UDC: 634.11:546.4/.8(497.115)
634.13:546.4/.8(497.115)
*Professional paper*

# ACCUMULATION OF HEAVY METALS IN APPLES AND PEARS FROM THE SUBURBS OF MITROVICA, KOSOVO

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**Abstract**

Intake of heavy metals through the food is a food safety problem that seriously affects consumer health. Therefore, information is needed on the intake of food contaminated with heavy metals and their concentrations, to assess the potential risk for human health. This paper aims to determine the accumulation of metals in apples and pears grown in the surroundings of Kosovska Mitrovica (Republic of Kosovo) and the bioconcentration factor (BF).

With the help of the ICP-MS technique, were determined the amounts of Cu, Fe, Co, Mn, Ni, and Cr in apples and pears grown in three regions - Zvečan , Frashër, and Polski.

From the conducted tests, the highest concentrations in apples and pears were determined for iron (on average 100.67 mg/kg for apples and 107.4 mg/kg for pears) and the lowest concentrations for cobalt (on average 0.13 mg/kg for apples and 0.18 mg/kg for pears). The lowest bioconcentration factor in apples is 0.01 (for Fe, Co, and Mn in all three regions), and the highest is 0.32 (for Cr in Zvečan). When determining the bioconcentration factor in pears, the lowest (0.01) was determined for iron (in all three regions) and manganese (in Zvečan and Frashër regions), and the highest bioconcentration factor was determined for copper – 0.46 (Polski region). There is a very high correlation between the values obtained for the analyzed metals in apples and pears.

According to BF values, pears extract twice as much Cu and Co from the soil compared to apples, and the extraction of other metals from the soil is the same for both types of fruit.

*Keywords:* heavy metals, apples, pears, bioconcentration.

## 1. Introduction

The nutritional value positions the fruit at the top of daily nutrition. The fruit contains vitamins and minerals in large quantities and their daily intake strengthens the body's vitality. Nutritionists advise consuming at least 120 grams of fruit every day (Khan, Arya, & Singh, 2021). Apples (Malus domestica) and pears (Pyrus communis L.) belong to the Rosaceae family and are one of the most important fruits in the world (Hong et al., 2024; Mousavi, Jafari, & Shirmardi, 2024). Apples contain important compounds such as vitamins, dietary fiber, minerals, organic acids, and sugars, as well as antioxidant compounds (Mousavi, Jafari, & Shirmardi, 2024). Pears contain significant amounts of sugars, organic and amino acids, vitamins, and minerals (Li, Li, Wang, & Gao, 2015). More than 10 million sites in the world covering more than 20 million hectares of land are considered contaminated sites, of which over 50% are contaminated with hazardous heavy metals and/or metalloids. The combined global economic impact of heavy metal pollution is estimated to exceed US$10 billion annually (Kumar et al., 2019). Heavy metal pollution is extremely harmful because of the toxic impact they have on humans, animals, and plants.

High concentrations of heavy metals have a negative effect on food production because they affect the metabolic activity of plants. Heavy metals have serious implications for human health, reaching the tissue through direct ingestion, dermal contact, inhalation, and adsorption (Sodhi, Mishra, Singh, & Kumar, 2022). The biochemical properties of heavy metals can change after they enter human organs. Liver, cardiovascular, and other damage can be caused by the

https://doi.org/10.62792/ut.jftn.v7.i13-14.p2700

accumulation of heavy metals above the safe threshold. In addition, heavy metals are also associated with cognitive impairment, neurological diseases, and malignancy (Rezvani Ghalhari et al., 2024). Lead (Pb) affects the normal activity of enzymes and is associated with carcinogenesis, mutagenesis, and teratogenesis in experimental animals. Lead poisoning is still a major public health risk, especially in developing countries. The toxic effect of lead is influenced by the chemical form in which the element is found, which is absorbed in the body by about 90%. (Scutarașu & Trincă, 2023). Cobalt (Co) is an important trace element for humans, but high doses can be harmful to their health. The high concentration of cobalt in the body can cause some health problems such as diarrhea, nausea, low blood pressure, damage to the thyroid gland, etc. Conversely, cobalt deficiency can lead to anorexia, chronic edema, and pernicious anemia (Genchi, Lauria, Catalano, Carocci, & Sinicropi, 2023). Manganese (Mn) is part of the group of heavy metals and is the fifth most abundant metal in the environment. It is important for several physiological processes that participate in enzymatic reactions as a cofactor (Peres et al., 2016).

