doi:10.14720/aas.2019.113.2.3 Original research article / izvirni znanstveni članek

Accumulation and dynamics of manganese in raspberry

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Received February 25, 2019; accepted April 23, 2019.
Delo je prispelo 25. februarja 2019, sprejeto 23. aprila 2019.

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Abstract: The aim of this study was to evaluate the dynamics of Mn in 'soil - raspberry' system on the area around the manganese ore deposits Radostovo in Bužim municipality. Atomic absorption spectroscopy was used to determine the concentration of Mn in soil and plant samples. Fe, Zn and Cu concentration in soil and raspberry plants was also subject of analysis, since these elements have antagonistic relationship with Mn in soils. The concentration of available Mn in soils was low, although the total Mn in the same soils exceeded the Mn toxic values noted in the scientific literature. The chemical and physical properties of the examined soils characterized by a relatively high pH value and good ability to store root-zone air certainly contributed to the decreasing release of available Mn^{2+} from manganese oxides in soils as well as Mn^{2+} oxidation to insoluble Mn^{3+} or Mn^{4+} ions, resulting in low uptake of Mn by plant roots. The results of study also showed that the absorbed Mn mostly accumulates in leaves and roots of raspberry, and much less in the stem and fruits. That rule in Mn distribution within raspberry plant is in fact identical to all food crops.

Key words: availability; nutrients; Mn; plant; soil; uptake

Kopičenje in dinamika mangana v malinjaku

Izvleček: Namen raziskave je bil ovrednotiti dinamiko Mn v sistemu tla-malinjak na območju z manganovo rudo Radostovo, v občini Bužim. Za določanje koncentracije Mn v vzorcih tal in rastlin je bila uporabljena atomska absorpcijska spektroskopija. Analizirane so bile tudi vsebnosti Fe, Zn in Cu v tleh in v malinjaku, ker imajo ti elementi antagonistično razmerje do Mn v tleh. Koncentracije razpoložljivega Mn v tleh so bile majhne, čeprav so vsebnosti celokupnega Mn v istih tleh presegale njegove toksične vrednosti, navedene v znanstveni literaturi. Analizirana tla so imela relativno visok pH in dobro prezračenost, kar je gotovo prispevalo k zmanjšanju razpoložljivega Mn^{2+} iz manganovih oksidov v tleh kot tudi k oksidaciji Mn^{2+} v netopni Mn^{3+} ali Mn^{4+}, kar je povzročilo majhen privzem Mn v korenine. Rezultati te raziskave so tudi pokazali, da se večina absorbiranega Mn kopiči v listih in koreninah malinjaka in veliko manj v steblu in plodovih. To pravilo v porazdelitvi Mn v malinjaku je dejansko enako za vse kmetijske rastline.

Ključne besede: razpoložljivost; hranila; Mn; rastlina; tla; privzem

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Acta agriculturae Slovenica, **113/2**, 221–229, Ljubljana 2019

1 INTRODUCTION

Manganese (Mn) is a mineral element that is both essential and potentially toxic for plant. It is essential for many plant functions, particularly for antioxidant defense system in plants as an enzyme antioxidant-cofactor (Millaleo et al., 2010). Furthermore, Mn participates in the structure of photosynthetic proteins and enzymes playing an important role in water-splitting system of photosystem II, which provides the necessary electrons for photosynthesis (Mousavi et al., 2011). In addition, Mn activates many enzymes that catalyzes decarboxylation, fatty acids synthesis or hydrolysis (Scăeţeanu et al., 2013). Nevertheless, an excess of Mn is toxic for plants. Kastori et al. (1997) reported that Mn concentration above 150 mg kg^{-1} in plant tissue can negatively affect life processes in plant whereas the concentration of 400 mg kg^{-1} dry matter is toxic. Excess of Mn in plants resulting in a reduction of biomass and photosynthesis, disturbances in absorption, translocation and utilization of mineral elements Ca, Mg, Fe, P and biochemical disorders such as oxidative stress (Lei et al, 2007).

