POLISH JOURNAL OF SOIL SCIENCE
VOL. XLIX/2 2016 PL ISSN 0079-2985

DOI: 10.17951/pjss/2016.49.2.181

MAJA RADZIEMSKA*, MIROSŁAW WYSZKOWSKI**

CHEMICAL COMPOSITION OF SOIL CONTAMINATED WITH TRI- AND HEXAVALENT CHROMIUM AMENDED WITH COMPOST, ZEOLITE AND CALCIUM OXIDE

Received: 2016.02.15
Accepted: 2017.04.21

Abstract. The studies involved determining the influence of Cr(III) and Cr(VI), as well as compost, zeolite and calcium oxide on the content of selected macronutrients and trace elements in soil in which oats were grown. An increase in the content of total chromium, manganese, zinc and nickel took place along with increasing contamination with Cr(III) and Cr(VI). In pots with Cr(VI), the addition of compost significantly increased the contents of copper, zinc and cobalt in the analyzed soil as compared to the control groups. The application of calcium oxide significantly limited the content of copper and cobalt in pots with trivalent chromium, and nickel in pots with Cr(VI); it also contributed to an increase in the contents of chromium and copper (pots with Cr(VI)).

Keywords: chromium contamination, heavy metals, compost, zeolite, calcium oxide

INTRODUCTION

The contamination of the soil environment with heavy metals and chromium compounds is a more and more frequently occurring problem throughout the world. Heavy metals are among the harmful groups of chemical compounds accumulated in soil as a result of anthropogenic activity (Adamcová *et al*. 2016;

---

* Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences, Nowoursynowska 159 St., 02-776 Warsaw, Poland, *Corresponding author, e-mail: maja_radziemska@sggw.pl

** Faculty of Environmental Management, University of Warmia and Mazury in Olsztyn, Pl. Łódzki 4, 10-718 Olsztyn, Poland

Sas *et al*. 2015; Radziemska *et al*. 2013). An additional source of this element are erosion processes and volcanic activity, as a result of which chromium compounds, mainly in the trivalent state of oxidation, are released into the atmosphere (Yu *et al*. 2014). Activities connected with the metallurgical industry, gas combustion, and steelmaking are yet another source of chromium compounds. In this case, in addition to Cr(III), the highly toxic form of Cr(VI), as well as metallic chromium also find their way into the atmosphere (Lukina *et al*. 2016).

In soils that are free of contamination, Cr(III) is present in greater proportions, which is connected with the occurring processes which lead to the reduction of Cr(VI). The transformation of Cr(VI) into Cr(III) takes place mainly with the involvement of microorganisms, indirectly by releasing reducing agents, such as iron ions or organic matter (Yilmaz and Soylak 2016).

There are three main routes by which chromium compounds make their way into the human body, i.e. oral, dermal and inhalation. In each case, chromium compounds at a higher state of oxidation are absorbed more effectively than those at lower states (Mathebula *et al*. 2017). Such a large difference in the level of absorption is connected with the ability of stomach acid to reduce Cr(VI) to Cr(III), which is characterized by poorer absorbability (Sasso and Schlosser 2015). Under physiological conditions, Cr(VI) occurs in the form of chromates, whereas Cr(III) is a cation. This difference of charge facilitates the passing of negatively charged Cr(VI) through the cell membrane (Guimarães *et al*. 2016).

Chromium is found in all plant tissues, as an essential microelement responsible for numerous physiological processes. The content of Cr(III) and Cr(VI) in plants is dependent on the abundance of this element in soil as well as the plant species (Wyszkowski and Radziemska 2009a; 2009b; 2010; 2013a; 2013b). Research focused on limiting the effects of chromium, especially Cr(VI) on soils as well as plants, which constitute an indirect link in the food chain, are important in all fields connected with environmental engineering and protection (Radziemska *et al*. 2016). In connection with the above, studies were carried out which aimed to determine the effects of Cr(III) and Cr(VI)compounds, as well as alleviating additives (compost, zeolite and CaO) on the contents of selected macronutrients and trace elements in soil after harvesting oat (*Avena sativa* L.).

