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CONTENT OF Cu, Zn, Co, Ni, Cr IN SOIL AND FRUITS OF APPLE AND PLUM

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Abstract

In plants, some metals play important role as micronutrient components, significant for growth in low concentrations. If present in higher concentrations than necessary, they can be phytotoxic and cause product contamination. Analysed soils are classified from clay loam to heavy clay, medium to high supply with soil basic fertility parameters, acid to neutral soil reaction. Analysing total content of Cu, Zn, Co, Ni, Cr in soils under apple and plum plantations, an averaged higher content of Cu (13,88 mg kg⁻¹), Zn (33,78 mg kg⁻¹), Co (22,05 mg kg⁻¹), Ni (52,38 mg kg⁻¹) has been measured under plum plantations and the content of Ni (9,55 mg kg⁻¹) under apple plantations. Results of the examination on the presence of the above elements in fruits have shown differences in relation to the content in the soil. Content of Cu, Zn, Co, Cr have had higher average values in fruits of apple and the Ni content has been higher in plums, with higher measured values in individual fruits of plum Cu 3,11 mg kg⁻¹ of dry matter), Zn (4,08 mg kg⁻¹ of dry matter), Ni (1,32 mg kg⁻¹ of dry matter). Adoption of metal from the soil depends on the pH value of the soil, organic composition, the soil type and the concentration of metals in the soil itself. It also depends on the percentage of metal adoption through the plant root, water, metabolic capacity, ion absorption and other. Monitoring the content of metals in soil and fruits is significant in sustainable land use and health food safety.

Keywords: *Metals, Apple, Plum, Soil fertility, Health food safety.*

Introduction

Fruit growing in Serbia is ever increasing with increased area under intensive fruit plantations. Most prevalent are plantations of stone fruits among which two thirds is under plum. Plum has long been the leading fruit species though apple, which is grown on 23.737 ha is dominant in modern production. In European scales, Serbia ranks 12th in areas under apple (Keserović et al., 2014).

For achieving high yields and production of health safe fruits, of particular importance is to choose land as a major source of nutritional substances necessary for plant growth and fruiting. Chemical analysis of soil is important for monitoring conditions of the environment and legislation. (Merry, 2010). Modern growing systems demand soil fertility monitoring but also the analysis of other nutrients of calcium, magnesium, sulphur and microelements: iron, manganese, zinc, copper, boron and molybdenum which plants need in smaller quantities than macroelements. Excess nutrients and those with no physiological significance belong to the group of hazardous and deleterious substances among which the most common are: Cu, Zn, Ni, Pb, Al, Cr. Natural content of hazardous and deleterious substances in soil is of geochemical origin and mostly so negligent that it has no significant effect on agroecosystem contamination. Hazardous and deleterious substances deriving from anthropogenic sources in soil are found in forms that are easily accessible. Accessibility of nutrients and their further transport in plants is affected by mechanical composition, soil reaction, humus content, calcium carbonate content and available phosphorous in the soil.

Different fruit types have different needs for adoption of biogenic elements. Deposition of certain elements is also different so in some plants, the largest concentration is in the root, in

others, in leaves or buds while the maximum allowable concentration in fruits is determined based on different parameters including human medicine. Absorption and accumulation of heavy metals in plants depend on bioaccessibility and contents in the soil, genetic properties of plants, edaphic and other ecological factors. These differences are mostly conditioned by plants' genetic base or other parameters.

The aim of the investigation is determining effects of Cu, Zn, Co, Ni, Cr presence in soil on the content of the same elements in fruits of plum and apple.

