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Professional paper

BIOACCUMULATION OF CU AND CO IN LEAFY AND FRUIT VEGETABLES FROM THE SUBURBS OF MITROVICA, KOSOVO

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Abstract

Contamination of vegetables with heavy metals is one of the basic environmental problems, especially in developing cities, primarily due to the uncontrolled level of pollution caused by industrial growth and the increase in the number of vehicles using petroleum fuels. This paper aims to determine the bioconcentration of heavy metals Cu and Co in leafy and fruit vegetables grown near Kosovska Mitrovica (Republic of Kosovo). Three places near Kosovska Mitrovica (Zvečan, Frashër, and Polski) are grown: parsley, spinach, lettuce, peppers, eggplant, and cucumber. All analyzed crops are from the 2023 harvest. In the same period, an analysis was made of the soil on which the crops were grown. The bioconversion factor (BF)of the selected leafy and fruit vegetables was also determined. The ICP-MS technique was used to determine the concentration of Cu and Co in soil and leafy and fruit vegetables.

From the obtained analyzes it was determined that the soil in Frashër contains the highest amount of Cu and Co - 58.4 mg/kg and 11.6 mg/kg respectively. The amount of Cu in the examined dry leafy and fruit vegetables is in the range from 5.38 mg/kg to 22.4 mg/kg, and of Co from 0.27 mg/kg to 2.99 mg/kg. The bioconcentration factor of the studied leafy and fruit vegetables of Cu and Co is in the range of 0.04 to 0.26 and 0.15 to 0.65 respectively.

The accumulation of Co in the analyzed vegetables is higher than the accumulation of Cu, due to the higher BF values for Co. The statistical processing of the results (t-test) showed that there is a difference in the concentration of Cu and Co between leafy and fruit vegetables, but there is no statistically significant difference because the obtained p-values are greater than the marginal p-values.

Keywords: bioconcentration, vegetables, heavy metals, Cu, Co.

1. Introduction

Vegetables and fruits are one of the basic components of human nutrition because they are a source of essential micronutrients such as copper, zinc, calcium, iron, magnesium, iodine, sodium, potassium, antioxidants, vitamins, and other metabolites. They can be consumed in fresh form or thermally processed (cooked) and therefore, vegetables containing toxic metals can cause harmful effects on human health (Mawari et al., 2022). The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous, even in small concentrations. "Heavy metals" is a generally accepted term that refers to metals and metalloids with an atomic density greater than 4 g/cm3, or five times or more, that of water. Heavy metals include: lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the group of elements of platinum (Duruibe, Ogwuegbu, & Egwukuri, 2007). Heavy metals are a group of metals with a relatively high density, atomic number, or weight ranging from 63.5 to 200.6 g mol-1 (Atitsogbey, Kyereh, Ofori, Johnson, & Steiner-Asiedu, 2023). Anthropogenic sources (non-ferrous metallurgical industry, mining, mineral processing, galvanization, etc.) are usually the main sources of release of hazardous metals such as heavy metals (Sarker et al., 2023). Although traces of copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), and zinc (Zn) are needed by plants, excessive amounts of these metals can be dangerous (Balkhair & Ashraf, 2016; Sonone, Jadhav, Sankhla, & Kumar, 2021). The use of polluted wastewater, fresh animal manure, and intensive use of

