

EXAMINATION OF ZINC AND IRON MOBILIZATION WITH ACID TREATMENTS AND THE METAL CONTENT OF MAIZE AND STINGING NETTLE IN THE ACTIVE FLOODPLAIN OF THE RIVER TISZA

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Abstract: In this paper the mobilization of zinc and iron was studied in soil samples from the Boroszló-kert Dead-Tisza region. Besides the determination of the soil characterizations, the effects of different acid treatments on the metal mobilization were examined with nitric acid in five concentrations and with three extraction times. $\text{HNO}_3 + \text{H}_2\text{O}_2$ digestion and NH_4 -acetate + EDTA extraction were also carried out. Moreover, the metal uptake of two plant species (*Zea mays* from ploughlands, and *Urtica dioica* L. from orchards) was also studied. The decrease of pH caused significant metal mobilization, and the change of the pH is closely related to the soil properties, especially to the granulometric composition. Fe was less mobilizable than Zn. More metal was mobilized from the samples derived from ploughlands, and maize accumulated more Zn and Fe. However, the samples of ploughlands contained more CaCO_3 than the samples from orchards.

Keywords: metal mobilization, active floodplain, zinc, iron, *Zea mays*, *Urtica dioica*

1. INTRODUCTION

The River Tisza is one of the most important rivers in Central Europe and in Hungary. Near the river bank, especially near the upper course of the river there are many activities which can be considered as potential pollution sources. There, the mining and processing of different metal ores are significant from the Middle Ages. Unfortunately, contaminated slurry from mines near the upper course of the river is drained off from time to time, generally at the high-water stage of rivers and brooks (Winkelmann-Oei et al., 2001). In addition to the continuous contamination, due to the irresponsible management and the disregard of the environmental and safety regulations, a great deal of waste water got into the river in the spring of 2000 contaminating the River Tisza with different heavy metals. These contaminants can be diluted in the water, and during floods they can be settled in the active floodplain attached to colloidal particles; but they do not cause significant harm while the pH of the soil

remains alkaline. However, if the soil pH decreases these metals can be mobilized, thus their bioavailability increases and getting into the food chain they can be accumulated by the living beings (Papp & Kümmel, 1992). Excessive heavy metal accumulation can hinder the growth of the different plants (Hung-Yu & Zueng-Sang, 2004). Acidification progresses naturally in soils of humid areas (decomposition products of plants, increased leaching). However, it can be accelerated by the application of fertilizers containing nitrogen and sulphur (Kádár, 1993), and through the presence of atmospheric nitrogen and sulphur deposited by acid rain (owing to the recently more and more considerable environmental pollution). During the acidification, the hydrogen ions can displace metal ions from the surface of humus molecules and clay minerals, so the metals normally attached to colloidal particles can be mobilized. These metals in solution can also reach areas (through leaching) where significant metal pollution has not occurred before.

The „buffering capacity” and the original pH of

the soil are also important factors to resist changes in pH. However, they are strongly dependent on several physical and chemical properties of the soil (clay content, the composition of the clay minerals, humus content etc.; Szabó, 2001).

In this paper the mobilization of two metals (zinc and iron) are studied. Both metals are important essential nutrients for plants; their solubility is a pH-dependant process. Our aim was to represent an easily and a hardly mobilizable element. Zinc is strongly attached to the organic matter accumulated in the upper layer of the soil but under the influence of acidification it is one of the most mobilizable metals (Csillag et al. 1998, Szabó & Szabó, 2004). Soil pH is also an important controlling factor in terms of the Zn uptake of plants (B. Jacobs Company LLC. 1998). Iron is proved to be easily mobilizable especially under the influence of concentrated acid (Szabó, 2004). Besides, both metals are able to create chelate complexes in soils thus they can detain each other (Mengel, 1976).

Our aim was to determine the metal content of the surface layer in the examined sample area in the Upper-Tisza region and, knowing the general soil characteristics, in what quantity and in what rate these metals are mobilized under the effect of different acid concentrations. The easily soluble metal content (with Lakanen-Erviö extraction) of the soil samples and the metal concentration in the different plant species as well as the correlations between them were also proposed to be determined.

2. METHODS AND SAMPLE AREA

The sample area is near Gulács (approximately

701 river km), in the surroundings of the Boroszló-kert Dead-Tisza region. It is situated in the southern part of Bereg-plain near the River Tisza.

The geological structure of the catchment area in the upper section of the river is rather heterogeneous. The north-eastern Carpathian Mountains consist of 9 structural units with paleogene-neogene volcanic rocks, flysch, metamorphites and limestones (Nagy et al. 2002; Stefanescu et al. 2005). Our sample area is situated in the Upper-Tisza Valley microregion that is covered by 5-15 m Holocene layers consisting of clay and silt, deposited on Pleistocene sediments that contain fluvial gravel as well. Its composition is influenced by the flood characteristics and the sediment carried by the river (in the concerned subcatchment area). Erosion sensitivity is also a determinant factor. 96% of the soils of the microregion are hydromorph soil formed in loamy clay.

