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CALCIUM AS A FACTOR MITIGATING NEGATIVE IMPACT OF HEAVY METALS ON SOIL AND PLANT

II. PHYTOTEST, TRANSFER FACTORS OF HEAVY METALS

WAPŃ JAKO CZYNNIK ŁAGODZĄCY UJEMNE DZIAŁANIE METALI CIĘŻKICH NA GLEBĘ I ROŚLINĘ

II. TEST ROŚLINNY, WSPÓŁCZYNNIKI TRANSFERU METALI CIĘŻKICH

Słowa kluczowe: test roślinny, żyto, wewnętrzne/zewnętrzne współczynniki transferu, biodostępne, wymienne metale.
Key words: phytotest, rye, intrinsic/extrinsic transfer factors, bioavailable, exchangeable metals.

Ocenę łagodzącego wpływu wapnia (Ca) na wybrane metale ciężkie przeprowadzono za pomocą fitotestu, przy użyciu żyta (Secale cereale). W tym celu, do pojemników zawierających 600 g gleby i odpowiednio związków zawierających wapń (CaBC) wysiano po 35 ziaren żyta. Obiekty przygotowano w czterech powtórzeniach. Wilgotność utrzymano na poziomie 75% ppw (polowej pojemności wodnej), a temperaturę w szklarni równą 18°C dla fazy ciemnej i 24°C dla fazy jasnej. Do stworzenia lepszych warunków wzrostu żyta, do każdego z badanych obiektów wprowadzono roztwór zawierający następujące sole: $(NH_4)_2SO_4$, KH_2PO_4, $Mg(NO_3)_2 \cdot 6H_2O$ *oraz* KNO_3. *Po 7 tygodniach wzrastania roślin, zebrano część nadziemną oraz korzenie żyta, które następnie wysuszono, zważono i zmielono oraz poddano analizie chemicznej na zawartość całkowitą metali. W zamieszczonej niżej tabeli podano średnie wartości całkowitej zawartości metali ze wszystkich obiektów, niezależnie od rodzaju i dawek CaBC.*

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Organ rośliny	Cu	Zn	Pb	Cd
	$mg \cdot kg^{-1}$ s.m.			
Część nadziemna	*243,4 ± 54,3	138,1 ± 24,7	15,0 ± 3,3	0,90 ± 0,20
Korzenie	1250,3 ± 282,4	201,2 ± 51,2	112,9 ± 13,0	2,17 ± 0,30

** Średnia ± odchylenie standardowe.*

Oznaczone wysokie zawartości metali, głównie miedzi (Cu), oddziaływały ujemnie najpierw na wschody a później wzrost żyta, poważnie zahamowany ze względu na skarłowacenie korzeni. Uzyskane wewnętrzne współczynniki transferu ($TF_{ex} = \frac{\text{Metal w części nadziemnej}}{\text{Metal w korzeniu}}$) *wahały się w przedziale:* $0{,}13 < 0{,}20 < 0{,}41 < 0{,}69$, *odpowiednio dla* $Pb < Cu < Cd < Zn$. *Te wyniki pokazują specyficzną rolę korzeni jako skuteczną przeszkodę przeciwko przemieszczeniu metali ciężkich, zwłaszcza Pb i Cu, do części nadziemnych. Zewnętrzne współczynniki transferu* $TF_{ex} = \frac{\text{Metal w części nadziemnej lub / i korzeniu}}{\text{Metal w glebie}}$, *obliczone dla metali ekstrahowanych przy użyciu 0,10 mola* $NaNO_3 \cdot dm^{-3}$ *oraz 0,005 mola* $DTPA \cdot dm^{-3}$ *ujawniły w sposób zróżnicowany łagodzący wpływ wapnia z CaBC.*

1. INTRODUCTION

Hot spots of soil contamination are located in areas of industrial activities, where surrounding agricultural lands are affected by atmospheric deposition of heavy metals. Also agricultural application of sewage sludge or phosphate fertilizers has led to increased metal content in soils [Kabata-Pendias and Pendias 1992; Adriano 2001]. Some surveys have pointed out, that on sites with low or medium contamination levels, metal concentration in crops is mostly not high o cause acute toxicity, but in the long term it may provoke chronic damage to health [NATO/CCMS 2002]. Due to the heavy metal burden in human and animal nutrition, there is a need for measures to retard or hamper metal transfer into agricultural plants.

