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Beata KUZIEMSKA[1] and Stanisław KALEMBASA[2]

EFFECT OF LIMING AND SEWAGE SLUDGE ADDITION ON THE DISTRIBUTION OF THE FRACTION OF HEAVY METALS IN SOIL CONTAMINATED WITH NICKEL

WPŁYW WAPNOWANIA I DODATKU OSADU ŚCIEKOWEGO NA ROZMIESZCZENIE FRAKCJI WYBRANYCH METALI CIĘŻKICH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Abstract: The total content of Zn and Cr and its distribution in fractions separated according to the BCR procedure was determined in soil taken after a three-year pot experiment. The following factors were taken into account in the experiment: I – liming (0 Ca and Ca according to 1 Hh of soil as $CaCO_3$); II – addition of sludge (without addition of sludge and addition of sludge from the wastewater treatment in Siedlce, applied at 2 gC $\cdot$ kg^{-1} of soil); III – varied level of contamination with nickel (0, 50 and 100 mgNi $\cdot$ kg^{-1} of soil as aqueous solution of $NiCl_2 \cdot 6\ H_2O$). Orchard grass (*Dactylis Glomerata* L.) was used as the test plant. The total content of Zn and Cr in soil was determined by ICP-AES, and the fractions of those metals by the 3-step BCR procedure. The total content of the metals in the analysed soil did not exceed the highest acceptable standards. Liming reduced the metal content in the exchangeable, reducible and organic matter-related fraction and increased their content in the residual fraction.

Addition of sludge reduced the Zn and Cr content in the reducible and residual fraction and increased their total content and share in the organic matter- and sulphides-related fraction. No effect of the varied Ni amount on the total content of Zn and Cr or their distribution in the fractions has been found.

Keywords: soil, nickel, liming, sewage sludge, sequential extraction procedure, zinc, chromium

Heavy metals play an important role in contamination and degradation of the natural environment, including the soil. Their characteristic features include accumulation in the environment, especially in live organisms, which increases the intensity of their interactions [1].

[1] Department of Soil Science and Plant Nutrition, Siedlce University of Natural Science and Humanities, ul. B. Prusa 14, 08–110 Siedlce, Poland, phone: +48 25 643 13 56, email: bak.kuz@interia.pl

[2] Department of Soil Science and Agricultural Chemistry, Siedlce University of Natural Science and Humanities, ul. B. Prusa 14, 08–110 Siedlce, Poland, email: kalembasa@uph.edu.pl

The behaviour of heavy metals in soils (solubility, mobility, availability) is affected mainly by: soil pH, red-ox potential and presence of mineral (iron and manganese compounds, silty minerals) and organic (soil humus) colloids [2–4].

The total content of heavy metals in the soil cannot be regarded as an indicator of their bioavailability [5]. Organic matter present in soil as humic substances as well as that introduced to the soil (substrate) with natural, organic, organic and mineral fertilisers, restricts the amount of heavy metals available to plants [6, 7].

Among soil's ecotoxicologic features, the speciation of heavy metals is of special importance as it can be related to their bioavailability. Commonly applied methods of sequential extraction enable identification of the chemical fraction of heavy metals in the soil environment as well as evaluation of their availability and potential toxicity to the biotic elements of the trophic chain [8–10].

Identification of element species combined with modern statistical methods allow a range of factors to be determined, such as bioavailability, accumulation, migration, toxicity, solubility and sorption [11].

The aim of this study was to determine the effect of liming and the application of sludge on the content of zinc and chromium in different fractions separated in accordance with the BCR procedure in soil contaminated with nickel.

Materials and methods

Soil after a three-year pot experiment, conducted in a random arrangement in triplicate, was used in the study. The experiment was conducted in the years 2006–2008 at the experimental facility of the Siedlce University of Natural Sciences and Humanities. The following factors were considered: I – liming (no liming and liming according to 1 Hh of soil as $CaCO_3$); II – addition of sludge (control and addition of sludge from a wastewater treatment plant in Siedlce, used in amounts corresponding to 2 gC $\cdot$ kg^{-1} of soil); III – varied contamination of soil with nickel (0, 50 and 100 mgNi $\cdot$ kg^{-1} of soil as aqueous solution of $NiCl_2 \cdot 6H_2O$). Liming, sludge and nickel were applied in April–May 2006. Orchard grass (*Dactylis glomerata* L.) whose 4 cuts were harvested each season, was used as the test plant. The soil material used in the experiment was taken from the layer of 0–20 cm of grey-brown podsolic soil with the granulometric composition of loamy sand [12]. The main properties of the soil before the experiment are shown in Table 1.

