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STUDY OF THE CHROMIUM, CADMIUM, COPPER, ZINC CONTENTS OF SOIL AND DOMINANT PLANT SPECIES IN THE FLOODPLAIN OF UPPER-TISZA AREA

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Abstract: As an effect of last decades' metal contaminations, the critical ecological levels were reached in several spots of the floodplain of the Upper Tisza. The aims of our study were to investigate the relationship of soil-plant-metal content in dominant plant species and soils of Upper Tisza floodplain. The sampling sites were at Tiszabecs, Vásárosnamény, Dombrád, and Tokaj. Between 2007-2009 in soils of flood-basin 20.6-24.6 mg/kg Cr, 0.40-1.15 mg/kg Cd, 28.4-66.7 mg/kg Cu, and 89.7-180.3 mg/kg Zn was found. The soil cadmium concentration in Dombrád floodplain exceeded the limit value according to Hungarian 6/2009. (IV.14.) KvVM-EüM-FVM regulation. The metal concentration range in roots of dominant plant species (Atremisia vulgaris L., Rubus caesius, Solidago canadensis) found in floodplains were 0.9-4.7 for Cr, 1.6-8.1 for Cd, 22.7-31.5 for Cu, and 106-186 for Zn in mg/kg. The leaves contained 0.7-3.9 Cr, 1.2-1.6 Cd, 0.6-42.8 Cu, and Zn 24.9-203.5 in mg/kg. It can be supposed that the metal excess found in soil originates from the water contamination of Tisza river. Soil contamination was reflected in the vegetation of floodplains.

Keywords: soil, plant, metal contamination, floodplain, Upper Tisza

INTRODUCTION

As a consequence of industrial pollution of recent years critical ecological status characterized the catchment area of Upper Tisza. Ecological accidents lead to extensive dispersion, deposition and accumulation of contaminants (heavy metals, cyanides and other industrial contaminants). This damaged living organisms of the river and catchment area not only when the contamination occurred, but for a long time. Soil can function as buffer to a certain extent, because it is able to soften the disadvantageous effects of contaminants through impeding their solubility and movement. This prevents them to get into the surface and subsurface waters. Soil buffer capacity can also prevent contaminants to enter into the food chain (plants → animals → humans) through transforming them into non-available compounds for plants (Várallyay, 2001; Kádár, 1995).

Spreading out of anthropogenic soil pollutants can lead to both punctual and non-punctual (diffuse) contamination (Simon, 1999). Considering inorganic micro-pollutants of the soil-plant system, the most dangerous heavy metals are Cd, Cu, Ni, Hg. Pb and Zn. These metals can be found in the soil of the flood area of River Tisza (Adriano et al., 2003; Prokisch et al., 2005).

Between 2000 and 2004 examinations began at the Hungarian reach of River Tisza, in Bereg Region and along the Tisza floodplains. The aim of this research was to survey the state of heavy metal contamination in catchment areas of Tisza. According to the results soil contamination is one of the degradation factors in this region, since the vegetation also accumulated the contaminants. Balázsy et al. (2007) measured 7.5-46 mg/kg of Cu, 11.3-106.5 mg/kg of Pb, 30.9-267.5 mg/kg of Zn, 0.1-1.33 mg/kg of Cd and 14.5-27 mg/kg of Ni in soil samples, which were taken from the catchment area of Upper Tisza. Considering plant species, the highest cadmium (1.7-11.6 mg/kg) and zinc (113-491 mg/kg) content was found n Salix and Populus species. According to Csathó (1994) and Kádár (1991) the leaves of plants which grow on soils with high heavy metal content reflects the available metal content in soil with enhanced metal accumulation in plant tissues.

It was supposed that the elevated heavy metal content in the soils of River Tisza floodplain is reflected in roots and leaves of dominant plants of a given area. In this research we examined the connections between

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metal contamination of soils and dominant plant species at 4 locations from Tiszabecs to Tokaj in floodplain areas of River Tisza.