Mn is not encountered as free element in the environment. It is found combined with other elements such as oxygen, carbon, silicon, Sulphur, chloride, and iron in various Mn-compounds, the most widespread one being pyrolusite (MnO_2) followed by rhodocrosite ($MnCO_3$), knebelite ($(MnFe)_2SiO_4$), hausmannite (Mn_3O_4), manganite ($Mn_2O_3 \cdot H_2O$) etc. (Wang et al., 2017). In soil Mn occurs in many oxidation states (from -3 up to +7) with widely divergent solubilities. Divalent manganese (Mn^{2+}) is the most soluble forms of Mn in soil and therefore the most available Mn form for plants, whereas the solubility of Mn^{3+} and Mn^{4+} are very low because these ions form insoluble hydrous oxides (Li et al., 1999).

The occurrence of Mn in various forms in soil depends on different physical, chemical and microbiological processes of which pH and redox conditions are more important (Husson, 2013). In acid soils at low pH (<5.5), Mn oxides are solubilized and release Mn^{2+} in soil solution, while in higher soil pH (up to pH 8), plant available Mn^{2+} is oxidized to insoluble Mn^{3+} or Mn^{4+} ions. Organic matter content and microbial activity also plays a very important rule in the solubility of Mn in soil. Bradl (2004) reported that the increase of organic matter in soil is correlated with the decrease of the available Mn^{2+} forms due to the formation of Mn complexes. Furthermore, higher organic matter also intensifies microbiological activity, which can further decrease the availability of Mn. Namely, some microbes can catalyze the oxidation of Mn^{2+} more fast than abiotic oxidation, resulting in increased insoluble Mn forms in soil. The availability of Mn in soil also depends on other soil properties such as soil moisture and aeration, and antagonistic interaction among Mn and some other elements in soil such as Cu, Zn and Fe (Sparrow and Uren, 2014).

Furthermore, the uptake of Mn^{2+} from soil solution by plants root, is also dependent on the genetic predisposition of the plants (Dučić and Polle, 2005). There are plant species considered more sensitive to excess Mn in soil: beans, lettuce, cabbage, soybean, cauliflower, potato; cucumber and watermelon are moderate; while field corn, rice, sugarcane, and tomato are tolerant on excess Mn in soils (Horst, 1988). According to available literature data, degree of tolerance of raspberry on excess Mn in soil has yet to be tested.

In the area of Bužim municipality, in the northwestern Bosnia, there are several deposits of Mn ore, so it is assumed that the soils in their vicinity contain high Mn levels. Also, in this area the raspberry cultivation is highly represented, and therefore this area is very suitable for testing the degree of tolerance of raspberry to excess Mn in soil.

The main purpose of this research was to evaluate the dynamics of Mn in system 'soil - raspberry' on the area near the manganese ore deposits Radostovo in Bužim municipality.

2 MATERIALS AND METHODS

2.1 STUDY AREA

The experiment was carried out during 2018 on the soils near Mn ore deposits Radostovo, located about 1 km northeast of the Bužim town area (45°3'17" N, 16°1'55" E). The geological structure of this area is mainly composed by limestones and dolomites and volcanic rocks. The Mn ore deposit occurs where the volcanogenic-sedimentary series overlie dolomites and dolomitic limestone. The deposit is dark-red in color, due to the high Mn concentration (Redžić et al., 2014). The climate in Bužim municipality is classified as Cfb by the Köppen-Geiger system. The average annual temperature is 10.7 °C and the average annual rainfall is 1061 mm. The study area included three soil plots in the immediate vicinity of the Mn ore deposits Radostovo. All selected soil plots are used for raspberry production and size of each plot is approximately 500 m^2. The natural profile of all examined soil may be designated as A-B(rz)-R. The color of A (humus accumulative horizon) in soils was dark-brown and its depth ranged from 10 to 15 cm. B(rz) (cambic horizon) was characterized by moderately fine texture and good water-holding capacity. The color of this horizon was dark-red, and depth ranged from 30 to 50 cm. Accordingly, these soils are classified as calcic cambisols (FAO, 2014).

