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The Risk Assessment of Fruit Copper Uptake from Soil

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Abstract

The heavy metals uptake from soil into the edible parts of plants represents an important problem, especially if their toxicity, non-biodegradability and the ability to be accumulated as the most dangerous characteristics that directly affect the consumer's health are concerned. The content of heavy metals in soil depends on the characteristic and the type of soil, heavy metals immission, the intake with fertilizers, pesticides, adsorption mechanism and/or fixation, type of fruit sort etc. The aim of the paper is to present the differences in the presence of copper in the soil with different pH values, and the content of organic substances and their influence on the copper content in the fresh plum fruits. The results of the conducted studies show that the accumulation of copper from soil into fruit depends not only on the type of soil content but also on the fruit sort. It can also be generally said that the increase, or the decrease in soil acidity contributes the increase of copper accumulation from soil into fruits in particular sorts, but its concentration in fresh plum is very low.

Keywords: copper; soil; fruit; risk assessment

1. Introduction

Copper (Cu) is one of the essential elements in traces having several important roles in human body metabolism, because it is the co-factor of several redox enzymes and a structural component of lots of metalloenzymes. There are about 100 mg of copper in healthy adult human, weighing 70 kg on average (Prashanth et al., 2015). Together with zinc and selenium it is involved in free radicals destruction (Chan et al., 1998), and it is essential for haematological and neurological system (Tan et al., 2006). Due to different enzymes containing copper as a cofactor, the symptoms of copper deficit are different and include haematological changes in the sense of normo and hypocromic anemias, hypercholesterolemia, skin and hair hypopigmentation, neurological changes due to neuromyelopathy, etc. There have also been changes in immunological functions and on bones noticed. Although it is an essential micronutrient for humans, copper is toxic in high levels. Acute toxicity as a result of short-term intake of large amounts of copper may result in several pathological conditions, while chronic toxicity may result in serious neurological defects (Uriu-Adams and Keen, 2005). Excessive dietary copper intake causes its accumulation in liver with a consequential decrease in haemoglobin concentration, and it may represent a problem in specific conditions such as *Wilson* disease.

Copper can be found in different kinds of food, and in different food supplements, too. Its concentration in food depends on local circumstances, and the concentration of copper in the soil is one of the factors influencing on its concentration in cereals, fruits and vegetables (Bost et al., 2016). Mean daily copper intake in European countries is between 1.27 and 1.67 mg/day in males older than 18, or 1.15-1.44 mg/day in non-pregnant women older than 18 on average. EFSA panel proposes the value of adequate daily copper intake of 1.6 mg/day for adult males and 1.3 mg/day for adult females (EFSA, 2015).

The intensity of copper intake and transport in the above-ground organs is in a positive correlation with its concentration in the soil. The process of copper intake is active and it is considered that there is a specific carrier (Lončarić, 2011) the competition for copper intake is manganese, ferrous and zinc, and it is also noticed that good nitrogen and phosphor supply in plants often leads to copper deficiency. According to overall concentrations, copper is the sixth heavy metal in the ground (behind ferrous, manganese, zinc, chromium and nickel). However, according to the overall concentrations of the available fraction, copper is on the third place, behind ferrous, manganese, and before zinc. Copper can be toxic in excessive amounts, and the anthropogenic input into the soil can be important, so the maximum permitted concentrations (MPC) have been stipulated for the agricultural land, where for the silt-loam grounds it is 90 mg/kg (Official Gazette of the Federation of Bosnia and Herzegovina, No 68/14). The root contains copper in significant amounts because the translocation of copper is medium in both directions. It is intaken as Cu^{2+} or in the form of chelates and belongs to the group of heavy metals that are hardly sorbated on soil colloids (Lončarić, 2010).

