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**EFFECT OF SOME SUBSTANCES ON CONTENT  
OF SELECTED COMPONENTS  
IN SOILS CONTAMINATED WITH CHROMIUM**

**WPLYW NIEKTÓRYCH SUBSTANCJI  
NA ZAWARTOŚĆ WYBRANYCH SKŁADNIKÓW  
W GLEBACH ZANIECZYSZCZONYCH CHROMEM**

**Abstract:** The effect of soil contamination with increasing doses of tri- and hexavalent chromium (0, 25, 50, 100 and 150 mg Cr · kg<sup>-1</sup> of soil) was determined on various properties of soil after cultivation of plants and the neutralizing effect of compost (3 %), zeolite (3 %) and calcium oxide (1 HA) on the contamination. Tri- and hexavalent chromium in soil, as well as the substances added to it significantly modified its basic physicochemical properties. Contamination of soil with tri- and hexavalent chromium reduced soil acidity and increased total exchangeable base cations, cation exchange capacity and base saturation. Hexavalent chromium had a greater effect on pH and hydrolytic acidity (but not on the total exchangeable base cation or cation exchange capacity) than trivalent forms of the metal. An addition of calcium oxide to the soil effectively neutralized the effect of contamination on the tested properties as it significantly decreased hydrolytic acidity. However, it also reduced total exchangeable base cations and cation exchange capacity – only with chromium(III) as compared with the control series (with no additives). The effect of the other substances was weaker and more positive in the case of compost than zeolite, especially in the objects with hexavalent chromium.

**Keywords:** contamination, chromium(III), chromium(VI), compost, zeolite, calcium oxide, soil, acidity, sorption properties

Dynamic industrial development, technological progress and agrochemization of agriculture have increased pollution of the environment with xenobiotics, which include heavy metals. One of the metals which is not neutral to the environment or humans is chromium, which, when present in excessive amounts, is a destructive factor, with a highly toxic effect on the biological properties of the soil [1]. The growing demand for chromium and its compounds along with the mining processes of this metal and other raw materials in which it is an accompanying metal, now pose a serious ecological threat [2]. In the soil it is found at various degrees of oxidation; the most durable are compounds of Cr(III), whereas the most toxic to plants are soluble forms of Cr(VI) [3].

The aim of the experiment was to determine the effect of soil contamination with increasing doses of tri- and hexavalent chromium on various soil properties after plant

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cultivation and the neutralizing effect of compost, zeolite and calcium oxide on the contamination.

## Material and methods

A pot experiment was conducted at the vegetation hall of the University of Warmia and Mazury in Olsztyn in polyethylene pots with a capacity of 9.5 kg each, on soil with a granulometric composition of light loamy sand with the following properties:  $\text{pH}_{\text{KCl}} - 4.8$ , hydrolytic acidity (HA) –  $33.75 \text{ mmol}(\text{H}^+) \cdot \text{kg}^{-1}$  of soil, total exchangeable base cations (EBC) –  $62.20 \text{ mmol} \cdot \text{kg}^{-1}$ , cation exchange capacity (CEC) –  $95.95 \text{ mmol} \cdot \text{kg}^{-1}$ , base saturation (BS) –  $64.80 \%$ ,  $\text{C}_{\text{org.}}$  –  $7.13 \text{ g} \cdot \text{kg}^{-1}$ , content of available: phosphorus –  $46.6 \text{ mg} \cdot \text{kg}^{-1}$ , potassium –  $8.2 \text{ mg} \cdot \text{kg}^{-1}$  and magnesium –  $33.9 \text{ mg} \cdot \text{kg}^{-1}$ . Under natural conditions it is brown soil. The soil was contaminated with aqueous solutions of chromium(III) as  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and chromium(VI) as  $\text{K}_2\text{Cr}_2\text{O}_7$  in the following amounts: 0, 25, 50, 100 and 150  $\text{mg Cr} \cdot \text{kg}^{-1}$  of soil. Substances neutralizing the effect of chromium were also introduced to the soil: compost and zeolite at 3 % of the soil mass, and calcium oxide in the amount equivalent to 1 hydrolytic acidity (HA), as well as basic macro- and microelements in the following amounts [ $\text{mg} \cdot \text{kg}^{-1}$  of soil]: N – 110 [ $\text{CO}(\text{NH}_2)_2 + (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} + (\text{NH}_4)_2\text{HPO}_4$ ], P – 50 [ $(\text{NH}_4)_2\text{HPO}_4$ ]; K – 110 [ $\text{KCl} + \text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} + \text{K}_2\text{Cr}_2\text{O}_7$ ], Mg – 50 [ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ], Mn – 5 [ $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ], Mo – 5 [ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ] and B – 0.33 [ $\text{H}_3\text{BO}_3$ ]. The following crops were cultivated in the experiment: spring barley (*Hordeum vulgare* L.) – the main crop, and maize (*Zea mays* L.) – the successive crop. The barley density was 15 plants per pot and for maize it was 8 plants per pot. During the vegetation of spring barley and maize, the soil humidity was maintained at 60 % of the capillary capacity with distilled water. Spring barley was harvested during the ear formation phase and maize was harvested during the stem elongation phase, after 56 and 67 days of vegetation, respectively. Samples of soil material for the laboratory analyses were taken during the maize harvest (123 days following contamination of the soil).

