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Heavy Metals in Fruits and Juice of Elstar Apple Variety

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Authors' contributions

This work was carried out in cooperation of all authors. Author EI designed the study, protocol, draft work and analyzed of the experiments. Author BS was responsible for selection of places for conducting the tour, preparation of the field for viewing, coordination of the study tour. Author HK performed the statistical data processing. Authors ES and AS were responsible for sampling of soil, applications of heavy metals, acidification and soil calcification agents, fruit reading and juice preparation. Author SN carried out the processing of work texts, charts and layout of work forms. All authors read and approved the final manuscript.

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ABSTRACT

The goal of the research was to determine the concentration of lead, copper, cadmium, zinc and iron in the soil of different pH, the degree of contamination in the intensive production of Elstar apples, as well as the impact of soil contamination on the concentration of heavy metals in fruits and apple juice. The stationary research was conducted during 2014-2015 in the fruit nursery Špionica near Srebrenik (Bosnia and Herzegovina).

Along with the standard agro-technology, acidification and calcification of soil were applied, as well as the simulation of soil contamination with heavy metals, on the experimental plot of apple plantations. The concentrations of heavy metals in the soil, fruits and apple juice were measured on an atomic absorption spectrophotometer (Analyst 200) and inductively coupled plasma by optical

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emission method ICP-OES (Optima 2100 DV) and by standard analytical methods. In tilted layer of soil in the width of the treetop, the heavy metal concentration ranged from 9.60 mg/kg for lead, 26.76 mg/kg for copper, 34.23 mg/kg zinc and 17852.00 mg/kg for iron. There was no cadmium. After zero soil sample analysis the acidity of sample soil were increased or decreased with ammonium sulfate, i.e. acidification (1.2 kg per apple tree) and with lime, i.e. calcification (3.2 kg per apple tree) and treated with solution of each metal in an amount of 800 mL per tree (10 mL of pure solution mixed with 10 L of distilled water). In soil samples where the acidification were done average concentration of heavy metals were: lead 12.70 mg/kg, copper 36.97 mg/kg, zinc 61.03 mg/kg and iron 24.00 mg/kg. In soil sample where the calcification were done average concentration of heavy metals were: lead 13.87 mg/kg, copper 38.50 mg/kg, zinc 65.03 mg/kg and iron 26193.00 mg/kg. In Elstar apples grown on demonstration plot, the highest was iron content with an average of 15 mg/kg. The content of zinc ranged from 2.36 to 4.40 mg / kg, with an average copper content of about 0.70 mg / kg while the lead content was 0.41-0.70 mg/kg. In juice, produced from the Elstar apples grown on the basic soil copper content was highest 0.668 mg/kg and that is the highest value recorded from all the values in the juice in general. The concentrations of these heavy metals in the soil before the experiment were below the maximum allowable concentration (MAC) for powdery-loamy soil. After acidification, calcification as well as simulation of soil contamination with heavy metals, there was a noticeable increase in the concentration of heavy metals in the soil, but after experiment concentrations of heavy metals in fruits and apple juice were very low, far below MAC. This research has shown that even with heavy metals in the soil there is no risk to consumers health to consume such fruits and products because coefficient of heavy metal transfer from the soil to the fruits is very low, below the limit values.

Keywords: Heavy metals; soil; MAC.

1. INTRODUCTION

The increasingly intensive application of mineral fertilisers (especially phosphoric) and plant protection products based on Cu and Zn in fruit production disrupt the natural balance of heavy metals and enable their smooth entry into the food chain through the plant. Intensive use of fungicides in fruit production increases the adverse effect on the environment [1-3]. The accumulation of heavy metals in the soil eventually increases the possibility of their translocation into surface and groundwater [4-7]. Even a small amount of heavy metals in the soil can be toxic to the agroecosystem due to its poor biodegradability and ability to attach to the adsorption complex of soil [8]. A special problem is fungicides, especially copper preparations that lead to the accumulation of copper in the soil, affecting soil organisms and, in the long term, negatively affect the fertility of the soil [9].

Determining the concentration of total heavy metals in the soil is the basic indicator for determining the degree of their pollution, although long-term risk assessments and direct effects of pollution rest on their bioaccessibility and/or mobility [10,11].