2. Material and Methods

The analysed soil samples were those within the treetop-width of two plum tree cultivars from *Fruit nursery garden in Srebrenik* (Bosnia and Herzegovina) with two experimental lots where alkalisation and calcification had been performed: experimental lot 1 (*Stanley cultivar*) and experimental lot 2 (*Cacanska rodna cultivar*). The soil samples were taken from the depth of 0-60 cm (silt-loam ground), than they were dried on air and grinded in ground mill. The basic chemical analysis was performed in the soil samples (five samples from each experimental lot): soil pH in H_2O and 1 M of KCl (ISO 10390, 1994), electrical conduction (μS) and organic matter (%), according to Tóth et al. (2013).
A concentration of copper was determined in *Stanley* (experimental lot 1) and *Cacanska rodna* (experimantal lot 2) cultivars of plum fruits (eight plum samples from each experimental lot).
The pH value of soil samples was determined electrometrically (ISO 10390, 1994) in soil suspension with distilled water (actual acidity) and in 1MKCl (substitution-potential acidity). Organic matter in soil is determined with samples burning till achieving the constant mass in a preheating furnace. After the soil samples analysis, the acidity of the experimental soil increased, i.e. decreased with the ammonium-sulphate (1 kg per plum tree) and lime (3.5 kg per plum tree) and it was treated with the copper metal solution in the amount of 600 ml per tree (10 ml of pure solution mixed with ten litres of distilled water). The total concentration of copper in soil after three months was determined by microwave technique where the soil was digested with aqua regia (ISO 11466, 1995), and EDTA extraction was used for heavy metals determination (Đurđević, 2014; Tomljanović, 2010). Copper concentrations obtained by measuring on ICP-OES represent its overall concentration in soil. The concentrations of heavy metals in soil and plum fruits were measured with atomic absorption spectrophotometer (*Analyst 200*) and in inductively coupled plasma with the method of optical emission ICP-OES (*Optima 2100 DV*).

3. Results and Discussion

The determination of the concentration of heavy metals in soil is the basic indicator of tracking the heavy metals migration from soil into the plant fruits. Bioavailability and bioaccumulation of heavy metals in plants and fruits is directly connected to their content and mobility in the soil (Teodorović et al., 2009). As the elements of basic soil analysis, the results of pH value determination in water and 1M KCl were presented, and the organic matter and electrical conduction as well.
The average pH value of the experimental lot 1 was 7.62 in water and 6.63 in KCl, while the average pH value of the experimental lot 2 was higher and it was 8.72 in water and 7.0 in KCl (figure 1).

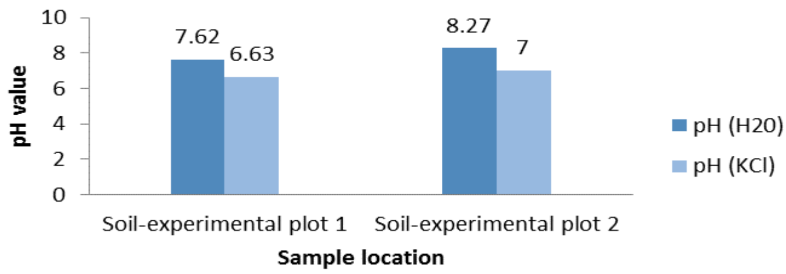

Figure 1. Average soil pH value in water and KCl

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The average content of organic matter was almost the same in both lots, i.e. in the experimental lot 1 it was 8.38%, and in the experimental lot 2 it was 7.89%. The average electrical conduction in the experimental lots was in the interval from 76.40 µS for the experimental lot 1, up to 36.30 µS for the experimental lot 2 (figure 2).

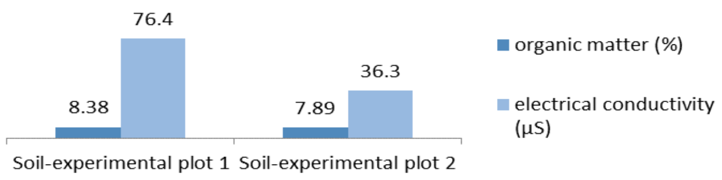

Figure 2. The average content of organic matter and the electrical conduction

Higher copper values were measured at the experimental lot 1 than in the experimental lot 2. The largest amount of copper in the experimental lot 1 was in sample 2, 68.57 mg/kg, and the largest amount of copper in the experimental lot 2 was in sample 5, 51.23 mg/kg. The lowest values of copper were noticed in sample 3 of the experimental lot 1, 55.96 mg/kg, and 38.89 mg/kg for the experimental lot 2, sample 2. The measured total concentrations of copper in the analysed experimental soils were significantly below the value of MPC with the average copper value for the experimental lot 2 of 46.3 mg/kg (figure 3).