Material and Methods

Investigations were carried out in September 2018 by sampling of the soil in the rural area of Čačak, in apple and plum orchards of the following cadastral municipalities: Baluga Trnavska, Trnava, Prislonica, Pridvorica, Vranići, Gornja Gorevnica, Vranići and Miokovci. Sampled orchards were marked by GPS coordinates: N from 4352028 to 4357480 and E from 2016305 to 2027156. Sampling depth was 0-30 cm. Analysed soil under plum plantations was classified as clay loam and light clay with 15.80-27.50% share of clay fraction and 42.10-58.00% of physical clay. Soils under apple plantations are classified as heavy clays on three sites with about 46.0% share of clay fraction and 71.40-79.20% physical clay. In apple orchards in Baluga Trnavska, the soil is classified as clay loam. Agrochemical characteristics of soil are analysed at the laboratory of the Fruit Research Institute, Čačak using the following methods: pH value in H₂O and 1N KCl-u (potentiometrically); humus (method by Kotzman); total nitrogen (method by Kjeldahl); easily accessible phosphorous and potassium (AL method, P₂O₅- colourmetrically, K₂O flame photometrically). The samples were previously dried at ambient/room temperature and sieved through a sieve ≤2 mm. The total content of macro and micro elements is specified by mineralization of soil samples with HCl and H₂SO₄, and the contents of the same elements in fruits upon a modified procedure (Morais et al., 2017) and reading on AAS (Perkin Elmer, 2018).

Results and Discussion

Numerous studies point to the influence of mechanical composition, soil reactions, humus content on the availability of nutrients. Strongly acidic soils are poor in available forms of macroelements and certain microelements for plants, while at the same time these soils contain higher amounts of ions of Al, Fe and Mn, available to plants, which in high concentrations, have toxic effect (on plants) (Dugalić et al., 2008). Research results (Tab. 1) have shown that the analysed soil is of weakly acid to weakly alkaline reaction. Average values of the active soil acidity (pH/H₂O) in the humus horizon (0-30cm) under plum and apple plantations is about 6.82. Substitutional soil acidity (pH/KCl) was higher in soils under apple plantations, which is caused by the mechanical composition of soil. Acidification process can be regarded as a primary cause of the reduced productivity of agricultural land (Mrvić et al., 2012), which was in the past substantially accelerated by anthropogenic factor, primarily increased emission and deposition of acidic contaminants, improper use of mineral fertilizers and other (Sparks et al., 2002). Humus supply is low to medium, of higher average values under apple plantations of 3.09%. Total nitrogen is, on average, of medium content up to 0.16%. The content of easily accessible phosphorous varies on the sampled parcels. The lowest value 4.15 mg/100g of soil is in acid reaction soil in Prislonica while the content of easily accessible P₂O₅ is high in other parcels. Under conditions of increased soil acidity, phosphorus as one of the most important macronutrients in the forms bound with Al and Fe becomes inaccessible to plants (Barber, 1995). The investigated soils are optimally supplied with easily available K₂O. The research results of all analysed parameters are consistent with the results of Milivojevic et al., 2017.

Table 1. Basic soil fertility

Site	Populated area	pH		CaCO ₃	Humus	Total N	AL-P ₂ O ₅	AL-K ₂ O
		H ₂ O	KCl	%	%	%	mg/100g adl	mg/100g adl
1	Baluga Trnavska	7.43	6.68	0.69	1.00	0.05	30.53	17.3
2	Trnava	6.47	5.78	0.69	3.59	0.18	45.42	55.4
3	Prislonica	5.82	4.68	0.00	2.24	0.11	4.15	34.8
4	Prislonica	7.50	6.60	1.57	5.54	0.28	57.88	52.5
	average	6,81	5,94	0,74	3,09	0,16	34,50	40,0
6	Pridvorica	6.43	5.82	0.82	3.89	0.19	74.81	55.8
7	Vranići	7.35	6.55	2.33	1.12	0.06	47.17	29.9
8	Gornja Gorevnica	6.89	6.23	1.37	4.18	0.21	26.04	34.1
9	Miokovci	6.60	5.86	0.00	2.65	0.13	29.06	31.3
	average	6,82	6,12	1,13	2,96	0,15	44,27	37,78

*parcels under apple (1-4)

*parcels under plum (6-9)