2.2 SOIL SAMPLING

The soil samples from each experimental plot were collected at February 2018 at a depth of 0 - 30 cm using a soil sampler probe. On each plot were collected individual soil samples from five spots (north, south, east, west and center of the plot), and then they were thoroughly mixed to obtain an average sample. After collection, soil samples were transferred to the laboratory of Faculty of Agriculture and Food Sciences University of Sarajevo. Soil samples were cleared of impurities, air-dried at room temperature, crushed and grinded using soil mortar and pestle, sifted through sieves (2 and 1 mm hole diameter) and then stored until the moment of laboratory analysis.

2.3 SOIL CHEMICAL ANALYSIS

The chemical analysis of the average soil sample included the determination of the following parameters: soil acidity, humus content, content of available forms of phosphorus (P_2O_5) and potassium (K_2O), as well as the most important parameter: the concentration of total and available forms of Mn in soil. The concentration of total and available forms of Fe, Zn and Cu in soil sample was also subject of this research, as it is known that these elements have the antagonistic relationship with Mn which can greatly affect the dynamics of manganese in the soil plant system.

Soil pH was determined in H_2O and 1 M KCl by pH meter according to ISO 10390 method (ISO, 2005), humus content by oxidation with potassium dichromate in the presence of sulphuric acid according to ISO 14235 method (ISO, 1998), content of available forms of phosphorus (P_2O_5) and potassium (K_2O) were determined by AL-method based on extraction with ammonium lactate-acetic acid (Egnér et al., 1960).

Analysis of total and available forms of Mn, Fe, Zn, Cu and in soils were performed using atomic absorption spectrophotometry on Shimadzu AA 7000 according to the instructions specified in the ISO 11047 method (ISO, 1998).

Previous extraction of total forms of Mn, Fe, Cu, Zn from the soil was performed using aqua regia solution (ISO, 1995), while the extraction of available forms of these elements was performed using the EDTA solution (ethylenediaminetetraacetic acid).

Aqua regia extraction was prepared as follows: 3 g of air-dried soil sample was transferred into 250 ml round bottom flask. Then, 28 ml of aqua regia (mixture of HNO_3 and HCl in 1: 3 ratio) was added. The flask was covered with a watch glass and allowed to stand 16 hours (overnight) in the digester. The solution was heated on hot plate under reflux and the temperature and digestion time was 270 °C and 2 hr. Thereafter, the flask allowed to cool to room temperature for 10 min and to this cooled solution was added 15 ml of distilled water to dilute the acid concentration. Then, the solution was filtered through quantitative filter paper into 100 ml flask and diluted to the mark with deionized water (ISO, 1995).

Extraction of available forms of Mn from the soil was performed as follows: 10 g of air-dried soils was transferred into 100 ml plastic bottle, then 20 ml EDTA solution (0.01 mol dm^{-3} ethylenediaminetetraacetic acid (EDTA) and 1 mol dm^{-3} $(NH_4)_2CO_3$, adjusted to pH 8.6) was added. The solution in bottle was shaken 30 min in an orbital shaker at 180 rpm. Thereafter the solution was filtered through quantitative filter paper into 25 ml flask and diluted to the mark with deionized water (Trierweler and Lindsay, 1969).

2.4 PLANT SAMPLING

Ten fresh raspberry plants (*Rubus idaeus* L. cultivar 'Willamette') from each examined soil plot were collected very carefully in August 2018 at the stage of commercial maturity, then placed in clean paper bags and transported to the laboratory.

Leaves, root, and fruits of each plant were separated, dried in oven at 40 °C until constant mass, grinded and then stored in little paper bags until analyzed. Three replicate measurements were performed to obtain mean and standard deviation of Mn, Fe, Zn and Cu concentration for each plant part.

2.5 PLANT ANALYSIS

Extraction of Mn, Fe, Zn and Cu from plant samples was performed as follows: 1 g of air-dried and grinded plant sample was placed in 100 ml round bottom flask. Then, 7 ml of a mixture of HNO_3 and H_2SO_4 with a volume ratio of 2.5: 1 (v / v) was added. The flask was left for a few hours at room temperature, and then gently heated on a hot plate for thirty minutes. The solution was cooled to room temperature, filtered through quantitative filter paper into 50 ml flask and made up to the mark with deionized water (Lisjak et al., 2009).