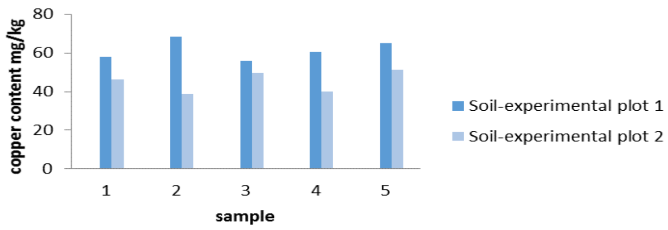

Figure 3. The soil copper content

The acidification with the purpose of soil acidification, i.e. calcification with the purpose of soil pH value increase, was performed on experimental lots. At the same time, dosing with copper within the treetop-width was performed, with the purpose of soil contamination. Only copper without acidification or calcification was dosed in the area of experimental lots, and there was no treatment in the other part of the lot and that part had the starting soil parameters of fruit nursery garden, in order to perform the comparison of the results obtained.
After the acidification, the average pH value of the experimental lot 1 was 6.99 in water and 6.27 in KCl. The average pH value of the experimental lot 2 was 6.57 in water and 6.28 in KCl (figure 4).

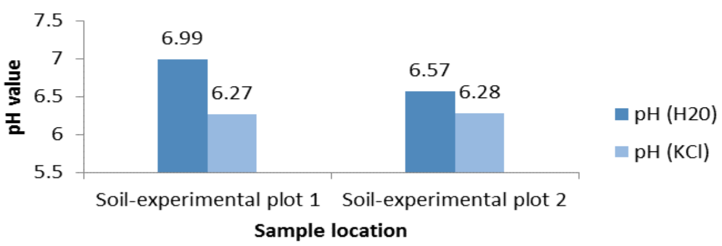

Figure 4. Average soil pH value in water and KCl after acidification

Compared with the starting parameters after soil acidification it can be concluded that there was a decrease in soil pH value, especially in the experimental lot 2, i.e. from 8.27 in water and 7.0 in KCl to 6.57 in water and 6.28 in KCl.

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After the calcification, the average pH value of the experimental lot 1 was 7.82 in water and 7.05 in KCl. The average pH value of the experimental lot 2 was 7.65 in water and 7.30 in KCl (figure 5).

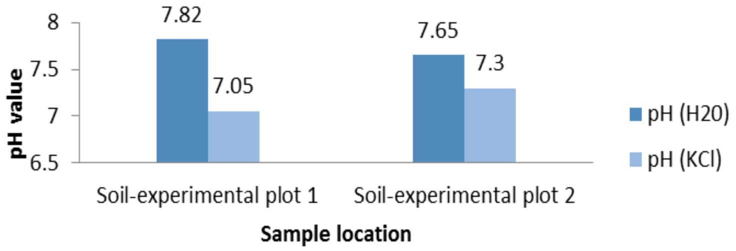

Figure 5. Average soil pH value in water and 1M KCl after calcification

Compared to the starting parameters after soil calcification it can be concluded that there was a slight increase of soil pH value in the experimental lot 1, i.e. from 7.62 in water and 6.63 in KCl to 7.82 in water and 7.05 in KCl.
The organic matter content was slightly higher in the experimental lot soil where the acidification had been performed and it was 7.6%, while in the soil where the calcification had been performed it was 6.84% (figure 6).

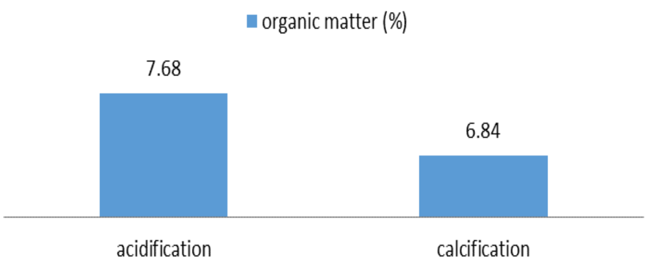

Figure 6. The average organic matter content in soil after acidification and calcification

