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EFFECT OF SOME SUBSTANCES ON THE CONTENT OF ORGANIC CARBON AND MINERAL COMPONENTS IN SOILS CONTAMINATED WITH CHROMIUM

WPŁYW NIEKTÓRYCH SUBSTANCJI NA ZAWARTOŚĆ WĘGLA ORGANICZNEGO I SKŁADNIKÓW MINERALNYCH W GLEBACH ZANIECZYSZCZONYCH CHROMEM

Abstract: The aim of the study was to determine the effects of compost, zeolite and CaO used as neutralizing substances on the content of organic carbon and mineral components in soils contaminated with Cr(III) and Cr(VI).

The content of organic carbon and mineral components varied depending on the form and the dose of chromium and neutralizing substances used. Increasing contamination of soil with Cr(III) and Cr(VI) resulted in the growth of the content of organic carbon and available forms of potassium and chromium(VI) resulted in a reduction of the content of available magnesium. Among the substances applied, compost and zeolite had larger effects than calcium oxide on the examined properties of soil, particularly in the case of organic carbon, phosphorus and magnesium. Compost and zeolite resulted in increasing the content of organic carbon and magnesium, and decreasing the content of phosphorus in the soil.

Keywords: chromium contamination, compost, zeolite, CaO, soil, organic carbon, available mineral components

Progressive degradation of the natural environment, a consequence of technological development, results in increasing contamination of the environment with xenobiotics. These include heavy metals detrimental to the natural environment, such as chromium. Chromium compounds most often found in the natural environment are of the +3 and +6 oxidation state. They differ in chemical properties as well as in their chemical and biological reactivity [1]. Chromium(III) found in a polluted natural environment is insoluble and mobile only to a slight extent, but the presence of organic ligands (*eg* humic, fulvic acids) causes complexation of Cr(III). This results in increasing solubility

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of trivalent chromium, hence its improved mobility and accessibility for living organisms. Chromium(VI) is regarded as more accessible due to its solubility, strong oxidizing properties and permeability through cell membranes [2].

The aim of the research conducted was to determine the effect of soil contamination with increasing doses of trivalent and hexavalent chromium on the content of organic carbon, available forms of phosphorus, magnesium and potassium in the soil, and to determine the role of the additives – compost, zeolite and calcium oxide – in mitigating the results of this contamination.

Material and methods

The experiment with 4 replicates was established in the vegetation hall of the University of Warmia and Mazury in Olsztyn (Poland) in polyethylene pots of 9.5 kg capacity in 2007. The soil of granulometric composition of loamy sand was characterized by the following properties: pH_{KCl} – 4.4, *hydrolytic acidity* (HA) – 44.00 $mmol(H^+) \cdot kg^{-1}$ soil, sum of *exchangeable base cations* (EBC) – 90.00 $mmol \cdot kg^{-1}$, *cation exchangeable capacity* (CEC) – 134.00 $mmol \cdot kg^{-1}$, *base saturation* (BS) – 67.16 %, content of C_{org} – 5.63 $g \cdot kg^{-1}$, content of available: phosphorus – 55.15 $mg \cdot kg^{-1}$, potassium – 56.27 $mg \cdot kg^{-1}$ and magnesium – 50.39 $mg \cdot kg^{-1}$. Normal brown soil under natural conditions was used. Before placing in pots, the soil was contaminated with water solutions of chromium(III) in the form of $KCr(SO_4)_2 \cdot 2H_2O$ and chromium(VI) in the form of $K_2Cr_2O_7$ in the following amounts: 0 (control), 25, 50, 100 and 150 $mg\ Cr \cdot kg^{-1}$ of the soil. Basic macro- and microelements were introduced to the soil in the following amounts (per 1 kg of the soil): 110 mg N [$CO(NH_2)_2$ + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ + $(NH_4)_2HPO_4$], 50 mg P [$(NH_4)_2HPO_4$], 110 mg K [KCl + $KCr(SO_4)_2 \cdot 12H_2O$ + $K_2Cr_2O_7$], 50 mg Mg [$MgSO_4 \cdot 7H_2O$], 5 mg Mn [$MnCl_2 \cdot 4H_2O$], 5 mg Mo [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] and 0.33 mg B [$H_3BO_3$], as well as additives mitigating the effects of chromium: compost and zeolite in the amount of 3 % in relation to the weight of the soil, and calcium oxide in the amount equal to 1 hydrolytic acidity (Hh). The experiment involved cultivation of spring rape (*Brassica napus* var. *oleifera*) – main crop and yellow lupin (*Lupinus luteus* L.) – successive crop. The density of spring rape was 25 pieces per pot, and yellow lupin was 18 pieces. Spring rape and yellow lupin were harvested in the blossoming phase.

