

HEAVY METAL ACCUMULATION IN FOOD CROPS CULTIVATED IN CONTAMINATED SOILS IN ALBANIA

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Abstract

The consumption of vegetables and fruits is a major pathway for human exposure to heavy metals, especially when these elements accumulate in edible plant parts. This study assessed the accumulation of nickel (Ni), chromium (Cr), zinc (Zn), iron (Fe), and manganese (Mn) in soils and food crops cultivated near a former metallurgical plant in Elbasan, Albania. The analyzed crops included onion, salad, potato, pepper, and strawberry. Bioconcentration factors (BCFs) were calculated to evaluate the capacity of each crop to uptake heavy metals from soil. Available metal concentrations in soil were determined using the Mehlich-1 extraction method and quantified by atomic absorption spectrometry. The results indicated that Mn, Zn, Fe, and Cr concentrations in potatoes, and Fe levels in pepper, were within WHO safety limits. However, Fe levels in onion, salad, and strawberry, Ni in all edible crops, and Cr in onion, salad, strawberry, and pepper exceeded recommended thresholds. The calculated BCFs confirmed notable metal accumulation, particularly for Ni and Cr. These findings highlight the need for regular monitoring of heavy metal levels in both soil and crops to safeguard food safety and public health.

Key words: accumulation; available metals; bioaccumulation factor plants (BFP); food crops; heavy metals.

INTRODUCTION

Heavy metals are naturally occurring elements with a density greater than 5 g/cm³ and are integral components of the Earth's crust. Their concentration in soil varies depending on the geochemical and mineralogical characteristics of the soil, as well as the extent of anthropogenic pollution. Soil contamination with heavy metals can result from numerous human activities, including mining, metallurgical and smelting processes, the application of organic and inorganic fertilizers, the use of pesticides and insecticides containing metal compounds, emissions from transportation, discharges from chemical plants, runoff, and waste from landfills (Hu et al., 2013; Osmani et al., 2015; Gjoka et al., 2022).

In recent years, the widespread use of heavy metals in industrial applications, and in the production of agrochemicals, has heightened the risk of environmental contamination and their subsequent entry into the food chain (Bradl, 2002). Fruits and vegetables are essential

components of the human diet, valued for their rich content of micronutrients, carbohydrates, vitamins, and fiber, all of which contribute positively to human health (Hu et al., 2013). However, elevated concentrations of heavy metals in edible plant parts pose significant health risks. Numerous studies have demonstrated that heavy metals can be absorbed by plant roots and transported to aerial parts, leading to accumulation in edible tissues, even when soil concentrations are relatively low (Jolly et al., 2013; Sharma et al., 2018; Zwolak et al., 2019).

Vegetables grown in agricultural soils located near industrial sites or in regions with naturally elevated metal content are particularly susceptible to contamination.

The metallurgical complex in Elbasan, central Albania, has long been identified as a major source of heavy metal pollution. Spanning an area of 155 hectares, this complex historically processed approximately 800,000 tons of ultramafic minerals (Fe-Ni), releasing an estimated 44.8 tons of toxic dust. Following

significant political and technological changes in the 1990s, many of the complex factories were shut down, and the surrounding area was repurposed for residential and agricultural use. Today, a variety of crops - including vegetables, fruits, and cereals - are cultivated on this land. As a result of the long-term processing and smelting of Fe-Ni-rich minerals, the soils surrounding the former industrial site are heavily contaminated with several heavy metals, including Fe, Mn, Ni, Zn, and Cr (Shallari et al., 1998; Sallaku et al., 1999; Osmani et al., 2015; Osmani et al., 2018). Despite this known contamination, limited research has been conducted on the accumulation of heavy metals in food crops grown in this area, or on the potential for selecting crop species or cultivars with low metal uptake.

Therefore, the present study aims to fill this gap by (1) investigating the concentration and bioavailability of selected heavy metals in the soils of the study area, and (2) assessing the accumulation of these metals in the edible parts of selected vegetables and fruit cultivated in this industrial region of Elbasan, Albania.