Soil contamination with heavy metals (Cu, Cd, Pb, Zn and Fe) in the conditions of intensive fruit production in Bosnia and Herzegovina is underdeveloped and inadequately treated scientific problem. According to the volume and dynamics of agro-technical measures, the presumption is that the quantity of these pollutants will be significantly more present in the soil and the possibility of transferring significant concentrations to the fruit.

In the modern apple production, heavy metal intake from soil to edible parts is an important issue, especially considering their toxicity, bio-non-gradability, and accumulation as the most dangerous characteristics that directly affect consumer health.

The importance of testing the bioavailability of heavy metals in fruits that are daily consumed as fresh fruits or used for further processing is very important due to the possibility of permanent accumulation of heavy metals in the human organs and possible death.

By examining the quality of agricultural soil and agricultural cultures as bioindicators for heavy metals intake and determination of Pb, Cd, Cu, Zn and Fe content, it is possible to introduce continuous monitoring, which is of particular importance for the development of agriculture and the production of healthy food.

This research will determine the correlation between the individual physical and chemical characteristics of the soil and the input of heavy metals in the conditions of their increased or normal soil content. Based on this it is the possible answer to the question whether fruits take heavy metals from soil and therefore become inadequate for consumption or further processing.

2. MATERIALS AND METHODS

The soil samples from the experimental plot in the width of the treetop were analysed. The samples were taken from the fruit tree nursery Srebrenik (Bosnia and Herzegovina)) on which acidification and calcification took place, as well as the simulation of soil contamination with heavy metals. Soil samples were taken from a depth of 0-60 cm (powdery- loamy soil), then dried in the air and milled in a ground mill. In soil samples (five samples), a basic chemical analysis was carried out: soil pH in H_2O and 1 M KCl (ISO 10390, 1994), electrical conductivity (μS/cm) and organic matter (%) [12].

The concentrations of Cu, Cd, Pb, Zn and Fe were determined in apple fruits of the Elstar variety (five samples of apples from experimental plots).

pH value of soil samples was determined electrometrically (ISO 10390, 1994) in a suspension of soil with distilled water (actual acidity) and in 1M KCl (substitution-potent acidity). Organic matter in the soil was determined by incineration of the samples to a constant mass in preheating furnace. After analysing the soil samples, in the experimental soil acidity was increased with ammonium sulfate, i.e. acidification (1.2 kg per apple tree) and with lime was reduced, calcification (3.2 kg per apple tree) and the same was treated with 800 mL of each metal solution (10 ml of pure solution mixed with 10 litres of distilled water). The total content of the investigated heavy metals in the soil was determined by microwave technique where the soil was destroyed with aqua regia (ISO 11466, 1995), and the extraction with EDTA was used for the determination of heavy metals [13,14].

The soil destruction with *aqua regia* gives the fastest, safest and most accurate analytical results with an accuracy of more than 5% for the determination of heavy metals in the soil. Concentrations of heavy metals obtained by measurement on ICP-OES represent their total soil content.

Soil samples were destroyed according to the following procedure (ISO 11466, 1995): 0.5 g of air- dried soil in Teflon cuvette was poured with 12 ml of freshly prepared *aqua regia* (1/3 HNO3 +2/3 HCl). After the destruction, extracts of the destroyed soil samples were filtered into 50 ml flask, which was then made up with distilled water to graduation mark. Heavy metal concentrations were measured on the atomic absorption spectrophotometer, AAS (Analyst 200) and inductively coupled plasma by the optical emission method ICP - OES (Optima 2100 DV). Control of the obtained results was performed by the electroanalytical method of Differential Pulse Anodic Stripping Voltammetry (DPASV) for several representative samples.

Soil samples before acidification, calcification and heavy metal dosing are shown in the pictures, marked with the following form:

Elstar - Soil plot
Acidification - dosing of ammonium sulphate and heavy metals into the experimental soil;
Calcification - dosing of lime and heavy metals into experimental soil;
Control - heavy metal dosing in experimental soil without acidification and calcification;

3. RESULTS AND DISCUSSION

As an element of basic soil analysis, the results of the acidity determination, shown as pH in water and 1M KCl, the content of organic matter and electrical conductivity, are presented in the Fig. 1.