Before establishing the experiment and after the harvest of crops, samples of soil were taken from each pot, dried at room temperature, crushed and sieved through a 1 mm mesh. In the material obtained, selected properties were analysed using the following methods: content of *organic carbon* (C_{org}) – according to the Tiurin method in potassium dichromate with dilute sulfuric(VI) acid [3], content of phosphorus and magnesium – according to the Egner-Riehm method [3], content of magnesium – according to Schachtschabel method [3]. The obtained results were statistically analysed with the use of STATISTICA software [4] using an ANOVA three-factor analysis of variance (1st factor – contamination type, 2nd factor – chromium dose, 3rd factor – type of neutralizing substance). The correlation between chromium dose and content of organic C and macroelements in soil was also calculated.

Results and discussion

Soil contamination with chromium(III) and chromium(VI) as well as the neutralizing additives applied significantly modified the content of organic carbon in the examined soil (Table 1).

In the series without neutralizing additives, increasing soil contamination with Cr(III) and Cr(VI) resulted in a significant growth of the content of organic carbon in the examined soil. Soil contaminated with trivalent chromium revealed a slightly higher content of organic carbon. Neutralizing additives in the form of compost, zeolite and calcium oxide significantly affected the content of the component under discussion. The application of zeolite in the series with chromium(VI) proved most beneficial, resulting in the growth of the mean content of organic carbon by 21 % in relation to the control series. The application of calcium oxide contributed to a significant reduction in the mean content of organic carbon in both contamination variants. However, the effect of CaO was larger in objects with chromium(III).

The content of available phosphorus was at a varied level, depending on the dose and the form of chromium, as well as on the application of compost, zeolite and calcium oxide (Table 2). Doses of 25 and 50 cm^3 of Cr(VI) $\cdot$ kg^{-1} of soil most strongly reduced the content of phosphorus with reference to the control object. In the series with Cr(III), a dose of 100 $cm^3 \cdot kg^{-1}$ of soil most strongly affected the content of the component under discussion, causing its 28 % reduction in relation to the control series. Compost and zeolite had a negative effect on the concentration of available phosphorus in soil contaminated both with trivalent and hexavalent chromium. Additionally, an increase of phosphorus content was also observed after applying CaO in objects with Cr(III).

The content of available potassium in the examined soil was affected by the dose and the form of chromium, as well as mitigating additives used in the experiment (Table 2).

A higher average content of potassium was revealed by objects contaminated with chromium(VI). Increasing doses of trivalent and hexavalent chromium in the control series had a positive effect on the content of available potassium in the soil. In objects with Cr(VI), this effect was higher, since it resulted in an almost three-fold increase in the content of the component under discussion. Among the substances applied, the strongest effects were caused by compost, which reduced the average content of available potassium in the soil, particularly in objects with chromium(VI). An increase in the potassium content in soil was also found after application of zeolite, but only in pots with chromium(III).

The effect of soil contamination with Cr(III) and Cr(VI) on the content of available magnesium was modified by the amount of the dose and by addition of neutralizing substances to the soil (Table 2). Hexavalent chromium in the control series resulted in a significant reduction in available magnesium concentration in the analysed soil, however, it was not a clearly oriented effect. An exception was contamination with 25 cm^3 Cr(VI) $\cdot$ kg^{-1} of soil, which increased the content of the component under discussion by a few percent. Among the mitigating substances, the addition of compost had the strongest effect on the average content of magnesium, and the lowest effect was the addition of zeolite.

