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EFFECT OF ORGANIC MATTER AND pH ON THE MOBILITY OF SOME HEAVY METALS IN SOILS OF PERMANENT GRASSLANDS IN THE FOOTHILLS OF THE HRUBY JESENIK MTS

WPŁYW MATERII ORGANICZNEJ I pH NA MOBILNOŚĆ NIEKTÓRYCH METALI CIĘŻKICH W GLEBACH TRWAŁYCH UŻYTKÓW ZIELONYCH NA POGÓRZU HRUBÝ JESENÍK

Abstract: In 2008 and 2009 total content of some heavy metals (Zn, Cu, Co, Pb, Cd and Mo) and their water-soluble forms were explored in soils of permanent grasslands of the foothills of the Hruby Jesenik Mts. Relationship between soil reaction and content and quality of organic matter was studied.

The total content of heavy metals ranged from 38.40 to 71.65 mg Zn $\cdot$ kg^{-1}; 10.47–17.46 mg Co $\cdot$ kg^{-1}; 14.30–41.42 mg Cu $\cdot$ kg^{-1}; 3.84–15.53 mg Pb $\cdot$ kg^{-1}; 0.104–0.323 mg Cd $\cdot$ kg^{-1} and 0.129–0.617 mg Mo $\cdot$ kg^{-1}. Content of water-soluble forms ranged from 0.0016 to 1.0100 mg Zn $\cdot$ kg^{-1}; 0.0204–0.2605 mg Co $\cdot$ kg^{-1}; 0.0085–0.2413 mg Cu $\cdot$ kg^{-1}, and 0.0108–0.0485 mg Cd $\cdot$ kg^{-1} of soil. Soil reaction ranged from 4.09 to 5.43 (ie from extremely acid to acid). Results showed that decreasing of pH value caused significant increase of water-soluble fractions of zinc and cobalt content, especially when mineral and organic fertilisers (slurry) were applied. After compost application the inverse relationship water-soluble zinc content and pH was found. Interrelations were not statistically significant in this case.

On permanent grassland soils total organic carbon (TOC) content ranged from 0.60 to 2.55 %. Sum of humic substances (HS) ranged from 4.5 to 8.0 mg $\cdot$ kg^{-1}; with a 1.5–3.3 mg $\cdot$ kg^{-1} and 2.5–5.5 mg $\cdot$ kg^{-1} proportion of humic acids (HA) and fulvic acids (FA), respectively. Humification degree was low (< 20 %). After organic and mineral fertilizers application on permanent grassland soils statistically significant differences were discovered in TOC and HA (compost) content (between the individual rates of organic fertilisers). Because of FA prevailed in humus fractional composition they mostly contributed to the transformation and migration of heavy metals mobile forms. During the experiment with mineral and organic fertilisers the dependence of water-soluble heavy metals and organic matter content was statistically

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significant for cobalt and copper. Cobalt content was inversely proportionate to HA content (r = –0.4021). In a similar way the copper content decreased due to increasing of FA in soils (r = –0.3803).

Keywords: total heavy metals, water-soluble heavy metals, soil reaction, total organic carbon content, humic substances, humic acids, fulvic acids

Soil is the key component of environment and irreplaceable source of most of the biochemical-active heavy metals**,** which have an effect on man *via* the food chain. As important biogenic elements the heavy metals are on the one hand essential in terms of plant metabolism and on the other hand at high concentrations they may have a toxic effect on the cell and they influence the quality of plant-based products. When studying their bio-accessibility it is of most importance to carry out simultaneous soil monitoring together with monitoring of qualitative and quantitative parameters of soil organic matter and agrochemical soil properties. As the most important component of the soil ecosystem affecting both transport and mobilisation, and mobilisation and local accumulation of soil heavy metals is, in all probability, the soil organic matter. Out of the most important components in the soil was monitored the total content of humus, *humic substances* (HS), particularly the amount of *humic acids* (HA) and *fulvic acids* (FA). These components have an extremely strong effect on the mobility, bio--accessibility and toxicity of the heavy metals [1, 2]. Another very important parameter of soil fertility, which affects the mobility of heavy metals, is the soil reaction [3–7].