The results of determining the content of organic matter and electrical conductivity are shown in Fig. 2.

The results of the heavy metal content in the soil of the experimental plots are presented in concentrations images for better examination and comparison.

In Fig. 3. lead concentrations in soil samples taken from the experimental plot for apple are shown.

The highest lead value in the experimental plot was recorded in sample 4, 16.87 mg/kg and the lowest value was in sample 1, 4.58 mg/kg. The average value of lead for the sample plot is 9.60 mg/kg.

Fig. 4 shows the concentrations of copper in soil samples taken from experimental plots for apple.

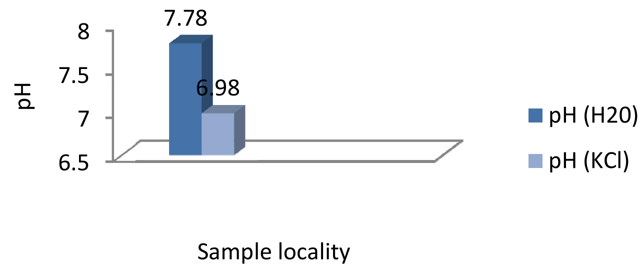

Fig. 1. Average pH soil value in H2O and 1M KCl

The highest value of copper in the experimental plots was recorded in sample 3, 34.79 mg/kg and the lowest value in the sample 5, 18.34 mg/kg. The average value of copper for the sample parcel is 26.76 mg/kg.

Cadmium was not present in any of the experimental soil samples.

Fig. 5 shows the concentrations of zinc in soil samples of the experimental plot for apple.

The highest value of zinc in the experimental plot was recorded in the sample 5, 44.15 mg/kg and the lowest in sample 3, 25.27 mg/kg. The average value of zinc for the test plot is 34.23 mg/kg.

Fig. 6 shows the concentrations of iron in soil samples of the experimental plot for apple.

The highest value of iron in the experimental plot was recorded in sample 4, 23781 mg/kg and the lowest was 1, 15656 mg/kg. The average values of iron for the experimental plot is 17852 mg/kg.

By the initial results of the pH of the soil, treatment of the experimental plots with the heavy metal solution was applied in the width of the treetop, as well as acidification and calcification, and part of the experimental plots was treated only with a heavy metal solution.