The concentration of Mn, Fe, Zn and Cu in the plant samples was also determined using atomic absorption spectrophotometry.

2.6 STATISTICAL ANALYSIS

All experimental measurements were performed in triplicate and the results were presented as mean ± standard deviation. Statistical analyses were carried out by one-way ANOVA and LSD comparison post hoc tests. Significant differences were accepted at $p < 0.05$. The analyses were performed using Microsoft Excel software.

3 RESULTS

3.1 CHEMICAL PROPERTIES OF THE EXAMINED SOILS

Selected chemical properties of the soil plots near the manganese ore deposits Radostovo are presented in Table 1.

Results of soil chemical analysis showed that soil 1 had a neutral reaction with moderate level of organic matter, while the soil plot 2 and 3 had a slightly acid reaction and a low level of organic matter. All examined soil had a low content of available forms of phosphorus (P_2O_5) and moderate level of available forms of potassium (K_2O).

3.2 MN, FE, ZN AND CU CONCENTRATIONS IN SOIL SAMPLES

Determined values of total and available forms of Mn, Fe, Zn, and Cu in soils are listed in Table 2.

The concentration of total Mn in soils greatly exceeded the permissible limit value for agricultural soils of 850 mg kg^{-1} noted by Pais and Jones (1997) or 1000 mg kg^{-1} noted by Vukadinović and Vukadinović (2001), and that result was expected since the examined soil plots were located near the manganese ore deposits. Fe concentration in analyzed soils was noticeably higher than the average value of Fe in soil (0.6 %) reported by Kabata-Pendias and Pendias (2001). Limit value of Fe in soils is not in the legislative rules or the main topic of discussion among scientists, because Fe is not direct contaminant of soil. Zn and Cu concentration in the examined soil samples did not exceed the maximum permissible value prescribed by the legislation in Bosnia and Herzegovina (Official Gazette of FBiH, 2009), indicating that the examined soils are not polluted by these elements.

The available Mn concentration in soils ranged between 13.4 and 14.7 mg kg^{-1} dry mass, and these amounts were relatively low compared with toxic level of 200 mg kg^{-1} reported by Lindsay and Cox (1985). In the soil samples extracted with EDTA solution, the concentration of Fe ranged from 11.99 to 19.1 mg kg^{-1} which was about 0.16 % of total Fe in soil. This data supports the hypothesis that only small fraction of Fe in the soil occurs in bioavailable forms (Violante et al., 2010). The

Table 1: Chemical properties of the examined soils

Parameter	measured value	soil plot 1	soil plot 2	soil plot 3
pH H_2O	pH unit	7.3	6.8	6.6
pH KCl	pH unit	6.6	5.7	5.4
humus	%	2.67	1.97	1.61
P_2O_5	mg 100 g^{-1}	0.71	0.77	0.66
K_2O	mg 100 g^{-1}	23.1	23.2	18.5

Table 2: Concentration of total and available forms of Mn, Fe, Zn, and Cu in soils

	Concentration (mg kg^{-1} dry mass)							
Soil plot	Mn*	Mn**	Fe*	Fe**	Zn*	Zn**	Cu*	Cu**
1	2034.8	14.7	10529.2	11.99	51.1	0.88	28.8	2.31
2	1849.9	13.4	10973.1	12.59	51.3	0.75	31.8	2.21
3	2228.2	14.4	11421.9	19.1	45.6	0.88	25.2	1.97
Permissible value	1000	-	-	-	200^2	-	80^2	-

* total forms; ** available forms

^{2}Permissible value prescribed by legislation in BIH availability ratio (percentage available fraction in relation to total concentration) for Cu and Zn was much higher and it ranged from 6.94% to 7.81% for Cu and from 1.46% to 1.93% for Zn.

3.3 MN, FE, ZN AND CU CONCENTRATIONS IN PLANT SAMPLES

Concentration of Mn, Fe, Zn and Cu in different parts of raspberry plants that have been grown in soil plots near the Mn ore deposits Radostovo is given in Table 3, 4 and 5.