In soils with alkaline reaction, mobility and accessibility of phosphorus, potassium, magnesium, iron, manganese, boron, cobalt, copper and zinc is decreased. Exceptions are (found in) molybdenum, sulphur, nitrogen, which are better adopted with an increase of pH value of the soil solution. Results of the content of macro and micro elements are shown in tab. 2. The average Cu content in the analysed parcels ranged from 9.2-25.3 mg kg⁻¹. According to the literature (Pendias Kabat et al., 2001) zinc content in soil should not be higher than 200-300 ppm. It is believed that high values of the content of total copper (> 60 mg kg⁻¹) are caused by fungicide application based on copper compounds (Schramel et al., 2000; Pietrzak and McPhail, 2004; Wightwick et al., 2006; Rusjan et al., 2007). The research results of the total copper content in smonitsas of Western Serbia (Milivojević et al. 2017) amounted to somewhat higher values in relation to our investigations. The content of Co was 12.8-31.0 mg kg⁻¹, and the content of Zn varied considerably between the analysed parcels 7.3-59.4 mg kg⁻¹.

Table 2. Content of micro elements in soil

No. of sample	Cu	Co	Zn	Cr	Ni
	mg kg ⁻¹				
1	10,4	12,8	26,5	10,2	60,8
2	9,2	18,5	51,8	9,8	30,8
3	17,2	21,3	13,0	8,9	63,9
4	17,5	18,5	21,5	9,3	2,9
average	13,58	17,80	28,2	9,55	39,6
6	8,8	16,0	34,9	9,2	35,2
7	9,8	16,4	7,3	9,2	11,2
8	11,6	24,8	33,5	9,0	50,8
9	25,3	31,0	59,4	10,1	112,3
average	13,88	22,05	33,78	9,38	52,38

*parcels under apple (1-4)

*parcels under plum (6-9)

The presence of the total Cr did not show greater interval variation from 8.9-10.2 mg kg⁻¹, in contrast to the presence of Ni, with the content from 2.9-112.3 mg kg⁻¹. Boskovic Rakočević

et al., 2014: found lower values of the Cu and Zn content in the soil, and the lower value of Zn in the fruits of plums, and an approximate value of Cu in relation to our investigations. Minerals and toxic element concentration in fruit are often variable and impacted by the species and cultivar, climatic conditions, geological origin of soil, the usage of fertilizers and other agricultural chemicals, plant growth stage and soil elements availability (Ekholm et al., 2007). The usage of fertilizers and pest control chemicals, urban industrial activities, and irrigation and fertilization type may affect the accumulation of microelements in soils (He et al., 2005). Microelements which have a role of regular enzyme functioning may also have adverse effects on human health depending on the intake quantity.

Investigation results show that, on average, the content of all analysed metals in apple fruits is higher in relation to plum fruits. However, looking at individual samples, there are deviations from previously mentioned. Cu content in the fruits apples ranged from 1.63-2.87 mg kg⁻¹, and in plum fruits 1.18-3.11 mg kg⁻¹. Miclean et al., 2000 report that the Cu content in agricultural products should be between 4 and 15 ppm, and according to the limit values of the World Health Organization, it is 3 mg kg⁻¹ and less. The presence of Co in certain samples is below the level of detection to a content of 0.55 mg kg⁻¹. Zn is present in the amounts of 1.88-2.95 mg kg⁻¹ in apple and 0.50-4.08 mg kg⁻¹ in plum. According to the FAO/WHO (1984) allowable Zn in fruits is up to 27.4 ppm. The content of Zn in our investigations is within the range of optimal values whereas the Cu content is above the values allowed according to FAO/WHO and optimal values, according to Miclean et al., 2000. There are not many data on levels of cobalt (Co) in foods of plant origin in the scientific literature. The available data showed low levels of this micronutrient, often under 0.001 mg/100 g.

