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VERTICAL ZINC MIGRATION IN VARIOUS SOIL TYPES

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In this contribution the zinc content in selected soil types and soil reaction on zinc loading in kinetic model conditions with knock–down columns filled with soil samples are evaluated. The total zinc content after their draining, finish and decomposition by HF + $HClO_4$ mixture and its fractions content in extract of 2 mol dm^{-3} HNO_3, in extract of 0.05 mol dm^{-3} EDTA and in extract of 0.01 mol dm^{-3} $CaCl_2$ using atomic absorption spectrometry method were determined.

The knock–down columns filled with soil samples in model kinetic conditions were used for observation of zinc sorption measure. The maximal water capacity of soils was determined and then solution of 280 mg zinc ($ZnSO_4.2H_2O$) per kilogram of soil was applied. The zinc contents in extraction solutions 2 mol dm^{-3} HNO_3, 0.05 mol dm^{-3} EDTA and 0.01 mol dm^{-3} $CaCl_2$ in drained 0.05 m high soil columns by atomic absorption spectrometry method were determined.

The obtained results were evaluated by mathematical-statistical methods – multiple range analysis and linear regression. Achieved data were compared to allowed limit values.

The results show different behavior of individual soil types against zinc loading. The soils showed different properties, where zinc migration to the lower column layers was determined. The accent is given to zinc dynamics in neutral and acid soils. The limit value A (140 mg kg^{-1}) was observed in Luvic Cambisol. The limit value A1 (40 mg kg^{-1}) was observed in Eutric Regosol and Luvic Cambisol in upper layer of soil in column. The obtained results show high mobility of zinc in tested soils and thus its risk for ecosystems.

Key words: zinc, soil mobility, migration, desorption

INTRODUCTION

Zinc belongs to the elements which are essential for humans, but on the other hand are potentially toxic. The amount of zinc entering every year the environment is about two million tons. The average concentration of zinc in the earth crust is about 50 mg kg^{-1} (Beneš 1994).

The zinc content in soils ranges from 2 to 100 mg kg^{-1} in natural conditions. The average content of zinc in soils ranges from 10 to 50 mg kg^{-1} in the world (Beneš & Pabiánová 1987). The highest average contents of zinc are in soils with higher humus and carbonate content (Chernozems and Fluvi-calcaric Phacozem, mainly carbonate). The zinc content in this soil types is under limit. Markedly contaminated area in the Middle Spiš is highlighted in the map of the zinc content in Slovak soils (Linkeš 1997). Other localities (with the zinc content from average value to hygiene limit 140 mg kg^{-1}) frame coherent territories, mainly in lowlands and depressions. Extremely high zinc content in soil extract of 2 mol dm^{-3} HNO_3 (100–150 mg kg^{-1}) occurs only in areas near Rudňany and Krompachy (Tomáš et al. 2000; Tóth 2007). High amount of zinc can be adsorbed on organic and inorganic soil colloids. Thus the zinc concentration in soil solution can be very high. The water-soluble fraction of zinc is lower than 1%, exchangeable zinc fraction 3%, zinc fraction adsorbed on Fe and Mn oxides 40% and residual fraction (zinc bounded in primary and secondary minerals) 25–75%

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from the total content (Alloway 1990). The zinc content in water – soluble fraction is quite low against zinc content in exchangeable fraction. Exchangeable or mobile zinc fraction is easily extracted by solutions of diluted acids, for example 2 mol dm^{-3} HNO_3 (Babčan & Švec 1997; Tóth et al. 2008).

In this contribution the total and mobile forms of zinc contents in selected soil types, soil reaction on

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Physical and chemical characteristics of used soils