The results have shown that the concentration of Fe, Zn and Cu in the examined plant parts was relatively low in comparison with the permissible limits of heavy metals in food crops reported by FAO/WHO (2001). Accordingly, the maximum permissible value for Fe, Zn and Cu is 425 mg kg^{-1}, 99.4 mg kg^{-1}, and Cu 73.3 mg kg^{-1}, respectively. Mn concentration in the parts of raspberry plants was also low and not even close to the toxic value for Mn in the plant (400 mg kg^{-1}) reported by Kastori et al. (1997). These findings were unexpected given the fact that the present study was conducted on soils containing high Mn concentration.

4 DISCUSSION

Total Mn and Fe concentration in soils differs considerably, primarily depending on the composition of the parent rock materials and the degree of weathering. Emsley (2001) reported that soil contains between 7 and 9000 mg kg^{-1} of Mn with an average of 440 mg kg^{-1}, while the average Fe concentration in soils is about 0.6% (Kabata-Pendias and Pendias, 1999).

Mn and Fe concentration in all examined soil contain much more Mn and Fe in relation to the average values for Mn and Fe in soils, indicating that the soils in the vicinity of the Mn ore deposits Radostovo have the potential to contaminate the agricultural crops by Mn and Fe. It is assumed that the parent material of these soils is characterized by Fe and Mn oxide minerals. This observation consistent with the result reported by Redžić et al. (2014) and Grigorova (2011) who stated the high presence of Mn and Fe oxide minerals such as romanechite, vernadite, pyrolusite, hematite and pyrite in the complex formations of the parent material in this area.

Although the total Mn concentration in soils was high, the concentration of available forms of Mn in the same soils was relatively low considering that values between 140 and 200 mg kg^{-1} regarded as excess (Lindsay

Table 3: Concentration of heavy metals in raspberry plants from soil plot 1

	Soil plot 1: Concentration (mg kg^{-1} dry mass)			
Part of the plant	Mn	Fe	Zn	Cu
root	56.89 ± 6.03^{b}	219.39 ± 30.92^{a}	36.82 ± 11.69^{a}	11.96 ± 1.78^{a}
stem	16.69 ± 3.18^{c}	52.59 ± 6.68^{c}	17.02 ± 3.88^{b}	2.62 ± 1.75^{b}
leaves	70.24 ± 8.88^{a}	110.62 ± 15.64^{b}	22.61 ± 4.75^{b}	4.37 ± 3.06^{b}
fruit	12.52 ± 2.93^{c}	66.32 ± 12.51^{c}	22.93 ± 12.78^{b}	4.11 ± 2.91^{b}
$LSD_{0.05}$	5.63	18.98	8.94	2.56

Values expressed as main ± standard deviation.
Different letters in each column represent significant difference among variants at 0.05 level of probability

Table 4: Concentration of heavy metals in raspberry plants from soil plot 2

	Soil plot 2: Concentration (mg kg^{-1} dry mass)			
Part of the plant	Mn	Fe	Zn	Cu
root	70.77 ± 8.78^{b}	252.83 ± 35.38^{a}	71.54 ± 15.65^{a}	13.22 ± 4.03^{a}
stem	30.71 ± 13.6^{c}	52.29 ± 13.56^{c}	19.23 ± 6.89^{b}	4.26 ± 2.02^{b}
leaves	111.45 ± 18.57^{a}	80.29 ± 16.75^{b}	18.06 ± 7.79^{b}	4.27 ± 2.72^{b}
fruit	21.23 ± 8.89^{c}	67.45 ± 14.87^{bc}	25.34 ± 6.3^{b}	4.73 ± 1.23^{b}
$LSD_{0.05}$	12.95	22.69	10.82	2.61

Values expressed as main ± standard deviation.
Different letters in each column represent significant difference among variants at 0.05 level of probability.

