, with additional potential for exploiting ore bodies whose conventional extraction is economically unfeasible.

Akinbile and Mbohwa (2025) noted that phytomining, i.e., the recovery of valuable metals from soils or wastes using plants, is attracting increasing attention as a sustainable and economically viable alternative to conventional mining methods. A key component of this approach is the use of metal-hyperaccumulating plants, which possess a remarkable ability to absorb and concentrate metals in their biomass. The use of hyperaccumulator plants has become an important component of phytomining at numerous mining sites worldwide. However, metal hyperaccumulator plants have certain limitations, including low biomass production and limited survival under harsh conditions, such as those found on mine sites. These limitations constrain their practical application under field conditions. Hyperaccumulator plants can contain valuable metals at concentrations comparable to those found in conventional metal ores, and the concentration of these metals can be substantially increased through combustion (Simonnot, Vaughan & Laubie, 2018). This provides an incentive to recover metals as valuable products, thereby partially offsetting the costs associated with the disposal of contaminated biomass originating from polluted soils, mining wastes, and processing residues. Metal recovery has been incorporated into the agromining value chain, which has developed over the past two decades, particularly for nickel and gold. More than 450 nickel hyperaccumulator plant species are known. Nickel recovery involves extraction, ashing and/or leaching of dried biomass, followed by refining using pyrometallurgical or hydrometallurgical processes. The final products may include ferronickel, metallic nickel, nickel salts, or nickel-based catalysts, all of which have widespread applications in various industrial sectors and everyday life. Gold can be recovered from mining wastes using several plant species, generally through the timely application of a gold-chelating extractant to the soil. The resulting dry biomass is subjected to ashing and smelting. This approach makes it possible to process resources that cannot be efficiently treated using conventional technologies.

Among the metals that can potentially be recovered through phytomining, rare earth elements (REEs) occupy a special position. REEs are essential for clean-energy technologies and advanced electronics; however, conventional extraction is often associated with substantial environmental and energy costs. Phytomining, based on the ability of hyperaccumulator plants to concentrate REEs from soils, offers a potentially sustainable alternative. Nevertheless, subsequent recovery of REEs from plant biomass remains a resource-intensive process. Xu et al. (2026) proposed a rapid electrothermal calcination (ETC) strategy for REE-enriched biomass, enabling rapid thermal activation, for example, at 1000 °C for 20 s, and enhancing REE recovery through dilute-acid leaching, with extraction efficiencies of up to approximately 97%. The ETC process was shown to be applicable to different hyperaccumulator biomass matrices, as demonstrated using *Blechnum orientale* and *Dicranopteris linearis*. A comparative life-cycle assessment indicated that ETC can reduce carbon emissions by more than 70% compared with conventional furnace-based methods. These findings demonstrate the potential of ETC as a sustainable and scalable platform for the development of circular REE recovery through phytomining.

In Kazakhstan, sunflower is a crop capable of actively accumulating non-ferrous metals. It can accumulate Cd, Pb, Zn, Cu, and Cr; however, the distribution of these elements between roots and aboveground organs depends on their chemical forms, plant developmental stage, soil properties, and the intensity of atmospheric deposition. Experimental studies have shown that Cd can be actively transferred into sunflower tissues, whereas Pb and Cr are more frequently retained in the roots, although under conditions of surface deposition, a substantial proportion of metals can also be detected in leaves (Abdullahi et al., 2021; Dhiman et al., 2017; Rai et al., 2019). A study conducted in the area of a metallurgical complex previously identified a relationship between soil contamination and the accumulation of Zn, Cd, Pb, and Cu in sunflower plants (Киршибаев et al., 2024).

It is expected that, with the further development and implementation of phytomining technologies for the efficient recovery of valuable metals from low-grade ores or metal-rich soils, this approach may become an environmentally and economically attractive technology for addressing the growing scarcity of metallic resources, as it enables both metal recovery and energy generation from biomass (Dang & Li, 2022). The product of phytomining is dried and combusted plant biomass, which is referred to as bio-ore. Bio-ore is plant biomass or the products of microbial activity containing elevated concentrations of valuable metals that have accumulated through biological processes.

The aim of this study was to investigate the elemental composition of soil and the seasonal accumulation of heavy metals in agricultural plants within an agricultural landscape of Eastern Kazakhstan located in the potential impact zone of a metallurgical enterprise. The objectives were to: characterize the agrochemical properties of the soil; describe the variability in metal concentrations in the collected soil samples; compare summer and autumn concentrations of non-ferrous metals in sunflower organs; compare the seasonal dynamics of metals, using Cd as an example, in sunflower, soybean, and maize; assess the prospects for developing phytomining-related approaches using the selected experimental agricultural site as a case study; and preliminarily evaluate the feasibility and potential for efficient processing of the resulting bio-ore.

LITERATURE REVIEW

Published data indicate that contamination of agricultural landscapes in Kazakhstan is driven by a combination of industrial and agricultural sources. In addition to emissions from mining and metallurgical enterprises, mineral and organic fertilizers, soil amendments, and irrigation water may contribute substantially to metal inputs. A review of global and Kazakhstan experience has noted that, for arable soils, it is important to consider not only local industrial sites but also the regular input of elements associated with agricultural chemicals (Ысқақ, 2025). Therefore, the proximity of an agricultural field to a metallurgical facility provides a basis for assessing potential industrial influence but does not replace the analysis of alternative sources. Regional studies demonstrate considerable spatial heterogeneity in environmental conditions. In irrigated agricultural soils of southern Kazakhstan, concentrations of most investigated metals were relatively low, whereas cadmium was identified as the most problematic element; its presence was associated by the authors with the quality of irrigation water (Suska-Malawska et al., 2022). For agricultural soils in the Kostanay Region, an integrated index indicated a range of risk levels from low to high, while abandoned areas associated with mining activities showed concentrations of As, Cd, Zn, and Pb exceeding national reference values (Zhyrgalova et al., 2024). These findings confirm that a uniform assessment for the entire country is not possible without considering land-use type and the history of anthropogenic impact.