Metals contained in the soil solution are those that are usually and directly taken up by plants. Metals solubility and transfer in soil solution is a complex process mediated by characteristics of soil and plants. The bioavailability of essential micronutrients such as copper and zinc is influenced first by their natural (bio)affinity for plants, which are able to solubilize insoluble forms as necessary. In the case of cadmium and lead, which are toxic by nature, their uptake by plants has no physiological basis, hence the rate of phytoaccumulation is a matter of their chemical specificity and geochemical processes [Freytag 1986].

The genotypic differences in plant ability for uptaking and accumulating mineral elements are sufficiently well documented [Kloke et al. 1984]. The transfer factor soil-plant, expressed as the ratio of plant concentration divided by the total concentration in soils may be an indicator of the plant accumulation behaviour [Freytag 1986; Kabata-Pendias and Pendias 1992]. Puschenreiter et al. [2005] reported significance in the transfer of Cd, Zn, Ni, Cu, Pb and Cr from soils to different plant parts. The lowest transfer factors of Cd were found for organs of maize, peas, oats and wheat, whereas the highest values were obtained for leaves of spinach and lettuce and the roots of various plants. On the other hand, low transfer factor of Zn have been found for carrot and grains of maize and pea, whereas the highest were detected for leaves of spinach and roots of radish and other plants.

Several researchers tested various amendments such as zeolite, Fe oxides, and biosolids as *in situ* Cd stabilizing agents [Gworek 1992a; 1992b]. Such amendments are inexpensive, readily available, and can be economically applied to large tracts of contaminated soil using standard agronomic practices without the need for expensive technical oversight and long-term management. The same applies also for calcium bearing compounds such as apatite, cement by-products, dredged lake sediments (lacustrine lime) and silicate as well [Brown et al. 2004; Cao et al. 2002; Diatta et al. 2007].

The effect of these compounds on retarding or decreasing heavy metals transfer to plants can be evaluated by plant growth, plant yield, and the metal concentration in plant tissues. These processes as frequently expressed by means of bioavailability factor (BF), and the transfer factor (TF), [Knox and Adriano 2000; Mâşu and Dragomir 2008]. The bioavailability factor (BF) is defined as the ratio of the metal content in the exchangeable phase ($[M]_{ex}$) to total metal content in the soil ($[M]_T$), BF = $[M]_{ex}/[M]_T$. This index indicates the fraction of the total content of a metal in the soil, that is considered readily available to plants. The transfer factor (TF) is the ratio of the metal content in plant tissue, ($[M]_P$), to the total content of metal in the soil ($[M]_T$), TF = $[M]_P/[M]_T$. It is normally considered as a measure of plant uptake by the roots and subsequent translocation to the aerial portion of the plant. In a large and detailed study, Machelett et al. [1993] have focused on differences between horticultural and agricultural plants in accumulating heavy metals. Selected data are listed in Table 1.

Table 1. Transfer factors (total content in plant ($mg \cdot kg^{-1}$)/total content in soil ($mg \cdot kg^{-1}$), [Machelett et al. 1993], (modified)

Tabela 1. Współczynniki transferu (zawartość całkowita w roślinie ($mg \cdot kg^{-1}$) / zawartość całkowita w glebie ($mg \cdot kg^{-1}$), [Machelett i in. 1993], (zmieniony)

Plant species	Organs	Cu	Zn	Pb	Cd	Ni
Winter rye	Grain	0.12	0.61	0.01	0.16	0.11
Maize	Straw	0.10	1.53	0.09	1.09	0.06
Maize	Cob	0.11	0.68	0.01	0.30	0.15

It is widely recognized, that metals accumulate in roots with less transfer to grain and other edible tissues; therefore, TF values may be expected to be highest for roots and lower for the shoots.