MATERIALS AND METHODS

Study area

This study was conducted in 2024 on contaminated farmland located in the Elbasan region of central Albania. The site, situated near the former metallurgical plant ($41^{\circ}09'18.12''N$, $20^{\circ}04'34.17''E$), lies to the west of Elbasan city and is characterized by flat topography (Figure 1). The area where the samples were collected is located about 500 meters from the former Ferro-nickel factory, which has not been operational for years. The local climate is typically Mediterranean, with an average annual temperature ranging between 15 and 16°C.

Sampling of Soil and Vegetables

Samples were collected from farmland adjacent to the metallurgical complex during the spring and summer of 2024. Three subsamples were taken for each of the four vegetable species and one fruit species cultivated in the area. Both soil and edible plant parts were collected.

The plant types and species included in the study are presented in Table 1.

Table 1. Vegetables type and species used in study

Vegetable Type	Vegetable Species
Bulb vegetable	<i>Allium cepa</i> (Onion)
Leafy vegetable	<i>Lactuca sativa</i> (Salad)
Tuber	<i>Solanum tuberosum</i> (Potato)
Fruits	<i>Fragaria vesca</i> (Strawberry)
Solanaceous	<i>Capsicum annuum</i> (Pepper)

Soil samples were taken from the rhizosphere (root zone) of each plant type, with three repetitions per crop. All samples were placed in clean polyethylene bags, clearly labeled by type, and transported to the Laboratory of the Department of Environment and Natural Resources at the Agricultural University of Tirana (AUT) for analysis.

Soil and Plant sample preparation and analysis

Plant samples were washed thoroughly with distilled water to remove the adhering dust. Soil samples were air-dried at room temperature to a constant weight and then finely ground using a mortar and pestle. The edible plant parts were chopped into small pieces using a pre-cleaned stainless-steel knife and oven-dried at 75°C for three days. Dried samples were then pulverized into a fine powder and stored in clean polyethylene (PE) bags for analysis.

Soil and plant analyses were performed at the Agricultural University of Tirana (AUT) and the University of Pristina in Kosovo. Soil pH was measured using a 0.01 M $CaCl_2$ solution at a 1:2.5 soil-to-solution ratio. Cation exchange capacity (CEC) was determined using the ammonium acetate method.

The Mehlich-1 extractant was used to determine the available concentrations of nickel (Ni) in soil, which were then analyzed using atomic absorption spectrometry (AAS). For total concentrations of macronutrients (P, K, Ca, Mg) and micronutrients (Fe, Mn, Zn, Ni, Cr, Co), 0.5 g of soil was digested in aqua regia (a 1:3 mixture of 65% HNO_3 and 37% HCl) at 200°C for 40 minutes, followed by analysis via AAS. To determine heavy metal concentrations in plant tissues, 0.2 g of dried plant material (edible parts and roots) was digested in a 4:1 mixture of 65% HNO_3 and 30% H_2O_2 using microwave digestion at 200°C for 25 minutes.

Digest solutions were analyzed using Atomic Absorption Spectrophotometry (AAS) with the Analytik Jena AAS 400 instrument. The elements analyzed included iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), chromium (Cr), zinc (Zn), and cobalt (Co). The limit of detection (LOD) for each element was defined as three times the standard deviation of the blank signal. We used the slope of the curve (absorbance per mg/L) to convert absorbance units in mg/L. The LOD values (in mg/L) for Fe, Mg, Mn, Zn, Ni, Cr, and Co were 0.009, 0.03, 0.0018, 0.012, 0.015, 0.012, and 0.02, respectively. The calibration ranges used in this study (in mg/L) were as follows: Fe: 0-10, Mg: 0-5, Mn: 0-5, Zn: 0-5, Ni: 0-5, Cr: 0-5, Co: 0-5. Dilution was applied to samples containing element concentrations above the upper limit of the calibration range. Quality control was ensured through the use of blanks and certified reference materials (CRMs), with recovery rates maintained within $\pm 10\%$ of the target values.