The following were determined in the soil samples: reaction (pH) of soil – by the potentiometric method in an aqueous solution of KCl at the concentration of  $1 \text{ mol} \cdot \text{dm}^{-3}$ , hydrolytic acidity (HA) and total exchangeable base cations (EBC) – by Kappen's method [4]. The hydrolytic acidity (HA) and total exchangeable base cations (EBC) were used to calculate the cation exchange capacity (CEC) and base saturation (BS) according to the following formulae:  $\text{CEC} = \text{EBC} + \text{HA}$ ;  $\text{BS} = \text{EBC} \cdot \text{CEC}^{-1} \cdot 100$ . The results were analyzed statistically with STATISTICA [5] software using a three-factor analysis of variance (ANOVA). The relationship was also determined between the contamination of soil with chromium and acidity and its other properties with the use of Pearson's simple correlation.

## Results and discussion

Contamination of soil with tri- and hexavalent chromium significantly affected the pH value, hydrolytic acidity, total exchangeable base cations, cation exchange capacity and base saturation of the examined soil (Tables 1, 2). In the series without neutralizing

additives, small amounts of tri- and hexavalent chromium brought about a gradual increase in the pH value (Table 1). Such relationships were observed up to the dose of 50 mg of Cr(III) and Cr(VI) per 1 kg of soil, while the relationships were negative in the soil with a higher chromium content. Slightly higher values of pH were measured in the soil contaminated with trivalent chromium. In the series without the neutralizing additives, increasing doses of tri- and hexavalent reduced the hydrolytic acidity (Table 1). The reduction was greater in the objects with hexavalent chromium than in the pots with trivalent chromium. The neutralizing additives – compost, zeolite and calcium oxide – significantly affected the pH value of the soil, both in pots with trivalent and with hexavalent chromium. The best results were achieved when calcium oxide was applied to the soil, both in the objects with trivalent and in those with hexavalent chromium; it considerably increased the pH value and reduced hydrolytic acidity as compared with the control variant. Zeolite and compost in the objects with trivalent chromium also produced good results.

Increasing doses of chromium(III) also positively affected the other properties of soil (Table 2). They produced an increase in total exchangeable base cations, cation exchange capacity and base saturation in soil. The highest dose of chromium(III) ( $150 \text{ mg} \cdot \text{kg}^{-1}$  of soil) resulted in their increase by 54 %, 43 % and 8 %, respectively, as compared with the control object (without chromium(III) addition to the soil). More ambiguous changes were observed when soil was contaminated with hexavalent chromium, although the highest values of total exchangeable base cations, cation exchange capacity and base saturation were observed in the soil with the highest dose of chromium(VI).