The purpose of the current phytotest was to assess the effect of calcium from calcium bearing compounds (CaBC) on shaping the uptake of selected heavy metals by rye (*Secale* *cereale*). Transfer factors have been calculated as the expression of the capacity of each metal for migrating from the soil to the plant. Intrinsic and extrinsic transfer factors are suggested.

2. MATERIALS AND METHODS

2.1. Concept, experimental design and soil incubation

Basic physical and chemical characteristics of the soil used in the current study have been outlined in details in Part I „*Soil chemical changes as induced by calcium-bearing compounds*", this issue.

It was assumed, that the low pH, i.e., high protons level favors metals activity and both may be counteracted by appropriated concentrations of calcium ions in the soil. Therefore calcium-bearing compounds (CaBC): quicklime (QL), phosphate rock (PR), lacustrine lime (LL) and silicate lime (SL) were incorporated into the acid soil on the basis of the hydrolytic acidity (HA). Prior to CaBC addition, their acid neutralizing capacity was determined and converted to CaO. Table 2 resumes basic information dealing with these details.

Table 2. Amounts of CaBC-based CaO incorporated to the investigated soil on the basis of hydrolytic acidity (HA)

Tabela 2. Ilości związków zawierających wapń (CaBC) dodane w oparciu o CaO do badanej gleby na podstawie kwasowości hydrolitycznej (HA)

Calcium-bearing compounds (CaBC)	CaO (%)	Amount of CaBC added on the basis of:			
		0.5 HA*	1.0 HA	0.5 HA	1.0 HA
		g CaBC 600 g^{-1}		t CaBC ha^{-1}	
Quicklime (QL)	83.7	0.18	0.36	0.905	1.81
Phosphate rock (PR)	9.0	1.68	3.36	8.39	16.78
Lacustrine lime (LL)	40.7	0.38	0.76	1.86	3.71
Silicate lime (SL)	41.1	0.37	0.74	1.84	3.68

* Hydrolytic acidity (HA).

Each treatment (i.e. CaBC x HA) consisted of 600 g soil and was replicated 4 times. The same applies for the control. These treatments were kept moist at 75% FWHC (Field water holding capacity) and incubated for 28 weeks at 18±2°C. The whole incubation period lasted 28 weeks of which soil sampling (120 g) was performed at each 7 weeks time interval.

2.2. Phytotest experiment with rye (*Secale cereale*)

The evaluation of Ca-based metal mitigation effect was additionally performed by a phytotest, where rye (*Secale cereale,* var. Dankowskie Złote) was grown on treatments as detailed in Table 1. For this purpose 35 rye grains were sown to each treatment containing 600 g soil. Pots, in 4 replications, were kept in a growth chamber, moistened at 75% FWHC (Field water holding capacity) with the ambient temperature 18°C the dark cycle and 24°C the bright cycle. A nutrient solution consisting of 2 g $(NH_4)_2SO_4 \cdot dm^{-3}$; 2 g $KH_2PO_4 \cdot dm^{-3}$; 2 g $Mg(NO_3)_2.6H_2O \cdot dm^{-3}$ and 0.25 g $KNO_3 \cdot dm^{-3}$ was supplemented in order to improve rye growth throughout 7 weeks. The phosphate rock (PR) treatment was not amended with the 2 g KH_2PO_4 dm^{-3} nutrient solution. Shoot and root biomass were collected, dried, weighted, ground and analysed for metal content.

Plant materials i.e., shoot (0.20 g) and roots (0.12 g) were digested in concentrated nitric acid by using MARS 5 CEM Corporation equipment. The recovered digests were filtered and metals were determined by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian Spectra 55B). All chemical tests were run in duplication and statistical evaluations were performed by using the Statgraphics® software and Excel® sheet facilities.