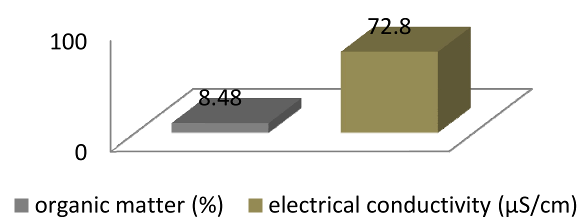

Fig. 2. Average content of organic matter in soil and electrical conductivity

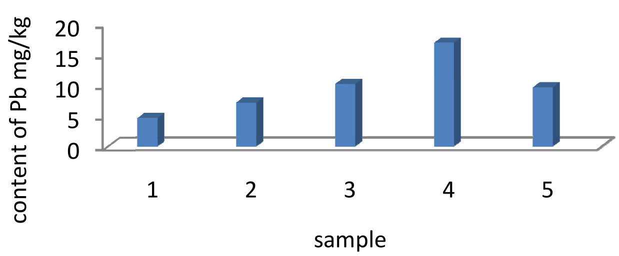

Fig. 3. Content of Pb in soil samples for apple

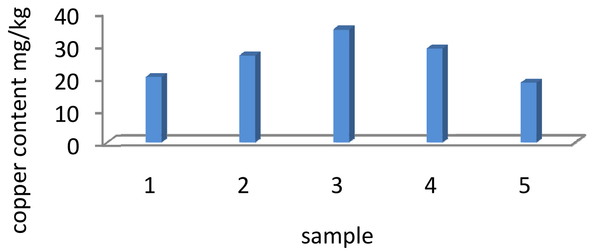

Fig. 4. The copper content in soil samples for apple

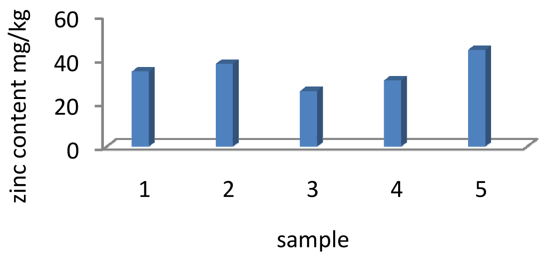

Fig. 5. Zinc content in soil samples for apple

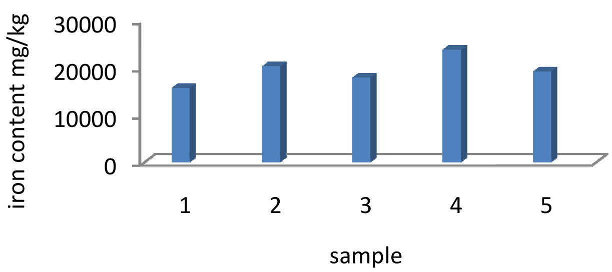

Fig. 6. Iron content in soil samples for apple

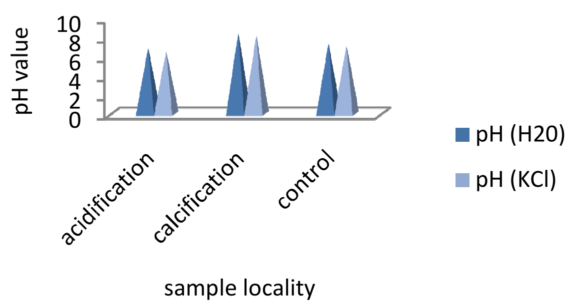

Fig. 7. Average soil pH in water and 1M KCl of variety Elstar

Soil samples were taken in September when the Elstar variety were harvested, i.e. four months after the acidification, calcification and dosing of the metal solution for soil contamination. The pH of the soil moved within the limits shown in the Fig. 7.

Fig. 7 shows the average pH values of the experimental plots, i.e. where acidification was applied on the experimental soil, the pH was 6.75 in water and 6.42 in KCl, hereinafter, moderately acidic soil. At the experimental soil where calcification was applied, the pH was 8.36 in water and 8.07 in KCl, hereinafter referred to as basic soil. On experimental soil treated with an only heavy metal solution, the pH was 7.23 in water and 7.05 in KCl.

Organic matter and electroconductivity is determined as well as the soil pH after four months and is shown in the Fig. 8.

The organic matter content was in the approximate ratio with a maximum value of 19.65% for experimental soil where only heavy metal dosage was performed without any change in the pH of the soil (control), and the lowest value of 13.4% was in the soil where the calcification was applied. Electroconductivity is by far the highest in the soil where calcification was applied at 285 µS/cm.

The content of copper in the experimental soil where the acidification was applied was 36.97 mg/kg and in the experimental soil where the calcification was applied was 38.50 mg/kg. The content of zinc in the experimental soil where the acidification was applied was 61.03 mg/kg and in the experimental soil where the calcification was applied was 65.03 mg/kg. Cadmium was not present in soil samples. The lead content was about the same in both soil samples, i.e. 12.70 mg/kg in soil with acidification and soil with calcification was 13.87 mg/kg. Because of the high value of iron content in soil samples, it was not possible to graphically represent it correctly about other metals, so that the iron content of the experimental soil was 24010 mg/kg and the experimental soil where the calcification was applied was 26193 mg/kg.

The Figs. [10,11,12,13] show the average values of heavy metals in the fruit of apple variety Elstar in experimental plots at different pH, organic matter content and electrical conductivity.