MATERIALS AND METHODS

Pot experiment layout

The experiment was carried out in a greenhouse belonging to the University of Warmia and Mazury in Olsztyn (Poland), in polyethylene pots with a holding capacity of 9.5 kg. The soil, with a granulometric composition of light loamy sand, was characterized by the following properties: pH_{KCl} – 5.0, hydrolytic acidity – 26.60 mmol(H^+) kg^{-1} soil, total exchangeable base cations – 100.00 mmol kg^{-1}, cation exchange capacity – 126.60 mmol kg^{-1}, saturation of the sorption complex with base cations – 79.00%, C_{org} content – 7.87 $mg \cdot kg^{-1}$, content of absorbable: phosphorus – 90.20 $mg \cdot kg^{-1}$, potassium – 37.90 $mg \cdot kg^{-1}$ and magnesium – 77.00 $mg \cdot kg^{-1}$, chromium – 12.95 $mg \cdot kg^{-1}$, manganese – 219.90 $mg \cdot kg^{-1}$, copper – 9.01 $mg \cdot kg^{-1}$, zinc – 24.25 $mg \cdot kg^{-1}$, nickel – 3.99 $mg \cdot kg^{-1}$, and cobalt – 2.37 $mg \cdot kg^{-1}$.

The soil was artificially contaminated with aqueous solutions of Cr(III) in the form of $KCr(SO_4)_2 \cdot 12H_2O$, and Cr(VI) in the form of $K_2Cr_2O_7$ in the following doses: 25, 50, 100 and 150 $mg \cdot kg^{-1}$. Macro- and micronutrients were also introduced into the soil in the following amounts in mg/kg soil: N – 110 [$CO(NH_2)_2$ + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ + $(NH_4)_2HPO_4$], P – 50 [$(NH_4)_2HPO_4$]; K – 110 [KCl + $KCr(SO_4)_2 \cdot 12H_2O$ + $K_2Cr_2O_7$], Mg – 50 [$MgSO_4 \cdot 7H_2O$], Mn – 5 [$MnCl_2 \cdot 4H_2O$], Mo – 5 [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], B – 0.33 [$H_3BO_3$], as well as additives: compost and zeolite in the amount of 3% of the soil mass and calcium oxide (CaO) in the amount equivalent to 1 hydrolytic acidity. Some values of chemical additives have been provided in Table 1. Oat (*Avena sativa* L.) of the Kasztan variety was grown at a seeding density of 25 seeds per pot. Harvest took place when the crop reached full maturity.

TABLE 1. CHEMICAL COMPOSITION OF AMENDMENTS USED IN THE EXPERIMENT

Parametr	Unit	Compost	Zeolite	CaO
Phosphorous	$g \cdot kg^{-1}$	2.32	0.11	0.10
Potassium		1.33	23.21	0.77
Magnesium		1.47	0.31	2.65
Calcium		15.80	15.20	347.00
Sodium		0.12	16.12	0.07
Chromium	$mg \cdot kg^{-1}$	3.48	1.81	2.70
Copper		38.13	12.38	2.26
Zinc		31.80	14.68	5.14
Nickel		18.75	408.70	6.64

Sample preparation and soil chemical analysis

Prior to setting up the pot experiment, as well as after harvesting the plants, soil samples were collected from each pot and then dried at room temperature, ground and strained through a 0.1 diameter sieve. The contents of: chromium, manganese, copper, zinc, nickel and cobalt were determined using the method of flame atomic absorption spectroscopy (FAAS) on an atomic absorption spectrometer using a SpectrAA 240FS type apparatus (VARIAN, Australia) in extracts obtained following the “wet” mineralization of soil in nitric acid (HNO_3 p.a.) at a concentration of 1.40 g·cm^{-3} in a MARS 5 type microwave oven (CEM Corporation, USA), in HP500 teflon dishes.