Table 1

C_{org} content in soil after crop harvest [g · kg^{-1} d.m. of soil]

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
0	6.00	6.08	9.75	5.85	6.92	6.00	6.08	9.75	5.85	6.92
25	6.98	6.23	8.85	5.48	6.89	6.83	7.28	7.50	7.13	7.19
50	7.50	8.10	7.80	5.10	7.13	7.20	7.88	7.73	6.23	7.26
100	7.65	8.33	6.23	6.15	7.09	7.58	8.18	8.33	6.00	7.52
150	7.88	8.85	6.00	5.85	7.15	7.80	9.68	9.60	5.78	8.22
Average	7.20	7.52	7.73	5.69	7.04	7.08	7.82	8.58	6.20	7.42
r	0.864**	0.905**	–0.961**	0.377	0.801**	0.921**	0.962**	0.229	–0.438	0.972**
LSD	a – 0.10**, b – 0.16**, c – 0.14**, a · b – 0.22**, a · c – 0.20**, b · c – 0.32**, a · b · c – 0.45**									

LSD for: a – contamination type, b – chromium dose, c – type of neutralizing substance; n.i. – insignificant differences; * and ** – difference significant at p = 0.05 and p = 0.015, respectively; r – correlation coefficient calculated between chromium dose and C_{org} content in soil.

Table 2

Content of available phosphorus, potassium and magnesium in soil after crop harvest [mg · kg^{-1} d.m. of soil]

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
Phosphorus										
0	137.8	84.4	62.6	179.7	116.1	137.8	84.4	62.6	179.7	116.1
25	101.6	79.4	65.4	159.6	101.5	83.6	83.0	68.3	110.0	86.2
50	100.9	68.6	75.6	176.4	105.4	97.3	84.6	75.7	94.6	88.1
100	99.7	63.7	80.9	152.9	99.3	122.3	90.1	97.1	89.5	99.8
150	102.7	59.5	84.0	129.0	93.8	129.8	95.8	112.9	85.8	106.1
Average	108.5	71.1	73.7	159.5	103.2	114.2	87.6	83.3	111.9	99.3
r	–0.588	–0.951**	0.952**	–0.893**	–0.726*	0.283	0.951**	0.996**	–0.753**	–0.314
LSD	a – 1.85**, b – 2.93**, c – 2.62**, a · b – 4.15**, a · c – 3.71**, b · c – 5.88**, a · b · c – 8.30**									
Potassium										
0	15.7	15.7	17.3	20.6	17.3	15.7	15.7	17.3	20.6	17.3
25	15.7	15.7	19.0	19.0	17.3	20.6	15.7	22.2	30.3	22.2
50	17.3	15.7	22.2	15.7	17.7	36.8	19.0	28.7	33.6	29.5
100	19.0	17.3	28.7	15.7	20.2	41.7	22.2	36.8	35.2	34.0
150	20.6	15.7	30.3	15.7	20.6	43.3	23.8	43.3	43.3	38.4
Average	17.7	16.0	23.5	17.3	18.6	31.6	19.3	29.7	32.6	28.3
r	0.987**	0.325	0.979**	–0.807**	0.893**	0.901**	0.974**	0.993**	0.936**	0.989**
LSD	a – 0.67**, b – 1.07**, c – 0.95**, a · b – 1.51**, a · c – 1.35**, b · c – 2.14**, a · b · c – 3.02**									

Table 2 contd.