Material and methods

In a long-term field trial in the spring and autumn of 2008 and 2009 we took soil samples from *permanent grasslands* (PG) in the locality Rapotin [50°00′12″ N, 17°00′29″ E] (in the foothills of the Hruby Jesenik Mts.) with a view to studying the effect of soil reaction and some parameters of organic matter on the total contents and water-soluble form of heavy metals (Zn, Co, Cu, Pb, Cd and Mo).

Basic soil properties of selected locality are given in Table 1.

Table 1

Characteristics of the locality Rapotin

Altitude a.s.l. [m]	Average temperature [°C]	Annual precipitation [mm]	Soil type	Texture classes [%]			< 0.01 [mm]
				clay	silt	sand	
315–340	7.25	693	Haplic Cambisol	9.4	32.8	57.9	21.4

During the experimental years three experiments, each applying 3 rates of mineral and organic fertilisers, were conducted on the permanent grasslands as shown in Table 2.

The experiment was established in the form of a precise small-plot experiment on experimental plots of 12.5 m^2 each. Apart from the intensity of land use of the PG we monitored burdening of soil with graded rates of fertilisers converted to so-called *livestock units* (LU). All fertilisation treatments were established in 4 replications.

Table 2

Treatments of the experiment with mineral and organic (slurry and compost) fertilization

Treatments of fertilization	Livestock Unit [LU · ha^{-1}]	Dose of nutrition in mineral and organic* fertilizers [kg · ha^{-1}]			Cutting frequency
		N	P	K	
Extensive	0.9	60	30	60	2
Middle intensive	1.4	90	30	60	3
Intensive	2.0	120	30	60	4

* With added fertilization of mineral fertilizers.

Soil samples were taken from a depth of 0.05–0.20 m. Texture was made by the pipette method. In soil soil reaction was determined by the potentiometric method. The total and labile contents of selected trace elements were determined by flame or electrothermal atomic absorption spectrometry after extraction of the soil samples in *aqua regia* (total content) and in the solution of 0.01 M $CaCl_2$ (labile form). *Total carbon content* (TOC) was determined by *oxidimetric titration* [8]. Humic substances (HS) sum, humic acids (HA) sum and fulvic acids (FA) sum were determined by short fractionation method [9]. *Humification degree* (HD) was calculated according to Orlov [10].

The results were assessed using the programme Statistica 7.1 CZ by the method of variance analysis (ANOVA) followed by Fisher's test at a 95 % ($p < 0.05$) and 99 % level of significance ($p < 0.01$).

Results and discussion

The effect of fertilisation on heavy metals content in PG soil was monitored during applying mineral fertilisers, slurry and compost. Total contents of metals corresponded with data given in literature [5].

Table 3

Total content of selected heavy metals in soil [mg · kg^{-1} soil];
values show mean of experiments ± standard error

Treatments of fertilization	Zn	Co	Cu	Pb	Cd	Mo
Extensive	$55.02^a \pm 1.22$	$14.06^a \pm 0.25$	$20.14^a \pm 0.50$	$7.89^a \pm 0.25$	$0.17^a \pm 0.05$	$0.30^a \pm 0.02$
Middle intensive	$53.97^a \pm 1.10$	$13.64^a \pm 0.25$	$20.66^a \pm 0.54$	$8.05^a \pm 0.26$	$0.17^a \pm 0.04$	$0.32^a \pm 0.02$
Intensive	$52.91^a \pm 0.91$	$14.07^a \pm 0.27$	$21.34^a \pm 0.80$	$8.34^a \pm 0.37$	$0.17^a \pm 0.05$	$0.30^a \pm 0.02$

$p < 0.05$ – statistically significant at a 95 %; variants with identical letters express statistically insignificant differences.

Table 3 shows that graded rates of fertilisers gradually increased total contents of Cu and Pb (by 2.6 to 6.0 % relatively and 2.0 to 5.7 % relatively, respectively). Likewise Jezierska-Tys and Frac [11] and Mantovi et al [12] reported that total contents of these metals increased after application of graded rates of fertilisers. However, the application of fertilisers did not significantly ($p < 0.05$) affect their amount in the soil. These findings corresponded with experiments carried out by Erhart et al [13] who discovered that application of compost increased total amounts of Cd, Cu and Pb but not statistically significantly.