The conditions of the process, i.e. weighted amounts, volume of nitric acid and mineralization temperature were assumed in accordance with US-EPA3051 methodology. Deionized water with an electrical conductivity of (0.055 µS cm^{-1}), purified using the Crystal 10 system (Adrona Laboratory System) was used for the analyses.

In addition to the above, the following were assessed in the soil prior to setting up the experiment: granulometric content of soil – laser method with Mastersizer 2000 measuring device, soil pH – potentiometrically in aqueous solution of KCl with a concentration of 1 mol·dm^{-1} (Klute 1996), sum of exchangeable base cations – Kappen's method (Klute 1996), total sorption capacity of the soil (Klute 1996), saturation of sorption complex with base cations (Klute 1996), organic carbon content – Tiurin's method in potassium dichromate with sulphuric acid (VI) (Mocek and Drzymała 2010), total nitrogen content – Kjeldahl's method after mineralization in concentrated sulphuric acid (VI) with the addition of H_2O_2 as the catalyst (Mocek and Drzymała 2010), total ammoniacal nitrogen – with Nessler's reagent (Mocek and Drzymała 2010), nitrate nitrogen content V – with application of Phenylanthranilic acid (Mocek and Drzymała 2010), content of absorbable forms of phosphorus and potassium – Egner-Riehm's method (Riehm 1958), content of absorbable magnesium – Schachteschabel's method (Mocek and Drzymała 2010).

Statistical analyses

The results of studies were subject to statistical calculations with Statistica 8.0 using three-way ANOVA analysis of variance and Duncan's test. Pearson's linear correlation coefficients (*r*) were also calculated between the analyzed variable.

RESULTS AND DISCUSSION

Influence of Cr(III) and Cr(VI) on contents of heavy metals in soil

The content of chromium in soil after harvesting the oats was dependent on the form of the introduced element (Tab. 2, Fig. 1). The average content of chromium in soils around the world is 54 mg·kg^{-1}, whereas its contents in the soils of Poland range from 0.007 to 0.024 mg·kg^{-1}. The highest concentration of chromium, reaching as much as 10,000 mg·kg^{-1}, are found in the Sudetes (Poland) (Kabata-Pendias and Pendias 2011). In soils of urban areas, as a result of industrial activity, the content of heavy metals, including chromium, can be significantly higher (Mazur *et al.* 2015). In the experiment carried out, in the series without neutralizing additives, chromium content was positively correlated (*r*=0.999) and (*r*=0.995) with increasing doses of Cr(III) and Cr(VI), however its influence was a bit stronger in the case of pots containing Cr(III). As compared to the control group, this increase was 11.5 fold – Cr(III) and eleven-fold Cr(VI). Chromium in contaminated soils is mainly present as residual chromium; in soils contaminated with, e.g. sewage sludge, the content of the from connected with Fe/Mn oxides increases manifold, with chromium bound with organic matter also increasing, though to a lesser extent. In the case of contaminated light soils, the majority of chromium is strongly connected with the crystalline network of primary and secondary minerals, occurring in the form of residuals (Arshad *et al.* 2017).

The applied dose and form of chromium, as well as neutralizing additives in the form of compost, zeolite and calcium oxide, influenced the contents of manganese in the analyzed soil (Tab. 2, Fig. 1). Manganese occurs in soil mainly in the form of free oxides or silicates. During the weathering of silicates, Mn^{2+} ions are released, which find their way into the soil complex. Moreover, manganese is an essential nutrient to plants. The physiological function of manganese involves the role of this nutrient in a series of enzymatic reactions. Manganese has an effect on the increase in the intensity of respiration, carbon dioxide assimilation and the synthesis of carbohydrates (Hao and Jiang 2015). In the series without the neutralizing additives, the soil in which oats were grown was characterized by a higher average manganese content in pots with Cr(VI) than their Cr(III) counterparts. The highest dose of Cr(III) and Cr(VI) (150 $mg \cdot kg^{-1}$ soil) had the strongest influence on the content of manganese in the control series (without neutralizing additives), leading to an increase of a few percent in the content of manganese, while the remaining doses did not have a targeted effect on the content of the above-mentioned component.