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agrochemicals causes the accumulation of heavy metals in the soil (Atitsogbey et al., 2023). Plants absorb Cu from the soil in the form of Cu2+ because it has a high affinity for binding organic matter compared to other Cu species (Ogunkunle et al., 2019). Eissa & Negim (2018) investigated the content of Cu in the roots and leaves of fresh lettuce. The authors determined 30 mg/kg in root and 15 mg/kg Cu in leaves of fresh lettuce. The content of Cu in fresh roots and leaves of spinach determined by Eissa & Negim (2018) is 35 mg/kg and 17 mg/kg Cu, respectively. When determining the content of Cu in dry onions by Bedassa, Abebaw, & Desalegn (2017), a quantity of 3.93±0.61 mg/kg was determined. Asafew & Chandravanshi (2021) determined a content of 4.3 to 10.0 mg/kg in dry eggplant. Murtić, Zahirović, Jurković, Karić, & Koleška (2019) determined an amount of 6.12±2.37 mg/kg of copper in dried cucumbers. Cobalt (Co) is an important trace element that participates in the production and regulation of red blood cells, platelets, and DNA, as well as the synthesis of fatty acids. Excessive intake can cause systemic toxicity affecting multiple organ systems. Cobalt toxicity occurs at blood levels of 7-10 μg/L and above. (Venkatraman, Wong, Shalita, Parente, & Lad, 2020). Un Nisa, Samiullah, Khan, & ur-Rehman (2020) determined 0.3841 mg/kg amount of cobalt in dried cucumbers grown in the city of Quetta (Pakistan). The mean lead content determined in spinach grown in Shiraz, Iran is 1.75 mg/kg of dry matter (Rahmdel et al., 2018). Using atomic absorption spectrophotometer Salhotra & Verma (2017) determined 5.32 mg/kg Co and 2.97 mg/kg Co in dry spinach and green pepper, respectively. This paper aims to determine the bioconcentration of heavy metals Cu and Co in leafy and fruit vegetables grown in the vicinity of Kosovska Mitrovica (Republic of Kosovo).

2. Materials and methods

2.1. Materials: Leafy vegetables (parsley, spinach, lettuce) and fruit vegetables (peppers, eggplant, and cucumber) were tested. The analyzes were made at the technological and nutritional maturity of the vegetables (harvest 2023). The soil on which this vegetable was grown was also analyzed.

2.2. Methods:

Study area

This study was conducted in three villages in the Kosovska Mitrovica region (42.883°N, 20.867°E) in Kosovo. Two of the villages - Zvečan (42°54'27"N, 20°50'25.01"E) and Frashër (42° 34' 59.88" N, 21° 00' 0.36" E) are near the lead and zinc smelter and the third - Polski (43 25' 00", 25 39' 00") is at a greater distance from the smelter.

Preparation of samples

All samples for analysis were dried to constant weight in an oven (Drying Oven SLN 15, Wodzisław Śląski, Poland) for 24-30 hours depending on the type of vegetable.

Determination of heavy metals Cu and Co

The determination of the concentration of Cu and Co in the selected types of vegetables was done with an accredited method MKC EN ISO/IEC 17025:2018 for determining the content of 35 elements in different samples using microwave digestion and inductively coupled plasma with ICP-MS mass spectrometry (model 7500cx, Agilent USA) - flexible range method.

Cu and Co in the soil are determined by the ISO 11464:2006(E) method; ISO 14869-1:2001; ICP-MS technique (ISO 17294-2:2009) - flexible range method.

Determination of Bioconcentration factor

The bioconcentration factor (BF) is determined using the formula:

$$BF = \frac{C_{dry\ vegetables}}{C_{soil}},$$

Where:
$C_{dry\ vegetables}$ = heavy metal concentration in dry vegetables, and
C_{soil} = heavy metal concentration in soil.

Statistical data processing

Statistical data processing was performed using Microsoft Excel 2016. Statistical correlation and student's t-test were performed on the concentration of Cu and Co between leafy and fruit vegetables.

3. Results and Discussion

Fig 1 presents copper concentrations in six types of dry vegetables: parsley, spinach, lettuce, peppers, eggplant, and cucumber.