Parameter	Horizon [m]	Soil type							
		Che	Je	Hcf	Re	Lgp	Lga	Bl	Lo
pH/H_2O	0.00–0.10	7.78	8.00	8.21	5.92	7.78	5.79	5.09	6.53
	0.20–0.30	7.34	8.00	8.29	5.84	7.85	5.75	5.48	6.40
	0.35–0.45	7.96	8.21	8.44	5.43	7.81	5.19	5.96	6.56
pH/KCl	0.00–0.10	7.27	7.34	7.60	5.00	6.88	4.75	3.82	5.29
	0.20–0.30	7.33	7.33	7.67	4.72	6.86	4.71	4.07	4.87
	0.35–0.45	7.38	7.42	7.79	4.61	6.53	3.91	4.30	5.17
C_{ox} [%]	0.00–0.10	1.43	1.87	2.60	1.43	1.87	1.93	6.67	1.72
	0.20–0.30	1.34	7.73	1.91	0.87	1.63	1.66	2.79	0.76
	0.35–0.45	1.01	1.42	1.20	0.55	1.01	0.52	1.85	0.36
Humus [%]	0.00–0.10	2.46	3.23	4.48	2.47	3.22	3.32	9.00	2.97
	0.20–0.30	2.30	2.98	3.30	1.50	2.81	2.85	5.86	1.31
	0.35–0.45	1.74	2.45	2.06	0.95	1.75	0.90	4.93	0.61
HA/FA	0.00–0.10	1.68	0.98	1.57	0.87	0.66	0.66	0.67	0.79
	0.20–0.30	1.43	0.85	1.45	0.73	0.60	0.89	0.46	0.82
	0.35–0.45	1.32	0.90	1.32	0.65	0.32	0.70	0.10	0.67
Carbonates [%]	0.00–0.10	0.33	1.63	3.10	0.00	0.00	0.00	0.00	0.00
	0.20–0.30	0.20	1.40	3.40	0.00	0.00	0.00	0.00	0.00
	0.35–0.45	0.40	1.40	4.30	0.00	0.00	0.00	0.00	0.00
Available P [mg kg^{-1}]	0.00–0.10	228.00	10.00	12.50	26.30	33.80	22.50	4.40	34.00
	0.20–0.30	190.00	12.50	13.75	31.30	23.80	17.50	4.70	30.00
	0.35–0.45	106.00	7.50	5.00	22.50	15.00	4.00	4.20	8.75
Available K [mg kg^{-1}]	0.00–0.10	412.00	179.00	91.50	90.80	107.00	256.00	148.00	366.00
	0.20–0.30	339.00	72.90	107.30	109.40	74.50	212.10	135.40	155.30
	0.35–0.45	347.00	38.10	27.70	79.80	59.50	98.20	128.70	102.40
Available Mg [mg kg^{-1}]	0.00–0.10	95.50	235.00	291.00	61.60	216.00	138.00	64.90	163.00
	0.20–0.30	95.00	233.80	303.00	59.10	195.70	152.00	85.50	171.90
	0.35–0.45	102.50	235.50	269.00	62.10	260.20	279.20	80.70	191.80

Soil types: Che – Calcero-haplic Chernozem (Trnovec nad Váhom); Je – Calcaric Fluvisols (Imeľ); Hcf – Fluvi-calcaric Phacozem (Dolný Štál); Re – Eutric Regosols (Veľké Leváre); Lgp – Plano-gleyic Luvisol (Čičarovce); Lga – Albo-gleyic Luvisol (Tomášovce); Bl – Luvic Cambisol (Stredný Spiš); Lo – Orthic Luvisol (Malanta)

pH/H_2O – exchangeable soil reaction,
pH/KCl – active soil reaction,
C_{ox} – oxidizable carbon,
HA/FA – ratio of humic acid and fulvic acid,
available for plants: P – according to Egner, K, Mg – according to Schachtschabel

zinc loading and zinc migration to the lower column layers in kinetic model conditions with knock-down columns filled with tested soil samples are evaluated.

MATERIAL AND METHODS

In this contribution the zinc contents in selected soil types Calcero-haplic Chernozem (Che), Trnovec nad Váhom; Calcaric Fluvisols (Je), Imeľ; Fluvi-calcaric Phacozem (Hcf), Dolný Štál; Eutric Regosols (Re), Veľké Leváre; Plano-gleyic Luvisol (Lgp), Čičarovce; Albo-gleyic Luvisol (Lga), Tomášovce; Luvic Cambisol (Bl), Stredný Spiš; Orthic Luvisol (Lo), Malanta (by Sobocká 2004, FAO–UNESCO, 1970–1978) and soil reaction on zinc loading in kinetic model conditions with knock–down columns filled with soil samples are evaluated. The agrochemical characteristics of the soils are presented in Table 1. In soil samples (taken in year 2002) from the horizons of 0.00–0.10 m, 0.20–0.30 m and 0.35–0.45 m the physical-chemical characteristics (active soil reaction (pH/H_2O), exchangeable soil