Table 1

Some properties of soil used in the pot experiment

pH 1 M KCl	C_{org}	N_{tot}	Available		Total		
			P	K	Ni	Cr	Zn
	[g $\cdot$ kg^{-1} of soil]		[mg $\cdot$ kg^{-1} of soil]		[mg $\cdot$ kg^{-1} of soil]		
5.6	7.9	0.98	69	75	5.67	2.46	7.93

The chemical composition of the sludge used in the experiment is shown in Table 2 [9].

Table 2

Chemical composition of sewage sludge from Siedlce

Component	[$g \cdot kg^{-1}$ d.m.]	Component	[$mg \cdot kg^{-1}$ d.m.]
N	60.5	Cd	1.99
P	31.2	Pb	50.5
K	4.28	Ni	20.6
Ca	39.6	Fe	10850
Mg	8.42	Cu	137.7
C_{org}	371	Zn	1276.8
MO	640	Cr	30.14
Dry matter [$g \cdot kg^{-1}$]		180	

To make the experiment results more accurate, 15 dm^3 pots, each containing 10 kg of soil, were put into additional containers to prevent the solution from leaking out of the pots. The pots were placed in the open and moisture of 60 % of field water capacity was maintained in them. The soil was analysed after the last cut of the test plant, in the third year of the experiment. The soil pH was determined in 1 mol/dm^3 KCl by the potentiometric method. The total zinc and chromium content in soil was determined by the ICP-AES method following the sample mineralisation in a muffle furnace at a temperature of 450 ^oC and dissolving the ash in a 10 % solution of HCl. The metal fractions were determined by the three-step method of sequential fractionation, proposed by *Community Bureau of Reference* (BCR) [13]. The method diagram is provided in Table 3.

Table 3

A diagram of the BCR metal sequential extraction method [10]

Fraction	Name fractions	Extraction reagents	pH
F_1	Exchangeable and acid soluble	0.1 M CH_3COOH	3.0
F_2	Reducible	0.5 M $NH_2OH \cdot HCl$	1.5
F_3	Oxidisable	8.8 M H_2O_2 + 1 M CH_3COONH_4	2.0
F_4	Residual	Calculated as difference between total content and sum three previously separated fractions	—

The results were worked out statistically by analysis of variance with the Fisher--Snedecor distribution, according to the F.R. Anal. Var 4.1 program and the value of $LSD_{0.05}$ was calculated by Tukey's test. Moreover, a linear correlation analysis was also performed to determine the relationship between the features under study.

Results and discussion

This study has shown clearly that the total content of the metals – zinc and chromium – in the analysed soil, taken after completion of a three-year pot experiment, did not exceed the value of the geochemical background and lay within the range of natural values [2, 14]. Similar values of chromium content in podsolic soils have been found by Kalembasa and Pakula [3] and Pakuła and Kalembasa [15].

The total zinc content in the soil under study (Table 4) ranged from 7.90 to 14.20 mg · kg^{-1} of soil and it significantly depended on liming and the addition of sludge. Liming resulted in a slight, yet statistically proven, increase in the content of the metal in the soil under study, which can be attributed to the fact that the calcium fertiliser introduced to the soil was probably contaminated with zinc compounds.