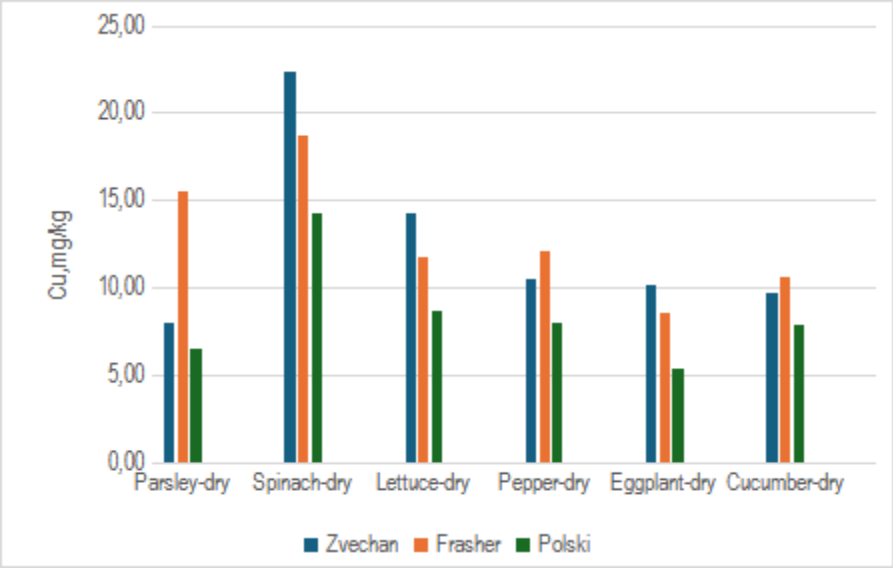

Figure 1. Concentration of Cu in dry vegetables in different regions in the surroundings of Kosovska Mitrovica

When comparing the areas where the vegetables were grown, it was determined that the vegetables grown in Poland contain the lowest concentration of copper.
The highest concentration of Cu was determined in spinach from Zvečan (22.4 mg/kg), and the lowest in eggplant from Polski (5.38 mg/kg). Leafy vegetables contain higher concentrations of Cu than fruit vegetables.
Fig 2 shows the concentration of Co in dry vegetables grown in three different regions in the vicinity of Kosovska Mitrovica.

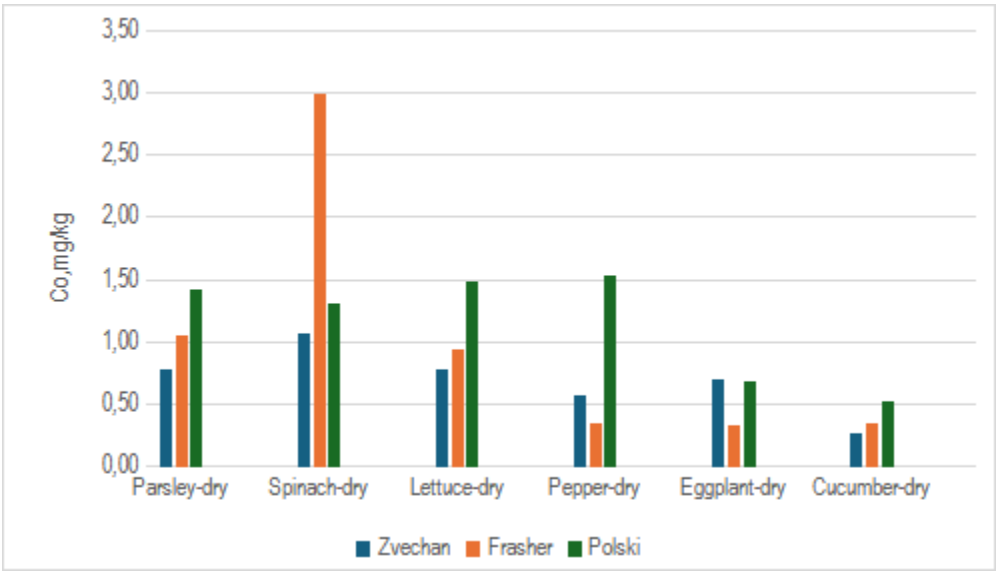

Figure 2. Concentration of Co in dry vegetables in different regions in the vicinity of Kosovska Mitrovica

In all the analyzed vegetables, Co is the most abundant in Polish samples, except for spinach where the highest Co concentration of 2.99 mg/kg was measured in Frashër spinach and eggplant where the Co concentration in Polish eggplant (0.68 mg/kg) is very close to the concentration of Co in the eggplant from Zvečan (0.78 mg/kg). In leafy vegetables, there is the least Co in leafy vegetables from Zvečan, and in fruit vegetables (except for cucumber), there is the least Co in fruit vegetables from Frashër.