Table 5: Concentration of heavy metals in raspberry plants from soil plot 3

	Soil plot 3: Concentration (mg kg^{-1} dry mass)			
Part of the plant	Mn	Fe	Zn	Cu
root	59.91 ± 11.28^{ab}	209.07 ± 22.98^{a}	33.15 ± 5.12^{a}	15.57 ± 5.56^{a}
stem	16.63 ± 6.82^{c}	63.32 ± 15.52^{c}	21.18 ± 8.41^{b}	2.79 ± 3.45^{b}
leaves	67.11 ± 19.8^{a}	90.85 ± 14.58^{b}	21.03 ± 4.8^{b}	2.78 ± 2.33^{b}
fruit	14.76 ±5.19^{c}	73.11 ± 11.94^{c}	21.63 ± 6.3^{b}	4.61 ± 2.71^{b}
$LSD_{0.05}$	11,32	16.81	6.43	3.81

Values expressed as main ± standard deviation.
Different letters in each column represent significant difference among variants at 0.05 level of probability.

and Norvell, 1978; Silanpaa, 1982; Esu, 1991). Podlesakova et al. (2002) noted that 100 mg kg^{-1} of available Mn in soil is also potentially harmful to food crops. In our study, determined values of available forms of Mn were not even close to above-mentioned critical value.

The concentration of available forms of Fe was also low, about 0.16 % of total Fe concentration in soil. These data indicate that the total concentration of elements in soils does not provide reliable information on their mobility, availability and consequently toxicity (Nunes et al., 2014). One of the main reasons for the low Mn and Fe availability in the examined soils are closely related to the soil redox potential and pH value (Dufey et al., 2009). It is well known that the release of most available Mn (Mn^{2+}) and Fe (Fe^{2+}) forms from Mn and Fe oxide minerals is only possible in acid soils and under anaerobic conditions resulting from waterlogging or very high organic matter content in soils (Rengel, 2015). Namely, when oxygen is depleted from the soil solution, the divalent state of Mn and Fe can be oxidized to the trivalent state, where it may form oxides or hydroxide precipitates and become unavailable to plants (Khabaz-Saberi and Rengel, 2010). It is assumed that the higher pH value (> 6.3 in H_2O) of examined soils contributed to the lower Fe and Mn solubility, and thus the availability of these elements in soils.

The availability of Mn, Fe and generally nutrients in soils is also dependent on plant exudates from roots, and the interactions of plant roots with microorganisms. Plants have potential to exude a variety of organic compounds (phenolics, carbohydrates, amino acids, enzymes, etc.) and inorganic ions (protons, phosphate, etc.) to change rhizosphere chemistry and biology and thus increase or decrease nutrient availability (Marschner et al., 2011). Some of these exudates can promote the activity of Mn-reducing microorganisms in the rhizosphere, increasing Mn availability (Guest et al., 2002). Contrarily, the higher presence of microorganisms that oxidize Mn in soil decreases its availability to plants (Porter et al., 2004). Comprehensive studies of interactions between microbe activity and plant nutrient can certainly contribute to making correct conclusions and quality solutions to increase manganese availability through the implementation of adequate agrotechnical measures such as inoculation of the Mn-reducing microorganisms in soils or similar.

As shown in Table 2, the concentration of total Zn and Cu in the examined soil plots did not exceed the maximum permissible value for agricultural soil prescribed by legislation in Bosnia and Herzegovina and ranged from 45.6 to 51.3 and from 25.2 to 31.8 mg kg–^{1}, respectively. These ranges are considered typical for Zn and Cu in soils. Available forms for these elements in examined soils were very low, especially for Zn, indicating that the chemical properties i.e. relatively high pH value and lower organic matter content of examined soils, are not favorable for Zn and Cu solubility and availability and consequently for their uptake by plant roots (Iratkar et al., 2014). An additional reason for the extremely low availability of Zn in examined soils could be potentially attributed to the interaction of Zn with Fe and Mn in soils, and these interactions in soils have been confirmed by numerous studies (Ghasemi-Fasaei and Ronaghi, 2008; Soltangheisi et al., 2014).