Table 2

The average zinc contents in different soil extracts

Soil type*	Horizon [m]	Zn content [mg kg^{-1}]				Zn content [%] (total content = 100 %)		
		total	in extract					
			2 mol dm^{-3} HNO_3	0.05 mol dm^{-3} EDTA	0.01 mol dm^{-3} $CaCl_2$	2 mol dm^{-3} HNO_3	0.05 mol dm^{-3} EDTA	0.01 mol dm^{-3} $CaCl_2$
Che	0.00–0.10	48.30	10.34	4.03	0.12	21.41	8.34	0.25
	0.20–0.30	46.80	9.86	4.00	0.07	21.07	8.54	0.15
	0.35–0.45	46.00	8.60	2.79	0.10	18.70	6.07	0.22
Je	0.00–0.10	76.80	11.78	1.79	0.14	15.34	2.33	0.18
	0.20–0.30	77.30	11.70	1.68	0.12	15.14	2.17	0.16
	0.35–0.45	35.90	7.48	0.53	0.12	20.84	1.48	0.33
Hcf	0.00–0.10	60.60	13.73	3.66	0.04	22.66	6.04	0.07
	0.20–0.30	56.40	13.47	2.34	0.14	23.88	4.15	0.25
	0.35–0.45	65.50	10.19	1.18	0.09	15.56	1.80	0.14
Re	0.00–0.10	22.80	5.32	3.16	0.02	23.33	13.86	0.03
	0.20–0.30	24.20	5.69	3.37	0.12	23.51	13.93	0.50
	0.35–0.45	11.80	2.09	0.79	0.06	17.71	6.69	0.51
Lgp	0.00–0.10	67.20	4.98	1.17	0.08	7.41	1.74	0.09
	0.20–0.30	60.00	3.30	0.63	0.07	2.59	0.49	0.49
	0.35–0.45	55.50	2.26	0.34	0.14	4.07	0.61	0.51
Lga	0.00–0.10	57.60	6.91	1.46	0.07	11.99	2.53	0.12
	0.20–0.30	59.50	7.05	1.51	0.05	11.85	2.54	0.06
	0.35–0.45	53.80	7.61	2.44	0.24	14.14	4.54	0.25
Bl	0.00–0.10	247.10	25.80	7.25	1.84	10.15	2.93	0.75
	0.20–0.30	236.10	20.35	3.18	1.07	8.62	1.34	0.45
	0.35–0.45	243.10	17.09	2.73	0.37	7.30	1.12	0.15
Lo	0.00–0.10	62.80	9.07	3.36	0.12	14.44	5.35	0.19
	0.20–0.30	60.90	9.38	2.92	0.16	15.40	4.79	0.26
	0.35–0.45	64.90	5.77	0.65	0.13	8.89	1.00	0.20

* legend of used soils as a Table 1

reaction (pH/KCl), C organic (C_{ox}), humus, ratio of humic acid: fulvic acid (HA/FA), available for plants P, K, Mg (P according to Egner; K, Mg – according to Schachtschabel) were determined. The tested soil belongs to Luvic Cambisol (extremely acid, and its humus content) corresponds to average values of Cambisols in Slovakia. A ratio of humic acid (HA) and fulvic acid (FA) is typical of the soils in moist and cold regions. The contents of zinc were determined according to the methodology for soil monitoring (Linkeš 1997). The total zinc content in soils after their draining, finish and decomposition by HF + $HClO_4$ mixture and its fractions content in extract of 2mol dm^{-3} HNO_3 (potentially mobile forms), in extract of 0.05mol dm^{-3} EDTA (actually mobile forms) and in extract of 0.01 mol dm^{-3} $CaCl_2$ (exchangeable forms) using by atomic absorption spectrometry method (AAS) by instrument PYE UNICAM SP9 were determined.