Studies of industrial centers in Kazakhstan demonstrate recurring multi-element metal associations, although the priority elements differ among industrial sectors. Near non-ferrous

metallurgical enterprises, Zn, Pb, Cu, and Cd are frequently detected in combination, whereas Cr, Ni, Sr, and other elements may occur at elevated levels near ferrous metallurgy and chromite-processing facilities. Therefore, monitoring programs should be designed according to the composition of the processed raw materials and the technological profile of the enterprise rather than being limited to a universal set of indicators. Recent reviews identify four interconnected directions for risk management: control of contaminant sources, regulation of metal bioavailability through soil properties, selection of crops with low transfer to economically utilized plant organs, and remediation of contaminated sites (Wan et al., 2024). For agricultural landscapes located near metallurgical enterprises, priority should be given to spatially referenced sampling, separate determination of total and mobile metal forms, monitoring of atmospheric deposition, and analysis of edible or feed plant parts. Phytoremediation measures should only be selected following such diagnostic assessment, since a high element concentration in plant tissue does not necessarily indicate high total removal without considering biomass production.

The industrial development of Ust-Kamenogorsk is associated with the processing of polymetallic and rare-metal raw materials. Metallurgical, energy, and mining and beneficiation facilities are concentrated within the urban agglomeration and adjacent territories. As a result, a complex mixture of technogenic flows is formed, and the contribution of an individual source is difficult to assess without a specialized monitoring network. For agricultural land, not only organized emissions from industrial stacks but also fugitive dust from open storage areas, roads, waste dumps, and disturbed surfaces are important. The mountainous terrain and river valleys of Eastern Kazakhstan may enhance the spatial heterogeneity of atmospheric deposition. Temperature inversions and periods of weak winds can promote the accumulation of pollutants in the near-surface atmospheric layer, whereas persistent airflows can transport aerosols beyond the industrial site. Therefore, equal distance from an industrial facility does not necessarily correspond to equal exposure. When selecting monitoring fields, the direction relative to the source, terrain elevation, protection provided by shelterbelts, and location within a valley should be considered. Agricultural landscapes differ from urban soils because of regular mechanical mixing of the cultivated horizon, fertilizer application, and removal of elements with harvested crops. Ploughing redistributes surface-deposited contaminants within the cultivated layer, while changes in soil acidity following fertilizer application affect metal mobility. Plant residues and organic matter can bind metal cations; however, subsequent mineralization may return part of these elements to an available state. Consequently, results obtained from urban monitoring cannot be directly transferred to arable land without field validation.

Land-use history is also important. Current soil concentrations reflect not only present-day inputs but also accumulated deposition from previous decades. A reduction in emissions does not result in the rapid disappearance of metals from the cultivated soil layer. Their subsequent fate is determined by erosion, vertical migration, plant uptake, and retention within mineral and organic matrices. Distinguishing current from accumulated impacts requires repeated observations at the same geographic coordinates. Remote sensing data do not replace laboratory measurements but can assist in designing sampling networks. Spectral indicators of vegetation and bare soil can be used to identify areas with anomalous vegetation conditions, after which laboratory sampling can be used to verify the underlying causes. The applicability of Sentinel-2 for the spatial assessment of metal concentrations and the integrated analysis of industrial factors has been demonstrated for Ust-Kamenogorsk (Felegari et al., 2023). Integration of field and remote-sensing data is particularly useful for surveying large agricultural areas.

Metallurgical enterprises affect agricultural landscapes through several pathways. Fine particulate matter can be transported by air currents and deposited on soil and leaf surfaces. Waste dumps and tailings storage facilities may act as secondary sources of dust, while surface runoff can transport dissolved and particulate forms of elements into topographic depressions

and watercourses. The composition of the technogenic metal association is determined by the raw materials and processing technology. The processing of polymetallic ores is commonly associated with the co-occurrence of Zn, Pb, Cd, and Cu. Correlations among these elements and the coincidence of spatial anomalies with prevailing transport directions can serve as indicators of a common source; however, these characteristics alone do not prove that the contamination originated from a specific enterprise (Zwolak, Szpyrka & Stawarczyk, 2019).

Metal behavior in the soil-plant system depends on pH, organic matter, particle-size distribution, redox conditions, and ion competition. Under neutral to slightly alkaline conditions, the mobility of many cationic metal forms decreases due to sorption and precipitation. Cadmium, however, retains relatively high bioavailability, while atmospheric dust may contaminate plant material independently of root uptake. Therefore, bioconcentration factors are valid only when analytical forms, units, and the basis for conversion to dry matter are comparable (Jakubus & Bakinowska, 2022; Wang et al., 2021).

Plant developmental stage affects element concentrations. Increasing biomass may reduce concentrations through a dilution effect, whereas prolonged uptake and redistribution among plant organs may lead to increasing concentrations toward the end of the growing season. Interpretation requires information on the biomass of each plant organ: the sum of concentrations in roots, stems, and leaves does not represent the total elemental removal by the plant. Therefore, in the present study, individual concentrations and the simple mean across three comparable organs are used only as descriptive indicators of seasonal dynamics.

