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TRANSPORT OF Cu, Zn, Pb AND Cd BY SPRING BARLEY CULTIVATION ON CONTAMINATED SOILS

TRANSPORT Cu, Zn, Pb A Cd PRI PESTOVANÍ JAČMEŇA JARNÉHO NA KONTAMINOVANÝCH PÔDACH

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The transport of copper, zinc, lead and cadmium between soil, roots and above ground phytomass of spring barley in dependence on the level of soil contamination was observed in pot experiments. Barley (variety Sladko) was cultivated on a substrate that had been contaminated with polymetallic imission dust at a dose of 48–150–300 g.m^{-2}. Atomic absorption spectrophotometry method was used to determine the Cu, Zn, Pb and Cd levels in the soil, roots and above ground phytomass of barley. The transfer coefficients were determined on the basis of these values.

Based on the transfer coefficients highest intensity of metallic ion transport was found to occur between soil and roots while the least of all transport activity was observed between roots and above ground phytomass. Ions of the investigated elements were transported between soil and above ground phytomass as well as between roots and above ground phytomass in the translocation order of Zn > Cd > Cu > Pb. With the increasing levels of heavy metals in the soil their accumulation in the plants increased, too (Cu 5.98 – 10.95 mg, Zn 19.25 – 31.35 mg, Pb 0.66 – 2.84 mg and Cd 0.05 – 0.11 mg per kilogram of dry matter). The higher concentrations of metals were found in roots and lowest concentrations in above ground phytomass of barley.

Key words: spring barley, contamination, Cu, Zn, Pb and Cd, transport of ions, accumulation

Natural occurrence of heavy metals is part of most ecosystems. According to the European Commission heavy metals include Cd, Cr, Cu, Pb, Ni, Tl, Hg, Zn and As. Trace elements such as B, Cu, Fe, Mo, Mn and Zn generally participate in the metabolic processes of plants as co-factors and activators of enzymatic reactions [15, 13]. Currently, however, the term heavy metals are mainly related to the negative effects of some elements originating in anthropogenic activities.

In industrial areas in which penetration of heterogeneous substances into the environment is excessive, soil and water are the primary recipients. Of all sources of risk elements atmospheric pollution accounts for 90 % of the arsenic, mercury and lead contamination and for about 60 % of the cadmium levels [1]. It is a specific feature of heavy metals that they do not undergo natural degradation but become a permanent component of the soil. Accumulation then leads to a manifold increase of heavy metal levels, thus causing considerable ecological and economic problems in agricultural production. Increased health risk for humans is one of the important results of the penetration

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of harmful substances into the food chain and therefore radical elimination of the existing contamination is a basic presupposition for improving the hygienic situation in imission areas. For the elimination of harmful substances it is inevitable to thoroughly understand the mechanisms of action, and also to study and apply more suitable systems of management. With respect to the considerable differences between the contaminants in different industrial areas a specific approach to environmental issues is required.

The transport of risk elements from the soil to plants depends on several factors, mainly on the chemical form in which the metal is bound, its solubility and concentration, pH-value of the soil, humus content of the soil, the redox-conditions around the root system that are related to the microbial decomposition processes of organic substances, humidity, temperature and density of the soil as well as on the fertilizers and plant protectives applied.

It is well known from literature and our experience also indicates that there exists a mutual acceptance as well as antagonism between plants and heavy metals. In a positive case we may speak of two mechanisms of communication between heavy metals and plants, the mechanisms of protection and tolerance. The former is based on the immobilization of metals in the cell walls, an altered permeability of membrane structures and increased secretion of substances producing metallic bonds. The mechanisms of tolerance are based on the synthesis of intracellular substances that serve as connecting substances for heavy metals, on the subcellular selection of metals or changes in the metabolism like activation of alternative ways of nitrogen exchange [18].

Heavy metals are mainly taken in by the root system of the plants. The heavy metal levels in the soil solution determine the rate of ion intake on the surface of the roots. After penetrating the roots the metallic ion is either deposited in the cell walls or transported to the over ground parts of the plants. For example in soya 98 % of cadmium received through the root system were retained and only about 2 % were transported to the sprouts [2].

The low translocation of metallic ions from the roots to the sprouts is considered [7] to result from the low production of phytochelatins in the roots, the binding of metals in the form of components with a high molecular weight and the retention of heavy metals in cortex cells, the xylem as well as in the covering tissues during long-lasting transport from the roots to the sprouts.

In spite of the great importance of the root barrier and other protective mechanisms risk elements are still transported to the plant phytomass. For this reason effective protection of the food chain from risk elements requires more detailed knowledge of their toxic effects in the emission areas as well as of their efficient elimination by decreasing risk element transfer from the air to the soil, water and plants and secondarily to the organism of animals and man.

