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EXAMINATION OF THE HEAVY METAL UPTAKE OF CARROT (*DAUCUS CAROTA*) IN DIFFERENT SOIL TYPES

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Abstract

In this paper the heavy metal uptake of carrot (*Daucus carota*) is studied in sample areas with different soil types. Our aim is to examine how the different soil types possessing different characteristics affect the heavy metal uptake and distribution in the plant. Correlation analyses were carried out in order to determine which of the total heavy metal concentrations and soil characteristics (pH, $CaCO_3$-content, humus content, granulometric composition) play the most important role in the uptake of the Co, Cu, Fe, Ni, Mn, Zn and in the metal distribution in the examined plant. Soil and plant samples were collected from 5 different Hungarian areas in July, 2008. In the cases of soils with different soil characteristics, the examined plants are supposed to give varied physiological responses. During the examination we proved that the genetic type and the heavy metal content of the soil do not significantly affect the heavy metal uptake of carrot. The granulometric composition of the soil has the most considerable effect but this factor only affects the rate of the metal uptake in 50% of the examined heavy metals (Ni, Mn, Zn).

Keywords: heavy metal, carrot (*Daucus carota*), soil-plant system, soil types

1. Introduction

Heavy metals play an important role in plant physiology since many of them are essential trace elements necessary for the optimal growth of the plants. The lack of them can result in different diseases (deficiency). On the other hand, above a certain concentration these heavy metals can have toxic effects on plants and other elements of the food chain (on the human beings as well). Most of the publications on the heavy metal uptake of plants studied the basic issues mentioned above. On the one hand, the chemical and physical characteristics and the trace element content of the soils are examined in terms of the optimal supply (Csathó, 1994; Alloway, 1995; Kádár, 1995; Szalai, 1998, 2005; Prokisch et al. 2006). On the other hand, they study how plant species respond to the various degrees of pollutions (Finster et al. 2004; Bíró and Takács, 2006; Rékási and Filep, 2006; Szabó and Szegedi, 2006; Farsang, 2007; Szabó et al. 2008). Small pot experiments are often carried out and it has advantages; however, more accurate results can be expected if the experiments are carried out in situ where plants can grow under natural conditions. In the cases of in-situ experiments such effects (e. g. weather, cultivation procedures, erosion and deflation processes etc.) can take place that can especially affect plant growth but we can not experience these effects during small pot experiments. Zhuang et al. (2009) traced heavy metals in the soil-plant-insect-pig food chain and proved that the amount of Pb and Cd was reduced a bit in the higher trophic levels but the concentration of Zn and Cu was higher and higher. Thus, in the cases of Zn and Cu bioaccumulation was proven. It can cause serious problems in contaminated areas especially when the lower levels of the food chain can tolerate the accumulated metal concentration well but toxic effects can occur in the higher levels. An example from 1957: near Toyama (Japan) rice lands were flooded with sewage especially contaminated with Zn and Cd, derived from a Zn mine. Cd accumulated by rice caused mass – often fatal – diseases (Yoshida et al. 1999).

According to special literature sources, vegetables (such as carrot) can accumulate some heavy metals to such degree that can have toxic effects on human beings (Clemens et al. 2002; Yang et al. 2009). In the case of 10 vegetables Monu et al (2008) studied how irrigation water deriving from different sources can affect the heavy metal uptake of plants. They observed that plants irrigated with sewage significantly accumulated heavy metals. Regarding Cu and Zn, the most significant accumulation was experienced in the carrot root. These researches prove that plants respond to the considerable heavy metal contaminations with the increase of the accumulation.

Less research studied the issue how plants accumulate heavy metals from slightly contaminated or non-contaminated soils, and whether there are provable significant differences among plants grown on different soil types, considering the accumulated heavy metal concentration and the distribution of these metals in plants. Kawada et al. (2002) carried out an extensive research in Japan about the Cu accumulation of carrot. 372 plant and soil samples were collected from 232 settlements of the country. The soils of the sample areas were classified into 7 types. It was proved that although there were differences in the Cu content of the soil types, significant difference was not observed concerning the Cu accumulation of carrot. In some cases it was showed that the higher Cu concentration of the soil resulted in more Cu uptake but this relation was more obvious in the cases of other heavy metals. Based on the geographical conditions and the vegetation, the authors divided the country into 9 provinces and they could show significant differences in the Cu accumulation of carrot among the provinces.