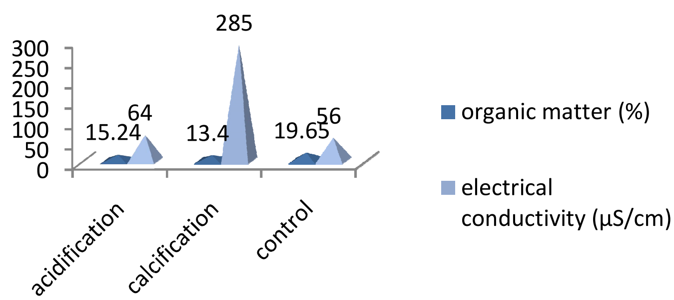

Fig. 8. Average content of organic matter in the soil and electrical conductivity for apple variety Elstar

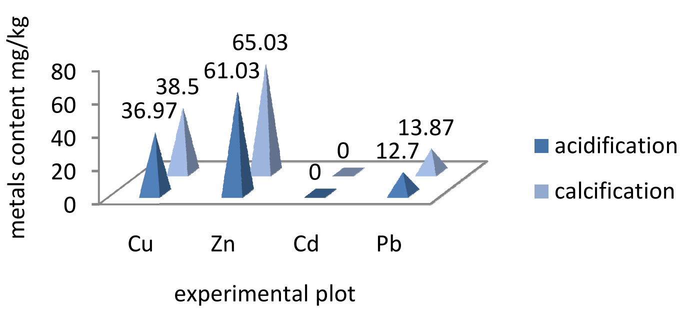

Fig. 9. The average content of heavy metals in soil samples for apple variety Elstar after acidification and calcification were applied (without iron)

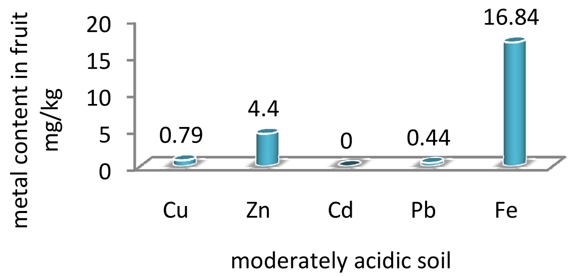

Fig. 10. The content of heavy metals in the fruit of the Elstar apples - moderately acidic soil

In the Elstar variety grown on moderately acidic soil, the highest iron content is 16.84 mg/kg, while the other metals are in insignificant quantities, with a slightly more expressed zinc content of 4.40 mg/kg.

In the Elstar variety grown on basic soil, the highest iron content of 14.29 mg/kg was recorded, while the smallest lead content was 0.57 mg/kg, taking into account that there was no cadmium.

In the Elstar apples cultivated on the neutral pH level, the highest iron content is 15.77 mg/kg, while the remaining quantities of metals are in insignificant quantities, with a slightly more expressed zinc content of 2.60 mg/kg.

In the Elstar apples cultivated on the experimental soil without any treatment, ie, soil with initial parameters where the pH was about an average of about 7, organic matter ranging from 7.99 to 8.48% and electrical conductivity from 33.30 to 72.80 μS/cm, maximum value of iron 16.84 mg/kg, zinc 4.40 mg/kg, copper 0.79 mg/kg and lead 0.70 mg/kg was noted. Cadmium was not present like in previous cases.

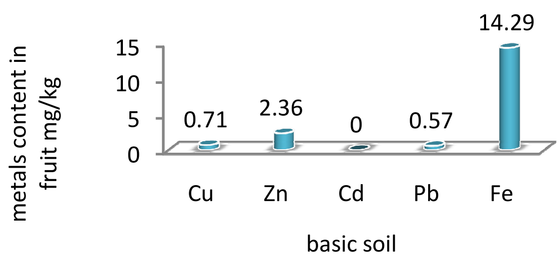

Fig. 11. The content of heavy metals in the fruit of the Elstar apples - basic soil

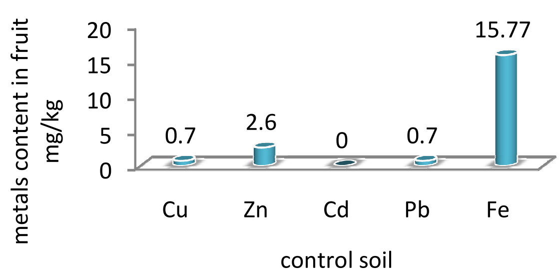

Fig. 12. The content of heavy metals in the fruit of the Elstar apples - control soil