In order to assess the ability of the plants to absorb heavy metal ions from the soil were suggested the transfer coefficients [12]. These coefficients suggest on the relation between metal levels in the plants and total metal concentration in the soil. High transfer coefficients result from decreased sorption of soil metals.

This study focused on the relations between Cu, Zn, Pb and Cd and their transport between soil and roots and above ground phytomass of spring barley as depending on the levels of soil contamination.

MATERIAL AND METHODS

In pot experiments the imission load in the Central Spiš region (north-eastern part of the Slovak Republic) was simulated since the latter is considered to be the area with the highest level of contamination by heavy metals. The observations were carried out on an uncontaminated site at an altitude of 700 m above sea level. The loamy substrate was contaminated with imission dust from a copper smelter that is the main source of contamination in the region. The chemical composition of the dust is presented in table 1.

The substrate (9 kg per pot) of the control variant was not contaminated whereas the substrate of variant P1 was homogenized with the imission dust at an amount of 48 g.m^{-2} that represented the yearly dust emission in uncon-

Table 1

Chemical composition of the imission dust
Chemické zloženie imisného prachu

Element (1)	Content (2) (g.kg^{-1})	Element	Content (g.kg^{-1})
Ca	8.354	Cu	96500.00
K	6.449	Zn	44384.00
Na	2.285	Pb	11410.00
Mg	0.568	Fe	3660.00
P	0.118	Cd	589.16
		Mn	145.50
		Cr	56.83
		Co	21.69

(1) Prvok, (2) obsah

taminated regions. The substrate of variant P2 was mixed with 150 g imissions per square meter. This amount corresponds to the maximum yearly admissible level set by the hygienic standard for dust emissions. The substrate of variant P3 was contaminated with the twofold amount of imissions, i.e. 300 g.m^{-2}.

Following contamination spring barley (variety Sladko) was sown (20th May) into the substrates at an amount of 44 g.m^{-2}, it was 54 grains into pot.

As soon as the plants in the control substrate reached the phenological stage of milk ripeness (day 78 after sow) the experiment was terminated and the crops were harvested. Samples of the overground matter and roots were taken for chemical analysis.

The concentrations of metals (Cu, Zn, Pb and Cd) in soil, the overground matter and roots of barley were determined by atomic absorption spectrophotometry.

The ability of plants to receive heavy metals from soil into the roots and the overground matter was expressed by transfer coefficients [12] that had been calculated according to the following formulas:

$$TC_{SB} = EC_B : EC_S$$
$$TC_{SR} = EC_R : EC_S$$
$$TC_{RB} = EC_B : EC_R$$

where TC – transfer coefficient
EC – concentration of element
S – soil
B – barley (above-ground part of plant)
R – root of barley

The results obtained were statistically evaluated by the single-factorial analysis and compared by Student's *t*-test.

RESULTS AND DISCUSSION

Levels of copper, zinc, lead and cadmium in the substrate of the experimental variants increased with the amount of imissions added (tab. 2). In the substrate of the control variant low levels of the investigated elements were stated that did not surpass the valid limits for risk substances in the soil. Variant P1 revealed copper levels that were above the middle value whereas in variants P2 and P3 zinc and cadmium levels surpassed the middle values. The copper level in the two latter variants surpassed the indicator value of contaminated soils, 100 mg Cu.kg^{-1}. The levels of lead in the substrates did not surpass the limits.

At different distances from the imission source in the Central Spiš region was found [16] copper levels to range from 27.9 to 420 mg.kg^{-1} whereas those of zinc, lead and cadmium were observed to oscillate in intervals of 45.3 – 388 mg Zn.kg^{-1}, 12.7 – 87.5 mg Pb.kg^{-1} and 0.16 – 2.19 mg Cd.kg^{-1} of dry soil, respectively. Other authors [5, 8, 11, 17] also observed similar concentrations of these metals in

Table 2

Concentration of observed metals in substrate of the experimental variants
Koncentrácia sledovaných kovov v substráte pokusných variantov

Variant	Concentration (koncentrácia) (mg.kg^{-1} d.s.)			
	Cu	Zn	Pb	Cd
C	12.98	13.70	8.025	0.041
P1	42.89	27.46	11.562	0.224
P2	106.45	56.69	19.077	0.612
P3	192.47	96.25	29.248	1.137

d.s. – dry soil – suchá pôda
C – control – kontrola
P1, P2, P3 – experimental variants
pokusné varianty

the given region. Coinciding with the findings of the above authors it can be stated that the heavy metal levels simulated in our study reflected the real situation in the region.