Helgesen and Larsen (1998) studied the As and Cu accumulation of carrot and found closer correlation between the As content of the soil and the As concentration accumulated by carrot than between the Cu content of the soil and the accumulated Cu concentration by carrot. Thus, clear connection can not always be found between the heavy metal content of soil and the metal concentration accumulated by plants since the transport processes are affected by other factors, too. Szalai (2008a) examined the heavy metal uptake of the dewberry (*Rubus caesius*) and concluded on the same.

In this paper the heavy metal uptake of carrot (*Daucus carota*) was investigated in 5 Hungarian sample areas with different soil types, regarding six essential heavy metals (Co, Cu, Fe, Ni, Mn, Zn). We studied whether the differences in the chosen soil types affect the heavy metal uptake of carrot and the metal distribution in the plant. Using correlation analysis we proposed to determine which soil characteristics play the most important role in the uptake of the different heavy metals. We also examined whether there is correlation between the total heavy metal content of the soil and the metal concentrations accumulated by carrot since the related special literature sources – as we demonstrated above - are not unambiguous.

2. Materials and methods

5 sample areas with different soil characteristics were chosen in Hungary (Fig. 1).

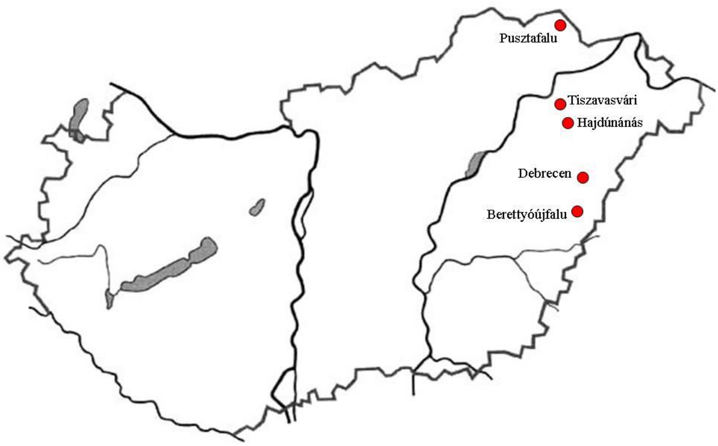

Fig. 1. The situation of the sample areas.

The first sample area is situated in Pusztafalu, in the northern part of Hegyköz where the soil and plant samples were collected from Luvisol. The second sample area can be found near Tiszavasvári where the main type of soil is Chernozem with lime incrustation formed on aeolian loess. The third sample area was designated in Hajdúnánás where the surface is also covered by Chernozem. However, here the dominant type of soil is Chernozem with lime incrustation formed on plain loess containing more silt and clay content; therefore it has finer granulometric composition and higher humus content (Stefanovits, 1981). The forth sample area is situated in the eastern part of Debrecen. This area belongs to the Nyírség; its dominant soil type is Arenosol with relatively high humus content. The last sample area can be found in Berettyóújfalu, situated in the former floodplain of the River Berettyó where the surface is covered by Gleysol.

Soil and plant samples were collected from 3 well-separated sample sites in every sample area. Thus, we had 15 sample sites altogether. The soil samples were taken from the depth of 0-15 cm, directly from the surroundings of the collected carrot roots. The samples were homogenized and transported in paper bags to the Geography Laboratory of the University of Debrecen where they were dried at 80°C in a drying oven and powdered in porcelain mortar.

The heavy metal content of the soil samples was determined according to the MSZ-08-1722-3:1989 with acid digestion (cc. HNO_3+H_2O_2). The measurements were carried out with a Perkin-Elmer 3000 FAAS appliance in the Department of Landscape Protection and Environmental Geography, University of Debrecen.

The granulometric composition (with Köhn-pipette, MSZ-08-0205-1978), the humus content (after Tyurin's scheme, MSZ-08-0210-1977) and the pH (with a pH-meter, MSZ-08-0206-2:1978) of the soil samples were also determined. The determination of the $CaCO_3$ content was carried out with Scheibler-calcimeter.

5-6 carrots were collected from every sample point. The roots were cleaned and washed properly, and then they were sliced up and dried at 80°C in a drying oven with the leaves. The dried root and leaf samples were homogenized separately in a porcelain mortar.