Sunflower is considered a promising crop for phytoextraction and phytomonitoring. It produces substantial biomass and can accumulate Cd and Zn; however, the efficiency of their translocation to aboveground organs varies depending on cultivar and growing conditions. Studies have shown that the addition of chelating compounds can increase the mobility of Cd and Pb while simultaneously increasing the risk of their migration. Conversely, the application of microorganisms and soil amendments can be used for controlled phytomonitoring and reduction of metal bioavailability (Shabaev & Ostroumov, 2025). For industrial agricultural landscapes, the primary task remains reproducible monitoring of soil, plants, and atmospheric deposition rather than remediation without prior diagnostic assessment.

Lead is considered a priority marker of the impact of non-ferrous metallurgical enterprises. In soils, it is generally strongly bound to organic matter and iron and manganese oxides and therefore exhibits limited downward mobility through the soil profile. High Pb concentrations in leaves may result not only from root uptake but also from particulate deposition on leaf surfaces. To identify the dominant pathway, it is advisable to compare washed and unwashed leaves and to analyze atmospheric dust deposition. Cadmium is characterized by greater mobility and can be taken up by plants even at relatively low soil concentrations. Its bioavailability increases under acidification and decreases when it is bound by organic matter or carbonates. In polymetallic ores, Cd commonly occurs together with Zn; therefore, the joint dynamics of these elements may have diagnostic significance. However, their correlation coefficient can only be reliably calculated when a sufficient number of independent samples is available.

Zinc and copper are essential micronutrients for plants, but excessive concentrations can disrupt physiological processes. Their concentrations depend on mineral nutrition, developmental stage, and the content of available forms in the soil. Therefore, exceeding the agronomic range is not equivalent to exceeding a sanitary standard. A correct assessment requires explicit identification of the criterion being applied: plant nutritional status, phytotoxicity, feed safety, or food safety. Chromium and nickel require particular attention to analytical speciation and measurement quality. The toxicity of Cr strongly depends on its oxidation state, and total Cr concentration does not reveal the proportion of the more mobile Cr(VI) form. Nickel participates in nitrogen metabolism at moderate concentrations, whereas excessive accumulation may inhibit

plant growth. Isolated extreme values should be confirmed by repeated sample digestion, analysis of blanks, and certified reference materials.

The global increase in stocks of low-grade ores and metal-contaminated soils observed over recent decades is expected to continue in the foreseeable future (Novo et al., 2017). However, the strategic and commercial importance of certain elements contained in these economically marginal ores and soils, together with their high market value and associated environmental concerns, has created opportunities for phytomining. This technology, based on phytoextraction, exploits the ability of certain plants to absorb valuable metals and produce bio-ore from harvested biomass, thereby enabling subsequent metal recovery through smelting. At a large scale, phytomining may operate as an independent process for recovering a target element or in combination with phytoremediation, helping to offset remediation costs.

Phytoremediation is currently a widely studied approach for the treatment of contaminated sites associated with previous rare-earth element (REE) extraction. However, the utilization of secondary resources such as plant biomass remaining after REE recovery remains a challenge. In a study by Feng et al. (2025), *Dicranopteris pedata* (Houtt.) Nakaike, a REE hyperaccumulator, was used to produce REE-rich carbonized materials (REEs/C) at different temperatures. The results showed that the removal efficiencies of Pb(II) using REE-rich carbonized materials prepared at 400 °C (REEs/C-4) and 800 °C (REEs/C-8) were 85.1% and 84.0%, respectively. These values were higher than the 67.0% removal efficiency obtained with REEs/C prepared at 600 °C (REEs/C-6).

Characterization analysis confirmed that the abundance of functional groups, including aromatic, hydroxyl, and C=C/C-C groups, in REEs/C-4 provided more chelation sites for effective complexation with Pb(II). The high Pb-removal capacity of REEs/C-8 was attributed to enrichment with larger amounts of rare earth elements and the development of a porous structure. Chemisorption processes, including ion exchange and chelation, played a significant role in adsorption. During carbonization, REEs enriched in *Dicranopteris pedata* promoted the formation of rare-earth oxides and oxygen vacancies in the material, enhancing the ability of REEs/C to remove Pb. Moreover, the REEs contained in the material did not leach during Pb removal, indicating that the material can be considered relatively safe and environmentally compatible. Finally, REEs/C was applied to wastewater treatment and demonstrated effective Pb adsorption.

Overall, this study provides new insights into two aspects: first, the utilization of REE-containing biomass obtained through phytoextraction as a valuable rare-earth-based carbon material; and second, the environmental benefits of technologies that promote the recycling and reuse of biomass-derived materials.

MATERIALS AND METHODS

The study was conducted based on the results of laboratory investigations carried out during 2025 - 2026. The study site was an agricultural field located 10 km from a non-ferrous metallurgical enterprise producing heavy metals, including Pb, Zn, Cu, and others. The experimental site was located northeast of the source of heavy non-ferrous metal emissions (Figure 1).

Soil sampling was carried out during the autumn–spring periods using the envelope sampling method at a depth of approximately 30 cm, in accordance with GOST 17.4.4.02-2017, «Environmental Protection. Soils. Methods for Sampling and Preparation of Samples for Chemical, Bacteriological, and Helminthological Analysis» For chemical analysis, a composite soil sample was prepared from five individual samples collected within a single sampling plot. The mass of each composite sample was at least 1 kg.