MATERIALS AND METHODS

Sampling sites

I. Tiszabecs floodplain. GPS coordinates: 48°11'N, 22°82'E.

The characteristic forest plants of this area were Salicetum albae-fragili, Salix alba, Salix fragilis, Populus canescens, Cornus sanguinea, Acer negundo, Fraxinus pennsylvanica, Robinia pseudocacia, and Populus species.

In the undergrowth the dominant plants were Humulus lupulus, Lamium purpureum, Symphytum officinale, Angelica silvestris, Ranunculus repens, Taraxacum officinale, Galium aparin. The highest number of plants were Solidago canadensis, Atremisia vulgaris L. and Rubus caesius.

Soil could be described by the following characteristics; 2 % (m/m) CaCO3, pHKCl 9.81; pHH2O 5.6, plasticity KA 60, water holding capacity 45 % (m/m), humus 3.2 % (m/m).

II. Vásárosnamény floodplain. GPS coordinates: 48°11'N, 22°33'E. The characteristic forest plants of this area were Salix alba, Salix fragilis, Populus canescens, Populus nigra, and Acer negundo species.

In the undergrowth the dominant plants were Humulus lupulus, Lamium purpureum, Symphytum officinale, Angelica silvestris, Ranunculus repens, Taraxacum officinale, Galium aparin. The highest number of plants were Solidago canadensis, Atremisia vulgaris L. and Rubus caesius.

Soil could be described by the following characteristics; 2 % (m/m) CaCO3, pHKCl 9.51; pHH2O 5.95, plasticity KA 58, water holding capacity 38 % (m/m), humus: 2.2 % (m/m).

III. Dombrád floodplain. GPS coordinata: 48°24'N, 21°89'E. The characteristic forest plants of this area were Populus canescens, Robinia pseudacacia, Salix alba, Salis fragilis, and Acer negundo species.

In the undergrowth the dominant plants were Urtica dioica, Galaium aparine, Ranunculus repens, Symphytum officinale, Gechoma hederacea, Plantago major, Chrysanrhemum vulgare, Rumex patientia, Equisetum aevense. The highest number of plants were Solidago canadensis, Atremisia vulgaris L. and Rubus caesius.

Soil could be described by the following characteristics; 2 % (m/m) CaCO3: 2 %, pHKCl 9.11, pHH2O 5.25, plasticity KA60, water holding capacity 35 % (m/m), humus: 2.1 % (m/m).

IV. Tokaj floodplain. The GPS coordinata: 48°12'N, 21°42'E.

The characteristic forest plants of this area were Fraxinus pennsylvanica, Salix fragilis, Robinia pseudacacia, Cornus sanguine and Amorpha fruticosa species.

In the undergrowth the dominant plants were Urtica dioica, Galaium aparine, Ranunculus repens, Ficaria verna, Gechoma hederacea, Plantago major. The highest number of plants were Solidago canadensis, Atremisia vulgaris L. and Rubus caesius.

Soil could be described by the following characteristics; 2 % (m/m) CaCO3, pHKCl 8.51, pHH2O 6.95, plasticity KA, water holding capacity 25 %(m/m), humus: 4.2 % (m/m).

Sampling and analysis of soil

The sample collecting was between 2007 and 2009. From every 100 m x 10 m sampling plots 15 soil sub-samples were taken randomly from 20 to 30 cm depth. The total chromium (Cr), cadmium (Cd), copper (Cu), and zinc (Zn) concentrations of the homogenised and air dried soil samples was determined with Lakanen-Erviö method (MSZ-20135:1999) in the certified laboratory of the Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences.

Sampling and analysis of plant

From each 100 m x 10 m experimental plots 5 dominant plant species were sampled. The roots of these plants were dried to constant weight at 70ºC after thorough washing them in water. The same drying procedure was applied to the leaves without washing. The "total" metal content of the homogenized samples was analysed by X-Ray fluorescent spectrophotometry (XRF) in the Agrar and Molecular Research Institute of the College of Nyíregyháza.