The homogenized plant samples were also digested (cc. HNO_3 and H_2O_2), then filtered through 288 μm filter papers into plastic storage tubes and diluted to 30 ml. The heavy metal content of the digested plant samples was also determined with the Perkin-Elmer 3000 FAAS appliance.

Excel 2003 software was applied to create the database and some diagrams. Statistical analyses were carried out with SPSS 8.0 software and diagrams were also made with this software. Since the examined data distribution is not normal (according to the Kolmogorov-Smirnov test), therefore Spearman's rho was applied during the correlation analysis.

3. Results and discussion

3.1. The examination results of the soil samples

The pH of the soil samples collected from the 5 sample areas vary within a narrow interval (Table 1): the mean values are neutral or slightly alkaline and only the pH

values of a few samples are slightly acid. The lowest pH was measured in the arenosol from Debrecen and the samples of the Gleysol in Berettyóújfalu have the highest pH. Regarding the $CaCO_3$-content, there were not significant differences among the sample areas; the samples are slightly and moderately calcareous. The lowest values – harmonizing with the pH – were measured in the samples of Debrecen and the most $CaCO_3$ was found in the samples from Berettyóújfalu.
More significant differences were found concerning the humus content: the highest percentages were experienced in the Luvisol samples from Pusztafalu and the samples from Debrecen contain the lowest amount of humus. Otherwise, low humus content is generally typical of Arenosols, and Chernozem soils can contain 6-8% of humus under natural conditions but the humus contents of the examined soil samples are below 4%, supposedly due to the intense tillage.

Table 1. Characteristics of soil samples (mean ± standard deviation)

Sample area	***pH*** (H_2O)	***$CaCO_3$*** %	***humus*** %
Pusztafalu	6.94 ± 0.47	5.07 ± 0.27	4.29 ± 1.83
Tiszavasvári	7.04 ± 0.29	3.99 ± 0.60	3.11 ± 0.61
Hajdúnánás	7.13 ± 0.16	5.24 ± 1.93	3.96 ± 0.43
Debrecen	6.79 ± 0.51	3.93 ± 0.60	2.37 ± 0.44
Berettyóújfalu	7.25 ± 0.04	5.80 ± 0.73	2.77 ± 0.89

Considerable differences in the granulometric composition of the soil samples were observed among the sample areas (Table 2, Fig. 2). The percentage of the sand fraction was the highest in the samples derived from Debrecen where the percentage of the coarse and fine sand fractions together was nearly 90%. In the samples from Berettyóújfalu, 60% was the percentage of the two sand fractions together but the clay fraction was also more than 10%. The percentage of clay fraction was the highest (nearly 20%) in the Luvisol of Pusztafalu. Samples were taken from the horizon A_1 and the upper part of the eluvial horizon (A_2) wherefrom most of the clay minerals are transferred to the level B. Thus, the percentage of the clay fraction is significantly higher in the lower levels of the soil; in the upper 15 cm of the soil the percentage of 20% can be considered common regarding the given soil type. On the other hand, the percentage of the coarse sand fraction was also the highest in the samples of Pusztafalu but it is not incredible since the denudation processes are intensive in upland areas, so the percentage of the coarser fractions can easily increase here.

Table 2. The granulometric composition of the soil samples (mean ± standard deviation, N=6)

Sample area	***granulometric composition (%)***			
	coarse sand	fine sand	silt	clay
Pusztafalu	16.1 ± 2.7	28.9 ± 4.7	35.7 ± 2.6	19.3 ± 2.1
Tiszavasvári	3.9 ± 2.1	37.2 ± 8.5	42.6 ± 11.2	16.3 ± 0.8
Hajdúnánás	4.0 ± 0.5	44.6 ± 1.2	41.3 ± 4.3	10.1 ± 3.6
Debrecen	13.4 ± 0.9	75.3 ± 5.0	9.6 ± 5.3	1.7 ± 1.0
Berettyóújfalu	5.6 ± 6.0	53.2 ± 7.1	29.9 ± 3.0	11.3 ± 2.7