In 2006 ten surface soil samples have been collected from the active floodplain, the exact locality of the samples was determined with GPS (Fig. 1). The samples derive from ploughlands and orchards (5-5 samples); the different land-use can cause differences in the physical and chemical soil characteristics (Kiss & Sándor, 2009).

From the sample area 5-6 stock of maize (*Zea mays*, from ploughlands) and stinging nettle (*Urtica dioica*, from orchards) was collected for metal content examinations. *Zea mays* was chosen because of its common presence throughout the ploughlands and *Urtica dioica* was the other species from orchards because, according to earlier experiments, it can be used as a biomonitor of bioavailable metal concentrations (Otte, 1991).

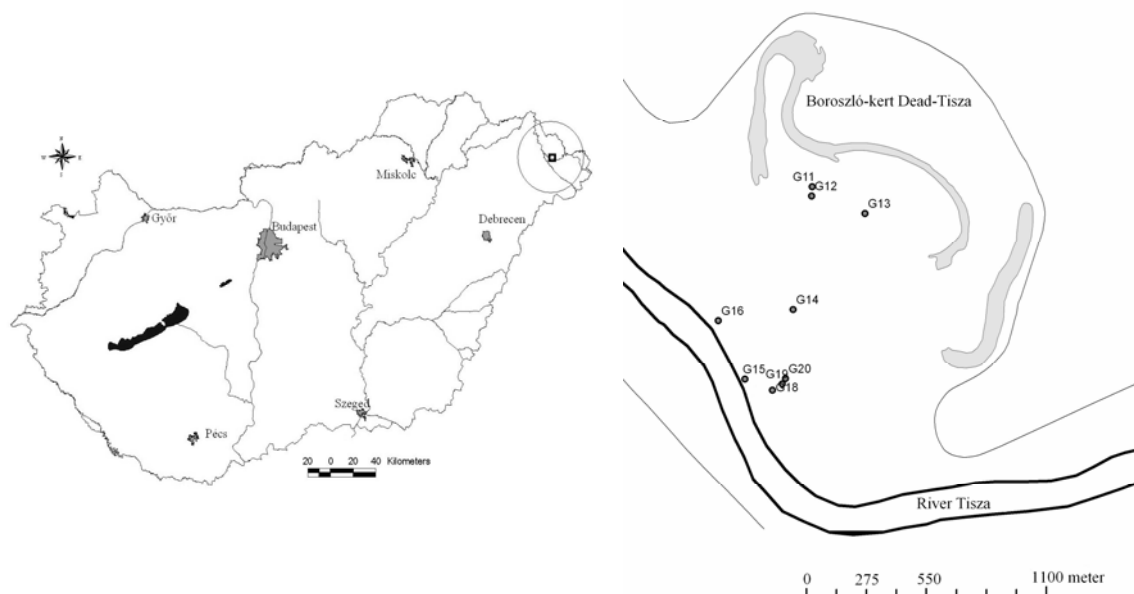


Figure 1. The situation of the examined area and the locality of the soil samples in the Boroszló-kert Dead-Tisza region. Legend: G11-20: surface soil samples; —: dyke

In the southern part of the microregion, where Gulács is also situated, Luvisols formed on sandy sediments with 2-10 cm brown bands of high clay content can be found as well (Marosi & Somogyi, 1990). As a control we examined 48 samples from outside the dyke. The mean Fe concentration of these samples was $29576 \pm 337.4 \text{ mg}\cdot\text{kg}^{-1}$, and the Zn content of them was $74.41 \pm 3.7 \text{ mg}\cdot\text{kg}^{-1}$ (on average).

The soil samples were cleaned from the bigger organic matter pieces in situ then dried at 40-60°C in drying oven for 24 hours in the laboratory. After that, the samples were homogenized in a mortar and passed through a 2 mm sieve (MSZ-08-1722/3-1989).

Since the metal mobilization greatly depends on the soil properties (Merino & Garcia-Rodeja, 1997), the granulometric composition (with Köhn-pipette), the CaCO_3 content (with Scheibler-calculator) and the humus content (after Tyurin's scheme) of the soil samples were determined according to the valid Hungarian standards (MSZ-08-0210:1977, MSZ-08-0205:1978, MSZ-08-0206-2:1978).

The effects of the soil acidification on the mobilization of metals were examined with nitric acid in five concentrations (distilled water; 0.001 M; 0.01 M; 0.05 M; 0.1 M) and with three extraction times (1 hour, 1 day, 1 week). The acid-soluble metal content was determined according to the MSZ-08-1722-3:1989 Hungarian standard with cc. $\text{HNO}_3+\text{H}_2\text{O}_2$ acid digestion.

Total acid-extractable metal content by itself does not give enough information about the dangers caused by metals since they are available for plants to a different extent depending on their form of occurrence. Therefore, in the soil samples the available quantity for plants has also been determined with Lakanen-Erviö extraction (NH_4 -acetate+EDTA, Lakanen & Erviö, 1971).