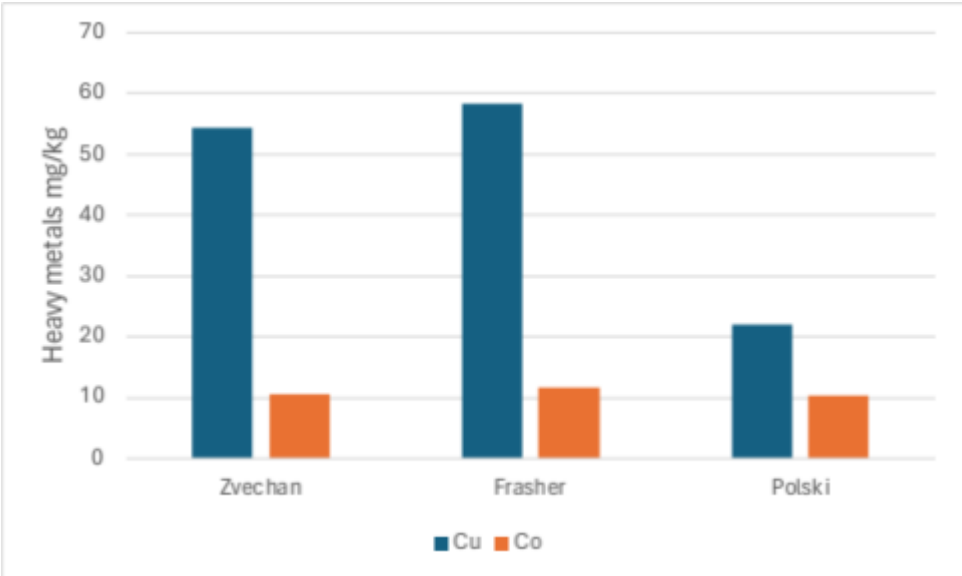

Figure 3. Concentration of Cu and Co in soil from the surroundings of Kosovska Mitrovica

Fig 3 presents the results for the concentration of Cu and Co in the soil on which the analyzed leafy and fruit vegetables were grown. The highest concentration of Cu was determined in Frashër (58.40 mg/kg), and the lowest in Polski (22.10 mg/kg). The concentration of Co in all three areas does not differ much and ranges from 10.4 mg/kg in Polski to 11.60 mg/kg in Frashër.

The bioconcentration factor (BF) describes the transfer of heavy metals from soil to plants and is key in assessing the possible health risks associated with heavy metals in plant products (Mng'ong'o et al., 2021). Table 1 presents the bioconcentration factor of Cu and Co in selected types of vegetables.

Table 1. Bioconcentration factor of Cu and Co in the analyzed vegetables from different regions

Bioconcentration factor		
Region	Cu	Co
Parsley		
Zvečan	0.07	0.15
Frashër	0.09	0.27
Polski	0.10	0.30
Spinach		
Zvečan	0.10	0.41
Frashër	0.26	0.32
Polski	0.13	0.65
Lettuce		
Zvečan	0.07	0.26
Frashër	0.08	0.20
Polski	0.14	0.39
Pepper		
Zvečan	0.05	0.19
Frashër	0.03	0.21
Polski	0.15	0.36
Eggplant		
Zvečan	0.07	0.19
Frashër	0.03	0.15
Polski	0.07	0.24
Cucumber		
Zvečan	0.03	0.18
Frashër	0.03	0.18
Polski	0.05	0.36