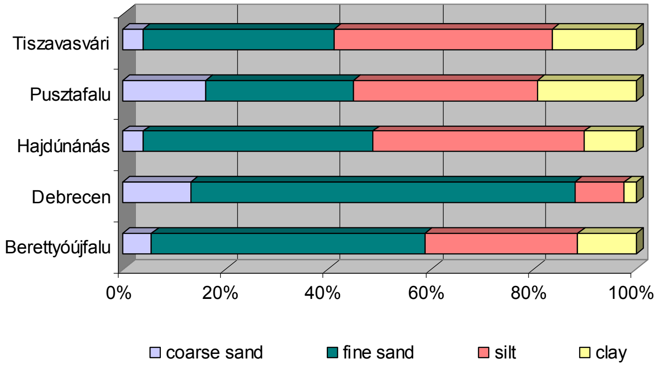

Fig. 2. The granulometric composition of the soil samples

3.2. Examination of the heavy metal content of the soil and plant

In every case of the examined heavy metals we experienced that the heavy metal concentrations were lower in the carrot leaves and roots than in the soil. This is also confirmed by the soil-plant transfer coefficients (Fig. 3) which are determined relevantly to the soil/leaf, and the soil/root. The coefficient is defined as the metal concentration in the plant organs divided by the total metal concentration in the soil. Based on the calculated coefficients it is proved that carrot leaves accumulated more heavy metal than roots. According to the special literature sources (Kloke et al. 1994; Alloway 1995), zinc and copper were the most mobilizable metals but the mobility of cobalt and nickel was also significant. The Mn and Fe reserves of the soil are relatively hardly available for carrot. For example, the Fe content of the plant was not more than 1-2% compared to the total Fe content of the soil.

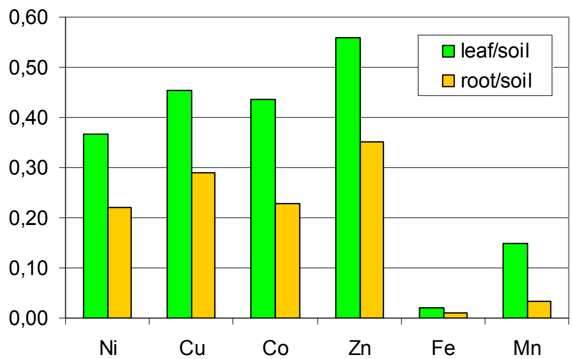

Fig. 3. The soil-plant transfer coefficients regarding the carrot leaf and root

Regarding the Co content of the soil samples, there were significant differences among the sample areas. The measured concentrations were between 5.1 and 16.4 mg·kg^{-1} (Fig. 4). The cobalt concentrations accumulated in the carrot leaves and roots did not correlate significantly with the total cobalt concentration of the soil. This is proved by the fact that the highest Co concentration was measured in the samples from Pusztafalu but the Co concentration of the carrot root was the lowest here.

The Ni concentrations of the soil samples varied between 12.0 and 37.4 mg·kg^{-1} (Fig. 5). Relatively strong significant correlation ($r=0.6$; $p<0.01$) was observed between the Ni concentrations of the soil and leaves but there was not significant connection between the Ni content of the soil and the carrot root.