Increasing levels of copper, zinc, lead and cadmium in the substrates lead to an increased concentration of these elements in both the phytomass and the roots of barley (tab. 3) where accumulation of the investigated elements was several times higher than in the overground mass. The finding according to which zinc, copper, cadmium and lead levels in the roots surpassed several times the concentrations in the soil substrate seems to be very interesting. The findings other authors [3, 4, 6] that plants may accumulate heavy metals in their roots and sometimes even in their overground parts at levels that considerably surpass those in soil or water coincide with our results. The intake of contaminants by the roots of the plants depends on the exchange capacity of the root that is determined by the production of H^+ and HCO^- ions in the root cells. The transport of heavy metals by the plants is to a certain extent regulated by the physiological barrier that restricts the transport of metals from the roots to the overground parts and from the vegetative to the reproductive organs, which becomes mainly visible in cereals [9].

The levels of contaminant accumulation in barley were characterized by the transfer coefficients (tab. 4). The lower the transfer coefficient of a given metal the firmer are the bonds of this metal and the more difficult is its trans-

Table 3

Concentration of observed metals in phytomass of spring barley
Koncentrácia sledovaných kovov vo fytomase jačmeňa jarného

Variant		Concentration (mg.kg^{-1} d.m.) (1)							
		in above-ground phytomass (2)				in roots (3)			
		Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
C (*n* = 6)	$\bar{x}$ ±SD	5.98 –	19.25 –	0.657 –	0.048 –	48.44 2.89	55.14 3.98	8.09 0.98	0.416 0.074
P1 (*n* = 6)	$\bar{x}$ ±SD	6.58 –	21.32 –	0.873 –	0.052 –	117.72 10.85	86.23 6.34	29.86 5.71	0.908 0.061
P2 (*n* = 6)	$\bar{x}$ ±SD	7.85 –	25.84 –	1.185 –	0.081 –	271.93 24.29	134.38 18.84	68.71 11.49	2.076 0.271
P3 (*n* = 6)	$\bar{x}$ ±SD	10.95 –	31.35 –	2.836 –	0.114 –	381.43 46.10	168.64 19.01	103.43 23.72	2.472 0.271
SSD						C : 1,2,3^{++} 1 : 2,3^{++} 2 : 3^{++}	C : 1,2,3^{++} 1 : 2,3^{++} 2 : 3^{++}	C : 2,3^{++} 1 : 2,3^{++} 2 : 3^{++}	2 : 3^{+} C : 1,2,3^{++} 1 : 2,3^{++}

$^{+}$SDD < 0.05 $^{++}$SDD < 0.01

d.m. – dry matter – sušina
n – number of samples – počet vzoriek
$\bar{x}$ – average – priemer
SD – standard deviation – smerodajná odchýlka
SSD – statistical significance difference at the level α = 0.05 or α = 0.01
Štatisticky preukazné rozdiely na hladine α = 0,05 alebo α = 0,01
Other symbols are identical with the table 2.
Ostatné symboly ako v tabuľke 2.

(1) Koncentrácia, (2) v nadzemnej fytomase, (3) v koreňoch

port. The highest coefficients and thus the most intensive transfer of the investigated elements were observed between the substrate and the roots whereas the lowest values were determined for metal transfer from the roots to the overground parts of barley.

Comparison of the transfer of trace elements revealed that increasing contamination of the substrate was accompanied by a relative decrease of the accumulation of a relative amount of risk elements in both the overground and the root parts of barley; at the same time the transfer rate of these elements from the roots to the plant was decreased. Lead was the only exception since transfer of trace elements between soil and the plant was rather balanced in all experimental variants.

Table 4

Transfer coefficients between soil, roots and above ground phytomass of barley
Transferové koeficienty medzi pôdou, koreňmi a nadzemnou fytomasou jačmeňa

Element (1)	Variant	Transfer coefficients (2)		
		ph./s.	r./s.	ph./r.
Cu	C	0.461	3.732	0.123
	P1	0.153	2.261	0.068
	P2	0.074	2.192	0.034
	P3	0.057	1.649	0.034
Zn	C	1.050	4.025	0.349
	P1	0.776	2.697	0.288
	P2	0.456	2.037	0.224
	P3	0.326	1.506	0.216
Pb	C	0.082	1.009	0.081
	P1	0.076	2.227	0.034
	P2	0.062	3.102	0.020
	P3	0.097	2.914	0.033
Cd	C	1.171	10.146	0.115
	P1	0.233	4.122	0.056
	P2	0.132	3.377	0.039
	P3	0.100	2.241	0.045

n = 6

n – number of samples – počet vzoriek
ph. – above-ground phytomass – nadzemná fytomasa
s. – soil – pôda
r. – roots – korene

(1) Prvok, (2) transferové koeficienty

In all variants of the experiment transfer of the investigated elements between the substrate and the plants took place in the order Zn > Cd > Cu > Pb. For all elements the coefficients were found to be the highest in the control variant and to decrease with increasing contamination. Investigating the transfer of lead and cadmium from the soil to barley [9] reported transfer coefficients between 0.09 – 0.11 and 0.94 – 3.26, respectively. On the contrary was found [19] the transfer coefficients of copper, zinc, lead and cadmium to reach 0.14 – 0.29, 0.34 – 0.54, 0.03 and 0.01 – 0.02, respectively. Comparison revealed the range of coefficients determined in our study to be wider and higher than that stated by the above authors. In our opinion this could result from the greater differences between the concentrations of the investigated elements in the substrates of the individual experimental variants.