The content of copper in soil following the harvest of oat was influenced by the form and dose of chromium, as well as compost, zeolite and calcium oxide (Tab. 2, Fig. 1). Copper content in soils amounts to an average of 2–40 mgCu kg^{-1} (Kabata-Pendias and Pendias 2011). Copper binds mainly with organic substances and Mn and Fe oxides, as well as silicates (Liu, 2016). In the series without additives, the average content of Cu was 19% higher in soils with Cr(III) than in pots with Cr(VI). In this series, in both variants of the experiment, a negative correlation occurred between the increasing contamination of soil with Cr(III) (*r*=-0.875) and Cr(VI) (*r*=-0.762), and the Cu content of the soil. In pots with Cr(VI), the highest dose (150 $mg \cdot kg^{-1}$ of soil) led to a 27% decrease in Cu content as compared to the control group, whereas in the case of Cr(III) contaminated soil, this decrease was only 10%.

The content of zinc in soil following the harvest of oat was dependent on the type and dose of soil contamination with chromium, as well as the addition of neutralizing substances – compost, zeolite and calcium oxide (Tab. 3, Fig. 1). The content of zinc in soil falls within the range of 10–80 $mg \cdot kg^{-1}$. Available zinc

TABLE 2. CONTENT OF CHROMIUM, MANGANESE AND COPPER IN MG·KG^{-1} OF SOIL AFTER OAT HARVEST

Cr dose in mg·kg^{-1} of soil	Kind of contamination									
	Chromium (III)					Chromium (VI)				
	Type of neutralizing substance									
	Without additives	Compost	Zeolite	CaO	Average	Without additives	Compost	Zeolite	CaO	Average
Chromium										
0	12.86	12.16	12.30	11.74	12.27	12.86	12.16	12.30	11.74	12.27
25	34.80	24.91	24.10	23.81	26.91	24.51	25.26	23.60	34.10	26.87
50	53.00	41.10	47.80	46.25	47.04	51.00	47.80	49.23	47.25	48.82
100	97.35	97.45	97.60	96.10	97.13	88.46	97.30	98.60	98.85	95.80
150	148.15	148.70	149.30	131.86	144.50	142.05	142.25	145.90	147.45	144.41
r	0.999**	0.993**	0.996**	0.996**	0.997**	0.995**	0.997**	0.997**	0.997**	0.998**
LSD	a – n.i., b – 3.59**, c – n.i., a·b – n.i., a·c – 4.54**, b·c – n.i., a·b·c – n.i.									
Manganese										
0	217.4	214.2	209.0	214.1	213.7	217.4	214.2	209.0	214.1	213.7
25	214.3	214.9	202.6	213.8	211.4	219.1	235.6	212.9	222.8	222.6
50	218.5	215.7	210.9	213.9	214.8	217.0	229.6	214.7	224.6	221.5
100	207.6	216.3	215.7	206.4	211.5	221.8	217.9	215.1	229.7	221.1
150	221.7	218.5	217.1	205.8	215.8	257.6	204.7	228.9	228.4	229.9
r	0.105	0.982**	0.824**	-0.927**	0.378	0.836**	-0.596	0.915**	0.847**	0.840**
LSD	a – 5.07**, b – n.i., c – n.i., a·b – n.i., a·c – n.i., b·c – n.i., a·b·c – n.i.									
Copper										
0	16.10	15.30	14.95	12.65	14.75	16.10	15.30	14.95	12.65	14.75
25	16.75	14.80	13.65	11.90	14.28	13.05	13.25	16.00	12.40	13.68
50	15.25	15.35	13.35	11.90	13.96	12.05	16.65	16.45	13.40	14.64
100	14.85	17.15	12.10	11.95	14.01	11.85	18.30	16.90	18.35	16.35
150	14.45	17.35	12.85	12.45	14.28	11.75	18.30	17.40	18.05	16.38
r	-0.875**	0.915**	-0.795**	-0.003	-0.470	-0.762**	0.816**	0.941**	0.918**	0.843**
LSD	a – 0.31**, b – 0.50**, c – 0.44**, a·b – 0.70**, a·c – 0.63**, b·c – 0.99**, a·b·c – 1.40**									