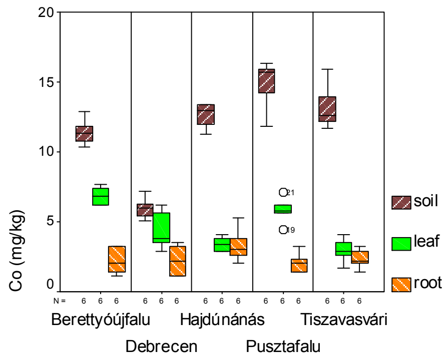

Fig. 4. The Co content of the soil, carrot leaf and root samples

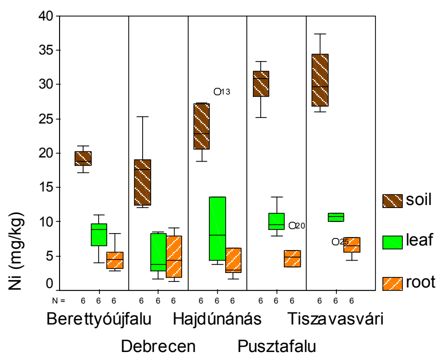

Fig. 5. The Ni content of the soil, carrot leaf and root samples

The concentrations of Zn and Cu considerably exceeded the limit values in the sample locality coded HNN1 of the sample area in Hajdúnánás (Fig. 6 and 7). These relatively high contamination values provided the opportunity to examine how the Cu and Zn content of the soils unusually exceeding the mean values influences the Cu and Zn accumulation of the plant. The Cu concentration in the carrot leaf is significantly higher in the plants grown in contaminated soil but the increase of the Cu concentration in the root was not observable. The results harmonize with Kádár’s (1995) statements: carrot root is genetically more protected against the harmful element accumulations; mainly leaves can accumulate the microelements to a toxic degree. In the case of Zn the effect of the contamination was provable neither in the leaves nor in the root. The former results are confirmed by correlation analyses: significant ($r=0.46$; $p<0.01$) correlation was found between the Cu concentration of the soil and the carrot leaves but the Cu content of the soil has no significant connection with the Cu content of the root. There was not significant correlation between the Zn concentrations of the soil and the examined carrot organs, too.

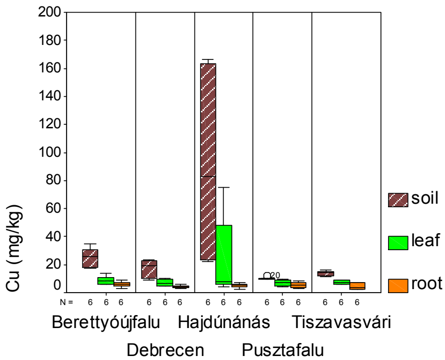

Fig. 6. The Cu content of the soil, carrot leaf and root samples

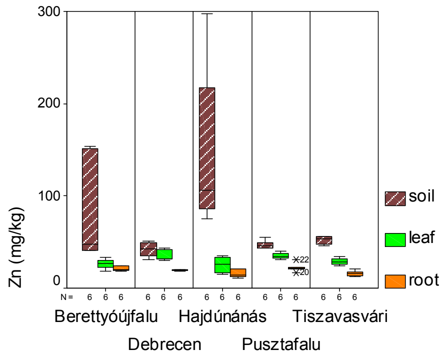

Fig. 7. The Zn content of the soil, carrot leaf and root samples

Although, in the case of manganese the soil-plant transfer coefficients are low (varies between 0.01-0.2, so carrot accumulates little Mn compared to the total Mn concentration of the soil), the Mn concentration has significant correlation with the Mn concentrations of the carrot leaf and root ($r=0.40$; $p<0.05$ and $r=0.67$; $p<0.01$ respectively). The connection between the Mn content of the soil and the Mn accumulation of the examined plant organs is observable in Fig. 8 and 9. Only the Mn concentration (among the examined heavy metals) of the soil influenced considerably the accumulated metal concentration in the carrot leaf and root.

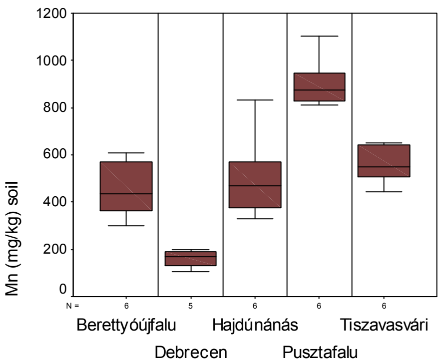

Fig. 8. The Mn concentrations of the soils

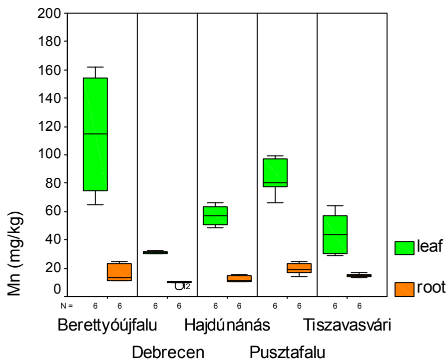

Fig. 9. The Mn concentrations of the carrot leaves and roots

The soil samples from Tiszavasvári contain Fe in high concentrations (Fig. 10). However, the plant samples collected in Tiszavasvári did not accumulate much iron, the concentration of this metal was especially low (compared to the samples from the other sample areas) in the leaves (Fig. 11). Correlation was found between the Fe concentration of the soil and the plant samples only in the case of the samples from Debrecen since carrot could accumulate less iron (compared to the other sample areas) from the sandy soil containing very little (3500-6500 mg·kg^{-1}) iron. However, regarding the whole database there was not significant correlation between the Fe concentration of the soil and the examined carrot organs.