2.3. Transfer factors (TF) of Cu, Pb, Zn and Cd: the concept of intrinsic and extrinsic TF

The effect of calcium in mitigating metals transfer to rye roots and further shoot was assessed by means of transfer factors divided, suggestively into two groups:

- Intrinsic transfer factor $TF_{ex} = \frac{\textit{Metal in shoot}}{\textit{Metal in root}}$, which specifically concerns the integrality of the plant and expresses metals mobility from roots to shoot only, i.e., internal turnover.
- Extrinsic transfer factor $TF_{ex} = \frac{\textit{Metal in shoot or / and root}}{\textit{Metal in soil}}$, generally expressed as transfer factor (TF) in the scientific literature, deals with two components: soil as a source and plant as a sink. In the current paper, Authors have suggested to compute this parameter with amounts of metals determined by using 0.10 mole $NaNO_3$ [bioavailable fraction; Gupta and Hani 1989] and 0.005 mole DTPA [chelated fraction; Lindsay and Norvell 1978, Kociałkowski et al. 1999]. This approach differs from those frequently outlined [Knox and Adriano 2000; Puschenreiter and Horak 2000; Mâşu and Dragomir 2008; Oyedele et al. 2008].

3. RESULTS AND DISCUSSION

3.1. Heavy metals phytoaccumulation shaping by CaBC

The availability of metals, and thus uptake by plants, is related both to their total concentrations, forms and associations with soil colloids, as well as to a number of geochemical factors operating at the soil-root interface. The influence of plant species on metal uptake may also be considerable and this is applied to the type of metal. Different species, and indeed different cultivars, regulate metal uptake at both the soil-root and root-shoot interfaces to varying degrees. As shown in Table 3, the total content of Cu, Pb, Zn and Cd depended both on the plant part, i.e., shoot or root and the rates of calcium bearing compounds (CaBC) applied (0.5 and 1.0 HA). Higher concentrations were found for the lowest rate as compared to the highest one, irrespective of the CaBC. Moreover, the highest recorded metals concentration for the control treatment requires due attention. Under extremely high metal levels, as does for Cu and Pb, the initiation of rootlets was hampered and the physiological function of cell walls could have been disturbed and destroyed, even. Therefore the uptake of Cu, Pb, Zn and Cd proceeded not selectively, basically at the roots level.

Table 3. Mean heavy metals content in shoots and roots of rye as influenced by CaBC application
Tabela 3. Średnia zawartość metali ciężkich w częściach nadziemnych oraz korzeniach żyta w zależności od zastosowanych CaBC

Treatments	HA[2]	Shoots				Roots			
		Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd
		$mg \cdot kg^{-1}$				$mg \cdot kg^{-1}$			
Control		357.75	19.50	183.00	1.02	1704.79	127.76	285.57	2.71
Mean	a[3]	249.19	17.14	156.19	0.98	1335.13	115.86	227.33	2.33
SD[1]		42.55	1.99	19.74	0.13	212.76	9.51	32.92	0.24
Mean	b[4]	218.75	12.56	120.00	0.79	1091.59	104.27	164.39	1.94
SD		32.06	1.88	12.56	0.14	192.86	11.81	22.83	0.16

[1] Standard deviation; [2] – Hydrolytic acidity (HA); [3] – 0.5 HA and [4] 1.0 HA.