Table 3. Content of micro elements in fruits

No of sample	Cu	Co	Zn	Cr	Ni
	mg kg ⁻¹				
1	2,87	<0,05	2,95	0,85	1,21
2	1,63	0,55	2,89	0,46	0,53
3	2,26	0,23	1,88	1,60	0,71
4	1,85	0,44	1,95	0,26	0,63
average	2,15	<0,05	2,42	0,79	0,77
6	1,72	0,05	4,08	0,49	0,76
7	3,11	<0,05	0,50	0,36	1,32
8	1,22	0,32	2,72	0,46	1,17
9	1,18	0,21	2,22	1,08	2,21
average	1,81	0,21	2,38	0,60	1,37

*apple fruits (1-4) *plum fruits (6-9)

Results of Osmanovic et al., 2014, show significantly higher levels of Zn and Cu, and the approximate values of Cu in the fruits of plum in relation to our investigations. Heghedüş-Mindru Ramona et al., 2014 found similar values of the Cu content in fruits of apple and plum, and the content of Zn and Co. was higher in our investigation results.

Average contents of Cr and Ni in apple is of approximately values (0.77-0.79 mg kg⁻¹), and in plum fruits the content of Ni is increased. FAO/WHO, 2001 anticipates a limit of 2.3 ppm for the content of Cr, which is within the limits of our values. An upper tolerance limit for the fruits of Ni is 0.5 mg to 100 g⁻¹ of Ni and the values are within the allowable value for our investigations. Fruits usually present Ni between <0.004 and 0.05 mg 100 g⁻¹ (Szefer and Grembecka, 2007). The recommended daily intake of Ni is in the range of 302–735 µg (Roychowdhury et al., 2003). A RDA for Cr is not well defined, but it is considered to be between 25–35 µg/day, fruits and vegetables being the major dietary contributors of Cr intake. Increased heavy metal concentrations in food may adversely affect human health due to the predominating soil-plant pathway for their entry into the human body (Liu et al. 2013).

According to the data from the studies on phytotoxicity (Kabata - Pendias, 2011), Ni is, unlike others, a very mobile element in plant (Cr), and its transfer to fruits is the result of the phloem mobility. Accessibility of heavy metals, as well as their adoption by plants, depends on a number of factors, primarily on their overall and available content in soil, followed by soil reaction, organic matter content, oxidation-reduction conditions and other (Adriano, 2001; Kabat - Pendias, 2011), while the uptake of heavy metals depends on the plant type too (Overesch et al., 2007). Particularly outstanding is the influence of soil pH where the higher the acidity the greater the adoption of metal and vice versa, i.e. alkalinity increase leads to metal immobilization.

Conclusions

Investigation results show that the analysed soil is slightly acid to slightly alkaline. Humus supply is low to medium, of higher values, on average, under apple plantations with 3.09%. Total nitrogen is, on average, of medium content up to 0.16%. The content of easily available phosphorus differs on sampled parcels with the lowest values 4.15 do 74,81 mg 100g⁻¹ of soil P₂O₅. The investigated soils are optimally supplied with easily available K₂O.

Total content of deleterious and hazardous substances in soil shows that the average Cu content in the analysed parcels ranged from 9.2-25.3 mg kg⁻¹. The content of Co was 12.8-31.0 mg kg⁻¹ and the content of Zn varied considerably between analysed parcels, 7.3-59.4 mg kg⁻¹. The presence of the total Cr did not show greater variation in the interval from 8.9-10.2 mg kg⁻¹, in contrast to the presence of Ni, having a content from 2.9-112.3 mg kg⁻¹.

The presence of heavy metals in fruits of apple and plum show that Cu in apple fruits ranged from 1.63-2.87 mg kg⁻¹, and in fruits of plum 1.18-3.11 mg kg⁻¹. The presence of Co is in certain samples below the level of detection up to 0.55 mg kg⁻¹. Zn is present in the amounts from 1.88-2.95 mg kg⁻¹ in apple and 0.50-4.08 mg kg⁻¹ in plum. Average content of Cr and Ni in apple is of approximate values (0.77-0.79 mg kg⁻¹), and in plum fruits, an increased Ni content is noticeable.

Availability of metals, as well as their adoption by plants, depending on their total and available content in soil, the reaction of soil, which has a significant effect, the content of organic matter, the oxidation-reduction conditions and the presence of heavy metals depend on the fruit type as well. In order to obtain health-safe food and assess the amount of fruit consumption, it is necessary to analyse each sample of soil and fruit individually.

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