The examined properties were significantly affected by the applied neutralizing additives – compost, zeolite and calcium oxide (Table 2). Total exchangeable base cations, cation exchange capacity and base saturation in the objects with trivalent chromium were higher than in those with hexavalent chromium. In the case of chromium(III), an addition of compost, zeolite and calcium oxide to the soil reduced total exchangeable base cations and cation exchange capacity compared to the control series (without additives), with the action of zeolite and calcium oxide being stronger. In the objects with hexavalent chromium, the effect of those substances (except compost) was weaker, but more positive. In the case of chromium(VI), the cation exchange capacity was most strongly affected by an addition of compost and less so by calcium oxide, with a higher mean value of total exchangeable base cations and cation exchange capacity than in the series without additives. The weakest effect of additives was observed for base saturation.

Cation exchange capacity and the reaction of soil are important factors which determine the growth and development of plants as well as the accumulation of heavy metals in their tissues [6]. The reaction of soil plays an essential role in controlling the share of bioavailable heavy metals by regulating their uptake and influence on plant growth and development [7]. A change in the reaction of soil may reduce the effect of heavy metals, including chromium, on plants. There is a close relationship between the soil sorptive properties and the population of soil microorganisms and their enzymatic activity. This in turn is closely related to microbiological transformations of metals of restricted availability to plants into their more easily available forms. However, soil

Table 1  
The pH and hydrolytic acidity of soil after harvest of the experimental plants

Dose [mg · kg <sup>-1</sup> of soil]	Chromium(III)					Chromium(VI)				
	Without additions	Compost	Zeolite	Calcium oxide	Average	Without additions	Compost	Zeolite	Calcium oxide	Average
pH <sub>KCl</sub>										
0	6.60	7.50	7.12	7.45		6.60	7.50	7.12	7.45	
25	6.90	7.32	7.20	7.70		7.36	7.22	7.21	7.53	
50	7.37	7.13	7.20	7.79		7.50	7.13	6.95	7.60	
100	7.23	7.14	7.20	7.78		7.30	7.30	7.15	7.57	
150	7.25	7.20	7.53	7.70		7.05	7.09	6.66	7.47	
Hydrolytic acidity (HA) [mmol · kg <sup>-1</sup> ]										
0	15.00	6.38	9.75	10.13	10.32	15.00	6.38	9.75	10.13	10.32
25	10.88	7.88	9.00	6.38	8.54	9.00	8.63	10.13	8.63	9.10
50	10.13	11.25	10.88	6.75	9.75	8.63	11.63	11.25	6.75	9.57
100	9.75	9.38	9.75	4.88	8.44	7.88	10.88	9.00	7.98	8.94
150	10.13	10.50	4.88	7.50	8.25	7.50	12.00	13.98	10.50	11.00
Average	11.18	9.08	8.85	7.13	9.06	9.60	9.90	10.82	8.80	9.78
LSD	a – 0.18**, b – 0.28**, c – 0.25**, a · b – 0.40**, a · c – 0.36**, b · c – 0.56**, a · b · c – 0.79**									

LSD for: a – kind of chromium, b – chromium dose, c – kind of neutralizing substance; \*\* – significant for p = 0.01, \* – significant for p = 0.05, r – correlation coefficient.

Table 2  
Total exchangeable base cations (EBC), cation exchange capacity (CEC) and base saturation (BS) of soil after harvest of the experimental plants