The addition of calcium *via* CaBC induced some chemical changes (see part I, this issue) and presumably physiological „restoration" of cell walls, due to Ca uptake and assimilation. This process resulted in the reduced transfer of metals through root barrier and hence the decrease of Cu, Zn, Pb and Cd levels along with Ca availability in the soil. This finding is outlined by the progressive decrease (relative values) as compared to the control treatment, accordingly:

Shoot:
0.5 HA: Cu – 30% > Zn – 15% > Pb – 12% > Cd – 4%
1.0 HA: Cu – 39% > Pb – 36% ≥ Zn – 34% > Cd – 23%
Roots:
0.5 HA: Cu – 22% ≥ Zn – 20% > Cd – 14% > Pb – 9%
1.0 HA: Zn – 42% > Cu – 36% > Cd – 28% > Pb – 18%

From these sequences, it appears clearly, that the role of Ca in shaping heavy metals contents in plant biomass was not uniform. Hence for shoot, the accumulation of Cd was less impacted by Ca levels in the soil, the same applied for Pb in the case of roots. Copper was the main pollutant of the investigated soils and it could be expected its highest levels in shoots and roots. This was consequently confirmed by data listed in Table 3. However, the first positions occupied by Cu in the reported sequences imply that its accumulation in rye biomass was in fact strictly related to Ca occurrence in the growth medium and higher relative values are indicative of this state.

3.2. Intrinsic transfer factors (TF_{in}) related to shoot versus root

The intrinsic transfer factor (TF_{in}) concept developed by Authors relies on the fact that significantly high levels of contaminants are retained by roots (Tab. 3). Therefore it should be assumed, that the higher the concentration of metals at the roots level, the highly probable their transfer to the shoots. Since the process performs within the plant biomass, is appears reasonable to express its intrinsic character.

Data reported in Table 4 tentatively show that the transfer of Zn and Cd from roots to shoot could have been mediated by Ca, as indicated by mean TF_{in} values at CaBC for 0.5 and 0.1 HA rates in comparison to the control treatment. This effect was not observed in the case of either copper or lead.

Table 4. Mean intrinsic transfer factors (**shoot to root**) for the respective heavy metals

Tabela 4. Średnie wewnętrzne współczynniki transferu (**części nadziemne do korzeni**) dla odpowiednich metali ciężkich

Treatment	HA	Cu	Pb	Zn	Cd
		$TF_{in} = \frac{Metal\ in\ shoot}{Metal\ in\ root}$			
Control		0.21	0.15	0.64	0.36
Mean	a	0.19	0.15	0.69	0.44
SD		0.02	0.02	0.09	0.05
Mean	b	0.20	0.12	0.74	0.40
SD		0.02	0.02	0.14	0.05

The TF_{in} range established for the control varies from 0.15 to 0.64 with Pb and Zn occupying the extremes positions. The same applies for CaBC-based transfer factors, which fluctuated in slightly larger ranges. The overall TF_{in} sequence, irrespective of the treatments, follows: Zn > Cd > Cu > Pb, which decidedly implies that Zn and Cd are easily whereas Cu and Pb hardly translocated from the root biomass to upper plant parts. Investigations carried out by Machelett et al. [1993] over a bulk of vegetables, fodder plant, cereals pertinently gave a similar sequence. This was recently confirmed also by data of Lukšienė and Račaitė [2008]*,* when studying heavy metals accumulation in spring wheat. It should be mentioned that the sequence obtained in the current study follows strictly the electronegativity feature of these heavy metals as reported by Sanderson [1983]: Zn – 1.65, Cd – 1.69, Cu – 1.90

and Pb – 2.33, which implies, that lead and copper are decidedly strongly attracted by soil colloids. The physiological nature and process of metals retention within the apparent free space (AFS) of plant roots seems similar and may be helpful in establishing remediation guidelines and phytotoxicity thresholds as well.