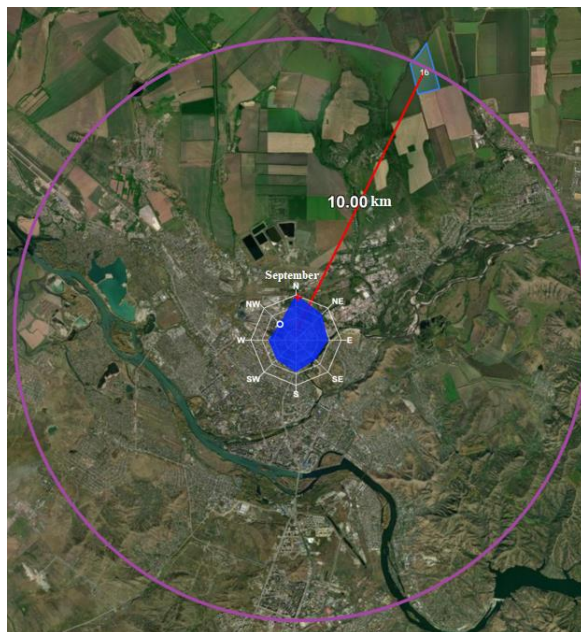


Figure 1. Map showing the location of the experimental site relative to the non-ferrous metallurgical enterprise

Note – compiled by the authors

In the laboratory, the samples were freed from large foreign inclusions and plant residues, ground, and passed through a sieve with a mesh size of 1 mm. For the determination of the organic matter content, additional sample preparation was performed in accordance with GOST 26213-2021, including thorough removal of plant residues, followed by grinding and sieving through a 0.25-mm mesh sieve.

The organic matter content of the soil was determined in accordance with GOST 26213-2021 (Measurement Procedure 66373620-005-2015). The method is based on the oxidation of organic matter with potassium dichromate in a sulfuric acid medium, followed by spectrophotometric determination of the resulting Cr(III) at a wavelength of 590 nm.

The total nitrogen content in the soil samples was determined using a modified Kjeldahl method in accordance with GOST 26107-84 (ST RK ISO 1986-2010). The method is based on the mineralization of organic nitrogen with concentrated sulfuric acid in the presence of a catalyst, resulting in the formation of ammonium salts, followed by distillation of ammonia in an alkaline medium and its absorption in a boric acid solution, with subsequent titrimetric determination.

The pH and dry residue of aqueous and salt extracts of the investigated soils were determined in accordance with GOST 26423-85 (GOST 26483-85) and ST RK ISO 10390-2007. The method is based on the extraction of water-soluble soil components using distilled water and a 1 M KCl solution (pH 5.6–6.0) at a soil-to-extractant ratio of 1:5, followed by potentiometric determination of pH.

The concentrations of Zn, Cu, Pb, Cd, Cr, Ni, Co, Mn, and Fe in the soil samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) in accordance with ISO 17586:2016, Soil quality - Extraction of trace elements using dilute nitric acid. Elemental concentrations are expressed in mg/kg.

During the summer and autumn periods, plant samples of sunflower, soybean, and maize were collected from the investigated site. The collected plant material was preliminarily separated into individual morphological parts-roots, stems, leaves, and generative organs (fruits)-after which each fraction was analyzed separately.

RESULTS AND DISCUSSION

It is well established that the primary sources of environmental contamination by heavy metals include industrial enterprises, such as metallurgical plants, the chemical industry, and waste disposal sites, as well as the use of chemical agents, including fertilizers and pesticides, and motor vehicles. Eastern Kazakhstan is one of the most industrially developed and anthropogenically impacted regions of the country. The long-term operation of non-ferrous metallurgical enterprises poses a risk of the input of lead, cadmium, zinc, copper, nickel, and chromium into the soil-plant system of adjacent agricultural landscapes.

In the present study, a preliminary assessment of the elemental composition of soil and the seasonal accumulation of metals in agricultural plants was carried out at a site located 10 km from a metallurgical enterprise in the vicinity of Ust-Kamenogorsk. Soil and plant samples were collected at the study site from spring to late autumn in 2025 and 2026. The collected plant material was preliminarily separated into individual morphological parts-roots, stems, leaves, and generative organs (fruits)-after which each fraction was analyzed separately.

This section presents the results obtained for sunflower as a representative crop. Photographs of the investigated plant material are presented in Figure 2.