Bioconcentration factor (BCF)

The Bioconcentration Factor (BCF) quantifies a plant's ability to accumulate metals from soil. It is calculated as the ratio of the metal concentration in the plant's edible part to its total concentration in the corresponding rhizospheric soil:

$$BCF = C_{\text{plant}} / C_{\text{soil}}$$

A BCF value below 1 indicates limited metal transfer from soil to plant, while a BCF greater than 1 suggests substantial uptake (Sharma et al., 2018; Ba et al., 2024).

Statistical analysis

Differences in the BCFs of heavy metals (Mn, Zn, Ni, and Cr) among the edible parts of the five crop species were evaluated using one-way ANOVA. A significance level of $p < 0.05$ was used to determine statistical relevance.

RESULTS AND DISCUSSIONS

Soil characteristics

Phosphorus (P) levels in the study soils were within the typical range, between 0.5 and 0.6 g/kg of dry soil. The total potassium (K) content in the upper 0.2 meters of agricultural soil generally ranges from 10 to 20 g/kg (Mandlo et al., 2022); however, in this study, values ranged

from 6 to 9.8 g/kg, which is slightly below the expected range.

Calcium (Ca) and Magnesium (Mg), though considered secondary nutrients, are essential for plant growth. In the study soils, Ca concentrations were consistently higher than Mg concentrations. This pattern suggests that the soils do not have a natural ultramafic origin, as ultramafic soils typically show higher Mg levels relative to Ca. Instead, the elevated presence of elements commonly associated with ultramafic rocks - such as Fe, Mg, Ni, Cr, and Co - can likely be attributed to anthropogenic contamination from the long-term processing of ultramafic minerals at the nearby metallurgical complex (Table 2A).

Iron (Fe) concentrations in the soil ranged from 18 to 26 g/kg, aligning with typical background levels reported for agricultural soils (Bodek et al., 1988).

The soils in the study area were found to be contaminated with several heavy metals, including manganese (Mn), zinc (Zn), nickel (Ni), chromium (Cr), and cobalt (Co), as detailed in Tables 2A and 2B. Nickel concentrations in rhizospheric soils ranged from 400 to 610 mg/kg, exceeding both the background level for Albanian agricultural soils (287.15 mg/kg) (Gjoka et al., 2022) and the intervention threshold of 210 mg/kg set by Denneman and Robberse (1990) and the Netherlands Ministry of Housing (1994).

Cobalt concentrations varied between 85 and 111 mg/kg across different sampling sites, also exceeding the background value of 83.10 mg/kg. Chromium levels ranged from 310 to 380 mg/kg, far above the target value of 100 mg/kg and the background level of 131.63 mg/kg reported for Albanian agricultural soils. These elevated concentrations of Ni, Cr, and Co are consistent with long-term emissions from metallurgical operations that processed ultramafic ores rich in these elements. Zinc concentrations ranged from 75 to 132 mg/kg. While these values are above the background concentration for Zn in Albanian soils (81.80 mg/kg) in the cases of soils under potato, strawberry, and pepper crops, they remain below the intervention threshold of 150-300 mg/kg established by the Council of the European Communities (1986).

As shown in Table 2, soils associated with all sampled crops exhibited elevated concentrations of Ni, Cr, and Co compared to both background levels and intervention thresholds.

Nickel and cobalt exceeded the permissible limits in all plots, with the highest Ni level recorded in strawberry soil (610 mg/kg), nearly three times the intervention threshold. Similarly,

chromium levels in onion and strawberry soil surpassed the 360 mg/kg intervention value. Zinc levels were highest in soils associated with strawberry and pepper but remained below the intervention limit of 300 mg/kg. Manganese concentrations were well below critical thresholds in all plots, though consistently elevated.