Table 4

The content [mg · kg^{-1} of soil] of zinc in fractions determined by the BCR method in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1 F_2 F_3 F_4	0.66 20.2 1.52 3.70	0.68 2.06 1.63 3.53	0.70 2.05 1.60 3.55	0.39 2.47 1.26 3.88	0.37 2.35 1.30 4.00	0.37 2.41 1.30 3.98
Sum of fractions	Σ	7.90	7.90	7.90	8.00	8.02	8.06
Sludge from Siedlce	F_1 F_2 F_3 F_4	0.47 4.78 4.04 4.61	0.45 4.81 4.06 4.48	0.47 4.74 4.05 4.64	0.37 4.19 3.50 6.14	0.39 4.27 3.51 6.03	0.38 4.22 3.55 5.95
Sum of fractions	Σ	13.9	13.8	13.9	14.2	14.2	14.1
			F_1	F_2	F_3	F_4	Σ
$LSD_{(0.05)}$ for: liming sludge from Siedlce doses of nickel			 0.013 0.013 n.s.	 0.047 0.047 n.s.	 0.053 0.053 n.s.	 0.196 0.196 n.s.	 0.157 0.157 n.s.

n.s. – not significant.

Sludge from the wastewater plant in Siedlce significantly increased the total zinc content in soil (the amount of zinc introduced to soil with the waste material is equal to 6.88 mg · kg^{-1}).

The content of the metal in the sequentially isolated fractions in soil (Table 4 and 5) varied significantly, with the variance being caused both by liming and by the addition of sludge. Liming significantly reduced the amount of zinc in the exchangeable fraction (F_1) and in that related to organic matter (F_3) and increased its amount in the residual fraction (F_4). The effect of the factor analysed here on the content of zinc in the fraction associated with iron and manganese oxides (F_2) was unclear. Liming in control pots significantly increased the content of the zinc fraction, whereas the opposite effect was observed in soils to which sludge was added, which can be attributed to the interaction of both the factors analysed in the experiment.

Table 5

The percentage share of the zinc fraction in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1 F_2 F_3 F_4	8.61 25.60 19.24 46.55	8.61 26.08 20.63 44.68	8.86 25.95 20.25 44.94	4.88 30.87 15.75 48.50	4.61 29.30 16.21 49.88	4.59 29.90 16.13 49.38
Sum of fractions	Σ	100	100	100	100	100	100
Sludge from Siedlce	F_1 F_2 F_3 F_4	3.38 34.39 29.06 33.17	3.26 34.86 29.42 32.47	3.38 34.10 29.14 33.38	2.61 29.51 24.65 43.23	2.75 30.07 24.72 42.46	2.70 29.93 25.18 42.19
Sum of fractions	Σ	100	100	100	100	100	100

Organic matter introduced into soil as sludge reduced the content of the analysed metal in the exchangeable fraction (F_1) and in the residual one (F_4), increased its content in the fraction associated with organic matter and with sulphides (F_3), without clearly differentiating its content in the reducible fraction (F_2).

Earlier studies [16] have provided similar findings concerning organic waste material.

This study did not find a significant effect of a varying content of nickel in soil on the total content of zinc or its distribution in different fractions. The average percentage of the metal under study in the isolated fractions can be shown in the following sequence of decreasing values: $F_4 > F_2 > F_3 > F_1$.

The total content of chromium in the analysed soil ranged from 2.40 to 2.61 mg · kg^{-1} of soil. Both the total content and its content in each fraction depended significantly on liming and the addition of sludge (Table 6 and 7). No effect of the factors under analysis were observed on the content of chromium in the residual fraction (F_4).

Introducing calcium carbonate to the soil resulted in a slight increase in the total chromium content, which – as with zinc (that has been discussed above) – can be attributed to contamination of the calcium fertilisers.

Since chromium in the amount of 0.16 mg · kg^{-1} of soil was introduced with sludge, this factor significantly differentiated the metal content.

A chemical analysis showed a varied content of chromium in the sequentially isolated fractions (Table 6 and 7). The smallest portion of the analysed metal was isolated in the exchangeable fraction (F_1): 2.28–4.28 % of its total content, and the largest was in the residual fraction (F_4): 24.72–58.81 % of the total content.