The knock–down columns filled with soil samples in model kinetic conditions were used for observation of zinc sorption measure. The maximal water capacity of soils was determined and then solution of 280 mg zinc ($ZnSO_4.2H_2O$) per kilogram of soil was applied in volume by up to 50 cm^3 higher than water capacity in every soil type. The migration time of solution in the column depended on the soil type. The zinc contents in extraction solutions 2 mol dm^{-3} HNO_3, 0.05 mol dm^{-3} EDTA and 0.01 mol dm^{-3} $CaCl_2$ in drained 0.05 m high soil columns after taking apart to pieces (a, b, c layers) by AAS method were determined. Achieved data were compared with the limit values (Decision of Ministry of Agriculture SR No. 531/1994-540).

The obtained results were compared with legislatively given limits (Decision of Ministry of Agriculture SR No. 531/1994-540) and by correlation analysis of zinc fractions and selected soil parameters testing.

RESULTS AND DISCUSSION

The results of total zinc in soils and its contents in extracts 2 mol dm^{-3} HNO_3, 0.05 mol dm^{-3} EDTA and 0.01 mol dm^{-3} $CaCl_2$ in used soils are presented in Table 2.

The results show different behaviour of individual soil types against zinc loading. The total Zn content in used soils was determined in range 11.80–67.20 mg kg^{-1}. The determined content of zinc in Luvic Cambisol in range 236.10–247.10 mg kg^{-1} were higher than the maximal allowed concentration A (140 mg kg^{-1}).

The total content of zinc in used soils presented uphill sequence: Luvic Cambisol > Calcaric Fluvisol > Orthic Luvisol > Albo-gleyic Luvisol > Fluvi-calcaric Phacozem > Plano-gleyic Luvisol > Calcero-haplic Chernozem > Eutric Regosol.

The zinc compounds in majority of tested soils are bonded in light released forms in extracts 2 mol dm^{-3} HNO_3 and 0.05 mol dm^{-3} EDTA. The mobile

T a b l e 3

Spearmann coefficients of individual zinc fractions and selected soil parameters

Parameter*	Zn content				pH/H_2O	Humus
	total	in extract 2 mol dm^{-3} HNO_3	in extract 0.05 mol dm^{-3} EDTA	in extract 0.01 mol dm^{-3} $CaCl_2$		
Total						
0.0–0.1 m	–	0.031	0.044	0.164	0.486	0.161
0.2–0.3 m	–	0.010	0.019	0.185	0.409	0.024
0.35–0.45 m	–	0.016	0.000	0.328	0.438	0.002
pH / KCl	0.419	0.167	0.266	0.670	–	–
C_{ox}	0.105	0.787	0.675	0.846	–	–
HK / FK	0.429	0.059	0.249	0.282	–	–

* legend of used soils as a Table 1

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Enhanced content and balance of zinc in observed extracts