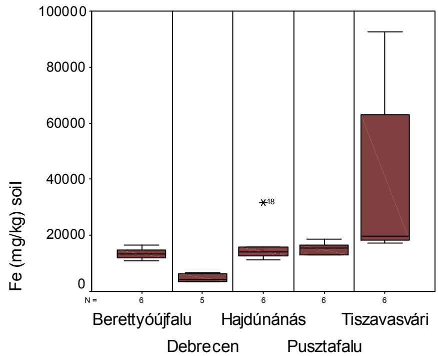

Fig. 10. The Fe concentration of the soils

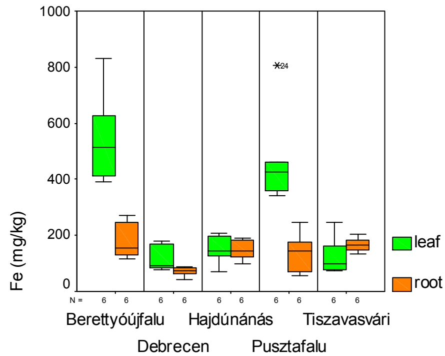

Fig. 11. The Fe concentrations of the carrot leaves and roots

3.3. The effects of the examined soil characterizations on the heavy metal uptake of the carrot

3.3.1. The effects of the soil pH

Soil pH is a considerable factor in terms of the heavy metal mobilization since it influences the solubility of the heavy metals, has effects on the stability and the cation bond ability of the colloids as well as on the activity of micro-organisms (Mengel, 1976; Stefanovits 1981; Szabó et al. 1987; Filep, 1988; Szalai, 2008). In the cases of our examined metals the decrease of the soil pH causes effective metal mobilization.

Fig. 12 shows the concentrations of the examined heavy metals in the soil samples classified into different pH categories. It is observable that the measured Ni, Co and Zn concentrations increase with the increasing soil pH since the mobility of these heavy metals is decreased at alkaline pH so plants can hardly take them up and they also resist leaching.

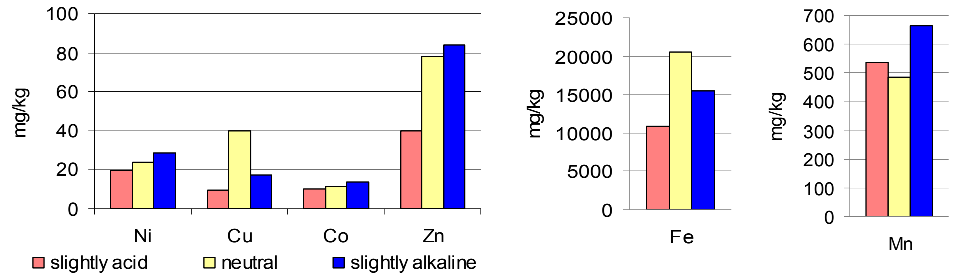

Fig. 12. The mean heavy metal concentrations in the soil samples classified into different pH categories

Although pH plays a very important role in the heavy metal transport, significant correlation was not observed between the soil pH and the accumulated metal concentrations in the carrot. This can be explained by the fact that the examined heavy metals are not mobilizable at this pH range, and since the pH of the soil samples collected in the different sample areas varied in a very narrow range, perceptible effects on the plant accumulation could not be proved.

3.3.2. The effects of the soil humus content

Humus plays an important role in the nutrient conservation and in the regulation of the nutrient availability since with the increase of the humus content the soil adsorption capacity is also increasing, and it results in the formation of metallo-organic complexes. According to Stefanovits et al. (1999), organic complexing agents promote the biological availability of heavy metals. But note that metallo-organic complexes do not definitely increase automatically the concentration of the easily soluble and available metals. It generally appears only in soils where humic materials small molecular mass humic materials dominate. In other cases the increase of the humus content increases the strongly bound metal concentration. The solubility is generally increased by small molecular mass organic acids (e. g. oxalate, malate, citrate etc).