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
	Magnesium									
0	53.6	55.6	48.6	41.4	49.8	53.6	55.6	48.6	41.4	49.8
25	50.4	61.6	48.2	51.3	52.9	58.6	60.1	66.4	42.9	57.0
50	52.1	63.1	53.3	50.7	54.8	51.3	69.2	63.4	43.5	57.9
100	53.8	66.4	60.3	49.9	57.6	49.6	76.4	56.2	45.2	56.9
150	54.8	69.6	63.8	50.5	59.7	43.0	76.8	61.2	45.6	56.6
Average	52.9	63.3	54.8	48.8	55.0	51.2	67.6	59.2	43.7	55.6
r	0.619*	0.956**	0.978**	0.538	0.979**	–0.879**	0.932**	0.241	0.964**	0.665*
LSD	a – 0.38*, b – 0.60**, c – 0.54**, a · b – 0.85**, a · c – 0.76**, b · c – 1.21**, a · b · c – 1.71**									

r – correlation coefficient calculated between chromium dose and content of macroelements (P or K or Mg) in soil. Other explanations under Table 1.

The accumulation of heavy metals in the soil can result in various changes to its properties [5]. On one hand, the soil fulfils the role of a filter which protects against contamination, while on the other, it acts as an intermediary in transporting contaminants [6]. In the authors' own research, soil contamination with compounds of chromium(III) and (VI) significantly modified the content of organic soil and mineral components in soils. Nutrient content affects the growth of cultivated crops to a large extent [7]. Chromium, especially high doses of chromium(VI), have a large negative effect on number of microorganisms [8–10] and enzymatic activity in soil [8–11]. Microorganisms take participation in biochemical transformations of nutrients in soil and in consequences they decided about content of available macroelements (eg phosphorus, calcium and magnesium) in soil. By applying various types of neutralizing substances to the soil, it is possible to positively affect soil conditions. The positive effect of zeolites results from their high porosity and sorptive capacity which, as in the authors' own research, was also confirmed by Ouki et al [12], Silva et al [13] and Leyva-Ramos et al [14]. Soil liming has a positive effect on their reaction, creates favourable conditions for the growth of microorganisms and consequently, accelerates processes of organic matter mineralization [15]. The application of calcium oxide in the experiment with Cr(III) had a favourable effect on the content of available phosphorus, but it significantly reduced the content of organic carbon in both contamination variants. The use of composts positively influences the physicochemical properties of soils, including soil contamination with chromium [16], which is also proved by own research.

Conclusions

1. The content of organic carbon and mineral component was varied depending on the form and the dose of chromium, as well as on the neutralizing substances used.

2. Increasing contamination of soil with Cr(III) and Cr(VI) resulted in the growth of the content of organic carbon and available forms of potassium, and Cr(VI) in a reduction of the content of available magnesium.

3. Among the substances applied, compost and zeolite had effects on the examined properties of soil larger than calcium oxide, particularly in the case of organic carbon, phosphorus and magnesium. Compost and zeolite resulted in increasing the content of organic carbon and magnesium and decreasing the content of phosphorus in soil.

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Abstrakt: Celem badań było określenie oddziaływania kompostu, zeolitu i CaO, stosowanych jako substancje neutralizujące, na zawartość węgla organicznego i składników mineralnych w glebach zanieczyszczonych Cr(III) i Cr(VI).

Zawartość węgla organicznego i składników mineralnych wykazywała znaczne zróżnicowanie w zależności od formy i dawki chromu oraz użytych substancji neutralizujących. Wzrastające zanieczyszczenie gleby Cr(III) i Cr(VI) spowodowało wzrost zawartości węgla organicznego oraz przyswajalnych form potasu, a chrom(VI) obniżenie zawartości przyswajalnego magnezu. Spośród zastosowanych substancji kompost i zeolit miały większy niż tlenek wapnia wpływ na badane właściwości gleby, zwłaszcza w przypadku węgla organicznego, fosforu i magnezu. Kompost i zeolit spowodowały wzrost zawartości węgla organicznego i magnezu oraz zmniejszenie zawartości fosforu w glebie.

Słowa kluczowe: zanieczyszczenie chromem, kompost, zeolit, CaO, gleba, węgiel organiczny, przyswajalne składniki mineralne