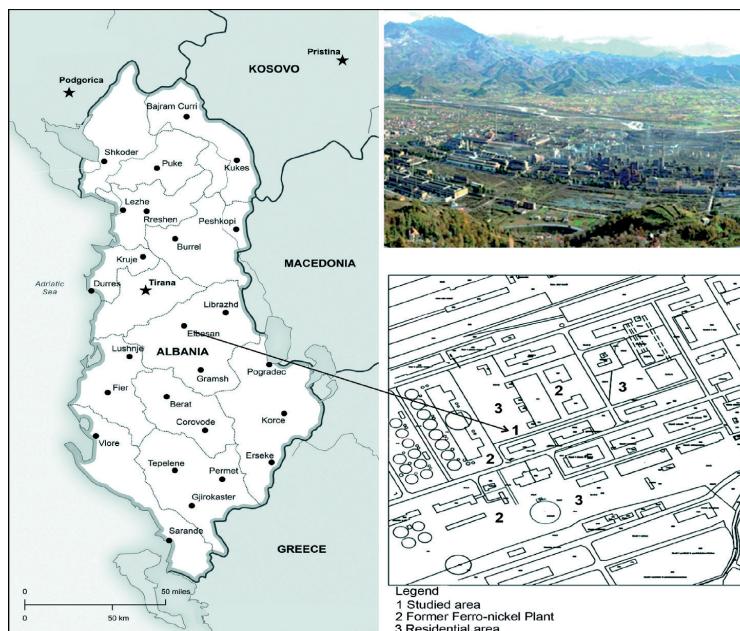


Figure 1. Map of Albania with the location of former Ferro-nickel plant and the study area.

Table 2. Total macronutrients and micronutrients (mean \pm SD) in soils of different sampling sites

A) Macronutrients (g/kg dry soil)					
Soil of Vegetable	P	K	Ca	Mg	Fe
Onion	0.5 \pm 0.04	8.1 \pm 1.0	31 \pm 2	14 \pm 2	26 \pm 6
Salad	0.7 \pm 0.01	7.2 \pm 0.5	29 \pm 5	13 \pm 3	18 \pm 1
Potato	0.6 \pm 0.01	9.8 \pm 0.5	30 \pm 4	14 \pm 5	19 \pm 5
Strawberry	0.6 \pm 0.02	6.0 \pm 1.0	41 \pm 8	15 \pm 4	19 \pm 2
Pepper	0.6 \pm 0.02	8.1 \pm 0.5	30 \pm 5	14 \pm 4	18 \pm 1

B) Micronutrients (mg/kg dry soil)					
Soil of Vegetable	Mn	Zn	Ni	Cr	Co
Onion	576 \pm 40	75 \pm 5	410 \pm 7	380 \pm 16	75 \pm 9
Salad	538 \pm 60	90 \pm 14	440 \pm 13	310 \pm 52	74 \pm 4
Potato	557 \pm 15	122 \pm 12	405 \pm 10	315 \pm 68	74 \pm 8
Strawberry	547 \pm 30	132 \pm 16	610 \pm 11	370 \pm 62	111 \pm 6
Pepper	565 \pm 23	123 \pm 8	400 \pm 20	360 \pm 19	85 \pm 5

*Intervention Threshold Values (mg/kg): Mn - 1500, Zn - 300, Ni - 210, Cr - 360, Co - 50

Macronutrient data showed moderate variability across sites, with phosphorus ranging from 0.5 to 0.7 g/kg and potassium from 6.0 to 9.8 g/kg. Notably, the strawberry plot had the highest

calcium concentration (41 g/kg), suggesting potential input differences or localized soil characteristics.

A soil pH between 6.0 and 7.2 is considered optimal for the growth of most garden crops, although many vegetable and fruit species can tolerate pH values between 7.0 and 8.0 (extension.usu.edu). The pH values in the rhizosphere of crops collected from the contaminated area in Elbasan (Table 3) fall within this acceptable range, suggesting that pH is not a limiting factor for plant growth in these soils. Cation exchange capacity (CEC) in the studied soils ranged from 15 to 26 cmol/kg, with an average of 20.6 cmol/kg. These values reflect a moderate-to-high nutrient-holding capacity, which is typical of fertile agricultural soils.