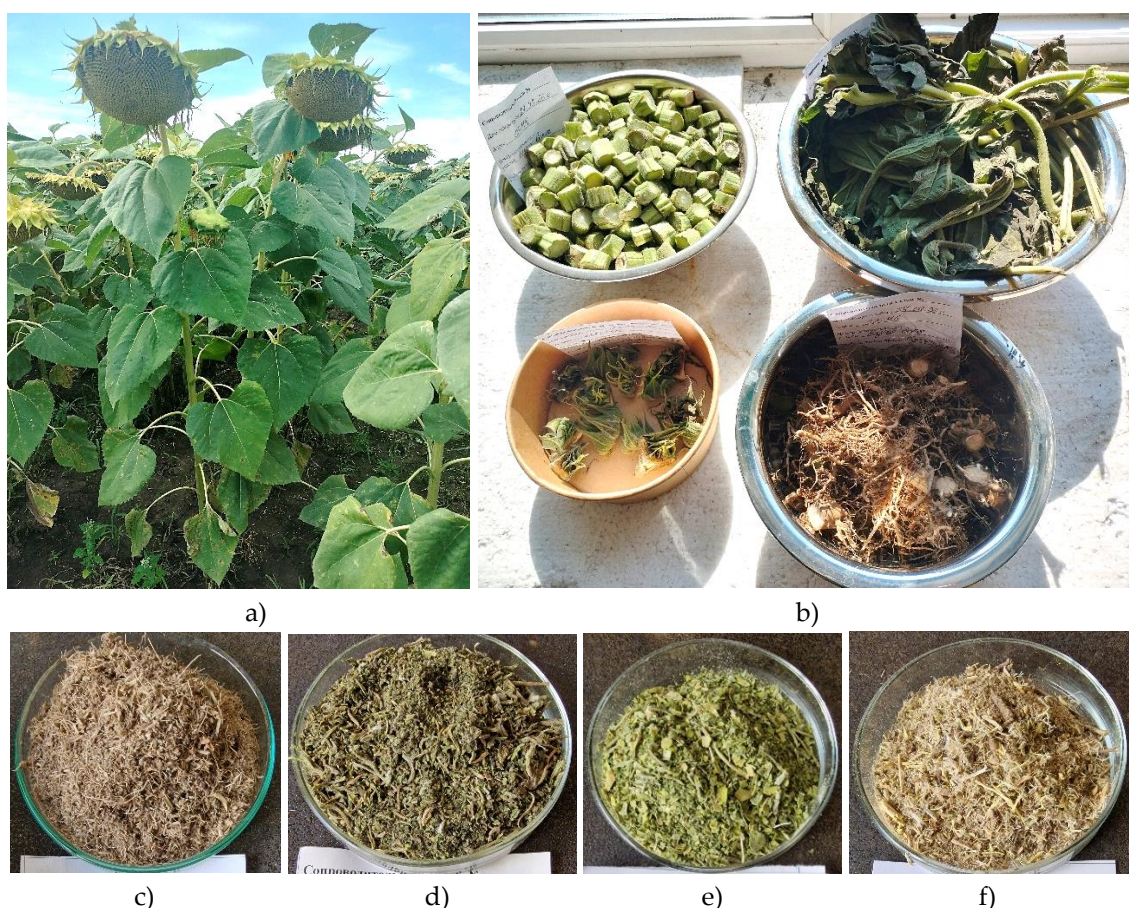


Figure 2. Samples of the investigated sunflower crop: (a) intact plant; (b) individual morphological parts of the plant-roots, stems, leaves, and fruits-during natural drying; (c-f) ground sunflower roots, stems, leaves, and fruits, respectively

Note – compiled by the authors

For the determination of heavy metal concentrations, the plant material was first dried to constant mass and ground using an electric laboratory knife mill to obtain a homogeneous

material with a particle size of no more than 2.0 mm. The prepared samples were thoroughly mixed, after which a 1.0-2.0 g aliquot was placed into pre-ashed and pre-weighed porcelain crucibles.

Ashing was performed in a muffle furnace (Figure 3) in several stages, with a gradual increase in temperature: 200–220 °C for 2 h, 300–350 °C for 1–2 h, and 450–500 °C for 3–6 h, until a homogeneous light-gray or white ash was obtained. After ashing, the crucibles were cooled in a desiccator and additionally heated at 500 °C for 30–60 min, followed by cooling and weighing.



Figure 3. Photographs of sunflower plant samples after ashing

Note – compiled by the authors

The completeness of ashing was controlled by the absence of visible organic residues and attainment of an essentially constant mass. Ashing of leaves and stems predominantly produced a white ash residue, whereas thermal treatment of roots resulted in the formation of brown-colored ash. Ashing of the fruits of the investigated agricultural crops resulted predominantly in the formation of a gray ash product. The resulting ash was homogenized and used for subsequent determination of the concentrations of Zn, Cu, Pb, Cd, Cr, Ni, Co, Mn, and Fe by inductively coupled plasma mass spectrometry (ICP-MS) following acid digestion of the samples in accordance with ISO 16965:2025, Environmental solid matrices - Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). Elemental concentrations are expressed in mg/kg. The results of the soil agrochemical analysis are presented in Table 1.

Table 1. Non-ferrous metal concentrations in soil during autumn and spring sampling

Sampling period	Non-ferrous metal concentrations in soil, mg/kg										
	Ca	Mg	Fe	Mn	Cu	Zn	Ni	Cr	Pb	Co	Cd
Autumn 2025	173,000	141,600	24,380	2,922	2,866	0,790	0,394	0,354	0,222	0,033	0,072
Spring 2026	133,280	130,960	9,185	1,779	1,264	0,943	0,221	0,167	0,762	0,011	0,012

Figure 4 presents a comparative characterization of the soil cover at the experimental site during the autumn-spring period of 2025–2026. The results show that the concentrations of all investigated elements in the soil decreased noticeably compared with their levels in autumn 2025, with the exception of zinc and lead, whose concentrations, in contrast, increased substantially, particularly that of lead.

To assess the concentrations and statistical characteristics of the distribution of heavy metals in the soil of the experimental field, including their concentration ranges and degree of

spatial heterogeneity, the arithmetic mean, standard deviation (SD), minimum and maximum concentrations, and coefficient of variation (CV) were calculated (Table 2).

For plant samples, the seasonal dynamics of elemental concentrations were assessed by calculating the ratio of the autumn concentration to the summer concentration for each plant organ.