Nickel is a transition element that is widely distributed in the environment, air, water, and soil. Contact with nickel can cause various side effects on human health, such as allergies, cardiovascular and kidney diseases, lung fibrosis, and lung and nose cancer. Depending on the dose and length of exposure, as an immunotoxic and carcinogenic agent, Ni can cause various health effects, such as contact dermatitis, cardiovascular disease, asthma, lung fibrosis, and cancer of the respiratory tract (Genchi, Carocci, Lauria, Sinicropi, & Catalano, 2020). Chromium (Cr) enters the body through its inhalation and also through the consumption of food and water containing chromium. High doses of exposure can cause a variety of cytotoxic and genotoxic reactions that affect the body's immune system (Shrivastava, Upreti, Seth, & Chaturvedi, 2002). This paper aims to determine the accumulation of Cu, Fe, Co, Mn, Ni, and Cr in apples and pears grown in the vicinity of Kosovska Mitrovica (Republic of Kosovo) and the bioconcentration factor.

## 2. Materials and methods

*2.1. Materials:* The following fruits were tested - apples and pears. The analyzes were made at the technological and nutritional maturity of the fruit (harvest 2023).

*2.2. Methods:*

*Study area*

This study was conducted in three areas in the Kosovska Mitrovica region (42.883°N, 20.867°E) in Kosovo. We expect that the two areas - Zvečan (42°54'27"N, 20°50'25.01"E) and Frashër (42° 34' 59.88" N, 21° 00' 0.36" E) are contaminated with heavy metals due to the proximity of the smelter for lead-zinc ore, and the third area - Polski (43 25' 00", 25 39' 00") is considered clean and uncontaminated by heavy metals due to the greater distance from the smelter.

*Preparation of samples*

The apples and pears used for the analysis of heavy metals were previously dried to a constant mass in a drying oven (Drying Oven SLN 15, Wodzisław Śląski, Poland) through a convective drying method. The drying time was 24-30 hours depending on the type of fruit.

*Determination of heavy metals*

The determination of the concentration of Cu, Fe, Co, Mn, Ni and Cr in apples and pears was performed using inductively coupled plasma with mass spectrometry ICP-MS (model 7500cx, Agilent, USA) according to the accredited method MKC EN ISO/IEC 17025 :2018.
The analyzed metals in the soil were 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:

$$BF = \frac{C_{dry\ fruit}}{C_{soil}}$$

Where:
$C_{dry\ fruit}$ = heavy metal concentration in dried fruit, 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, Fe, Co, Mn, Ni and Cr in apples and pears.

## 3. Results and Discussion

The content of heavy metals (Cu, Fe, Co, Mn, Ni and Cr) in dry apples grown in the three different regions (Zvečan, Frashër and Polski) near Kosovska Mitrovica are presented in Fig 1.