Statistical analysis

Statistical analysis of the experimental data was made with SPSS 14.0 software, using analysis of variance with Tukey's b-test. The statistical significance was defined at $P<0.05$.

RESULTS AND DISCUSSION

Considering soil analytical results differences were found among Tiszabecs, Vásárosnamény, Dombrád and Tokaj sampilng sites. In floodplain soils zinc and copper were found in the largest quantities (Table 1). On the basis of the limit values for metal soil contamination (6/2009. (IV.14.) KvVM-EüM-FVM reg-

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ulation), and according to metal concentrations which are considered to be contaminated (Alloway, 1990), soils of the examined floodplains were not contaminated with chromium, cadmium, copper and zinc. Cadmium concentrations in soil samples from Dombrád slightly exceeded the limit values for this metal (Table 1).The largest amount of chromium and cadmium was measured in the roots of Rubus caesius

Table 1. Chromium, cadmium, cooper and zinc concentrations (mg/kg) of soils from floodplains. Means are the averages of three years (2007–2009)

Sampling sites	Heavy metals			
	Cr	Cd	Cu	Zn
Tiszabecs	24.0b	0.48a	41.8b	89.7a
Vásárosnamény	20.6a	0.40a	66.6c	110ab
Dombrád	24.6b	1.15b	28.4a	180c
Tokaj	21.6a	0.43a	30.1a	122b
Average	23.5b	0.61a	41.7c	125d

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at P<0.05.

Chromium concentrations in soil samples from Tiszabecs and Dombrád are significantly higher than chromium content in the soil samples from Vásárosnamény and Tokaj. The largest amount of cadmium and zinc was measured in the samples from Dombrád, while the largest quantities of copper could be found in the soil samples from Vásárosnamény. Differences are significant.

Metal concentrations of the root system of dominant plants are demonstrated in Table 2. Among the four examined metals zinc was found in the largest quantity in the roots of dominant plants. The highest Zn concentration was found in plants grown in Tiszabecs floodplain. Copper and cadmium were measured in smaller amounts, while chromium was found in smallest quantity. Similar tendency could be observed in metal concentrations of dominant plants' roots from the floodplains of Vásárosnamény, Dombrád and Tokaj (Table 2).

Table 2. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in roots of dominant plant species. Means are averages of three years (2007–2009)

Plant species	Sampling sites				Average
	Tiszabecs	Vásárosnamény	Dombrád	Tokaj	
	Cr				
Rubus caesius	4.50b	4.70b	3.90a	3.55a	4.41b
Solidago canadensis,	0.80a	0.90a	0.70a	0.70a	0.77a
Artemisia vulgaris L.	0.80a	0.90a	0.90a	0.80a	0.86a
	Cd				
Rubus caesius	6.00b	8.10c	2.70a	2.50a	4.82b
Solidago canadensis,	1.60a	5.50b	1.70a	1.70a	2.62a
Artemisia vulgaris L.	1.70a	6.20b	1.70a	1.60a	2.80a
	Cu				
Rubus caesius	28.00a	29.10a	28.10a	31.50a	29.17a
Solidago canadensis,	30.10b	22.90a	22.80a	21.10a	24.22a
Artemisia vulgaris L.	22.70a	24.40a	22.70 a	21.20a	22.75a
	Zn				
Rubus caesius	185.00a	184.00a	180.10a	185.00b	181.85c
Solidago canadensis,	101.21a	113.90a	186.00b	178.33a	146.52b
Artemisia vulgaris L.	106.00a	109.30a	106.00a	117.00a	109.57a

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at $P<0.05$.