LSD for: a – contamination type, b – chromium dose, c – type of neutralizing substance; n.i. – insignificant differences, ** – significant for p=0.01, * – significant for p=0.05; r – correlation coefficient.

found in the soil complex binds, above all, with organic matter. Moreover, zinc is absorbed by iron, manganese and aluminum oxides, as well as clay minerals and silicates. Additional immobilization of zinc is the effect of higher contents of sulphates and phosphates in the soil complex (Dumoulin *et al*. 2017). Following the harvest of oat, the Zn contents of soil from the series without additives were found to be similar in pots with Cr(III) and Cr(VI). In those with Cr(VI), a positive correlation between increasing soil contamination and zinc content was noted, with the highest dose of the contaminant (150 mg·kg^{-1} of soil) result-

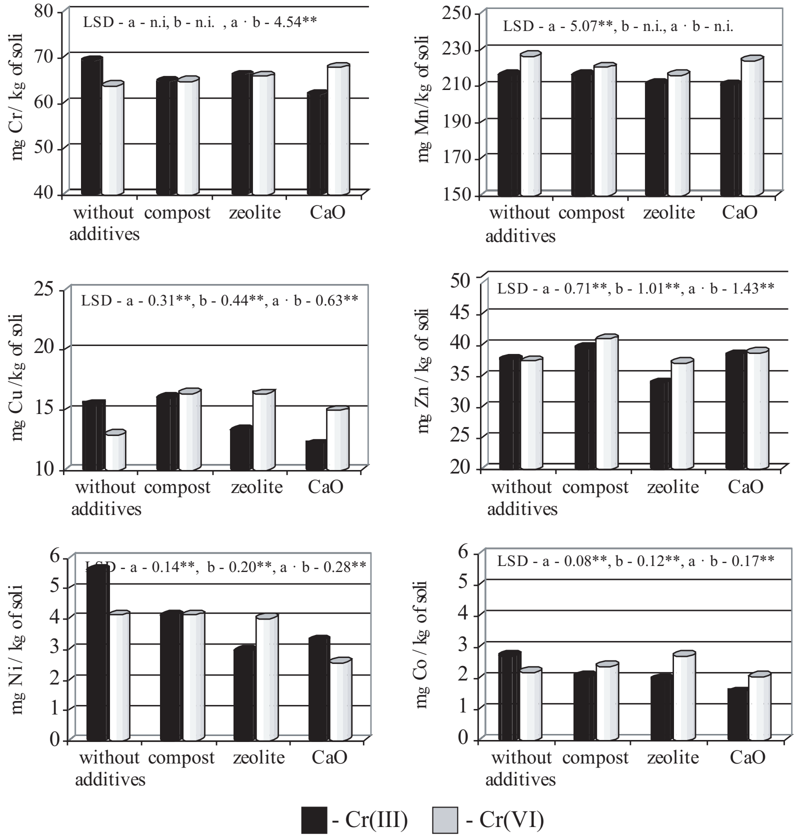

Fig. 1. Average content of Cr, Mn, Cu, Zn, Ni, Co in soil after plants harvest in dependence from addition of a different substances , mg·kg^{-1} d.m.

NIR for: a – contamination type, b – chromium dose, c – type of neutralizing substance; n.i. – insignificant differences, ** – significant for p=0.01, * – significant for p=0.05; *r* – correlation coefficient

ing in a 15% increase in the described element as compared to the control. In the case of pots with Cr(III), a 100 mg·kg^{-1} of soil dose applied to the series without neutralizing additives increased Zn content in the analyzed soil by 17%. The strongest effect on the content of Zn in soil was noted following the application of zeolite and compost in pots with Cr(III) and Cr(VI), respectively. Literature confirms the effectiveness of removing contamination with chromium compounds from soil with the use of zeolites (Antoniadis *et al.* 2017).