Table 4 shows that graded applications of fertilisers increased water-soluble zinc, cobalt and copper content. The highest fertiliser rate (equivalent to 2.0 LU per ha) increased the content of Zn, Co and Cu by 61.2 %, 16.2 % and 19.1 %, respectively.

Table 4

Water-soluble content of selected heavy metals in soil [$mg \cdot kg^{-1}$ soil]; values show mean of experiments ± standard error

Treatments of fertilization	Zn	Co	Cu	Cd
Extensive	0.085 ± 0.007	0.068 ± 0.005	0.068 ± 0.005	0.028 ± 0.001
Middle intensive	0.114 ± 0.014	0.071 ± 0.007	0.068 ± 0.004	0.030 ±0.001
Intensive	0.137 ± 0.031	0.079 ± 0.009	0.081 ± 0.007	0.029 ±0.001

Figure 1 shows that in terms of heavy metals the content of copper increased significantly ($p < 0.05$) in the experiment where slurry was applied. Erhart et al [13] also discovered that compost fertilisation significantly increased the content of copper.

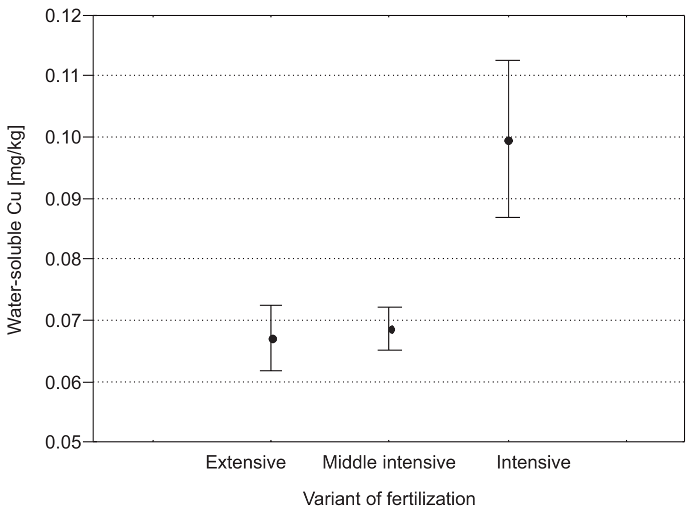

Fig. 1. Effect of fertilization on contents of water-soluble copper [$mg \cdot kg^{-1}$ soil]; errors bars represent Fisher test at $p < 0.05$

During experiments the dependence of water-soluble forms of total elements content was not high. In the slurry-fertilised experiment the most marked statistically highly significant correlation ($p < 0.01$) was found with copper ($r = 0.6311$). The proportion of water-soluble forms of Zn and Co in their total contents increased after the application of fertilisers (Zn from 0.155 % in the extensively loaded treatment to 0.259 % in the intensively loaded treatment and Co from 0.484 to 0.561 %).

During experiments the effect of pH on heavy metals content was also evaluated. Table 5 shows that particularly the water-soluble forms of heavy metals were significantly ($p < 0.05$, $p < 0.01$) dependent on the soil reaction.

Table 5

Effect of pH on the total content and soluble forms of heavy metals in soil

Heavy metals	Mineral fertilization	Compost	Slurry
Total content			
Zn	–0.5212**	0.2033	–0.2058
Co	–0.0324	0.0942	–0.0204
Cu	–0.0556	–0.0236	0.0598
Pb	0.1255	–0.1874	0.3492*
Cd	0.0018	–0.0445	–0.1456
Mo	0.2466	–0.0122	–0.2800
Water-soluble forms			
Zn	–0.5320**	–0.1464	–0.3319*
Co	–0.3628*	0.1822	–0.6253**
Cu	0.2458	0.0037	0.3225
Cd	0.1991	–0.1488	0.1368

* and ** – correlation coefficient significant at the 0.05 level ($p < 0.05$) and 0.01 level ($p < 0.01$), respectively.