Dose [mg · kg <sup>-1</sup> of soil]	Chromium(III)					Chromium(VI)				
	Without additions	Compost	Zeolite	Calcium oxide	Average	Without additions	Compost	Zeolite	Calcium oxide	Average
Total exchangeable base cations (EBC) [mmol · kg <sup>-1</sup> ]										
0	104.40	157.80	123.20	98.00	120.85	104.40	157.80	123.20	98.00	120.85
25	144.80	137.20	125.20	121.60	132.20	85.20	137.00	131.80	140.80	123.70
50	144.00	128.80	125.40	124.80	130.75	90.00	133.60	124.80	142.60	122.75
100	159.20	120.20	128.60	145.20	138.30	114.20	133.60	90.20	133.80	117.95
150	161.00	132.40	140.00	152.40	146.45	124.40	121.00	65.80	59.80	92.75
Average	142.68	135.28	128.48	128.40	133.71	103.64	136.60	107.16	115.00	115.60
LSD	a – 3.58 <sup>**</sup> , b – 5.66 <sup>**</sup> , c – 5.07 <sup>**</sup> , a · b – 8.01 <sup>**</sup> , a · c – 7.17 <sup>**</sup> , b · c – 11.33 <sup>**</sup> , a · b · c – 16.02 <sup>**</sup>									
Cation exchange capacity (CEC) [mmol · kg <sup>-1</sup> ]										
0	119.40	164.18	132.95	108.13	131.17	119.40	164.18	132.95	108.13	131.17
25	155.68	145.08	134.20	127.98	140.74	94.20	145.63	141.93	149.43	132.80
50	154.13	140.05	136.28	131.55	140.50	98.63	145.23	136.05	149.35	132.32
100	168.95	129.58	138.35	150.08	146.74	122.08	144.48	99.20	141.68	126.86
150	171.13	142.90	148.63	159.90	155.64	131.90	133.00	79.68	70.30	103.72
Average	153.86	144.36	138.08	135.53	142.96	113.24	146.50	117.96	123.78	125.37
LSD	a – 3.56 <sup>**</sup> , b – 5.64 <sup>**</sup> , c – 5.04 <sup>**</sup> , a · b – 7.97 <sup>**</sup> , a · c – 7.13 <sup>**</sup> , b · c – 11.27 <sup>**</sup> , a · b · c – 15.94 <sup>**</sup>									

Table 2 contd.

Dose [mg · kg <sup>-1</sup> of soil]	Chromium(III)					Chromium(VI)				
	Without additions	Compost	Zeolite	Calcium oxide	Average	Without additions	Compost	Zeolite	Calcium oxide	Average
	Base saturation (BS) [%]									
0	87.44	96.12	92.67	90.64	91.72	87.44	96.12	92.67	90.64	91.72
25	93.01	94.57	93.29	95.02	93.97	90.45	94.08	92.87	94.23	92.91
50	93.43	91.97	92.02	94.87	93.07	91.25	92.00	91.73	95.48	92.62
100	94.23	92.76	92.95	96.75	94.17	93.55	92.47	90.93	94.44	92.85
150	94.08	92.65	94.20	95.31	94.06	94.31	90.98	82.59	85.06	88.24
Average	92.44	93.61	93.03	94.52	93.40	91.40	93.13	90.16	91.97	91.66
LSD	a – 0.52 <sup>**</sup> , b – 0.83 <sup>**</sup> , c – 0.74 <sup>**</sup> , a · b – 1.17 <sup>**</sup> , a · c – 1.05 <sup>**</sup> , b · c – 1.66 <sup>**</sup> , a · b · c – 2.34 <sup>**</sup>									

Explanations under Table 1.