Table 6

The content [mg · kg^{-1} of soil] of chromium in fractions determined by the BCR method in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1	0.099	0.102	0.100	0.085	0.087	0.084
	F_2	0.289	0.286	0.290	0.358	0.350	0.357
	F_3	0.660	0.680	0.690	0.580	0.570	0.570
	F_4	1.352	1.342	1.350	1.417	1.438	1.429
Sum of fractions	Σ	2.40	2.41	2.43	2.44	2.44	2.44
Sludge from Siedlce	F_1	0.073	0.070	0.075	0.059	0.062	0.064
	F_2	0.376	0.362	0.360	0.305	0.273	0.294
	F_3	0.861	0.873	0.878	0.730	0.740	0.780
	F_4	1.220	1.255	1.247	1.496	1.565	1.462
Sum of fractions	Σ	2.53	2.56	2.56	2.59	2.61	2.60
			F_1	F_2	F_3	F_4	Σ
$LSD_{(0,05)}$ for:							
liming			0.003	n.s.	0.017	n.s.	0.015
sludge from Siedlce			0.003	0.006	0.017	n.s.	0.015
doses of nickel			n.s.	0.008	n.s.	n.s.	n.s.

n.s. – not significant.

Table 7

The percentage share of the chromium fraction in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1	4.13	4.23	4.12	3.48	3.57	3.44
	F_2	12.04	11.87	11.93	14.67	14.34	14.63
	F_3	27.50	28.22	28.40	23.77	23.36	23.36
	F_4	56.33	55.68	55.55	58.08	58.73	58.57
Sum of fractions	Σ	100	100	100	100	100	100
Sludge from Siedlce	F_1	2.89	2.73	2.93	2.28	2.38	2.46
	F_2	14.86	14.14	14.06	11.78	10.46	11.31
	F_3	34.03	34.10	34.29	28.19	28.35	30.00
	F_4	51.11	49.03	48.72	57.75	58.81	56.23
Sum of fractions	Σ	100	100	100	100	100	100

The average percentage of the chromium fractions can be shown in the following sequence of decreasing values: $F_4 > F_2 > F_3 > F_1$. A similar sequence has been presented in studies by Bacon et al [17], Kalembasa and Pakula [3] and Pakula and Kalembasa [16].

Wherever liming was applied, it reduced the portion of the metal in the exchangeable fraction (F_1), which leads one to the conclusion that it is a good method to immobilise chromium, and to reduce its toxicity as a result. This factor also reduced the portion of the metal in the fraction bound with organic matter and sulphides (F_3).

Sludge introduced into soil reduced the portion of chromium in the exchangeable fraction (F_1) and in the reducible fraction (F_2) and increased its content in the fraction bound with organic matter and with sulphides (F_3). No effect of the factor under analysis was observed on the content of chromium in the residual fraction (F_4).

The statistical analysis did not confirm any significant effect of increasing the content of nickel in soil on the total content of chromium and its portion in the fractions determined according to the BCR procedure, except for the fractions associated with iron and manganese oxides (F_2), but the effect was not clearly defined.

Table 8 shows the values of pH of the soil, determined in 1M KCl solution, ranging from 5.80 to 6.80.

Table 8

pH of soil in 1 M KCl

Fertilisation	Liming					
	0 Ca			Ca to 1 Hh		
	Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
	0	50	100	0	50	100
Without organic fertilisation	5.97	5.84	5.80	6.64	6.59	6.80
Sludge from Siedlce	5.99	5.80	5.80	6.60	6.71	6.72
$LSD_{(0,05)}$ for:						
liming	0.165					
sludge from Siedlce	n.s.					
doses of nickel	n.s.					

n.s. – not significant.

The pH value of limed soil was significantly higher than that of unlimed soil. No effect of the other two factors on the feature was observed.

Significant relationships were observed in the analysed soil between the parameters under examination, which were confirmed by the analysis of correlation.

The values of the correlation coefficient are given in Tables 9 and 10.

Particularly noteworthy is a highly significant negative correlation coefficient between the pH of soil and the portion of zinc in the exchangeable fraction (F_1).

Table 9

Simple correlation coefficients between fractions of zinc and selected properties of soil

Parameter	Fractions			
	F_1	F_2	F_3	F_4
Zn_{tot}	n.s.	0.974**	0.976**	0.840**
pH	–0.766**	n.s.	n.s.	n.s.

n.s. – not significant; ** α = 0.01.