(Table 2). Differences were statistically significant. The chromium and cadmium concentrations were similar in the roots of Solidago canadensis and Artemisia vulgaris L. on all sampling sites. Significantly highest cadmium concentration of investigated plants was measured in Vásárosnamény sampling site. Similar tendency could be observed in copper concentration of investigated plants. We measured significant differences in Cu concentrations of Solidago canadensis roots from Tiszabecs. The zinc content of Rubus caesius plant roots was significantly larger in all sampling sites. Similarly to Rubus the zinc concentration of Solidago canadensis roots was the highest in Dombrád and Tokaj area. In general metals are accumulating mostly in plant roots (Csathó, 1994; Kádár, 1995; Pitchel et al., 2000, Keresztúri et al., 2003; Simon, 2003). This trend was valid for cadmium concentrations in our samples.

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The metal concentrations of investigated plant's leaves were statistically different in investigated areas (Table 3). In plants, zinc and copper were found in largest quantities.

Table 3. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in leaves of dominant plant species. Means are averages of three years (2007–2009).

Plant samples	Sampling sites				Average
	Tiszabecs	Vásárosnamény	Dombrád	Tokaj	
	Cr				
Rubus caesius	0.70a	0.90a	1.10a	0.90a	0.90a
Solidago canadensis,	0.90a	1.10a	3.90b	1.20a	1.75b
Artemisia vulgaris L	0.80b	0.90b	1.10b	0.40a	0.80a
	Cd				
Rubus caesius	1.20a	1.21a	1.20a	1.20a	1.20a
Solidago canadensis,	1.20a	1.40b	1.60c	1.60c	1.35a
Artemisia vulgaris L	1.60b	1.60b	1.50b	1.20a	1.47a
	Cu				
Rubus caesius	2.01b	3.12b	7.60c	0.60a	3.33a
Solidago canadensis,	42.8b	42.0b	13.2a	12.6a	27.8b
Artemisia vulgaris L	42.1b	40.3b	12.3a	13.1a	26.9b
	Zn				
Rubus caesius	24.9a	25.0a	26.1a	187b	65.8a
Solidago canadensis,	81.0a	106a	191b	203b	145b
Artemisia vulgaris L	73.0a	78.2a	95.3a	201b	112b

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at $P<0.05$.

Chromium concentration of plants in non-polluted soils is between 0.02 and 0.2 mg/kg (Csathó, 1994; Kádár 1995; Keresztúri et al., 2003; Pitchel et al., 2000). Considering our results, chromium content of all plant roots and leaves exceeded these aforementioned values in all sampling sites (Table 3). Significantly largest amount of chromium was measured in Solidago canadensis' leaves in samples from Dombrád. Cadmium concentration of plants from non-polluted soils is usually 0.3-0.5 mg/kg (Simon, 1999, 2003). Considering our results, cadmium content of all plant leaves exceeded the aforementioned values

in all sampling sites. Cadmium content was similar in Rubus caesius leaves at all investigated sampling sites. Compared to Tiszabecs Solidago canadensis leaves were found significantly higher cadmium quantities in samples from Vásárosnamény, Dombrád and Tokaj. In Artemisia vulgaris L. leaves were accumulated the significantly highest cadmium quantities from Tiszabecs, Vásárosnamény, and Dombrád sampling sites. Copper accumulates mainly in plant roots, while in the aboveground plant organs it can be found in relatively small amounts (Várallyay, 2001; SIMON, 1999). Copper concentrations in Solidago canadensis and Artemisia vulgaris L. leaves were higher than of Rubus caseius. This was significant for all sampling sites. The largest concentrations of zinc were measured in the samples from Tokaj. Differences are significant (Table 3).

Chromium, cadmium, copper and zinc concentrations in roots and leaves of dominant plant species from Tiszabecs area are presented in Table 4.