It is observable in Fig. 13 that parallel with the increase of the humus content, the metal concentration of the soil is also increasing in the examined soil samples. The good adsorbing capacity of the humus is indicated by the fact that positive significant correlation was found between the humus and the Ni, Co, Zn and Mn content of the soil. The strongest connection ($r=0.69$; $p<0.01$) was observed between the humus and the Zn content. It is proved by special literature sources that Zn is strongly organophillic (Kloke, 1994; Stefanovits et al. 1999).

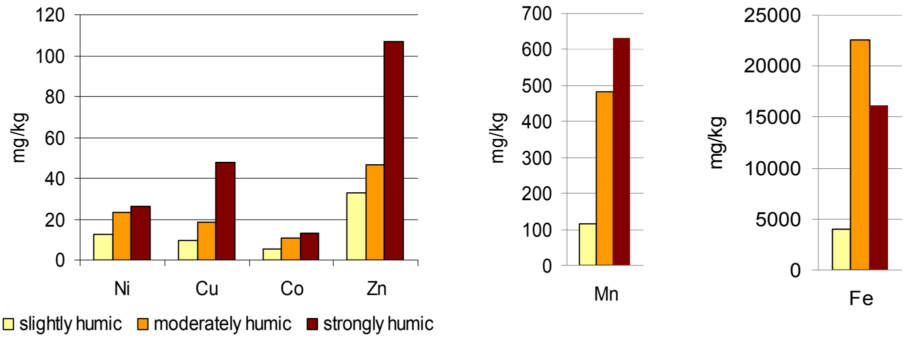

Fig. 13. The mean heavy metal content in the soil samples with different humus content

Similarly to the pH, significant correlation was not proved between the humus content and the concentration of the heavy metals accumulated by the carrot.

3.3.3. The effects of the granulometric composition

The physical characteristics of the soil are considerably influenced by the size distribution of the mineral grains since different conditions are formed in the soil when e. g. coarse sand fraction dominates or when fine clay fraction prevails (Stefanovits et al. 1999). Granulometric composition also plays an important role in terms of physiology because the bioavailable heavy metal concentration can be different in soils with dissimilar granulometric composition but similar metal content (Csathó, 1994).

The effects of the granulometric composition on the heavy metal concentration of the soil can be seen in Fig. 14. It is observable that sandy soils consisting of coarser grains and possessing small adsorbing capacity have the lowest heavy metal concentration, and with the decrease of the grain size, the heavy metal content of the soils is increasing. The highest metal concentration was determined in silty loam consisting of the finest grains.

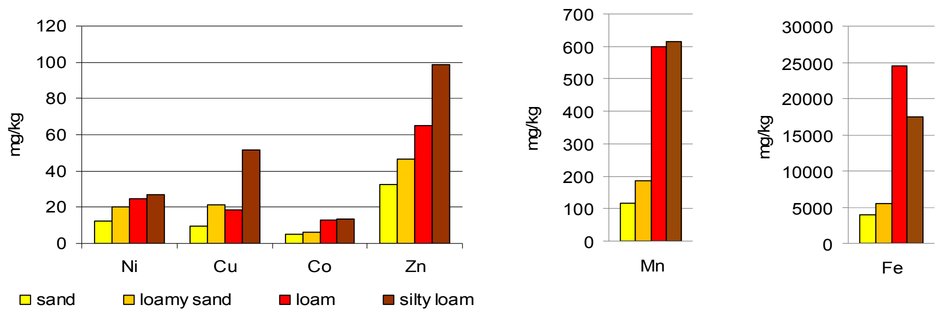

Fig. 14. The mean heavy metal concentration in the soil samples with different granulometric

composition

The correlation coefficients (Table 3) also illustrate well the connection shown in Fig. 14 since the examined heavy metals have strong positive correlation with the silt and clay fractions. However, strong negative connection is found with the coarse and fine sand fractions. The exception of the Cu can be explained by the fact that some of the samples from the sample area of Hajdúnánás was contaminated with Cu (supposedly due to the close vineyard), thus the Cu content of the samples was increased independently of the granulometric composition.