The plants were cleaned (it was especially

important in the case of roots), dried and separated into root and shoot. The samples were digested with the same method as in the cases of soil samples (cc. $\text{HNO}_3+\text{H}_2\text{O}_2$). All experiments (both with the soil and plant samples) were performed in triplicate and blanks were run simultaneously. The metal analysis of samples was carried out with ICP-OES at the laboratory of Analab Kft (Debrecen, Hungary).

The data processing was executed with Microsoft Excel and SPSS for Windows 16.0. The normal distribution of the data was analysed with Shapiro-Wilks test and since none of the examined variables (Mn, Zn, granulometric composition fractions, humus content, pH and CaCO_3 -content) met this criterion therefore non-parametric tests were applied. Mann-Whitney test was carried out in order to demonstrate the differences between the groups and Spearman's rank correlation coefficient was used in the correlation analyses.

3. RESULTS AND DISCUSSION

Table 1 contains the characteristics of the collected soil samples. These are little clayey, sandy-silty samples with neutral, slightly acid pH and various humus contents. Distilled water and HNO_3 in different concentrations (0.001 M; 0.01 M; 0.05 M; 0.1 M) were used in order to study the mobilization of different metals in soils from the active floodplain.

Furthermore, these experiments were carried out with 3 extraction times (1 hour, 1 day, 1 week). Such acid impact does not take place under natural conditions; it can occur more frequently in highly polluted areas such as industrial areas. However, examining the metal mobilization of uncontaminated soils is also as much important since we can learn how these soils react upon acid affections.

Table 1. The soil characteristics of the analysed samples according to the land use

Land use	Sand	Silt	Clay	Humus	CaCO ₃	pH (H ₂ O)
	%					
ploughland	47.9 ± 2.7	41.0 ± 2.3	11.0 ± 0.7	3.6 ± 0.2	6.0 ± 0.6	6.8 ± 0.2
orchard	37.5 ± 2.4	50.9 ± 1.7	11.4 ± 0.9	6.1 ± 0.3	4.8 ± 0.4	6.9 ± 0.1

Table 2. The effects of the acid treatments in different concentrations and extraction times on the metal mobilization in the ploughland (the means of 5 samples, with standard deviation values)

Leaching medium		Zn (mg/kg)			Fe (mg/kg)		
		1 hour	1 day	1 week	1 hour	1 day	1 week
Distilled water		<0.001	0.005 ± 0.005	0.014 ± 0.001	<0.001	<0.001	<0.001
HNO_3	0.001 M	1.669 ± 0.8	1.768 ± 0.5	2.963 ± 1.4	0.722 ± 0.1	0.370 ± 0.1	<0.001
	0.01 M	7.439 ± 1.6	11.96 ± 2.2	17.75 ± 2.5	21.92 ± 3.3	49.42 ± 6.0	156.6 ± 18.0
	0.05 M	9.382 ± 1.8	14.80 ± 2.8	22.29 ± 3.7	58.31 ± 5.3	159.0 ± 16.1	507.3 ± 62.9
	0.1 M	9.227 ± 1.7	17.72 ± 3.0	23.46 ± 3.4	87.18 ± 9.2	318.8 ± 28.1	895.6 ± 73.4
Lakanen-Erviö		16.13 ± 2.2			1449 ± 156.2		
Acid-digested		92.40 ± 5.1			23358 ± 2403.0		

Table 3. The effects of the acid treatments in different concentrations and extraction times on the metal mobilization in the orchard (the means of 5 samples, with standard deviation values)

Leaching medium		Zn (mg/kg)			Fe (mg/kg)		
		1 hour	1 day	1 week	1 hour	1 day	1 week
Distilled water		<0.001	0.032 ± 0.01	<0.001	<0.001	<0.001	<0.001
HNO ₃	0.001 M	0.668 ± 0.3	0.525 ± 0.3	0.789 ± 0.4	<0.001	<0.001	1.692 ± 0.8
	0.01 M	11.88 ± 2.7	15.20 ± 2.5	22.91 ± 3.8	18.25 ± 3.6	34.48 ± 3.7	108.7 ± 10.4
	0.05 M	14.69 ± 2.8	20.97 ± 3.8	32.81 ± 5.9	58.19 ± 7.0	101.7 ± 5.0	364.1 ± 11.4
	0.1 M	14.94 ± 2.3	26.05 ± 4.8	35.20 ± 6.1	81.76 ± 10.1	242.6 ± 15.9	854.0 ± 56.8
Lakanen-Erviö		27.12 ± 5.2			1717 ± 203.2		
Acid-digested		114.9 ± 7.5			27344 ± 1206.8		

Table 2 and 3 contain the mean concentrations of the acid-extracted metals in the examined area, according to the land use. It can be seen that increasing the acid concentration and the extraction time the extracted amount is also increasing.