While total metal concentrations are useful for identifying long-term contamination and possible sources, they do not accurately represent the portion of metals available for plant uptake. To evaluate bioavailability, the Mehlich-1 extraction method was used to assess the potentially available fractions of Fe, Mn, Zn, Ni, Cr, and Co. The results indicate that available Fe concentrations ranged from 16 to 58 mg/kg, Mn from 4 to 15 mg/kg, and Ni from 2.4 to 4.5 mg/kg. Notably, Co and Cr showed very low extractable concentrations across all sampled soils, a finding consistent with their limited uptake by plants in this study.

Table 3. Soil pH, CEC, and available metal concentrations (mean values)

Soil of vegetable	pH	CEC (cmol/kg)	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Co (mg/kg)
Onion	7.5	15	38	4	3.8	3.6	0.1	0.2
Salad	8.0	17	57	5	3.0	4.0	0.1	0.2
Potato	7.7	14	16	3	3.7	3.6	0.1	0.2
Strawberry	7.5	16	58	12	2.9	4.5	0.1	0.2
Pepper	7.5	26	28	15	3.9	2.4	0.1	0.2

Nickel concentrations in edible plants and roots of food crops

The mean concentrations of iron (Fe), manganese (Mn), zinc (Zn), nickel (Ni), and chromium (Cr) in the edible parts of the sampled food crops ranged as follows: Fe (99-765 mg/kg), Mn (6.2-90 mg/kg), Zn (3.6-12 mg/kg), Ni (10-26 mg/kg), Cr (0.5-19 mg/kg) (Table 4).

Among these, the Mn, Zn, Fe, and Cr concentrations in potatoes, and Fe in peppers, remained below the permissible limits set by the World Health Organization (WHO). However, Fe levels in onion, salad, and strawberry, Ni concentrations in all edible samples, and Cr concentrations in onion, salad, strawberry, and pepper exceeded the WHO safety thresholds.

Table 4. Heavy Metal concentrations in edible parts of crops (mean \pm SD)

Vegetable	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
Onion	200 \pm 4	6.4 \pm 2	8 \pm 2	12 \pm 2	2.0 \pm 0.1
Salad	646 \pm 41	25 \pm 3	3.6 \pm 0.2	16 \pm 1	5.0 \pm 0.7
Potato	59.5 \pm 9	6.2 \pm 1	10.0 \pm 0.7	10 \pm 0.5	0.5 \pm 0.3
Strawberry	765 \pm 59	90 \pm 2	7 \pm 0.1	26 \pm 3	19.0 \pm 3.0
Pepper	99 \pm 3	21 \pm 4	12 \pm 2	15 \pm 1	4.0 \pm 0.6
WHO Limits	270	300	300	10	1.3

These findings indicate a significant health concern, particularly regarding Ni and Cr accumulation. The order of Ni accumulation in edible parts of the crops was as follows: Strawberry (fruit) > Salad (leafy vegetable) > Pepper (solanaceous) > Onion (bulb) > Potato

(tuber). The metal concentrations in the roots of these food crops were significantly higher than in the edible parts, ranging as follows: Fe (1899-2658 mg/kg), Mn (25-97 mg/kg), Zn (6-28 mg/kg), Ni (16-56 mg/kg), Cr (4.2-24 mg/kg) (Table 5).

Table 5. Heavy Metal concentrations in roots of crops from contaminated soil (mean \pm SD)

Vegetable	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
Onion	2658 \pm 4	97 \pm 2	26 \pm 0.06	56 \pm 0.4	21.0 \pm 0.1
Salad	2494 \pm 41	25 \pm 3	6 \pm 0.2	16 \pm 0.8	23.0 \pm 0.7
Potato	2239	87 \pm 0.7	20.0 \pm 0.7	42 \pm 0.5	24.0 \pm 0.3
Strawberry	2487 \pm 59	70 \pm 0.7	11 \pm 0.1	27 \pm 2.6	12.0 \pm 3.0
Pepper	1899 \pm 3	41 \pm 4	28 \pm 2	25 \pm 1.2	4.2 \pm 0.6

This pattern reflects the bioaccumulation of metals in root tissues and is consistent with the elevated levels of available metals in the rhizospheric soils. In all cases, root concentrations of Fe, Mn, Zn, Ni, and Cr exceeded WHO safety thresholds (FAO/WHO, 2001).