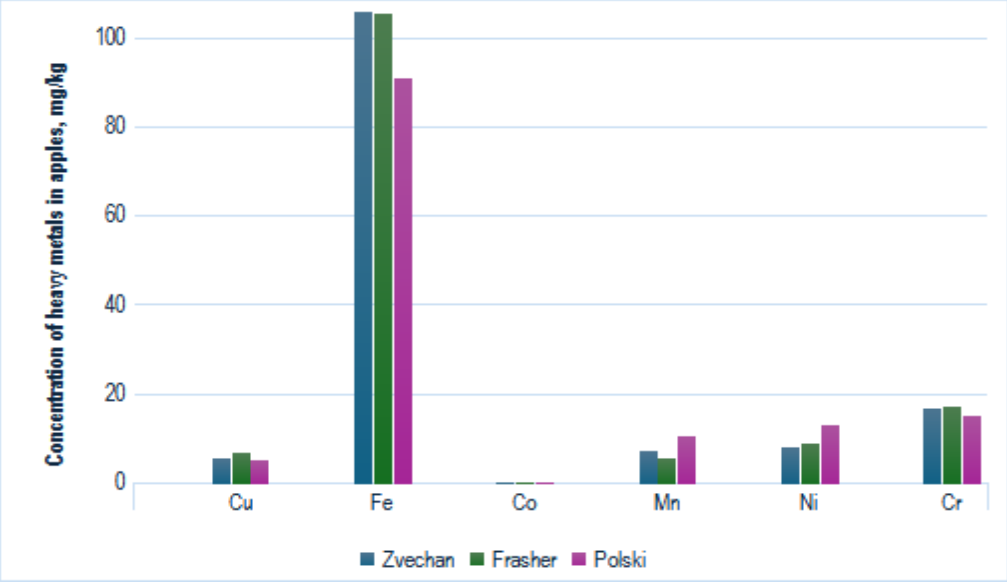


**Figure 1**. Concentration of Cu, Fe, Co, Mn, Ni and Cr in apples from different regions in the surroundings of Kosovska Mitrovica

The results presented in Graph 1 show that the tested apples contain the most iron (average 100.67 mg/kg). The lowest content in apples was determined for Co (average 0.02 mg/kg). Apple samples from the Polski region have the lowest concentration of: Cu, Fe, Co, and Cr, and the highest of Mn and Ni. The presence of heavy metals Pb, Cd, Cr, Ni, As, Zn, Cu and Fe in

soil and dried apples grown in different parts of the Mitrovica region in Kosovo was determined by Imeri, Kullaj, Duhani, & Millaku, (2019). They determined the highest values of Cr and Ni in the area "mm106" 6.88±1.63 mg/kg and 8.03±1.91mg/kg, respectively, for apples. Compared to our results, the concentration of Cr is higher in our samples, while the concentration of Ni is approximately the same. The highest concentration of Cu was determined in the area "M106" – 4.36±1.16 mg/kg, which is approximately the same as the concentration of Cu determined in apples from the Polski region (4.89). On the other hand, the same authors determined the highest concentration of Fe in the area "M9" – 4.13±2.66 mg/kg, which is much lower than the concentration of iron in apples that we determined.

Fig 2 shows the content of heavy metals (Cu, Fe, Co, Mn, Ni, and Cr) in pears grown in three different regions (Zvečan, Frashër, and Polski) near Kosovska Mitrovica.

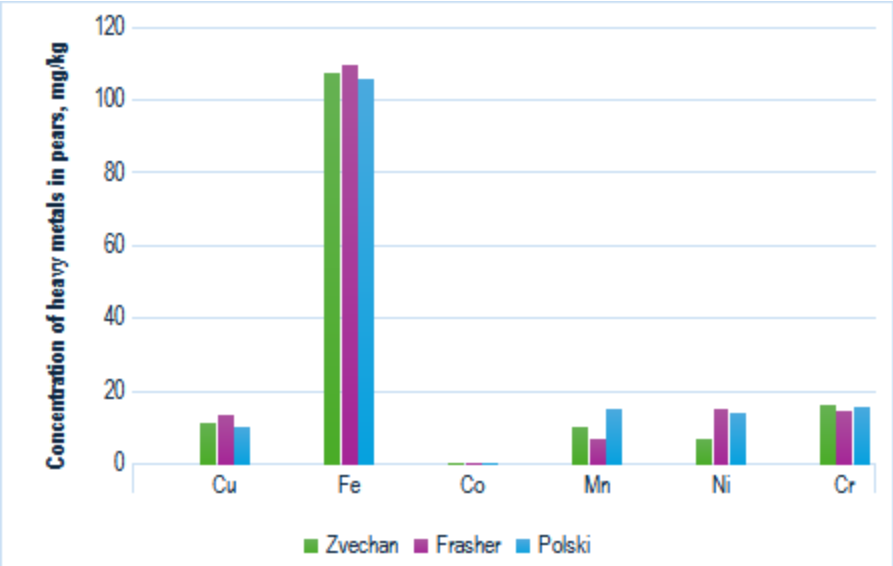


**Figure 2**. Concentration of Cu, Fe, Co, Mn, Ni and Cr in pears from different regions in the vicinity of Kosovska Mitrovica

As with apples, also in pears the highest concentration of the examined heavy metals was determined for iron (average 107.40 mg/kg), and the lowest is the concentration of cobalt (average 0.02 mg/kg). Pears from Frashër have the highest concentrations of Cu, Fe and Ni, pears from Zvečan contain the most Co and Cr, and pears from Polski contain the most Mn.