Table 4. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in roots and leaves of dominant plant species from Tiszabecs area. Means are averages of three years (2007–2009)

Plant samples	*Rubus caesius*	*Solidago canadensis*	*Artemisia vulgaris* L.	Average
	Cr			
root	4.50b	0.80a	0.80a	2.03b
leaf	0.70a	0.90a	0.80a	0.80a
	Cd			
root	6.00b	1.60a	1.70a	3.10b
leaf	1.20a	1.20a	1.60b	1.33a
	Cu			
root	28.0ab	30.1b	22.7a	26.9a
leaf	2.01a	42.8b	42.1b	28.9a
	Zn			
root	185b	101a	106a	130b
leaf	24.9a	81.0b	73.0b	59.6a

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at $P<0.05$

Metal content in roots of Rubus caseius was significantly higher than metal concentration in leaves (Table 4). In three dominant plant species the highest chromium, cadmium and zinc concentrations were found in Rubus caseius roots. In the leaves of all plant species similarly low chromium content was found.

Among three dominant plant species the highest metal concentrations were found in the roots of Rubus caseius from Vásárosnamény area (Table 5).

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Table 5. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in roots and leaves of dominant plant species from Vásárosnamény area. Means are averages of three years (2007–2009)

Plant samples	*Rubus caesius*	*Solidago canadensis*	*Artemisia vulgaris* L.	Average
	Cr			
root	4.70b	0.90a	0.90a	2.16b
leaf	0.90a	1.10a	0.90a	0.96a
	Cd			
root	8.10b	5.50a	6.20a	6.60b
leaf	1.21a	1.40a	1.60a	1.40a
	Cu			
root	29.1b	22.9a	24.4a	25.5a
leaf	3.12a	42.0b	40.3b	28.5a
	Zn			
root	184b	113a	109a	135b
leaf	25.0a	106.3c	78.2b	69.8a

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at P<0.05.

Chromium and cadmium concentrations of leaves were similar in plant species from Dombrád area (Table 6). Copper zinc concentrations in Solidago canadensis and Artemisia vulgaris L. leaves were significantly higher than in Rubus caesius leaves. In Rubus caseius roots significantly more Cr, Cd, Cu, and Zn was accumulated than in roots of other plant species (Table 6).

Table 6. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in roots and leaves of dominant plant species from Dombrád area (mg/kg). Means are averages of three years (2007–2009)

Plant samples	*Rubus caesius*	*Solidago canadensis*	*Artemisia vulgaris* L.	Average
	Cr			
root	3.90b	0.70a	0.90a	1.83a
leaf	1.10a	3.90b	1.10a	2.03b
	Cd			
root	2.70b	1.70a	1.70a	1.66a
leaf	1.20a	1.60b	1.50b	1.43a
	Cu			
root	28.1b	22.0a	22.7a	24.5b
leaf	7.60a	13.2b	12.3b	11.0a
	Zn			
root	180b	186b	106a	157b
leaf	26.1a	191c	95.3b	104a

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at P<0.05.

Among three dominant plant species sampled in Tokaj area the highest metal concentrations were detected in Solidago canadensis leaves (Table 7). Largest metal concentrations were found in Rubus caseius roots from Tokaj area. Differences are significant.

Table 7. Chromium, cadmium, cooper and zinc concentrations (mg/kg) in roots and leaves of dominant plant species from Tokaj area (mg/kg). Means are averages of three years (2007–2009)

Plant samples	*Rubus caesius*	*Solidago canadensis*	*Artemisia vulgaris* L.	Average
	Cr			
root	3.55b	0.70a	0.80a	1.68b
leaf	0.90b	1.20c	0.40a	0.83a
	Cd			
root	2.50b	1.70a	1.60a	1.66a
leaf	1.20a	1.60b	1.20a	1.33a
	Cu			
root	31.5b	21.1a	21.2a	24.3b
leaf	0.60a	12.6b	13.1b	8.78a
	Zn			
root	185b	178b	117a	160a
leaf	187a	203a	201a	197a

Statistical analysis was done by ANOVA with Tukey's b-test. Means within the rows followed by the same letter are not statistically significant at $P<0.05$.