The lowest value for BF of Cu (0.03) was determined in the analyzed peppers from Frashër, eggplant from Frashër, and cucumbers from Zvečan and Frashër, and the highest value for BF for Cu was determined in spinach grown in Frashër (0.26). The BF values for Co are higher and range from 0.15 (parsley in Zvečan and eggplant in Frashër) to 0.65 (spinach in Polski). The BF for Co in all the analyzed vegetables are several times higher than the BF for Cu, which means that Co is more easily incorporated into the analyzed vegetables than Cu. Fruit vegetables have lower BF values than leafy vegetables for both Cu and Co. High values for BF (greater than 1) suggest greater uptake of heavy metals into the plant, and lower values (less than 1) mean greater concentration of heavy metals in soil than in plants. (Mng'ong'o et al., 2021).
Table 2 presents the correlation coefficients for Cu and Co concentration between leafy vegetables (parsley, lettuce, spinach) and fruit vegetables (peppers, eggplant and cucumbers).

Table 2. Correlation coefficient between leafy and fruit vegetables for Cu and Co.

	Correlation coefficient
Correlation between leafy and fruit vegetables for Cu concentration	0.16608475
Correlation between leafy and fruit vegetables for Co concentration	-0.007504195

The results in Table 2 show the correlation between leafy and fruit vegetables for Cu and Co. It can be said that there is a small positive correlation between the concentration of Cu in leafy and fruit vegetables and a very small negative correlation between the concentration of Co in leafy and fruit vegetables. The negative correlation for Co is due to the extremely high value of Co in Frashër spinach.
Table 3 presents the results of the student's t-test for the concentration of Cu and Co in leafy (parsley, lettuce and spinach) and fruit vegetables (peppers, eggplant and cucumbers).

Table 3. Student's t-test between Cu and Co concentration separately for leafy and fruit vegetables

	Cu		Co	
	Leafy vegetables	Fruity vegetables	Leafy vegetables	Fruity vegetables
Mean value	13.35	9.21	1.31	0.59
Value of t-test	2.2277533		2.771795567	
Critical value for t	0.040596993		0.013609903	
Obtained p – value	2.119905299		2.119905299	

From the student's t-test results shown between Cu concentration in leafy and fruit vegetables (2.2277533 ＞0.040596993) it can be determined that there is a difference between Cu concentration in leafy and fruit vegetables. The obtained p-value 2.119905299 > limit p-value (0.05) indicating that there is no statistically significant difference between Cu concentrations in leafy and fruit vegetables. From the statistical processing of Co results, the t-test values (2.771795567＞0.013609903) show that there is a difference in Co concentration between leafy and fruit vegetables, but there is no statistically significant difference because the obtained p-value 2.119905299 > limit p-value (0.05).

4. Conclusions

This paper aimed to determine the bioconcentration of heavy metals Cu and Co in three different areas of the environment of Kosovska Mitrovica. The highest concentration of Cu was determined in spinach grown in the Zvečan region (22.4 mg/kg), and the lowest in eggplant from Polski (5.38 mg/kg). The concentration of Co is the highest in spinach from Frashër (2.99 mg/kg), and the lowest in cucumber from Zvečan (0.27 mg/kg). The soil in all three areas contains a higher concentration of Cu compared to Co. The bioconcentration factor for all vegetables was less than 1 indicating that the soil in which the vegetables were grown contained more Cu and Co than these heavy metals accumulated in the vegetables. The higher BF values for Co compared to Cu indicate that Co accumulates more easily in the analyzed vegetables than Cu. Leafy vegetables accumulate more Cu and Co than fruit vegetables. The t-test values for Cu and Co show that there is a difference in the concentration of Cu and Co between leafy and fruit vegetables, but there is no statistically significant difference because the obtained p-values>limit p-values.

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