Table 3. Spearman correlation coefficients of the connection between the heavy metal content of the soils and the granulometric composition

	coarse sand	***fine sand***	***silt***	***clay***
Ni	0.11	-0.85*	0.61*	0.79*
Cu	-0.58*	0.31	0.12	-0.47*
Co	-0.07	-0.78*	0.68*	0.76*
Zn	-0.31	-0.34	0.59*	0.03
Fe	-0.28	-0.48*	0.54*	0.65*
Mn	0.05	-0.77*	0.48*	0.87*

** Correlation is significant at the 0.01 level*

The effects on the heavy metal accumulation of the carrot are not that obvious, the provable correlations are less strong. The Ni and Mn concentrations of the carrot leaf correlate with the clay fraction ($r=0.45$; $p<0.05$ and $r=0.44$; $p<0.05$ respectively) but only the Ni content of the leaf has significant connection with the silt fraction ($r=0.52$; $p<0.01$). The Zn content of the leaf correlates with the coarse sand fraction ($r=0.52$; $p<0.01$). This harmonizes with the special literature data: the adsorption capacity of the soils with coarser granulometric composition is lower but heavy metals generally occur in easily mobilizable forms that makes the plant uptake easier (Szabó et al. 1987; Csathó, 1984; Szalai, 2005). It is conceivable that Zn appears bound to Fe and Mn oxide colloids (carrot can easily take up Zn) in the examined soils with coarse granulometric composition.

Among the heavy metals accumulated in the carrot root, only manganese correlated strongly with the granulometric composition. The Mn content of the root has strong positive correlation ($r=0.75$; $p<0.01$) with the clay fraction but negative correlation is observable with the sand fraction ($r=-0.65$; $p<0.01$).

4. Conclusions

Comparing the main characteristics of the soil samples collected from 5 different sample areas it is proved that regarding pH and $CaCO_3$-content, there was not significant difference among the different soil types, but examining the humus content and the granulometric composition considerable differences were observed. The Luvisols and Chernozems contain more humus (3.5-4.5%) but only 2-3% humus was found in the Gleysol and Arenosols. Regarding the granulometric composition, sand fractions dominate in the Arenosols and Gleysol while silt and clay fractions prevail in the Chernozems and Luvisols.

The measured heavy metal concentrations of the examined soils are higher in the Luvisols and Chernozems, thus more heavy metal can be found in soils with finer granulometric composition and higher humus content than in Gleysol and Arenosols with coarser granulometric composition and lower humus content.

Our examinations show that in every case of the examined heavy metals the concentrations found in the soil exceeded the concentrations measured in the carrot root and leaf, thus all of the soil-plant transfer coefficients (both in the case of leaf/soil and root/soil) were below 0.5 apart from an exception.

The calculated order of mobility is the following: Zn > Cu > Co > Ni > Mn > Fe.

Investigating the distribution of the heavy metals within the plants it is stated that the carrot leaves accumulated heavy metals in higher concentrations than the roots. The less metal accumulation of the consumable organ is favourable in terms of human health since the consumption of a carrot grown in contaminated soil can involve less toxicological risk against a plant that can accumulate heavy metals in higher concentrations.

During the examination of the factors affecting the heavy metal uptake of the carrot, it is proved that the total metal content of the soil has more considerable effect on the heavy metal concentration of the leaf than that of the root. In the cases of Ni, Cu and Mn positive significant correlation was found between the metal content of the soil and leaves, however, the metal content of the soil correlated with the metal concentration of the root only in the case of Mn.

Based on our results it is shown that although the pH and the humus content of the soil significantly affect the heavy metal concentration of the soil, they have no considerable effects on the heavy metal uptake of the carrot.

Our results confirm that the granulometric composition is one of the most important factors in terms of the heavy metal content of the soils, and its effect on the heavy metal uptake of the carrot is also proved regarding some metals. The Ni and Mn uptake was more significant from soils with finer granulometric composition. This can be explained by the fact that these metals are mainly bound to clay minerals so they are accumulated in the finer fraction in bioavailable form. However, positive significant correlation was found between the Zn content of the carrot leaf and the coarse sand fraction since Zn can be more mobilizable in sandy soils, and it makes the metal uptake of the plants easier.

This research confirmed the special literature sources stated that the genetic soil type and the heavy metal content of the soil do not considerably influence the heavy metal uptake of the carrot. Granulometric composition has the most significant effect but this factor affected the rate of the metal uptake only in 50% of the examined heavy metals (Ni, Mn, Zn).

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