Comparing the metal concentrations in plant leaves, the highest chromium and cadmium amount was in Solidago canadensis, while cooper concentrations were the highest in Artemisia vulgaris L. leaves. Differences except of zinc are significant.

CONCLUSIONS

On the basis of the limit values for soil metal contamination (6/2009. (IV.14.) KvVM-EüM-FVM regulation) and according to metal concentrations which are referred to be under the background level (Alloway, 1990) soils of the examined floodplains were not contaminated with chromium, cadmium, copper and zinc. The cadmium concentration in soil samples from Dombrád exceeded the limit values for soil contamination.

In addition to the effects of a Romanian mining accident a flood occurred in River Tisza by March 23, 2000, which led to significantly increased amounts of zinc and copper in floodplain soils. Between 2000 and 2004, the largest copper content was measured in Vásárosnamény (66.6 mg/kg). This value is similar to copper content (58 mg/kg) measured by Boyko et al. (2007) in the floodplain of Upper Tisza. Zinc concentration of soil samples significantly decreased in relation to the largest zinc concentration (452 mg/kg) which was measured just after the mining accident. According to our measurements, the largest zinc concentration was 185 mg/kg. In spite of the similar physicochemical properties of the soil, chromium and zinc content is larger on the floodplain soil of Dombrád, which can be found on a low-lying area, farther from the mouth of River Szamos (Sucharev, 2007). This probably can be explained by the large amount of contaminating elements which are released by the non-ferrous metallurgical companies. In accordance with the results of Sucharev (2007), largest amounts of chromium, cadmium and zinc were measured in the soil samples from Dombrád. Soils can be contaminated with chromium through industrial activities.

Chromium content of plants on non-polluted soils is between 0.02-0.2 mg/kg (Csathó, 1994; Kádár 1995; Keresztúri et al., 2003; Pitchel et al., 2000). Considering our results, chromium content of all plant roots and leaves exceeded the aforementioned values in all sampling sites.

As cadmium does not move in the soil, it can critically accumulate in the upper soil layers. Generally, cadmium content of soils is in linear relation with the cadmium content of plants (Kabata-Pendias et al., 1992; Simon, 1999). In the examined floodplains of

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Upper Tisza, accumulation of cadmium could be mainly detected in plant roots. According to Kabata-Pendias et al., (1992), average cadmium content of plant leaves is 0.05-0.2 mg/kg, referring to dry matter content. Multiples of these values were measured in dominant plants of floodplains.

Copper accumulates mainly in plant roots, while in the aboveground plant organs it can be found in relatively small amounts (Várallyay, 2001). In several cases, our results support the data of other scientists. However, on the floodplains of Vásárosnamény and Tiszabecs, copper concentration in the leaves of Solidago canadensis and Artemisia vulgaris L. exceeded the upper value of 5-30 mg/kg concentrations, which were determined by Kabata-Pendias et al., (1992) referred to dry matter content. In case of air pollution zinc accumulates in plant shoots, while in case of soil pollution it accumulates in roots (Simon, 1999; Csathó, 1994; Kádár, 1995; Várallyay, 2001).

Zinc accumulated mostly in plant roots in the examined floodplains, except the floodplain area of Tokaj. In Tokaj, zinc concentration in the leaves of all three plants was significantly higher than zinc concentration of the roots. Zinc concentration in plant leaves exceeded the upper value of 27-150 mg/kg, which were determined by Kabata-Pendias et al., (1992) referred to dry matter content.

Considering the river section of Upper Tisza between Tiszabecs and Tokaj, chromium, cadmium (except of Dombrád area), copper and zinc concentrations of soil samples did not exceeded the limit values of metal soil contamination, which was determined by 6/2009. (IV.14.) KvVM-EüM-FVM regulation. However, chromium, cadmium and copper concentrations (in Tiszabecs and Vásárosnamény), and zinc concentrations (in Tokaj) in plant leaves were larger than metal contents in plants of non-contaminated soils, which was determined by Kabata-Pendias et al., (1992).

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