There was a decrease in value of the organic matter content after the calcification was performed by 10% in average, compared to the starting parameters of the experimental soil.
The results of soil analysis after acidification and soil contamination, i.e. copper dosing into the soil within the treetop width, show that the lot where the *Stanley* plum cultivar had been grown has a pH value of 6.99 in water and 6.27 in KCl, while the pH value for *Cacanska rodna* cultivar was 6.57 in water and 6.28 in KCl. The share of copper in the soil for *Stanley* plum cultivar increased from 60.6 mg/kg to 951.52 mg/kg, which shows that there was a considerable increase of Cu in the soil (high above the MPC of 90 mg/kg for silt-loam ground).
The results of soil analysis after calcification and simulated soil contamination, i.e. copper dosing into the soil, show that the lot where the *Stanley* plum cultivar had been grown has a pH value of 7.82 in water and 7.05 in KCl, while the pH value for Cacanska rodna *cultivar was 7.65 in water and 7.30 in KCl. The share of copper in the soil for Cacanska rodna* plum cultivar was several times higher compared to starting parameters, i.e. from 46.3 mg/kg to 2002.6 mg/kg.
The availability of copper in soil was a bit lower in *Stanley* plum cultivar, but much above MPC of 90 mg/kg for silt-loam soil. The variability of relative availability of copper in soil is extremely high. In order to have better monitoring of heavy metal transfer into the fruit, copper in this case, the analysis was performed during the plum harvesting. The average pH values of experimental lots during plum harvesting are shown in figure 7, so the pH value of the experimental soil during plum harvesting where the acidification was performed was 5.96 in water and 5.43 in KCl and, therefore, it is a moderate acid soil. The pH value of the experimental lot where the calcification was performed was 7.81 in water and 7.48 in KCl, and it belongs to a basic soil. The pH value in the soil treated only with heavy metal solution was 7.65 in water and 7.01 in KCl, which is classified as neutral soil, experimental control in our case.

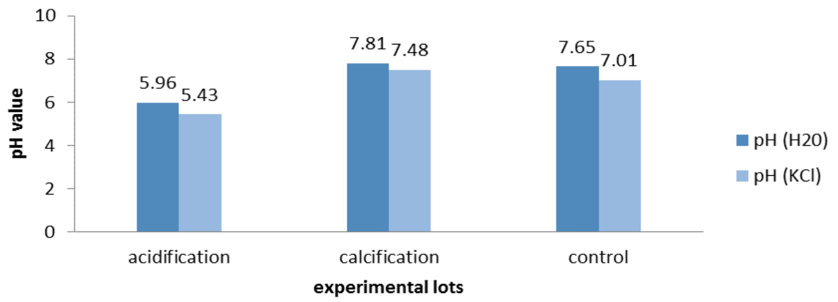

Figure 7. Average soil pH value in water and 1M of KCl during plum harvesting

The highest value of organic matter in the experimental soil treated only with heavy metal solution was 7.95%, while the lowest value of organic matter in the experimental soil where the calcification was performed wa 6.35% (figure 8).

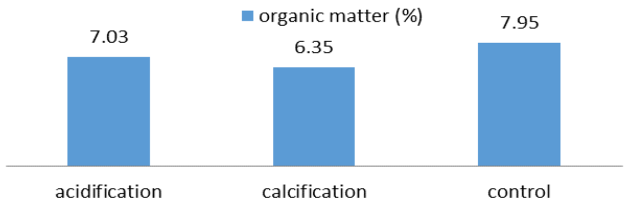

Figure 8. Average content of organic matter in the experimental soil

The comparative relation of copper content in *Stanley* plum cultivar at different soil conditions is shown in figure 9. The experimental soil samples are marked as follows: *Moderate acid soil-S1, Basic soil-S2, Control soil-S3 and Neutral soil-S4 (without any treatment with the average starting parameters of fruit nursery garden condition).* Copper concentrations in *Stanley* plum cultivar fruit at different soil conditions in the first three samples are nearly the same and the highest value for S1 grown in the acid soil was 0.02 mg/kg, while for S4 grown in neutral soil without any treatment and any soil contamination simulation with copper was 0.001 mg/kg. The average values of copper in *Stanley* plum cultivar at given conditions were very low, i.e. much below MPC.