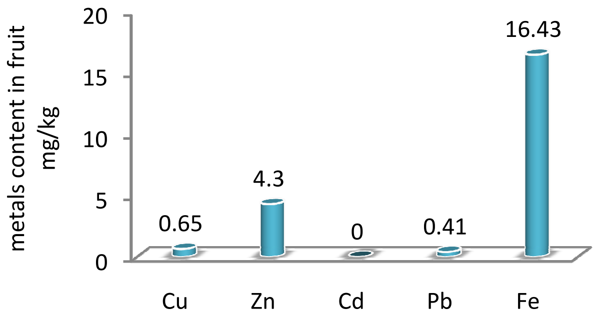

Fig. 13. The content of heavy metals in the fruit of the Elstar apples – initial parameters of soil

It can be concluded that in the Elstar variety, which was cultivated on experimental plots, had recorded the highest iron content, in average 15 mg/kg. The zinc content ranged from 2.36 to 4.40 mg/kg, the copper content ranged from 0.65 to 0.79 mg/kg, while the lead content was in the range 0.41 to 0.70 mg/kg. Cadmium was not present in any of the samples of the Elstar apples.

In the Fig. [14,15,16,17] are represented the average concentrations of heavy metals in the apple juice of the Elstar variety from different soils.

In the juice produced from the Elstar variety grown on moderately acidic soil, the copper concentration was highestin amount of 0.208 mg/kg, while the lowest was zinc value 0.064 mg/kg. The lead was 0.194 mg/kg and iron 0.126 mg/kg, with not cadmium.

In the juice produced from the Elstar variety grown on basic soil, the highest was copper content 0.668 mg/kg, while the lowest was lead content 0.058 mg/kg, with no cadmium.

In the juice produced from the Elstar variety grown on control soil, the highest copper content was 0.438 mg/kg, while the lowest was lead content of 0.055 mg/kg, the proportion of other metals was in the approximate ratio. There was also a concentration of cadmium of 0.131 mg/kg, which was not the case in the previous samples of the juice, which certainly indicates that its origin is not from the original raw material of the apple, but as a consequence of the production of the juice itself, and the probability of migration from the dishes and equipment used to produce juice.

In the juice produced from apples of the Elstar variety grown on experimental soil without any treatment, the highest was copper 0.221 mg/kg and the lowest was lead 0.052 mg/kg although cadmium was not present at all.

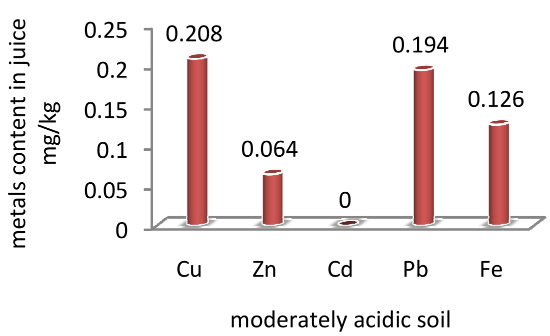

Fig. 14. The content of heavy metals in fruit juice of the Elstar variety - moderately acidic soil

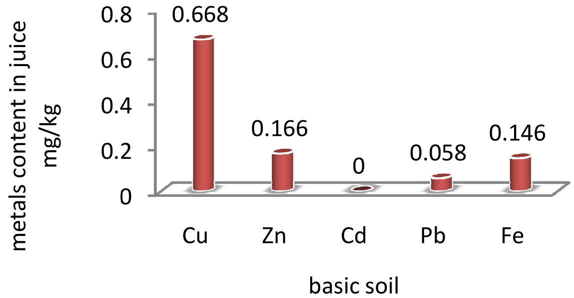

Fig. 15. The content of heavy metals in fruit juice of the Elstar variety - basic soil

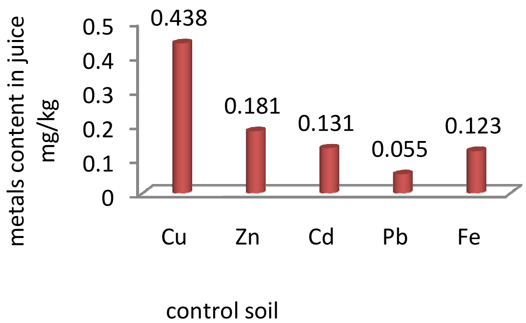

Fig. 16. The content of heavy metals in fruit juice of the Elstar variety - control soil