3.1. Zinc content of the acid-extracted soil samples

The mean acid extractable zinc content of the digested soils is 102.7 mg·kg⁻¹. Neither of the zinc concentrations measured in the different soil samples exceeds the critical contamination level (200 mg·kg⁻¹, joint decree no. 6/2009 IV.14. KöM-EüM-FVM-KHVM). Distilled water and the 0.001 M HNO₃ did not mobilize much zinc in an hour, the proportion is almost zero compared to the total acid extractable Zn amount (Fig. 2).

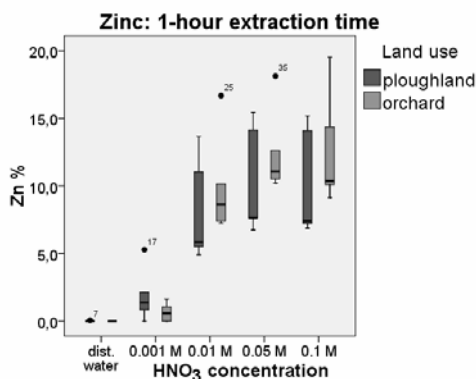


Figure 2. The percentage of Zn extracted by the different acid concentrations in an hour compared to the total acid-extractable Zn content of soils, according to land use (median, interquartile range)

Regarding the treatment with 0.01 M HNO₃ significant increase can be observed in the mobilized Zn concentration (9.1% on average). 0.1 M HNO₃ mobilized the most zinc during an hour but it was just a bit more than the proportion extracted by the 0.05 M acid (11.5% and 11.4%, respectively). Regarding the other two extraction times (1-day and 1-week) it is observable that the distilled water-extracted zinc is almost zero and it did not increase significantly under

the effect of the 0.001 M acid (Fig. 3, 4).

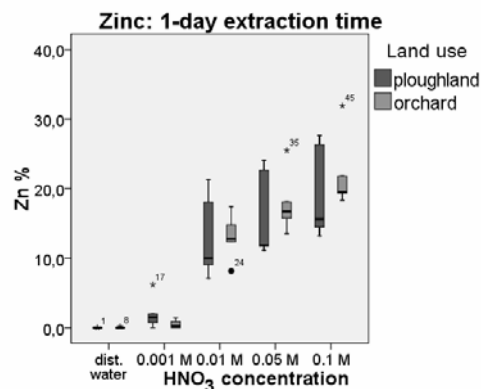


Figure 3. The percentage of Zn extracted by the different acid concentrations in a day compared to the total acid-extractable Zn content of soils, according to land use (median, interquartile range)

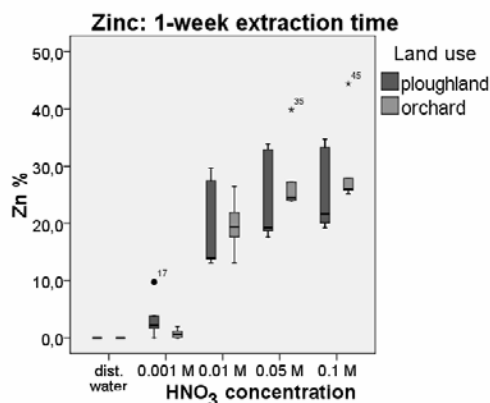


Figure 4. The percentage of Zn extracted by the different acid concentrations in a week compared to the total acid-extractable Zn content of soils, according to land use (median, interquartile range)

However, 0.01 M HNO₃ mobilized 13.1% of the total acid-extractable amount in a day and 19.7% in a week. Comparing the higher concentrations (0.05 M and 0.1 M) greater increase can be experienced in a day: the mean percentage of zinc extracted by the 0.05 M acid is 17.1% and regarding the 0.1 M HNO₃ it is 20.8%. However, if we study the amounts

extracted with 1-week extraction time it can be seen that the proportions are increased slightly by the increase of the acid concentrations (the percentages are 26.2% and 27.8%). Regarding the land use more total acid-extractable zinc concentration was measured in the samples of orchards ($114.9 \text{ mg}\cdot\text{kg}^{-1}$) than that of ploughlands ($92.4 \text{ mg}\cdot\text{kg}^{-1}$) and more zinc was also mobilized in samples from orchards, based on the mean concentrations.

3.2. Iron content of the acid-extracted soil samples

The mean iron concentration of the soil samples is $25068.4 \text{ mg}\cdot\text{kg}^{-1}$. Studying the results iron was proved to be less mobilizable under acid effect than zinc (Fig. 5, 6 and 7).