3.3. Extrinsic transfer factors (TF_{ex})

3.3.1. Metals in shoots versus $NaNO_3$ and DTPA-extracted metals

It is generally contented that transfer factors operationally outlined in the scientific literature are obtained by dividing concentrations of metals accumulated in a given plant part to the *total content* of the same metals in the soil. The levels of these metals are expressed in mg kg^{-1} [Knox (formerly Chlopecka), Adriano 2000; Puschenreiter and Horak 2000; Mâşu and Dragomir 2008]. From the physiological point of view, only metals soluble in the soil solution or exchangeable as well as weakly bound to soil colloids are expected to be taken up by the root system and translocated further to the shoot. Therefore the so-called labile or potentially available metals forms may be considered as more representative and indicative of the direct impact of metals on the whole plant growth. The use of total metals content in soil for calculating transfer factors overestimates availability process and implies that quite all metals are practically available! Such consideration is basically confusing and the generated data hardly realistic. Hence Authors have suggested to calculate transfer factors on the basis of $NaNO_3$ and DTPA-extracted metals and to be expressed as extrinsic transfer factors (TF_{ex}), (Tab. 5).

Table 5. Mean extrinsic transfer factors for shoot to bioavailable (Bio) and chelated (Chel.) heavy metals

Tabela 5. Średnie wewnętrzne współczynniki transferu do części nadziemnych w stosunku do biodostępnych (Bio) oraz schelatowanych (Chel.) metali ciężkich

Treatments	HA	Cu	Pb	Zn	Cu	Pb	Zn
		$TF_{ex} = \frac{Metal\ in\ shoot}{Metal\ extracted\ in\ 0.10\ mole\ NaNO_3}$			$TF_{ex} = \frac{Metal\ in\ shoot}{Metal\ extracted\ in\ 0.005\ mole\ DTPA}$		
Control		35.66	9.44	60.33	0.62	0.28	7.66
Mean	a	32.26	9.07	75.54	0.47	0.36	12.18
SD		6.00	1.05	9.59	0.07	0.07	1.98
Mean	b	33.48	7.98	86.76	0.44	0.29	11.45
SD		6.87	1.05	20.34	0.06	0.02	1.42

The TF_{ex} values differ markedly, with the highest recorded for bioavailable-based TF_{ex} as compared to the chelated-based TF_{ex} ones. These data are strikingly important, since they reflect the magnitude of the possible impact of each metal fraction in soil over the shoot (*via* roots). Practically, chelated metal forms may be intended to be accumulated progressively within a relatively longer time and hence affect more heavily plant growth and due to their long-lasting availability as compared to the bioavailable forms. The latter ones interact directly with plant roots and their prompt availability shortens their pools along with time.

Metals translocation to the shoot operated according to the sequence Zn > Cu > Pb, irrespective of CaBC rates and metal forms. This sequence is similar to that established for the intrinsic transfer factors (TF_{in}), (Tab. 4) and is fully in line with that outlined by Machelett et al. [1993], (Tab. 1, the current paper), but not consistent at all with those reported by Lukšienė and Račaitė [2008] in the case of spring wheat sprouts (Zn > Pb > Cu) and Puschenreiter and Horak [2000] for the straw of wheat (Cd > Cu > Zn) and rye (Cu > Cd = Zn). The disparities in these sequences depend on some critical factors such as soil content of investigated metals, accumulating plant organs and their age.

3.3.2. Metals in roots versus $NaNO_3$ and DTPA-extracted metals

The accumulation of Cu, Zn and Pb took place preponderantly in the root biomass, which can be designated as the main „metal storage organ" as listed in Table 3. This strategy was developed by rye plants for overcoming excessive metals transfer to the shoot biomass, being naturally „designed" for extending the life cycle, i.e., grain production. Consequently, any relationship established between heavy metals in soils and their potential (bio) availability should be of great value for estimating a possible occurrence of metal phytotoxicity [Vera et al. 2003; Pečiulytė et al. 2006].