Observations on the transfer of trace elements from the substrate to the roots revealed a changed order of transfer. In the control and the first experimental variant transfer took place in the order Cd > Zn > Cu > Pb whereas in the second and third experimental variant the orders of transfer were Cd > Pb > Zn > Cu and Pb > Cd > Cu > Zn, respectively.

In the control and first experimental variant the transfer coefficients revealed transfer of trace elements between roots and plants to take place in the order Zn > Cu > Cd > Pb. Copper and cadmium transfer was balanced. In the second and third variant of the experiment transfer of copper from the roots to the plants slightly decreased whereas that of cadmium increased. In these experimental variants the translocation order of trace elements was Zn > Cd > Cu > Pb.

It is worthy to note that the transfer of trace elements between the substrate and the plants and the roots and plants took place in the same order but that between substrate and roots was altered. The lowest intensity of transfer was stated for lead. According to Xiong [20], the lead is considered to be a passive metal and its translocation from the roots to other parts of the plant to be very low. He reported only 10–20 % of this metal present in a soil solution to be transferred to the roots where usually as much as 90 % of this amount are retained. Markert [14] considered the transfer of lead to highly depend on the physiological state of the plant. In adult plants and under suitable conditions the highest amounts of lead in the roots are found as clusters in the cell walls.

Similarly to lead translocation of cadmium in the plant occurs only after it had been sufficiently absorbed by the roots. The cadmium to be intensively accumulated in the root tissues, to easily undergo transport in the plant and get into all organs. In comparison to other metals it is also easily accumulated in the grain of cereals [21].

In contamination experiments with barley was observed, that the levels of cadmium and lead increase in the plant parts with increasing soil contamination [10]. The lowest accumulation was seen in the grain, then in straw and the highest one was stated in the roots. The latter seemed to be an efficient barrier of heavy metal transfer to the overground parts of plants.

CONCLUSION

Our results confirm that most of the amount of copper, zinc, lead and cadmium that entered the plant from the soil was retained in the root tissue. However, in spite of the blockage of the transport of risk elements by the root system of plants increasing substrate contamination resulted in increased accumulation of heavy metals in the overground mass of barley.

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SÚHRN

V nádobových pokusoch sa sledoval transport vybraných ťažkých kovov (Cu, Zn, Pb a Cd) medzi pôdou, koreňmi a fytomasou jačmeňa jarného v závislosti od úrovne kontaminácie pôdy. Jačmeň (odroda Sladko) sa pestoval na substrátoch kontaminovaných polymetalickým imisným prachom (dávky 48–150–300 g.m^{-2}) a metódou atómovej absorpčnej spektrofotometrie sa sledovala koncentrácia kovov v pôde, koreňoch a fytomase jačmeňa. Miera kumulácie kontaminantov sa vyjadrila transferovými koeficientmi.

Na základe transferových koeficientov sa zistilo, že intenzita transportu kovových iónov bola najvyššia medzi pôdou a koreňmi, najnižšia medzi koreňmi a fytomasou. Ióny sledovaných prvkov boli medzi pôdou a fytomasou i medzi koreňmi a fytomasou transportované v rovnakom translokačnom slede: Zn > Cd > Cu > Pb. S nárastom obsahu ťažkých kovov v pôde stúpala aj ich kumulácia v rastlinách (pri medi 5,98 – 10,95, pri zinku 19,25 – 31,35, pri olove 0,66 – 2,84 a pri kadmiu 0,05 – 0,11 mg.kg^{-1} suš.). Koncentrácia kovov dosiahla najvyššie hodnoty v koreňoch, najnižšie vo fytomase.

Získané výsledky potvrdili, že prevažná časť sledovaných minerálov bola po vstupe z pôdy do rastlín zabudovaná do koreňových pletív. Aj napriek blokovaniu transportu rizikových prvkov koreňovým systémom rastlín však so zvyšujúcou sa kontamináciou substrátu dochádzalo k zvyšovaniu kumulácie ťažkých kovov v nadzemnej hmote jačmeňa.

Kľúčové slová: jačmeň jarný, kontaminácia, Cu, Zn, Pb a Cd, transport iónov, akumulácia