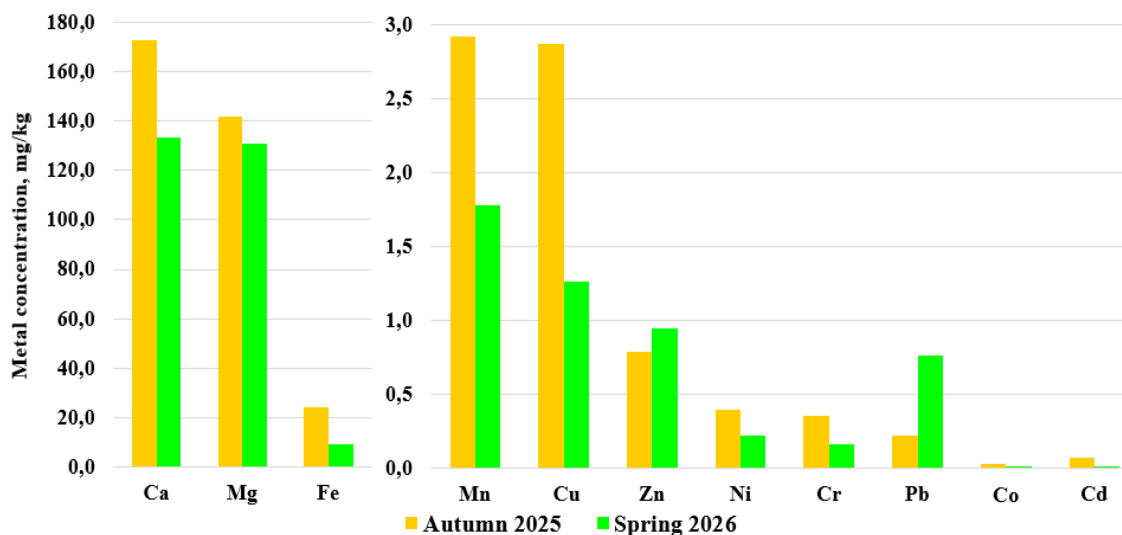


Figure 4. Relationship between non-ferrous metal concentrations in soil and sampling time

Note – compiled by the authors

The coefficient of variation (CV) additionally enabled the assessment of the relative variability in the concentrations of individual elements and comparison of the variability of metals characterized by different mean concentrations.

Table 2. Descriptive statistics of soil parameters at the experimental field

Parameter	Mean	SD	Range	CV, %
Humus, %	3,828	0,385	3,60–4,40	10,1
Water pH	7,078	0,662	6,51–8,03	9,4
Salt pH	6,568	0,673	6,03–7,55	10,2
Pb, mg/kg	0,485	0,036	0,433–0,517	7,5
Cu, mg/kg	1,629	0,198	1,418–1,842	12,1
Zn, mg/kg	0,955	0,111	0,830–1,082	11,6
Ni, mg/kg	0,264	0,030	0,234–0,300	11,5
Mn, mg/kg	0,697	0,252	0,421–1,026	36,1
Cr, mg/kg	0,148	0,020	0,133–0,177	13,4

Note – n = 4; calculated by the authors based on the original laboratory data

The soil of the experimental field was characterized by a mean humus content of 3.83%, with a range of 3.60-4.40%. The mean water pH was 7.08, whereas the salt pH was 6.57. The soil reaction ranged from slightly acidic to slightly alkaline, indicating spatial heterogeneity within the experimental site and potentially affecting metal availability.

The total nitrogen content was relatively stable, ranging from 0.20 to 0.22%, with a coefficient of variation of 3.9%. Among the determined elements, Mn, Mg, Ca, and Fe exhibited the greatest variability. The mean concentrations of Pb, Cu, Zn, Ni, and Cr in the specified analytical form were 0.485, 1.629, 0.955, 0.264, and 0.148 mg/kg, respectively.

The mean water pH of 7.08 indicates conditions under which the solubility of many cationic forms of Pb, Cu, Zn, and Ni is generally limited by sorption and the formation of sparingly soluble compounds. The humus content of 3.60–4.40% indicates that the soil has a considerable sorption capacity. Organic matter can reduce the immediate availability of metals; however, its effect is not unambiguous, as soluble organic complexes may in some cases enhance the mobility of Cu and Zn.

Total nitrogen and available forms of phosphorus and potassium are important for interpreting plant status. Nutrient deficiency may reduce biomass production and thereby increase the measured metal concentration per unit of dry mass. Conversely, intensive plant growth may result in a dilution effect. In the present study, the total nitrogen content of the soil was relatively stable, whereas the concentrations of N, P, and K in the plants decreased in autumn. This observation may reflect the redistribution of nutrients during plant maturation rather than solely indicating nutrient deficiency.

Among the soil elements presented, Mn had the highest coefficient of variation, at 36.1%. Manganese is associated with redox conditions and may undergo localized redistribution depending on soil moisture conditions. The high variability of Mg and Ca may also indicate heterogeneity of the parent material or differences in agronomic management across the site.

At the next stage of the study, the concentrations of these metals in the organs of sunflower plants were investigated (Table 3).

Table 3. Concentrations of priority metals in sunflower plant organs

Plant organ	Sampling period	Pb	Cu	Zn	Ni	Cr	Cd
Roots	Summer	24,27	128,60	200,80	42,87	84,25	2,70
Roots	Autumn	45,90	114,10	337,80	30,72	144,40	5,44
Stems	Summer	14,87	116,70	420,50	347,70	24,73	2,10
Stems	Autumn	47,46	66,77	534,30	15,11	137,20	9,80
Leaves	Summer	30,06	95,74	234,40	16,06	15,77	2,61
Leaves	Autumn	83,10	101,70	395,10	22,72	64,57	4,19
<i>Note – All concentrations are expressed in mg/kg; compiled by the authors based on the original data</i>							

According to the results of the study conducted in 2025 on agricultural fields located approximately 10 km from the metallurgical enterprise, the total content of the investigated heavy metals in the ash products obtained from soybean, sunflower, and maize biomass amounted to 315.5, 305.5, and 165.0 kg, respectively, per 1,000 kg of ash. Calcium, magnesium, and iron accounted for the predominant fraction of the elemental composition of the ash products, with their contents substantially exceeding those of the other investigated elements (Figures 5 and 6). In addition to their contribution to the mineral composition of the biomass, these elements are of particular interest from the perspective of metallurgical processing and the potential recovery of valuable components. At the same time, the presence of non-ferrous and other metals in the ash products, including zinc, copper, manganese, chromium, nickel, lead, cobalt, and cadmium, indicates the potential for considering plant biomass (bio-ore) as a non-traditional technogenic–biogenic raw material for integrated metal recovery.