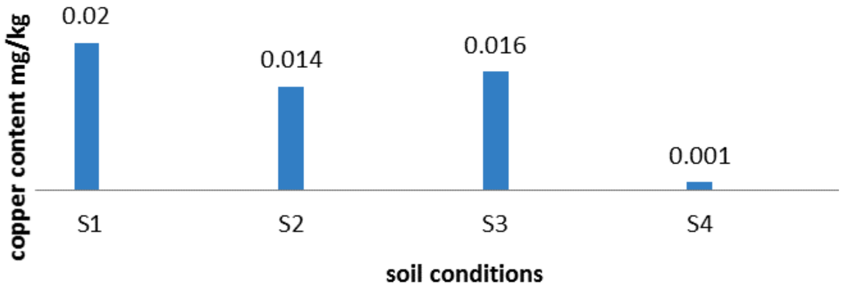

Figure 9. The relation of copper content in *Stanley* plum cultivar in different conditions

Figure 10 shows the comparative content of copper in *Cacanska rodna* plum cultivar in different soil conditions given. The experimental soil samples are marked as follows: *Moderate acid acid soil-R1, Basic soil-R2, Control soil-R3 and Neutral soil-R4 (without any treatment with the average starting parameters of fruit nursery garden condition).* The highest concentration of cooper in *Cacanska rodna* plum cultivar was measured in R4 soil-0.2 mg/kg, and it was the fruit sample from the tree grown in neutral soil without any treatment and soil contamination with copper, but this sample was sprayed with copper preparations for the purpose of annual protection, which can be the cause for higher copper concentration. A much lower concentration of copper was noticed in other samples, for R1 grown in the acid soil-0.066 mg/kg, for R2 grown in the basic soil-0.033 mg/kg, and 0.02 mg/kg for R3 grown in neutral pH value soil.

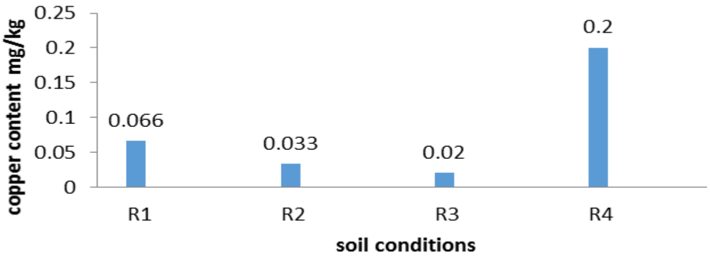

Figure 10. The relation of copper content in *Cacanska rodna* plum cultivar in different conditions

Higher values of copper were recorded in the given soil conditions for *Cacanska rodna* plum cultivar, but those values are much below MPC, which represents a serious danger for consumers, since the daily copper intake in European countries is between 1.27 and 1.67 mg/day on average in males older than 18, or 1.15-1.44 mg/day in non-pregnant females older than 18. EFSA panel proposes the value of adequate daily copper intake of 1.6 mg/day for adult males and 1.3 mg/day for adult females (EFSA 2015).

4. Conclusion

The mobility of heavy metals in soil represents a complex process which basically depends on the nature of metal itself, the type of interaction of solid phase and the soil, and other factors such as acidity, oxidation and/or reduction conditions, ionic content of soil solution. It is known that chemical and physical soil characteristics and their interactions, i.e. specific ability of particular plant types to accumulate metals can considerably affect the heavy metals intake from the ground and their accumulation in plants and fruits. The presence of helate agents, organic matter content and amount, cation capacity and pH values are particularly important among physical and chemical factors. The mobility and availability of heavy metals is usually low, especially in the case of low ground pH value and high organic matter and clay. Through soil acidification, which is frequently present in agriculture as an inevitable measure of soil acidity repair, the conditions where heavy metals will be more available to the plant root and their content increased in the fruit itself are made in the ground. The aforementioned fact is manifested when it is taken into consideration that the mechanisms of heavy metal intake into plant cultures and the factors affecting their intake have not been completely clarified. Copper is firstly accumulated in the cell wall of root cells, and while some plants have the ability to accumulate those metals in their vacuoles to a large extent, some plants accumulate them in their mitochondrias. The results of the conducted studies show that the accumulation of copper from soil into fruit depends not only on the type of soil content but also on the fruit sort. It can be concluded that the increase, or the decrease in soil acidity contributed the increase of copper accumulation from soil into fruits in particular sorts, but its concentration in fresh plum is very low. Soil pH value has a considerable effect on the availability of microelements in basic grounds, especially copper. All these facts support the fact that copper concentration, i.e. its speciation in soil can vary depending on soil profile. Copper is one of the essential elements in traces having several important roles in human body metabolism, because it is the co-factor of several redox enzymes and a structural component of lots of metalloenzymes. For that reason it is very important to human organism but in normal quantities. Although being an essential nutrient for humans, copper is toxic in high levels, and therefore it is essential to continuously perform control and risk assessment for copper intake through food.

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