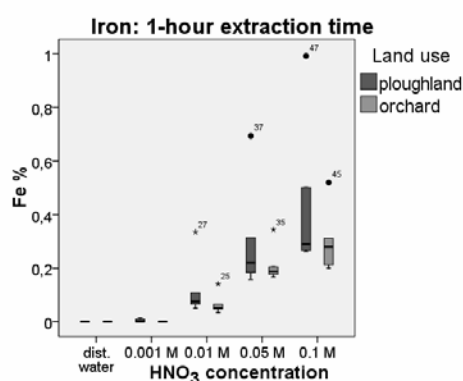


Figure 5. The percentage of Fe extracted by the different acid concentrations in an hour compared to the total acid-extractable Fe content of soils, according to land use (median, interquartile range)

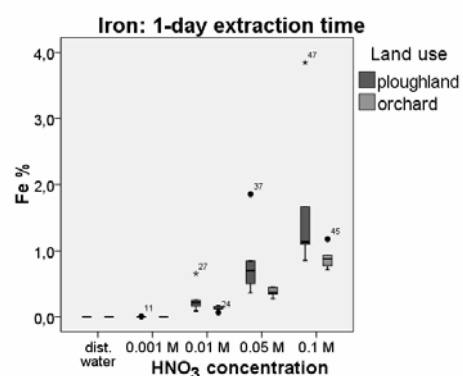


Figure 6. The percentage of Fe extracted by the different acid concentrations in a day compared to the total acid-extractable Fe content of soils, according to land use (median, interquartile range)

The extracted iron with distilled water and even with the 0.001 M HNO_3 is almost zero in every cases of the extraction times. In an hour neither the acids in higher concentrations mobilized more iron

than 0.6% of the total acid-extractable concentration. Increasing the extraction time the mobilized iron amount is not increasing significantly. Regarding the 1-day extraction time the mean percentage extracted by the 0.1 M HNO_3 is only 1.3% and considering the 1-week extraction this proportion is 3.9%.

Comparing the land use types it is observable that more iron is mobilized from the samples of ploughlands. However, examining the mean total acid-extractable concentrations samples from orchards contain a bit more iron ($27344.3 \text{ mg}\cdot\text{kg}^{-1}$) than the samples from ploughlands ($22792.5 \text{ mg}\cdot\text{kg}^{-1}$).

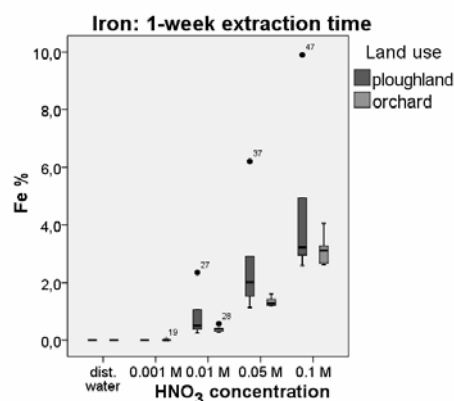


Figure 7. The percentage of Fe extracted by the different acid concentrations in a week compared to the total acid-extractable Fe content of soils, according to land use (median, interquartile range)

3.3. The evaluation of metal mobilization according to the extraction times

First, we examined whether there is significant difference among the concentrations according to the extraction times. Table 4 contains the results. In the case of the 0.001 M nitric acid concentrations the differences in the times were not significant. It raised the question whether the significant difference between the 1-day and 1-week treatments in the case of the distilled water was perhaps measurement error.

Probably this is the point since the deviation of the measured concentrations near the detection limit can cause significant difference. However, the differences that we found examining the concentrated acid extraction were correct and yielded interesting results. Considering iron the time counts in every acid concentration but regarding zinc 0.01 M - 0.05 M nitric acid mobilized significant concentration only in the case of the 1-week extraction time, and with 0.1 M acid this treatment had no effect. So prospectively more iron would be mobilized in every extraction increasing the time, but as for zinc it would be typical only in the case of 0.01 - 0.05 M HNO_3 leaching media, using 0.1 M acid more mobilization is not expectable.

Table 4. The significance of the extraction time differences considering iron and zinc (bold emphasis: $p < 0.05$)

Leaching medium		Concentration			
		Zn		Fe	
		1 hour – 1 day	1 day – 1 week	1 hour – 1 day	1 day – 1 week
Distilled water		0.971	0.481	1.000	1.000
HNO ₃	0.001 M	0.853	0.315	0.971	0.796
	0.01 M	0.089	0.043	0.001	0.001
	0.05 M	0.063	0.023	0.001	0.001
	0.1 M	0.011	0.063	0.001	0.001

3.4. The evaluation of the metal mobilization according to the acid concentrations

Regarding zinc (Table 5), significant differences are observable between the distilled water-0.001 M acid and the 0.001 M-0.01 M acid in every extraction times (distilled water mobilized concentrations were managed under reserve). Examining iron distilled water and 0.001 M nitric acid do not show differences in any case of the extraction times. Considering every other acid extractions, significant differences can be found.

3.5. The evaluation of the Lakanen-Erviö extractions and metal content of the plant samples

According to earlier experiments zinc is more easily mobilizable with EDTA than Fe (Table 6) thus the bioavailability of Zn is higher (Peris et al., 2007). Zinc (Fig. 8) is an essential element; plants can accumulate more zinc in their roots and shoots than the amount found in soils (Szabó, 2004). This is true regarding the ploughlands: Lakanen-Erviö extractable mean percentage (17.8%) is less than the mean percentage accumulated by maize root (76.6%) and shoot (54.8%). According to Gorlach's

experiment maize root can accumulate two times more zinc than its shoot (Gorlach, 1994). This is not typical of the orchards: plants accumulated less Zn (stinging nettle root: 14.1%, shoot: 22.2%, mean percentages) comparing to the percentage found in the easily soluble fraction (22.9%).