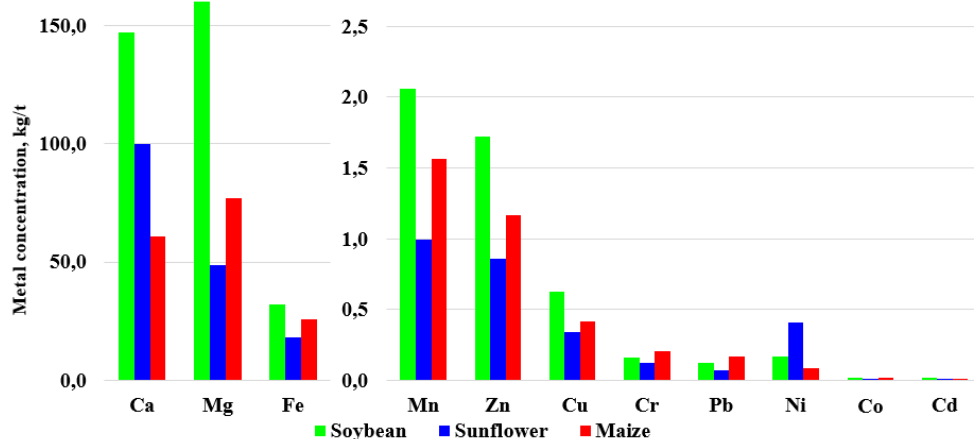


Figure 5. Concentrations of non-ferrous metals in the ash products of sunflower, soybean, and maize biomass in summer 2025

Note – compiled by the authors

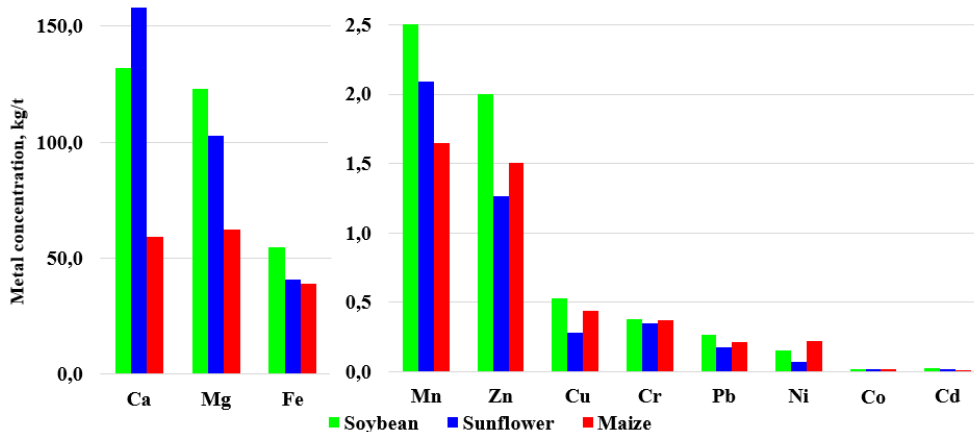


Figure 6. Concentrations of non-ferrous metals in the ash products of sunflower, soybean, and maize biomass in autumn 2025

Note – compiled by the authors

The results of the study showed organ-specific and seasonal patterns in the distribution of metals within the plant biomass. By autumn, Pb concentrations increased in all plant organs: from 24.27 to 45.90 mg/kg in roots, from 14.87 to 47.46 mg/kg in stems, and from 30.06 to 83.10 mg/kg in leaves. The highest autumn concentration was recorded in the leaves. This pattern may be attributed to a combination of root uptake, internal translocation, and deposition of aerosol particles on the leaf surface. Zinc also accumulated by autumn: its concentration increased by 1.68-fold in roots, 1.27-fold in stems, and 1.69-fold in leaves. The seasonal increase in Cr was even more pronounced, reaching 1.71-fold in roots, 5.55-fold in stems, and 4.09-fold in leaves. Cd concentrations increased by 2.01-fold in roots, 4.67-fold in stems, and 1.61-fold in leaves. The highest autumn Cd concentration was recorded in stems, at 9.80 mg/kg. The dynamics of Ni were heterogeneous. In stems, its concentration decreased from 347.70 to 15.11 mg/kg, whereas in leaves it increased from 16.06 to 22.72 mg/kg, and in roots it decreased from 42.87 to 30.72 mg/kg.

Comparison with the reported concentration ranges showed that, in autumn, the upper limit for Pb was exceeded by 2.30-fold in roots, 4.75-fold in stems, and 8.31-fold in leaves. For Cr, the corresponding ratios were 14.44, 17.15, and 8.07, respectively. For Cd, the upper limit was

exceeded by 1.09-fold in roots and 3.27-fold in stems, whereas the concentration in leaves remained within the reported range. The distribution pattern of Pb shifted from relatively similar summer concentrations to a pronounced maximum in leaves during autumn. The leaf-to-root concentration ratio increased from 1.24 in summer to 1.81 in autumn. For an element that is often retained by the root barrier, this result supports the hypothesis of surface deposition and/or enhanced uptake during the later period of the growing season. For Zn, the highest concentrations were observed in stems during both sampling periods, reaching 420.50 mg/kg in summer and 534.30 mg/kg in autumn. This distribution pattern differs from that of Pb and may be associated with the physiological mobility of Zn. In autumn, Zn concentrations reached 395.10 mg/kg in leaves and 337.80 mg/kg in roots. The simultaneous increase in all plant organs is consistent with prolonged metal input but does not allow the soil and atmospheric pathways to be distinguished.