The soil reaction affected particularly zinc content. After mineral fertilisers application total zinc content significantly ($p < 0.01$) correlated with pH – see Table 5. Total content of Zn and its soluble forms content increased due to soil acidification. Barancikova and Makovníkova [14] and Chukwuma et al [15] reported similar results. The same trend was monitored in the treatment fertilised with slurry. However a significant dependence ($p < 0.05$) on the soil reaction was discovered only with water-soluble zinc. Mosquera-Losada et al [16] likewise reported a significant effect of fertiliser application on Zn content. Correlation between water-soluble cobalt content and soil acidity was also important. The correlation coefficient $r = –0.6253$ demonstrates the strong effect of pH on water-soluble Co forms.

In Table 6 one may see that in average during experiments a significant ($p < 0.05$**)** effect of fertilisation with organic and mineral fertilisers on the content of C_{ox} was discovered. While in the treatment applying the lowest rate of fertilisers C_{ox} ranged at 1.35 %, the relative amount in the treatment with an intensive level of nutrition was by 12.6 % higher. In terms of the fractional composition of humus one may see a prevalence of fulvic acids (Table 6)**,** which had a predominant effect on the transformation and migration of heavy metals mobile forms.

Table 6

Fractional composition of humic substances in soil;
values show mean of experiments ± standard error

Treatments of fertilization	TOC [%]	HS	HA	FA
		[mg · kg^{-1}]		
Extensive	1.35^{a} ± 0.04	6.17^{a} ± 0.12	2.19^{a} ± 0.05	3.98^{a} ± 0.10
Middle intensive	1.37^{a} ± 0.03	6.20^{a} ± 0.11	2.25^{a} ± 0.05	3.90^{a} ± 0.09
Intensive	1.52^{b} ± 0.05	6.18^{a} ± 0.12	2.28^{a} ± 0.07	3.88^{a} ± 0.09

$p \le 0.05$ – statistical significance at a 95 % level of significance; variants with identical letters express statistically insignificant differences.

The effect of fertilisation on HA content was found to be significant ($p < 0.05$) in the experiment where compost was applied. Based on the rate of compost fertilisation HA content increased from 2.09 (extensive) to 2.45 % (intensive); ie by 17.2 % relatively. Zhang et al [17] also reported that high-quality humus substances (HS) increased due to the application of organic fertilisers.

The sum of humic substances, sum of humic acids and fulvic acids had a significant effect ($p < 0.05$, $p < 0.01$) on the content of water-soluble forms of heavy metals. In the experiment with slurry cobalt content decreased significantly due to HA content ($r = –0.4021$). During experiment with mineral fertilisers a significant correlation was discovered between FA content and the amount of water-soluble copper ($r = –0.3803$), as one may see in Fig. 2.

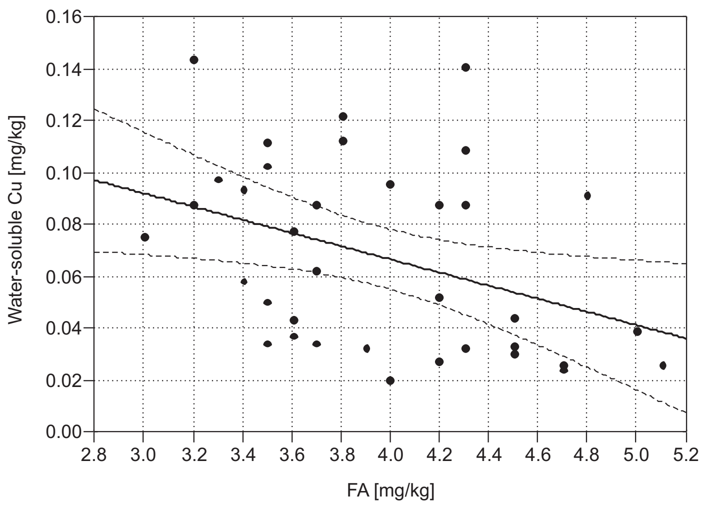

Fig. 2. Correlation between FA content and water-soluble copper [mg · kg^{-1} soil]

After compost amendment no significant ($p < 0.05$) correlation between the organic matter and content of heavy metals was detected.