From data reported in Table 3 and Table 6, it appears that roots have accumulated relatively to extremely high amounts of metals, Cu particularly, whose level extracted by using 6 moles $HCl \cdot dm^{-3}$ was 2041.3 $mg \cdot kg^{-1}$ soil as compared to lead, 540.0 $mg \cdot kg^{-1}$ soil. Ecotoxicological research [Moffett and Brand 1996; Römkens et al. 1999] revealed, that copper uptake and toxicity are closely related to the speciation in solution, and especially „free" metal ions are considered important species that can be taken up by organisms and plants. Such approach has been reported by Boon et al. [1998] who stated that tolerance exhibited by a copper-tolerant grass (*Agrostis capillaries*) was a matter of intrinsic metals translocation capacity as well as their ready solution concentrations and activity as well. The same applied to the results of this study, where Cu solution concentrations (bioavailable forms extracted in 0.10 $NaNO_3$, data not listed) were in strict position to exert direct toxicity over the root. Moreover it should be mentioned the relatively low pH_{CaCl_2} range 5.3 – 5.9, being one of the factors controlling the activity of Cu as well as Pb and Zn in the rhizosphere.

Extrinsic transfer factors (TF_{ex}) for roots (Table 6) decreased along with CaBC incorporation, i.e., Ca occurrence in rye growth medium. The practical meaning of these data is that Ca acted as cell wall „renovating agent" resulting in a further improvement of selectivity in metal uptake. The latter one may lead to a relative decrease of metals transfer to the roots and in turn increase of their respective concentrations in the ambient solution. This explained lower TF_{ex} values at 1.0 HA as compared to 0.5 HA. However, the lowest values recorded in the case of control treatments are attributed typically to the highest pools of extractable bioavailable metal forms in soil. The relatively low levels of Ca for controlling/lowering metals activity was similarly outlined by Römkens and Dolfing [1998].

Table 6. Mean extrinsic transfer factors for roots to bioavailable (Bio) and chelated (Chel.) heavy metals

Tabela 6. Wewnętrzne współczynniki transferu do korzeni w stosunku do biodostępnych (Bio) oraz schelatowanych (Chel.) metali ciężkich

Treatments	HA	Cu	Pb	Zn	Cu	Pb	Zn
		$TF_{ex} = \frac{Metal\ in\ root}{Metal\ extracted\ in\ 0.10\ mole\ NaNO_3}$			$TF_{ex} = \frac{Metal\ in\ root}{Metal\ extracted\ in\ 0.005\ mole\ DTPA}$		
Control		169.95	57.82	94.14	2.46	1.86	11.96
Mean	a	173.27	66.03	117.08	2.95	2.42	17.50
SD		33.49	4.47	8.93	0.33	0.14	0.66
Mean	b	167.35	61.25	109.28	2.50	2.19	15.57
SD		38.60	0.82	15.70	0.39	0.35	1.10

4. CONCLUSIONS

1. The addition of calcium *via* CaBC induced some presumable physiological „restoration" of root cell walls, due to Ca uptake and assimilation. This process resulted in the reduced transfer of metals through root barrier and hence the decrease of Cu, Pb, Zn and Cd levels in rye along with Ca availability in the soil.
2. Extremely high Cu concentrations, impacted significantly emergence and further rye growth was seriously impaired as a result of root stuntedness.
3. The overall *intrinsic* transfer factors (TF_{in}), irrespective of the CaBC treatments, follows the sequence: Zn > Cd > Cu > Pb, which decidedly implies, that Zn and Cd are easily, whereas Cu and Pb hardly translocated from the root biomass to upper plant parts.
4. Shoot *extrinsic* transfer factors (TF_{ex}) values differ markedly, with the highest recorded for bioavailable-based TF_{ex} as compared to the chelated-based TF_{ex} ones. Metals translocation to the shoot operated according to the sequence Zn > Cu > Pb, irrespective of CaBC rates and metal forms (i.e., extracted by 0.10 mole $NaNO_3$ or 0.005 mole DTPA).
5. *Extrinsic* transfer factors (TF_{ex}) for roots decreased along with CaBC incorporation, i.e., Ca occurrence in rye growth medium – lower TF_{ex} values at 1.0 HA as compared to 0.5 HA. This outlines the role of Ca as cell wall "renovating agent" resulting in a further improvement of selectivity in metal uptake.

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