Soil type		Horizon [m]	In extract								
			2 mol dm^{-3} HNO_3			0.05 mol dm^{-3} EDTA			0.01 mol dm^{-3} $CaCl_2$		
			a	b	c	a	b	c	a	b	c
Zn content [mg.kg $^{-1}$]	Che	0.00–0.10	19.27	3.02	1.35	16.35	2.40	1.04	4.58	0.42	0.31
		0.20–0.30	19.17	4.06	2.29	15.31	3.23	1.77	5.52	0.73	0.31
		0.35–0.45	20.73	1.88	0.73	16.67	1.35	0.63	2.71	0.10	ND
	Je	0.00–0.10	24.48	ND	0.10	29.06	0.52	0.52	0.52	0.10	ND
		0.20–0.30	25.10	0.10	0.10	26.35	0.42	0.42	0.52	0.21	0.10
		0.35–0.45	25.00	0.10	0.10	26.98	0.31	0.31	0.52	0.10	0.21
	Hcf	0.00–0.10	26.98	ND	ND	21.15	0.31	0.21	ND	ND	ND
		0.20–0.30	27.19	ND	ND	23.75	ND	ND	2.50	0.10	0.10
		0.35–0.45	14.58	ND	ND	15.63	0.10	ND	0.21	0.10	ND
	Re	0.00–0.10	41.77	0.31	0.21	39.38	0.52	0.73	0.63	0.21	ND
		0.20–0.30	25.21	0.10	0.52	28.33	0.52	0.42	0.31	ND	ND
		0.35–0.45	32.71	0.42	0.21	26.04	0.63	0.21	0.63	ND	ND
	Lgp	0.00–0.10	51.88	0.31	0.31	46.04	0.21	0.21	2.60	ND	ND
		0.20–0.30	37.08	0.10	0.10	35.52	0.31	0.21	9.17	0.21	ND
		0.35–0.45	35.21	ND	ND	29.17	0.10	0.10	9.79	ND	ND
	Lga	0.00–0.10	25.10	0.21	0.21	24.38	0.31	0.31	0.63	0.21	0.31
		0.20–0.30	19.69	ND	ND	18.75	0.10	0.10	0.31	0.21	0.31
		0.35–0.45	29.69	0.21	0.21	27.60	0.42	0.10	0.31	0.21	0.21
Zn balance % (percent of added amount, 100 % = 280 mg kg^{-1})	Che	0.00–0.10	6.88	1.08	0.48	5.84	0.86	0.37	1.64	0.15	0.11
		0.20–0.30	6.85	1.45	0.82	5.46	1.15	0.63	1.97	0.26	0.11
		0.35–0.45	7.40	0.67	0.26	5.95	0.48	0.23	0.97	0.04	ND
	Je	0.00–0.10	8.74	ND	0.04	10.38	0.19	0.19	0.19	0.04	ND
		0.20–0.30	8.96	0.04	0.04	9.41	0.16	0.15	0.19	0.08	0.04
		0.35–0.45	8.93	0.04	0.04	9.64	0.11	0.11	0.19	0.04	0.08
	Hcf	0.00–0.10	9.64	ND	ND	7.55	0.11	0.08	ND	ND	ND
		0.20–0.30	9.71	ND	ND	8.48	ND	ND	0.89	0.04	0.04
		0.35–0.45	5.21	ND	ND	5.58	0.04	ND	0.08	0.04	ND
	Re	0.00–0.10	14.92	0.11	0.08	14.06	0.19	0.26	0.23	0.08	ND
		0.20–0.30	9.00	0.04	0.19	10.12	0.19	0.15	0.11	ND	ND
		0.35–0.45	11.68	0.15	0.08	9.30	0.23	0.08	0.23	ND	ND
	Lgp	0.00–0.10	18.53	0.11	0.11	16.44	0.08	0.08	0.93	ND	ND
		0.20–0.30	13.24	0.04	0.04	19.11	0.11	0.08	3.28	0.08	ND
		0.35–0.45	12.58	ND	ND	10.42	0.04	0.04	3.50	ND	ND
	Lga	0.00–0.10	8.96	0.08	0.08	8.71	0.11	0.11	0.23	0.08	0.11
		0.20–0.30	7.03	ND	ND	6.70	0.04	0.04	0.11	0.08	0.11
		0.35–0.45	10.60	0.08	0.08	9.86	0.15	0.04	0.11	0.08	0.08

Soil type: Che – Calcero-haplic Chernozem, Je – Calcaric Fluvisol, Hcf – Fluvi-calcaric Phacozem, Re – Eutric Regosol, Lgp – Plano-gleyic Luvisol, Lga – Albo-gleyic Luvisol,

a, b, c – layers of soil in column (height of every one 0.05 m),
a – upper , b – central, c – below,
ND – non detected

zinc forms in extract 2 mol dm^{-3} HNO_3 were in range 2.26–25.08 mg kg^{-1}, e.g. 4.07–23.88% of the total content. The potentially mobile zinc forms in extract 0.05 mol dm^{-3} EDTA were in range 0.53–7.25 mg kg^{-1}, i e. 0.50–13.93% of the total content. The exchangeable Zn forms in extract 0.01 mol dm^{-3} $CaCl_2$ were in range 0.02–1.84 mg kg^{-1}, i.e. 0.06–0.75% of the total content. The mobile forms of Zn in used extracts presented uphill sequence:

2 mol dm^{-3} HNO_3 > 0.05 mol dm^{-3} EDTA >
0.01 mol dm^{-3} $CaCl_2$.