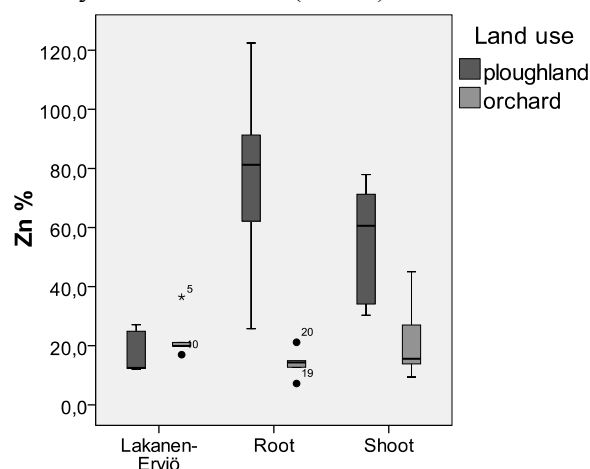


Figure 8. The percentage of Zn extracted by the Lakanen-Erviö extraction and accumulated by the plant's root and shoot compared to the total acid-extractable Zn content of soils, according to land use (median, interquartile range).

Table 5. The significance of differences in metal concentrations extracted with the different acid concentrations (bold emphasis: $p < 0.05$)

Leaching medium		Concentration					
		Zn			Fe		
		1 hour	1 day	1 week	1 hour	1 day	1 week
HNO ₃	0.001 M	0.015	0.015	0.001	0.481	0.481	0.739
	0.001M-0.01M	0.001	0.001	0.001	0.001	0.001	0.001
	0.01 M-0.05M	0.123	0.280	0.143	0.001	0.001	0.001
	0.05 M-0.1M	0.912	0.190	0.529	0.003	0.001	0.001

Table 6. The metal concentration of the Lakanen-Erviö extractions and the examined plants in $\text{mg}\cdot\text{kg}^{-1}$ and compared to the total acid extractable metal concentration (%), according to the land use (the means of 5 samples, with standard deviation values)

	Ploughland				Orchard	
	Lakanen-Erviö	Zea mays		Lakanen-Erviö	Urtica dioica	
		Root	Shoot		Root	Shoot
Zn (mg/kg)	16.13 ± 3.1 (17.8%)	70.48 ± 14.6 (76.6%)	50.26 ± 9.7 (54.8%)	27.12 ± 6.2 (22.9%)	16.18 ± 2.7 (14.1%)	24.89 ± 9.5 (22.2%)
Fe (mg/kg)	1449 ± 156.2 (6.3%)	2271 ± 514.1 (10.4%)	177.1 ± 77.7 (0.8%)	1717 ± 203.2 (7.3%)	453.4 ± 190.5 (1.6%)	301.5 ± 94.6 (1.1%)

In the case of iron (Fig. 9) the difference between the Lakanen-Erviö extractable amounts of the two land-use types is only approximately 1% (6.3% in ploughlands and 7.3% in orchards). Regarding plants it is observable that maize roots accumulate more iron on average (10.4% of the total acid extractable amount) than their shoots (0.8%, it is less than the amount accumulated by the shoots of stinging nettles). Stinging nettles from orchards do not accumulate more iron than the easily soluble amount: 1.6% of the total acid-extractable amount was found in roots and only 1.1% was in shoots, on average

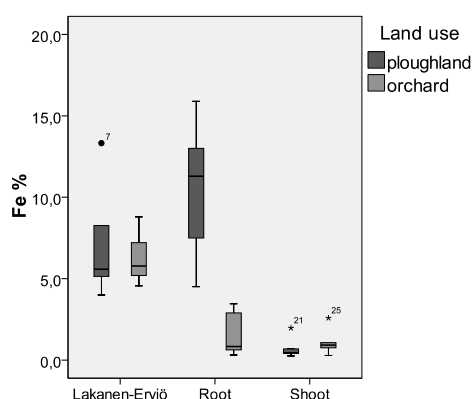


Figure 9. The percentage of Fe extracted by the Lakanen-Erviö extraction and accumulated by the plants' root and shoot compared to the total acid-extractable Fe content of soils, according to land use (median, interquartile range).

3.6. Correlations

Since the distribution of the examined data was not normal (according to the Shapiro-Wilks test), Spearman's rho was carried out in order to examine the correlation between the different data. The probability level of every given correlation coefficients is $p < 0.05$.

In the case of the distilled water extraction, we did not examine correlations since the concentrations extracted by distilled water were so low that the measurement error is perhaps very considerable.

Regarding the 0.001 M acid extraction, Zn strongly correlates with the silt fractions, one of the clay fractions (< 0.01 mm), the humus content and the pH (H_2O and KCl as well). The correlation coefficients are 0.75; 0.5; 0.6 and 0.5, respectively. Iron also correlates with the 0.01-0.005 mm and 0.005-0.002 mm silt fractions. The metals did not correlate with each other.