Nickel is an element characterized by high mobility in the natural environment through the soil – plant system. Grzywnowicz (1997) stated that naturally derived nickel, in soils contaminated anthropogenically, is less soluble and less mobile than other elements. Moreover, this author in his studies showed that the total content of nickel is connected with the pH of the soil, the capacity of the sorption complex, and organic carbon content. The applied doses of Cr(III) and Cr(VI) and neutralizing additives in the form of compost, zeolite and calcium oxide significantly affected nickel content in soil on which oat was grown (Tab. 3, Fig. 1). Soil samples taken after harvesting the plants from the series without neutralizing additives were characterized by a 36% higher content of Ni in pots with Cr(III) than in their Cr(VI) counterparts. In the series without additives, the first dose of Cr(III) resulted in an increase of nickel content in the analyzed soil, with the following doses decreasing the content of this element. In the analogous series with Cr(VI), the existence of a negative correlation (*r*=-0.871) between increasing contamination and nickel content was observed, with the highest dose of the contaminant (150 mg·kg^{-1} soil) decreasing its content by more than twofold.

The contamination of soil with Cr(III) and Cr(VI), as well as compost, zeolite and calcium oxide all significantly influenced the content of cobalt in the soil after harvesting the test plant (Tab. 3, Fig. 1). In the natural environment, cobalt is found in sulfide, oxide and arsenide minerals. The presence of cobalt in soil is dependent on local geochemical processes and the application of phosphatic fertilizers containing this element (Jalali and Majeri 2016). In the series without neutralizing additives, soil in pots with Cr(III) was characterized by a higher average chromium content after harvesting oat. In the control series (without neutralizing additives), the content of the analyzed component in the soil was negatively correlated with increasing Cr(III) - *r*=-0.816 and Cr(VI) - *r*=-0.883. Cr(VI) most noticeably limited (by 59%) the content of cobalt in the analyzed soil. Its influence was over twice higher than that of Cr(III).

Effect of amendments on heavy metal content in soil polluted with Cr(III) and Cr(VI)

Serving as a filter protecting against containments, the soil is also an intermediary in their transport; moreover, the accumulation of heavy metals in soil can lead to significant changes in their physicochemical properties (Hewelke *et al*. 2014; Hewelke *et al*. 2015; Radziemska and Fronczyk 2015). The organic matter found in soils forms stable compounds, decreasing their uptake by plants. Chromium, as compared to other heavy metals, is most strongly connected with the organic fraction of soil (Arshad *et al*. 2017). Applying composts has a positive effect on the physicochemical properties of soil, also in the case of chromium contamination (Wyszkowski and Radziemska 2009c). Organic matter has the ability to reduce Cr(VI) to Cr(III) as well as having a major influence on the bioavailability of metals (Thacher *et al*. 2015).

Compost, zeolite and CaO significantly influenced the chromium content of the analyzed soils (Tab. 2, Fig. 1). Calcium oxide and zeolite did not have a positive influence on the average content of chromium in pots with Cr(VI) in soil in which oats were grown, as they led to a small decrease in the content