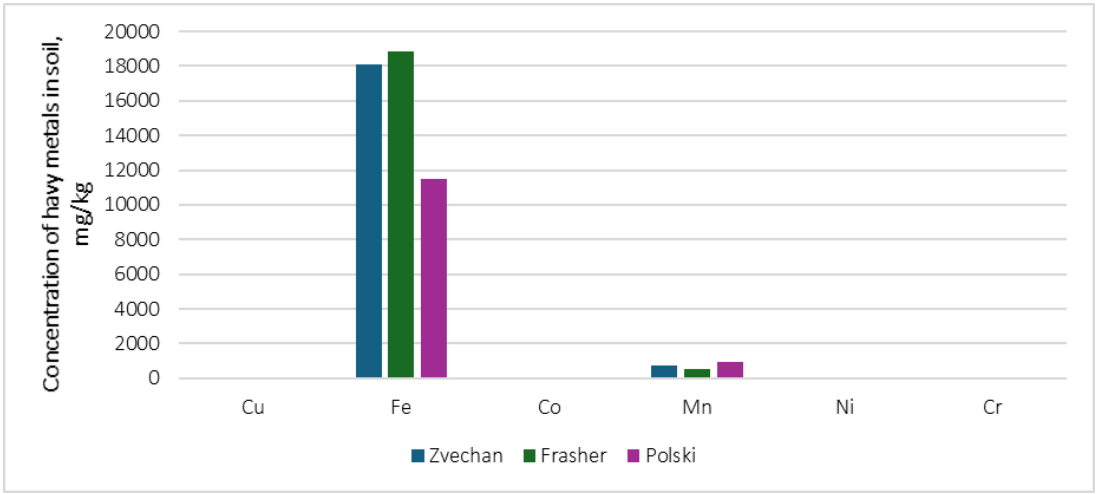


**Figure 3**. Concentration of Cu, Fe, Co, Mn, Ni and Cr in soil from different regions in the surroundings of Kosovska Mitrovica

Fig 3 shows the concentration of Cu, Fe, Co, Mn, Ni and Cr in soil from Zvečan, Frashër and Polski. In all three areas, the highest is the concentration of Fe (18 100 mg/kg - Zvečan , 18841 mg/kg - Frashër and 11470 mg/kg - Polski. The lowest concentration of the heavy metals analyzed in the soil was determined for Co (10.6 mg/kg - Zvečan ; 11.6 mg/kg – Frashër and 10.4 mg/kg – Polski).

**Table 1**. Bioconcentration factor of Cu, Fe, Co, Mn, Ni and Cr in apples and pears

| Heavy metals | Regions | BF apples | BF pears |
|---|---|---|---|
| Cu | Zvečan | 0.10 | 0.20 |
| | Frashër | 0.11 | 0.23 |
| | Polski | 0.22 | 0.46 |
| Fe | Zvečan | 0.01 | 0.01 |
| | Frashër | 0.01 | 0.01 |
| | Polski | 0.01 | 0.01 |
| Co | Zvečan | 0.01 | 0.02 |
| | Frashër | 0.01 | 0.02 |
| | Polski | 0.01 | 0.02 |
| Mn | Zvečan | 0.01 | 0.01 |
| | Frashër | 0.01 | 0.01 |
| | Polski | 0.01 | 0.02 |
| Ni | Zvečan | 0.15 | 0.13 |
| | Frashër | 0.18 | 0.31 |
| | Polski | 0.20 | 0.21 |
| Cr | Zvečan | 0.32 | 0.31 |
| | Frashër | 0.30 | 0.26 |
| | Polski | 0.22 | 0.22 |

The bioconcentration factor is an important parameter in phytoremediation that shows the absorption of heavy metals from soil into plant tissues. Values higher than 1 indicate higher absorption of heavy metals in plants (Maiti, Ghosh, & Raj, 2022).
From the results presented in Table 1, it can be seen that all values are lower than 1, i.e. the soil on which the analyzed apples and pears were grown contains more heavy metals than are absorbed in the fruit itself. From the obtained results, it can be seen that the BF for Cu and Co in pears are two times higher than those in apples. It shows that pears, compared to apples, extract twice as much Cu and Co from the soil and therefore contain two times higher concentrations of Cu and Co than apples. The BF values for Fe for apples and pears are the same, and for Mn, Ni, and Cr they are very similar, which means that the extraction of these metals from the soil for both types of fruit is the same, that is, these metals are equally incorporated into apples and in pears.