Plant genetic potential is also important for nutrients uptake, especially if the manganese subject of research (Blamey et al., 2015). Different plant species have different degrees of tolerance on excess Mn in soil. Sonneveld and Voogt (1975) rated lettuce and beans as sensitive, cucumber as less sensitive and tomato as tolerant to excess Mn in soils. Degree of tolerance of raspberry on excess Mn in soil have not yet been sufficiently investigated, so the main purpose of this study is to contribute to a better understanding the dynamics of Mn in soil-raspberry system.

The mechanisms of Mn uptake, transport and accumulation in raspberry and generally in plant tissues are still poorly understood. It is known that Mn as many other ions enter the root either through the plasma membrane of the root cells (symplastic transport) or through the free space between cells (apoplastic transport), and that Mn can not pass through membranes without the aid of membrane transporter proteins (Rengel, 2000). These transporter proteins occur naturally in cell membranes and plants possess many transporters for Mn transport. The abundance and activity of each transporter varies with types of plant tissues, development stage of plant, and environmental conditions, making the mechanism of Mn uptake, transport and accumulation in plant even more complicated. For example, when a low Mn concentration is in the soil solution, Mn uptake usually requires a high-affinity transporter or vice-versa, low-affinity transporters are more useful when high concentrations of Mn are present in soil solution (Cailliatte et al., 2010).

Plants have developed many types of mechanisms for identifying and involving Mn and other nutrients into essential cellular processes, but also for blocking them if their presence is harmful to the plant. The general rule in plant nutrition is that the elements useful for essential cellular processes are transported in tissues where they are needed, whereas the elements toxic for plant are stored in places where they cause the least harm to essential cellular processes (Pinto et al., 2014). The fact is that there is a tendency for Mn to easily translocate form roots to the leaves, indicating that Mn is needed in higher amounts for physiological processes in the plant, especially for photosynthesis where the Mn playing an important role in water-splitting system of photosystem II. The results of the present study confirm that fact as well as the fact that the Mn mostly accumulates in leaves, then in roots, and much less in the stem and fruits of raspberry. These findings are consistent with other research on the topic (Dou et al., 2009; Lambers et al., 2015).

An interesting finding of this study was that the Mn concentration in raspberry fruit was lower than the average Mn concentration for raspberry reported by many scientists (Tešović and Dulić, 1989; Ekholm et al., 2007). It is obvious that the low accumulation of Mn in the fruits was related to the physical and chemical characteristics of the examined soil as well as the climate conditions of the examined region.

Sharma et al. (2004) noted that Mn availability increased with a high increase in organic matter content and moisture in soil surface and subsurface horizons. Our assumption is that the properties of the studied soil (Cambisol) characterized by the absence of organic matter and appreciable quantities of clay fractions, do not favor the formation of reducing conditions in soil, thus resulting in lower Mn availability in soil and consequently lower accumulation in the fruit.

Another interesting finding of this study was that the concentration of Cu was about threefold higher in the root than in other parts of raspberry, while the difference in distribution within the plant was lower for other examined elements. This observation leads to the conclusion that the Cu in higher concentrations in leaves and fruits may have adverse effects on plant growth and development, and therefore the plant tends to keep Cu in the root where it cannot to a large extent negatively affect essential cellular processes. Emamverdian et al. (2015) have reported that the difference between the accumulation in root and the leaves is even higher for hazardous heavy metals such as Cd, Cr, and Pb. It is evident that the plants possess different mechanisms to prevent or reduce the transport of hazardous heavy metals from roots to the to the above-ground parts of plants. Some of these mechanisms are precipitation, binding of metals by strong ligands, changing the harmful forms of heavy metals to less toxic form by redox mechanisms, as well as export of heavy metals out of the cells and plants (Leitenmaier and Küpper, 2013).

5 CONCLUSIONS

The concentration of Mn available forms in the examined soils was low, resulting in a low degree of Mn uptake and accumulation in the raspberry plants, although the concentration of total Mn in soils was high compared to the average as well as the potential toxic value of Mn in soil. It is assumed that the chemical and physical properties of examined soils characterized by relatively high pH value and good ability to store root-zone air, contributed to them. From the point of view of Mn distribution within the plant, it is evident that the Mn mostly accumulates in leaves and roots of raspberry, and much less in the stem and fruits.

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