Copper concentrations decreased by autumn in roots and stems but increased slightly in leaves. This pattern demonstrates that seasonal accumulation cannot be generalized across all elements. Cu participates in enzymatic reactions and may be redistributed during tissue senescence. Differences between summer and autumn sampling may also be influenced by variations in the proportion of structural tissues and the degree of sample drying. The analytical results showed an increase in Cd concentrations in vegetative organs by the autumn period. The mean Cd concentration in sunflower leaves, stems, and roots increased from 2.47 mg/kg in summer to 6.48 mg/kg in autumn, corresponding to a 2.62-fold increase. Analysis of Cd distribution among individual plant organs showed that its concentration in stems increased from 2.10 to 9.80 mg/kg, i.e., by 4.67-fold. In leaves, the concentration increased from 2.61 to 4.19 mg/kg, whereas in roots it increased from 2.70 to 5.44 mg/kg.

Based on the experimental data obtained and the calculated parameters, the potential yield of ash products and the quantities of the investigated metals contained therein were estimated on a per-unit-area basis for the agricultural site (Table 4). Taking into account the reported ranges of dry biomass production and biomass ash content, calculated using the approach described by Pagliuso et al. (2025), Lisý et al. (2020), and Lizotte, Savoie and De Champlain (2015), it was established that the potential ash product yield from 1 ha of soybean crops could range from 200 to 480 kg, from sunflower from 640 to 1,440 kg, and from maize from 480 to 1,260 kg. Considering the total concentrations of the investigated metals determined in the ash products, the potential quantities of these metals that could be concentrated in the ash residue generated from 1 ha were subsequently calculated.

Table 4. Potential yield of ash products and the investigated metals from 1 ha of agricultural crops

No.	Crop	Dry biomass, t/ha	Ash content, %	Ash product, kg/ha	Potential content of the investigated metals, kg/ha
1	Soybean	5 - 8	4 - 6	200 – 480	63,096 - 151,430
2	Sunflower	8 - 12	8 - 12	640 - 1440	195,558 - 440,006
3	Maize	8 - 14	6 - 9	480 – 1260	79,157 - 207,787

For soybean, this parameter ranged from 63.096 to 151.430 kg/ha; for sunflower, from 195.558 to 440.006 kg/ha; and for maize, from 79.157 to 207.787 kg/ha. Thus, the calculated values demonstrate the presence of substantial quantities of mineral components in the plant biomass, which become concentrated in the ash product during thermal processing.

The high concentrations of heavy metals are likely associated with the atmospheric deposition of substantial quantities of metal-containing aerosol particles originating from industrial sources, thereby contributing to the formation of zones of contamination in soil, water,

and vegetation. An important factor in this context is the regional wind rose, which determines the direction, transport distance, and intensity of air-mass movement. Prevailing winds form a «plume» of pollutants extending over considerable distances, with the development of a near-source zone characterized by intensive and spatially heterogeneous contamination and a more extensive deposition zone.

The wind rose is a critical factor in environmental mapping and risk assessment, as it makes it possible to predict the likely directions of atmospheric transport of metals such as lead, cadmium, copper, and mercury. The wind regime of Ust-Kamenogorsk is characterized by seasonal variability and changing prevailing directions, with northwestern and southeastern winds occurring most frequently. This pattern is associated with the topographic features of the Irtysh River valley. The local wind regime has a substantial influence on the dispersion of industrial emissions within the city.

Ust-Kamenogorsk is located in a basin surrounded by the Altai Mountains, which contributes to specific meteorological conditions favorable to periods of calm. According to data from the Republican State Enterprise «Kazhydromet» the total annual atmospheric emissions of pollutants in Ust-Kamenogorsk amounted, for example, to 164,369 tonnes in 2022. Motor vehicles accounted for 90,031 tonnes per year, while emissions from various industrial and other enterprises amounted to 54,548 tonnes per year.

Under these conditions, atmospheric deposition of metal-containing particulate matter is likely to occur. This mechanism is indirectly supported by the elevated concentrations of Pb and Cr detected in plant leaves during the autumn period, as well as by data from previous studies conducted in the industrial zone of Ust-Kamenogorsk.

CONCLUSION

The soil of the investigated field, located 10 km from the metallurgical enterprise, was characterized by a mean humus content of 3.83%, a water pH of 7.08, and a salt pH of 6.57. In the autumn samples, the concentrations of Pb, Cu, Zn, Ni, and Cr in the analytical form specified in the original laboratory records exhibited moderate variability, with the exception of the higher variability observed for Mn.

A seasonal increase in the concentrations of Pb, Zn, Cr, and Cd was observed in sunflower organs. The highest autumn Pb concentration was recorded in the leaves (83.10 mg/kg), whereas the highest Cd concentration was detected in the stems (9.80 mg/kg). The mean Cd concentration in sunflower roots, stems, and leaves increased 2.62-fold between the summer and autumn sampling periods.

The obtained data indicate the accumulation of metals during the growing season and support the potential for developing an alternative metallurgical technology for the recovery of non-ferrous metals from bio-ore. It should be noted that the reported values represent potential metal contents estimated from the approximate dry biomass yield, its ash content, and the determined elemental composition of the ash.

The obtained results can be considered an initial assessment of the resource potential of plant biomass as a non-traditional source of metallurgical raw materials. However, the actual metal recovery during subsequent processing will depend on their mineral forms, distribution within the ash product, solubility, and the efficiency of the extraction technology. The latter will be investigated in subsequent studies by the authors.

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DATA AVAILABILITY STATEMENT: The data supporting the results of this technical study are available from the corresponding author upon reasonable request.

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