**Table 2**. Correlation coefficient between the content of heavy metals (Cu, Fe, Co, Mn, Ni and Cr) in apples and pears

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

Table 2 shows that there is a strong positive correlation between the content of heavy metals (Cu, Fe, Co, Mn, Ni and Cr) determined in apples with the content of heavy metals contained in the analyzed types of pears.

Table 3 presents the results of the student's t-test for the total concentration of heavy metals determined in apples and pears.

**Table 3**. Student's t-test between the concentration of heavy metals (Cu, Fe, Co, Mn, Ni and Cr) in apples and pears

| Cu | | |
|---|---|---|
| | Apples | Pears |
| Mean value | 5.68 | 11.57 |
| Value of t-test | -5.518211778 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.005264925 | |
| **Fe** | | |
| | Apples | Pears |
| Mean value | 100.67 | 107.4 |
| Value of t-test | -1.328343817 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.254784839 | |
| **Co** | | |
| | Apples | Pears |
| Mean value | 0.128 | 0.182 |
| Value of t-test | -5.185720818 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.006580372 | |
| **Mn** | | |
| | Apples | Pears |
| Mean value | 7.57 | 10.57 |
| Value of t-test | -1.07356077 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.343468832 | |
| **Ni** | | |
| | Apples | Pears |
| Mean value | 9.82 | 11.93 |
| Value of t-test | -0.690141128 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.528060313 | |
| **Cr** | | |
| | Apples | Pears |
| Mean value | 16.2 | 15.43 |
| Value of t-test | 1.062041322 | |
| Critical value for t | 2.776445105 | |
| Obtained p – value | 0.348084073 | |

The results in the table show that the value of the t-test for all analyzed metals is lower than the critical value for t, which means that there is no difference in the concentration of analyzed metals in apples and pears from these areas. The obtained p-value for all analyzed metals is higher than 0.005, which means that the obtained results for the analyzed metals in apples and pears do not statistically differ significantly.The t-test values for all analyzed metals show that there is no difference in their concentration in apples and pears and there is no statistically significant difference because the obtained p-values are greater than the critical p-values.

## 4. Conclusions

Six heavy metals (Cu, Fe, Co, Mn, Ni, and Cr) in apples and pears from three different areas around Kosovska Mitrovica were analyzed. The goal is to see the accumulation of heavy metals in apples and pears from this region.

The tested apples contain the most Fe (average 100.67 mg/kg) and the least Co (average 0.02 mg/kg). In apples, the highest concentrations for Cu, Co, and Cr were determined from Frashër (6.55, 0.135, and 16.8 mg/kg respectively), of Mn and Ni (10.4 and 13 mg/kg respectively) in apples from Polski, and in Fe in apples from Zvečan (105.8 mg/kg).

The highest concentration of Cu (13.4 mg/kg), Fe (109.5 mg/kg), and Ni (15 mg/kg) was determined in pears from Frashër, of Co and Cr was determined in pears from Zvečan (0.201 and 16.3 mg/kg respectively), and the most Mn was determined in pears from Polski (15 mg/kg).

The bioconcentration factor for the analyzed apples and pears is less than 1, which indicates that the soil on which they were grown contains a higher concentration of the analyzed heavy metals than that accumulated in the apples and pears. BF for Cu and Co in pears are twice as large as those in apples, for Fe they are the same, and for Mn, Ni, and Cr they are very similar. This means that compared to apples, pears extract twice as much Cu and Co from the soil, and the extraction of other metals from the soil is the same for both types of fruit.

The high correlation value (0.995122041) shows that there is a strong positive correlation between the content of heavy metals (Cu, Fe, Co, Mn, Ni, and Cr) in apples and pears.

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