The experimental results signal the zinc risk for ecosystems. Achieved data corresponds to the results of Makovníková (2005), Vácha et al. (2002), Tomáš et al. (2000), Linkeš et al. (1997), Lahučký et al. (2005, 2007).

The results of correlation analysis are in Table 3. The relations between total zinc content, zinc content in different extract solutions 2 mol dm^{-3} HNO_3, 0.05 mol dm^{-3} EDTA, 0.01 mol dm^{-3} $CaCl_2$ and soil parameters (pH/H_2O, pH/KCl, humus content, C_{ox}, ratio HA/FA) from the horizons of 0.00–0.10 m, 0.20–0.30 m and 0.35–0.45 m are not distinct and statistically not demonstrative due to variability of soil properties and soil-ecological conditions of chosen localities of soil types.

Increasing of zinc content in individual soils after application of 280 mg Zn per kilogram of soil is presented in Table 4. The soil behavior towards zinc was variable but relatively similar. The Zn content in extract 2 mol dm^{-3} HNO_3 was in range ND (not detected) – 51.88 mg kg^{-1} (ND – 18.53% of added amount). The Zn content in extract 0.05 mol dm^{-3} EDTA was in range ND – 46.04 mg kg^{-1} (ND – 19.11% of added amount). The Zn content in extract 0.01 mol dm^{-3} $CaCl_2$ was in range ND – 9.79 mg kg^{-1} (ND – 3.50% of added amount).

The soil shows different properties in relationship to zinc migration to the lower column layers. The accent is given to zinc dynamics in neutral and acid soils. The limit value A_1 (40 mg kg^{-1}) was observed in Eutric Regosol and Luvic Cambisol in upper layer of soil in column. The similar results are presented by Tóth et al. (2008) and Tomáš et al. (2001). They explored the zinc content in soils near metallurgical factory Krompachy in Middle Spiš region, due to massive antrophic immision load.

Our results show different properties of individual soil types against zinc loading. The zinc compounds in majority of tested soils are bonded in lightly released forms in extracts 2 mol dm^{-3} HNO_3 and 0.05 mol dm^{-3} EDTA. The carbonate and weakly alkaline Calcero-haplic Chernozem, Calcaric Fluvisols, Fluvi-calcaric Phacozem and also neutral and acid Eutric Regosols, Albo-gleyic Luvisol, Plano-gleyic Luvisol, in which zinc migration to the lower column layers was detected, seemed like risky soils. The limit value A (140 mg kg^{-1}) was observed in Luvic Cambisol. The limit value A_1 (40 mg kg^{-1}) was observed in Eutric Regosol and Luvic Cambisol in upper layer of soil in column. The obtained results show high mobility of zinc in soils and thus its risk for ecosystems.

CONCLUSION

The results show different properties of individual soil types against zinc loading. The zinc compounds in majority of tested soils are bounded in lightly released forms in extracts 2 mol dm^{-3} HNO_3 and 0.05 mol dm^{-3} EDTA. The contents of potentially mobile Zn forms in 2 mol dm^{-3} HNO_3 (Fluvi-calcaric Phacozem, Calcero-haplic Chernozem, Calcaric Fluvisol, Albo-gleyic Luvisol) and in 0.05 mol dm^{-3} EDTA (Albo-gleyic Luvisol, Plano-gleyic Luvisol) were especially high. The accent is given to zinc dynamics first of all in acid and neutral soil reaction. The mobile forms of Zn in used extracts presented uphill sequence:

2 mol dm^{-3} HNO_3 > 0.05 mol dm^{-3} EDTA >
0.01 mol dm^{-3} $CaCl_2$.

The soil behavior towards zinc was variable but relatively similar. Different properties shown Eutric Regosol, Albo-gleyic Luvisol, Plano-gleyic Luvisol, Calcero-haplic Chernozem and Calcaric Fluvisol, in which zinc migration to the lower column layers were find out.

However, the content of zinc were higher in Eutric Regosol and Luvic Cambisol than the allowed limit value A_1 (40 mg kg^{-1}), therefore a higher attention has to be drawn to these locations. The obtained results show higher mobility of zinc in soils and thus its risk for ecosystems.

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