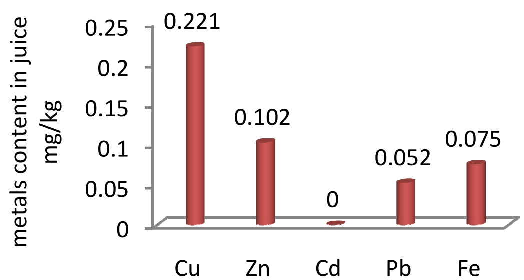

Fig. 17. The content of heavy metals in fruit juice of the Elstar variety – without treatment

The heavy metal mobility in the soil is a complex process that basically depends on the nature of the metal itself, the type of solid phase interaction and soil, and other factors such as acidity, oxidation and / or reduction conditions, ionic content of the soil solution, etc. [15]. The presence of chelating agents, content and quantity of organic matter, cationic capacity and pH value are of particular importance from physical and chemical factors. The mobility and availability of heavy metals are usually low, especially in the case of low soil pH and high content of organic matter and clay [16]. Through soil acidification, which is often present in agricultural production and as an indispensable soil acidity correction measure, soil conditions are created in which heavy metals will be more accessible to the root of the plant, thereby increasing their content in the fruit itself. This fact comes to light when taking into account that the mechanisms of the input of heavy metals into plant crops are not completely clarified, nor the factors that influence their input [16].

Table 1. Transfer coefficient of heavy metals from soil to fruits of Elstar apple

Metal	Elstar acidification	Elstar calcification	Elstar control
Pb	0,0346	0,0411	0,0729
Cu	0,0214	0,0184	0,0261
Cd	0	0	0
Zn	0,0721	0,0363	0,0759
Fe	0,0007	0,0005	0,0008

The transfer coefficient (Tc) of metals from soil to fruit is the best way to show metal absorption from the soil by the plants. The transfer coefficient of metals from soil to fruits is defined as a relation of concentrations of a certain metal in plant/ fruit and soil (mg/kg) [17]. The transfer coefficient is different in different metals, high values have Cd and Zn (1-10), lower Tc values show Cu and Ni (0.1-1), and Co and Pb have the lowest value of Tc (0.01-0.1) [18]. The conducted research shows that the transfer coefficient of heavy metals from soil to edible apple parts is very low, i.e. below the limit values.

4. CONCLUSION

It is known that the absorbance of heavy metals from the soil and their accumulation in plants and fruits can significantly affect the chemical and physical characteristics of the soil and their interaction, or the specific ability of certain plant species to accumulate metals.

This research has shown that in the fruit of the Elstar variety in all four fruit samples, iron recorded the highest content, which on average was around 15 mg/kg. The zinc content ranged from 2.36 to 4.40 mg/kg, the copper content ranged from 0.65 to 0.79 mg/kg, while the lead content was in the range 0.41 to 0.70 mg/kg. Cadmium was not present in any of the samples.

The content of metals is noticeable in the fruit juice of the Elstar variety by different conditions of the soil, the highest was copper content of 0.668 mg/kg in the case of juice produced from apples from the basic soil as well as the highest iron concentration of 0.146 mg/kg. The highest zinc concentration of 0.181 mg/kg was observed in fruit juice from the control soil and lead in apple juice from the moderate acidic soil of 0.194 mg/kg. Cadmium is only registered in the case of apple juice from the control soil at a concentration of 0.131 mg/kg.

The general conclusion is that the volume of the absorption of the tested heavy metals into the fruit and processed apple juice depends not only on the type of soil but also on the applied agro-technical measure. It can also generally be said that increasing soil acidity and complexing (acidic and base soils) contributed to the mild absorbtion of heavy metals by the tested apple variety which was within the limit points of MAC. [19]

Growing apples on such soils do not present a hazard to the consumer when consuming apples and products from apples. The transfer coefficient of heavy metal from the soil to the edible parts is very low i.e. below the permitted limit values.

5. RECOMMENDATION

Such research should also be carried out on other types of fruit such as plum, pear, strawberries etc. to determine the possibility of absorbing the heavy metals from soil to fruits.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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