Zinc extracted by the 0.01 M HNO_3 has positive significant correlation with the extracted iron concentration ($r = 0.70$) and the pH (both H_2O and KCl; the coefficients are 0.44 and 0.47). Regarding Fe, there was not observed any correlation with the soil

characteristics.

The correlation between the two metals is significant at the 0.01 level ($r = 0.71$) examining the 0.05 M nitric acid extraction. Besides, Zn has negative connection with the 0.2-0.5 mm and the 0.05-0.1 mm sand fractions and positive correlation with the smallest clay fraction (< 0.01 mm) and the pH (both H_2O and KCl).

Regarding the 0.1 M extractions almost the same trend is observable as with the 0.05 M acid. Zn has connection with the same parameters and positive significant correlation between the two examined metals is also observable ($r = 0.76$; $p < 0.01$).

Considering the extraction times positive significant correlations were found between the examined metals in all the cases. The correlation coefficient is 0.87 in the case of the 1-hour extraction time, 0.86 in the case of the 1-day extraction and $r = 0.85$ regarding the 1-week extraction time (the level of the significance is 0.01). Examining the 1-hour extraction there was no connection observed among the metals and the soil characteristics.

Examining the Lakanen-Erviö extractions the two metals have significant correlation with the pH (both H_2O and KCl); the correlation is strong especially with the pH_{KCl} . The coefficients are the followings: $r_{Zn-pHKCl} = 0.83$ and $r_{Fe-pHKCl} = 0.82$.

In the followings, the results of the correlation analysis are examined in terms of the digested samples. Both metals have negative correlation with the 0.1-0.2 mm sand fraction. Besides, strong correlation was found between the Zn and the 0.05-0.1 mm sand fraction ($r = -0.98$; $p < 0.01$) and between the Fe and the 0.01-0.005 mm silt fraction (positive correlation: $r = 0.99$; $p < 0.01$).

During the correlation analysis the examined plant species were studied separately. The Zn content of the maize samples the 0.02-0.05 mm sand fraction ($r = -0.89$). Fe has negative significant correlation with the coarse (0.5-2.0 mm) sand fraction ($r = -0.89$) and positive connection with two of the silt fractions (0.02-0.01 mm and 0.01-0.005 mm). The correlation coefficient is 0.90 in both cases. Examining the stinging nettle no correlation was found regarding Zn. Fe has strong correlation with the smallest clay fraction (< 0.001 mm). Correlation between the examined metals was not observed.

4. CONCLUSION

Five acid concentrations (distilled water, 0.001 M, 0.01 M, 0.05 M, 0.1 M) were applied in every sample and the treatments were carried out with different extraction times (1 hour, 1 day, 1 week) and every sample was digested with $HNO_3 + H_2O_2$ acid

digestion.

The concentrations of the examined metals do not exceed the critical contamination level (joint decree no. 6/2009 IV.14. KöM-EüM-FVM-KHVM on limit values established for the protection of groundwater and the geological medium).

Zn was proved to be more mobilizable than Fe (the HNO₃ acid extractions mobilized Zn in higher percentage than Fe). In the case of the iron almost zero percentage of the total metal content of the soil was mobilized with the distilled water and the 0.001 M HNO₃ in every extraction time. According to earlier experiments with HCl solutions the same was proved: Fe was dissolved minimally while approximately 50% of the total Zn concentration was extracted under the effect of 0.01 M HCl (Kuo et al., 2006).

The ploughlands and the orchards reacted to the acid extraction nearly the same way but higher metal concentration was mobilized from the samples of ploughlands. It was expected since according to the granulometric composition the samples from the ploughlands contain more sand (these samples belong to the medium/sandy loam category according to the soil triangle), and it is proved that Zn adsorption is increased in soils containing more colloidal particles (Alloway, 1995). However, more CaCO₃ was also found in ploughlands so the areas of this land use have better buffering capacity than orchards.

Maize root and shoot accumulated more Zn, and root also holds more Fe than the Lakanen-Erviö extracted concentration. This is not typical of the stinging nettle.

Among the soil characterizations granulometric composition plays the most important role in the heavy metal mobilization of the examined soil samples. The role of granulometric composition is examined by several earlier publications (Szalai et al., 2005). It is proved that more metal is adsorbed on soils with smaller granulometric composition (Sipos, 2010) and we experienced the same considering the correlation analyses. According to our correlation analyses, in the cases of the 0.01 M, 0.05 M and 0.1 M nitric acid treatments, examining the extraction times, significant correlation was found between the two metals and pH also played an important role in some cases.

Summarizing the results we can say that the decrease of pH in the soil cause effective metal mobilization and the change of the pH closely related to the soil characterizations (especially to the granulometric composition).