Bioconcentration Factor (BCF)

Bioconcentration Factors (BCFs) are used to evaluate the capacity of food crops to accumulate heavy metals in their edible tissues. The transfer of metals from soil to plants, and specifically into the edible parts, represents the principal route through which potentially toxic elements enter the human food chain. This process is influenced by several factors, including the type and concentration of the metal, plant species, soil physicochemical properties, and environmental conditions (Gebeyehu & Bayissa, 2020).

Figure 2 presents the BCF values calculated for Fe, Mn, Zn, Ni, and Cr in the edible parts of the crops analyzed in this study. Notably, the BCFs for Mn, Ni, and Cr were significantly higher in

the fruit crop (strawberry) compared to the four vegetable types, indicating a greater potential for metal accumulation in fruit tissues under similar soil contamination conditions.

In all tested vegetables and fruits, BCF values were below 1.0 when calculated using the total metal concentrations in rhizospheric soil, suggesting that while metals were taken up, the transfer efficiency was relatively low. However, values close to or approaching 1 may still indicate concern when paired with high soil concentrations.

The relative order of metal transfer based on BCFs differed across plant types: Onion (Zn > Ni > Mn > Cr), Salad (Mn > Zn > Ni > Cr), Potato (Zn > Ni > Mn > Cr), Pepper (Zn > Ni > Mn > Cr). These differences highlight species-specific metal uptake mechanisms and the importance of crop selection when cultivating in contaminated areas.

Statistical analysis using one-way ANOVA revealed significant differences ($p < 0.05$) in the BCFs of Mn, Zn, Ni, and Cr among the five food crop types analyzed, as shown in Table 6.

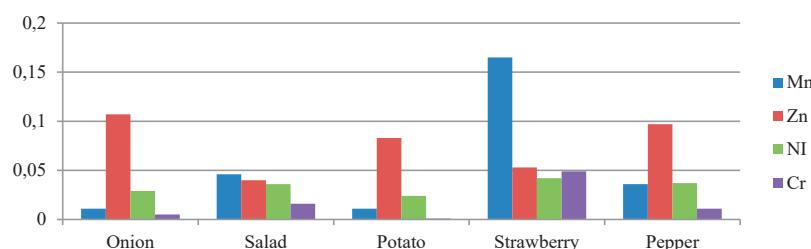


Figure 2. Bioconcentration Factor (BCF) in food plants

Table 6. ANOVA results: Significant differences in BCFs of Heavy Metals among edible parts of five food crops

Metal	Degrees of Freedom (df)	F-value	P-value	Critical F-value
Mn	4	208	0.000	3.47805
Zn	4	16.7	0.0002	3.47805
Ni	4	11.2	0.001	3.47805
Cr	4	153	0.000	3.47805

CONCLUSIONS

This study investigated the accumulation of heavy metals in four vegetable species and one fruit species cultivated on farmland contaminated with iron (Fe), manganese (Mn), zinc (Zn), and nickel (Ni) in Elbasan, Albania. The concentrations of these metals in the soil exceeded the typical background levels reported for Albanian agricultural soils.

Among the edible parts of the analyzed crops, metal concentrations decreased in the following order: Fruit (Strawberry) > Leafy vegetable (Salad) (except for Zn) > Solanaceous (Pepper) > Bulb (Onion) > Tuber (Potato). This gradient indicates that certain crop types, particularly fruits and leafy vegetables, are more prone to accumulating heavy metals and may therefore pose greater health risks when grown in contaminated environments.

These findings support the selection of low-accumulator plant species - such as onions and potatoes - for cultivation in areas with known soil contamination. Conversely, high-accumulator species should be avoided or managed carefully to reduce human exposure to toxic metals through the food chain.

Future research should focus on identifying the chemical forms and mineral phases of metals - especially Ni, soil to better understand their bioavailability, environmental mobility, and potential risks. This knowledge will be crucial for developing effective mitigation strategies and improving food safety in contaminated regions.

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