contamination with heavy metals may modify the relations negatively. In the experiments conducted by Kizilkaya et al [8] with soil contaminated with metals, only the activity of urease was strongly correlated with cation exchange capacity; on the other hand, a significant negative correlation was observed between heavy metal content in soil and microbiological properties of soil. In the present experiment, contamination of soil with tri- and hexavalent chromium reduced the acidity of soil and increased its pH value, cation exchange capacity, total exchangeable base cations and base saturation. The application of calcium oxide increased the pH value after the crop harvest, confirming the positive effect of liming on the soil reaction, as reported in other papers, eg Czekala [9] and Kuziemska and Kalembasa [10]. The strong correlation between chromium content in soil and its reaction is indicated by Zarcinas et al [11]. Their findings include a positive correlation between the content of the metal and application of organic substances to soil, for example, compost and manure. The positive effect of zeolite results from its high porosity and cation exchange capacity [12]. The soil reaction, organic matter content and soil cation exchange capacity have a great effect on the bioavailability of metals and their influence on plants [13]. Pils et al [14] also indicate pH and cation exchange capacity as the main factors which determine metal retention in soil. According to Karathanasis and Pils [15], the bonds between chromium and the organic fraction of the soil are stronger than those of any other heavy metals, therefore, the application of calcium and organic matter to soil should produce a positive effect on its properties, which has been confirmed in previous studies by the authors. Wyzkowska [16] also showed an improvement in the sorptive properties of soil following the application of straw. In a laboratory experiment conducted by Castilhos et al [17], the application of organic substance as cattle manure to soil completely reduced Cr(VI) to Cr(III) within 42 days, with microbiological activity in non-sterilized soil decreased chromium content by 16 % as compared with sterilized soil. Organic substances in soil create durable combinations with heavy metals, thereby decreasing their uptake by plants. Liming and the addition of organic substance to soil may be effective methods (*in-situ*) of restricting the effect of hexavalent chromium on the properties of soil and on plants.

## Conclusions

1. Tri- and hexavalent chromium in soil, as well as the substances added to it, significantly modified its basic physicochemical properties.
2. Contamination of soil with tri- and hexavalent chromium reduced soil acidity and increased total exchangeable base cations, cation exchange capacity and base saturation.
3. Hexavalent chromium had a greater effect on pH and hydrolytic acidity (but not on total exchangeable base cations or cation exchange capacity) than trivalent forms of the metal.
4. An addition of calcium oxide to the soil effectively neutralized the effect of contamination on the tested properties as it significantly decreased hydrolytic acidity. However, it also reduced total exchangeable base cations and cation exchange capacity, but only with chromium(III) as compared with the control series (with no additives).

The effect of the other substances was weaker and more positive in the case of compost than zeolite, especially in the objects with hexavalent chromium.

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### WPLYW NIEKTÓRYCH SUBSTANCJI NA ZAWARTOŚĆ WYBRANYCH SKŁADNIKÓW W GLEBACH ZANIECZYSZCZONYCH CHROMEM

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**Abstrakt:** W doświadczeniu wazonowym badano wpływ zanieczyszczenia gleby wzrastającymi dawkami chromu trój- i sześciowartościowego (0, 25, 50, 100 i 150 [mg Cr · kg<sup>-1</sup> gleby]) na wybrane właściwości gleby po zbiorze roślin oraz oddziaływania kompostu (3 %), zeolitu (3 %) i tlenku wapnia (1 Hh) na łagodzenie skutków tego zanieczyszczenia. Zanieczyszczenie gleby chromem trój- i sześciowartościowym miało duży wpływ na pH, kwasowość hydrolityczną i pozostałe właściwości badanej gleby. Zanieczyszczenie gleby chromem trój- i sześciowartościowym spowodowało zmniejszenie zakwaszenia gleby oraz zwiększenie sumy wymiennych kationów zasadowych, całkowitej pojemności wymiennej i stopnia wysycenia kationami zasadowymi. Chrom sześciowartościowy w stosunku do trójwartościowego znacznie silniej oddziaływał na pH i kwasowość hydrolityczną, w odróżnieniu od sumy wymiennych kationów zasadowych i całkowitej pojemności wymiennej. Dodatek do gleby tlenku wapnia skutecznie łagodził oddziaływanie zanieczyszczenia gleby chromem na badane właściwości gleby, gdyż znacznie zmniejszył kwasowość hydrolityczną. Jednakże ograniczył także sumę wymiennych kationów zasadowych oraz pojemność wymienną – tylko w przypadku chromu(III), w porównaniu z serią kontrolną (bez dodatków). Wpływ pozostałych substancji był mniejszy i bardziej korzystny w przypadku kompostu niż zeolitu, szczególnie w obiektach z chromem sześciowartościowym.

**Słowa kluczowe:** zanieczyszczenie, chrom(III), chrom(VI), kompost, zeolit, tlenek wapnia, kwasowość, właściwości sorpcyjne