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REFERENCES

- Alloway, B. J.,** 1995. *Heavy metals in soils*. Blackie Academic and Professional, London, 292-302.
- Bechtel Jacobs Company LLC.,** 1998. *Empirical Models for the Uptake of Inorganic Chemicals from Soil by Plants*. Bechtel Jacobs Company LLC, Oak Ridge, TN. BJC/OR-133.
- Csillag, J., Lukács, A., Bujtás, K. & Németh T.,** 1998. *Impact of soil contamination and acidification on heavy metal concentration in the soil solution*. Filep Gy. ed.: Soil Pollution; Soil, Water and Environmental Relationships, DATE, Debrecen, 65-73.
- Gorlach E.,** 1994. *Phytoavailability of heavy metals as affected by liming and plant species*. Pol. J. Soil Sci. 27 (1), 59.
- Hung-Yu Lai & Zueng-Sang Chen,** 2004. *Effects of EDTA on solubility of cadmium, zinc, and lead and their uptake by rainbow pink and vetiver grass*. Chemosphere 55, 421-430.
- Kádár, I.,** 1993. *The relations between the fertilization and the environmental pollution regarding the duration experiments in Rothamsted*. (in Hungarian) Agrokémia és Talajtan, 42 (3-4) 421-431.
- Kiss, T. & Sándor, A.,** 2009. *Land-use changes and their effect on floodplain aggradation along the Middle-Tisza River, Hungary*. AGD Landscape and Environment 3(1), 1-10.
- Kuo, S., Lai, M. S. & Lin, C. W.,** 2006. *Influence of solution acidity and CaCl₂ concentration on the removal of heavy metals from metal-contaminated rice soils*. Environmental Pollution, 144(3), 918-925.
- Marosi, S. & Somogyi, S.,** 1990. *The cadaster of the Hungarian microregions*. (in Hungarian) MTA FKI, Budapest, 153-161.
- Mengel, K.,** 1976. *Plant nutrition and metabolism*. (in Hungarian) Mezőgazdasági kiadó, Budapest, p. 365.
- Merino, A. & Garcia-Rodeja E.,** 1997. *Heavy metal and aluminium mobilization in soils from Galicia (NW Spain) as a consequence of experimental acidification*. Applied Geochemistry, Vol. 12, Elsevier Science Ltd. 225-228.
- Nagy, B., Komonyi, É., Molnár, J., Izsák, T., Gönczy, S., Kucsinka, I. & Sándor, A.,** 2002. *Factors of floods of the Upper-Tisza - focusing on the catastrophes of the recent years and the prevention*. Ferenc Rákóczi II. Transcarpathian Hungarian Institute, Berehovo, p. 56.
- Otte, M.L.,** 1991. *Heavy metals and arsenic in vegetation of salt marshes and floodplains*. PhD thesis. Vrije Universiteit Amsterdam, Amsterdam.
- Papp, S. & Kümmel R.,** 1992. *Environmental chemistry*. (in Hungarian) Tankönyvkiadó, Budapest, p. 359.
- Peris, M., Micó, C., Recatalá, L., Sánchez, R. & Sánchez, J.,** 2007. *Heavy metal contents in horticultural crops of a representative area of the*

- European Mediterranean region. Science of the Total Environment* 378, 42-48.
- Sipos, P.,** 2010. *Sorption of copper and lead on soils and soil clay fractions with different clay mineralogy.* Carpathian Journal of Earth and Environmental Sciences, 5(2), 111-118.
- Stefanescu, M., Dicea, O., Butac, A. & Ciulavu, D.,** 2005. *Hydrocarbon geology of the Romanian Carpathians, their foreland, and the Transylvanian Basin.* In Golonka, I. and Picha J.F. eds. *The Carpathians and their forelands: Geology and hydrocarbon resources.* AAPG Memoir 84., 521-567.
- Szalai, Z., Baloghné Di Gléria, M., Jakab, G., Csuták M., Bádonyi, K. & Tóth A.,** 2005. *Physical speciation of sediment associated heavy metals in active floodplains of the Danube and Tisza rivers, Hungary.* (in Hungarian) Földrajzi Értesítő LIV. 1-2, 61-84.
- Szabó, Sz.,** 2001. *Connection between Soil and Landscape Sensitivity.* Ekológia 20, 285-291.
- Szabó, Sz.,** 2004. *Evaluation of the role of the soil characterizations with the example of a landscape sensitivity examination.* (in Hungarian) *Studia Geographica*, Kossuth Egyetemi Kiadó, Debrecen, 87-108.
- Szabó, Sz. & Szabó, Gy.,** 2004. *Evaluation of acid effects with examining the copper and manganese mobilization of soils.* (in Hungarian) II. Magyar Földrajzi Konferencia közleményei – Szegedi Egyetem, Természeti Földrajzi Tanszék, Konferencia CD ROM, p. 8.
- Winkelmann-Oei, G., Varduca, A., Geisbacher, D., Pinter, Gy. & Liska, I.,** 2001. *Analysis of Accidental Risk Spots in the Catchment area of the Danube, In, Inventory of Potential Accidental Risk Spots in the Danube River Basin.* International Commission for the Protection of the Danube River, ARS-ad-hoc Expert Panel of the AEPWS EG p. 131.

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