Conclusions

Graded rates of fertilisers gradually increased the total contents of Cu and Pb but not statistically significantly. A fertiliser rate equivalent to 2.0 LU per ha increased the water-soluble contents of Zn and Co by 61.2 % and 16.2 %, respectively. In slurry-fertilised experiments also significantly increased of Cu by 19.1 % was found. Significantly dependent on soil reaction were particularly heavy metals in water-soluble form, most markedly zinc. Water-soluble Zn content was increasing due the effect soil acidification. Important was the correlation between water-soluble cobalt and soil acidity (r = 0.6253). Fertilisation increased TOC content in soil by 12.6 %, relatively. In terms of fractional composition of humus it is evident the prevalence of fulvic acids. During compost application the effect of fertilisation on HA content was significant. After slurry application content of cobalt considerably decreased due to increasing of HA content (r = –0.4021).

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WPŁYW MATERII ORGANICZNEJ I pH NA MOBILNOŚĆ NIEKTÓRYCH MIKROSKŁADNIKÓW W GLEBACH TRWAŁYCH UŻYTKÓW ZIELONYCH NA POGÓRZU HRUBÝ JESENÍK

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Abstrakt: W latach 2008–2009 oceniano ogólną zawartość niektórych metali ciężkich (Zn, Cu, Co, Pb, Cd i Mo) oraz ich form wodnorozpuszczalnych w glebach trwałych użytków zielonych Pogórza Hrubý Jeseník. Badano zależności między odczynem gleb i zawartością oraz jakością materii organicznej.

Ogólna zawartość metali ciężkich mieściła się w zakresach: 38,40–71,65 mg Zn · kg^{-1}; 10,47–17,46 mg Co · kg^{-1}; 14,30–41,42 mg Cu · kg^{-1}; 3,84–15,53 mg Pb · kg^{-1}; 0,104–0,323 mg Cd · kg^{-1} i 0,129–0,617 mg Mo · kg^{-1} gleby. Zawartość form wodnorozpuszczalnych wahała się w granicach: 0,0016 to 1,0100 mg Zn · kg^{-1}; 0,0204–0,2605 mg Co · kg^{-1}; 0,0085–0,2413 mg Cu · kg^{-1} i 0,0108–0,0485 mg Cd · kg^{-1} gleby. pH gleb wahało się od 4,09 do 5,43 (tj. odczyn od bardzo kwaśnego do kwaśnego). Wykazano, że obniżenie wartości pH powodowało istotny wzrost zawartości frakcji wodnorozpuszczalnych cynku i kobaltu, zwłaszcza gdy zastosowano nawozy mineralne i organiczne (gnojowicę). Po zastosowaniu kompostu stwierdzono odwrotną zależność między zawartością frakcji wodnorozpuszczalnego cynku i pH. Zależności te nie były istotne statystycznie.

Całkowita zawartość węgla organicznego (TOC) w glebach trwałych użytków zielonych wahała się od 6,0 do 25,5 g · kg^{-1}. Suma substancji humusowych (HS) wahała się od 4,5 do 8,0 mg · kg^{-1}; z udziałem odpowiednio 1,5–3,3 mg · kg^{-1} kwasów huminowych (HA) i 2,5–5,5 mg · kg^{-1} kwasów fulwowych (FA). Stopień humifikacji był niski (< 20%). Po zastosowaniu nawozów organicznych i mineralnych na glebach trwałych użytkach zielonych wykazano statystycznie istotne różnice w zawartości TOC i HA (kompost) (między poszczególnymi dawkami nawozów organicznych). Ponieważ FA przeważają w składzie frakcyjnym próchnicy, najczęściej one biorą udział w przemianach i przemieszczaniu się mobilnych form metali ciężkich. W trakcie doświadczenia z nawozami mineralnymi i organicznymi zależność między zawartością frakcji wodnorozpuszczalnych metali ciężkich i materii organicznej była statystycznie istotna dla kobaltu i miedzi. Zawartość kobaltu była odwrotnie proporcjonalna do zawartości HA ($r = -0{,}4021$). Podobnie zawartość miedzi obniżała się wraz ze zwiększającą się zawartością FA w glebach ($r = -0{,}3803$).

Słowa kluczowe: zawartość całkowita metali ciężkich, wodnorozpuszczalne formy metali ciężkich, odczyn gleby, zawartość całkowita węgla organicznego, substancje humusowe, kwasy huminowe, kwasy fulwowe