Table 10

Simple correlation coefficients between fractions of chromium and selected properties of soil

Parameter	Fractions			
	F_1	F_2	F_3	F_4
Pb_{tot}	–0.943**	n.s.	0.691*	n.s.
pH	n.s.	n.s.	n.s.	n.s.

n.s. – not significant; * α = 0.05; ** α = 0.01.

It can be concluded that both of the factors examined in the experiment (liming and applying sludge) modified the total content of zinc and chromium in soil and their portion in fractions isolated according to the BCR procedure. Both lime and sludge increased the total amount of both the metals under study in the soil. Liming significantly reduced the amount of both metals in the exchangeable fraction (F_1) and in that bound to organic matter and sulphides (F_3); it also reduced the portion of zinc in the fraction associated with iron and manganese oxides (F_2).

Sludge reduced the portion of both metals in the exchangeable fraction (F_1) and increased its content in the fraction bound to organic matter and sulphides (F_3).

Both calcium carbonate and sludge reduced the mobility of the heavy metals under study in soil, which is in line with the findings of a study conducted by Karczewska et al [18].

This study has not shown a significant effect of an increasing content of nickel in soil on the total content of zinc and chromium in the soil and their portion in fractions isolated according to the BCR procedure.

Conclusions

1. The total content of zinc and chromium did not exceed the value of the geochemical background.

2. The smallest amount of zinc and chromium in the analysed soil was found in the exchangeable fraction (F_1), and the largest amount was in the residual fraction (F_4).

3. Liming reduced the portion of both metals in the exchangeable fraction (F_1) and in the fraction associated with organic matter and with sulphides (F_3); it also increased their total content.

4. Sludge reduced the portion of zinc and chromium in the exchangeable fraction (F_1) and increased its content in the fraction bound to organic matter and with sulphides (F_3).

5. This study did not find a significant effect of a varying content of nickel in soil on the total content of zinc and chromium in soil and its distribution in different fractions.

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WPŁYW WAPNOWANIA I DODATKU OSADU ŚCIEKOWEGO NA ROZMIESZCZENIE FRAKCJI WYBRANYCH METALI CIĘŻKICH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Katedra Gleboznawstwa i Chemii Rolniczej
Uniwersytet Przyrodniczo-Humanistyczny w Siedlcach

Abstrakt: W glebie branej po trzyletnim doświadczeniu wazonowym badano ogólną zawartość Zn i Cr oraz ich rozmieszczenie we frakcjach wydzielonych według procedury BCR. W doświadczeniu uwzględniono następujące czynniki: I – wapnowanie (0 Ca i Ca wg 1 Hh gleby w formie $CaCO_3$); II – dodatek osadu ściekowego (bez dodatku osadu ściekowego i dodatek osadu ściekowego pochodzącego z oczyszczalni ścieków w Siedlcach, stosowanego w dawce odpowiadającej ilości 2 gC $\cdot$ kg^{-1} gleby); III – zróżnicowane zanieczyszczenie gleby niklem (0, 50 i 100 mgNi $\cdot$ kg^{-1} gleby w formie roztworu wodnego $NiCl_2 \cdot 6H_2O$). Rośliną testową była trawa – kupkówka pospolita (*Dactylis glomerata* L.). Ogólną zawartość Zn i Cr w glebie oznaczono metodą ICP-AES, a frakcje tych metali 3-stopniową metodą BCR. Ogólna zawartość badanych metali w analizowanej glebie nie przekraczała dopuszczalnych norm. Wapnowanie spowodowało zmniejszenie udziału obu metali we frakcji wymiennej, redukowalnej i związanej z substancją organiczną oraz zwiększenie ich ogólnej zawartości i udziału we frakcji rezydualnej.

Dodatek osadu ściekowego wpłynął na zmniejszenie ilości Zn i Cr we frakcji redukowalnej i rezydualnej oraz zwiększenie ich ogólnej zawartości i udziału we frakcji związanej z materią organiczną i siarczkami. Nie wykazano wpływu zróżnicowanej ilości Ni w glebie na ogólną zawartość Zn i Cr oraz ich rozmieszczenia w wydzielonych frakcjach.

Słowa kluczowe: gleba, nikiel, wapnowanie, osad ściekowy, analiza sekwencyjna, cynk, chrom