TABLE 3. CONTENT OF ZINC, NICKEL AND COBALT IN MG$\cdot$KG^{-1} OF SOIL AFTER OAT HARVEST

Cr dose in mg$\cdot$kg^{-1} of soil	Kind of contamination									
	Chromium (III)					Chromium (VI)				
	Type of neutralizing substance									
	Without additives	Compost	Zeolite	CaO	Average	Without additives	Compost	Zeolite	CaO	Average
	Zinc									
0	34.89	40.65	36.38	40.76	38.17	34.89	40.65	36.38	40.76	38.17
25	37.11	39.07	31.65	38.30	36.53	36.45	39.08	38.91	36.42	37.72
50	39.22	39.60	32.65	38.08	37.39	37.94	46.03	37.70	35.55	39.31
100	40.73	39.10	33.94	38.05	37.96	37.99	42.48	36.69	40.80	39.49
150	36.71	38.97	34.93	37.02	36.91	40.10	37.09	36.12	40.71	38.51
r	0.375	-0.701*	0.081	-0.821**	-0.227	0.947**	-0.311	-0.479	0.392	0.419
LSD	a – 0.71**, b – n.i., c – 1.01*, a$\cdot$b – n.i., a$\cdot$c – 1.43**, b$\cdot$c – 2.26**, a$\cdot$b$\cdot$c – 3.19**									
	Nickel									
0	5.44	4.27	3.25	2.71	3.92	6.15	4.31	3.27	3.05	4.20
25	6.95	3.99	2.84	4.53	4.58	4.30	3.54	3.54	2.93	3.58
50	5.65	3.97	2.73	3.94	4.07	3.91	3.94	3.90	2.60	3.59
100	5.51	4.07	2.31	2.75	3.66	3.28	4.17	4.58	2.22	3.56
150	4.62	4.37	3.61	2.62	3.81	3.01	4.68	4.88	2.01	3.65
r	-0.648*	0.403	0.184	-0.465	-0.556	-0.871**	0.614	0.989**	-0.986**	-0.537
LSD	a – 0.14**, b – 0.22**,c – 0.20**, a$\cdot$b – 0.31**, a$\cdot$c – 0.28**, b$\cdot$c – 0.44**, a$\cdot$b$\cdot$c – 0.63**									
	Cobalt									
0	3.35	1.75	1.66	1.29	2.01	3.35	1.75	1.66	1.29	2.01
25	3.09	1.78	1.52	1.33	1.93	2.87	2.06	3.39	1.83	2.54
50	2.54	1.90	1.67	1.60	1.93	1.73	2.33	3.03	2.12	2.30
100	2.15	2.20	2.35	1.65	2.09	1.63	2.65	2.84	2.29	2.35
150	2.44	2.50	2.59	1.86	2.35	1.38	3.10	2.63	2.73	2.46
r	-0.816**	0.989**	0.942**	0.960**	0.855**	-0.883**	0.994**	0.216	0.954**	0.507
LSD	a – 0.08**, b – 0.13**, c – 0.12**, a$\cdot$b – 0.19**, a$\cdot$c – 0.17**, b$\cdot$c – 0.27**, a$\cdot$b$\cdot$c – 0.38**									

Explanatory notes under Table 1.

of the analyzed element by 6% and 4% respectively as compared to the control series (without neutralizing additives). According to Otabbong (1990), liming increases the amount of non-organic compounds – chromium hydroxides and phosphates, and decreases the amount of organic Cr(III) compounds. Literature contains findings which confirm the efficiency of removing chromium soil contamination using zeolites (Silva *et al*. 2008), which are characterized by high porosity and sorption capacity (Król and Mikuła 2017). Their use is also supported by the fact that, introduced into the soil, they do not undergo biochemical decomposition and can be removed from the soil at any time, along with the absorbed contaminants (Vareda *et al*. 2016).

The application of alleviating substances in the form of compost, zeolite and calcium oxide significantly affected the content of manganese in the analyzed soils (Tab. 2, Fig. 1). In soil in which oats were grown, the addition of zeolite had the most noticeable limiting effect on manganese content in pots with Cr(VI), causing a 5% average decrease in the content of the above element as compared to the series without the application of such substances.

In series containing neutralizing additives (compost, zeolite, CaO) and various doses of Cr(III) and Cr(VI), significant differences in the content of copper (Cu) were observed following the harvest of oat (Tab. 2, Fig. 1). Zeolite and CaO had a negative effect on the average Cu content in pots with Cr(III). Compost, zeolite and CaO in the series with Cr(VI) influenced the average Cu content in the analyzed soil positively. The application of composts has a positive influence on the physico-chemical properties of soils, including the contamination of soil with chromium (Banks *et al*. 2006), which has also been confirmed by the authors' own studies. Shortages of copper in soils occur as a result of its immobilization by organic matter on recently cultivated peat soils. Some shortages are also exhibited by calcareous soils (Yoo *et al*. 2016).

Alleviating substances (compost, zeolite, CaO) affect the content of zinc in soil following the harvest of the grown crop in different ways (Tab. 3, Fig. 1). Among the applied substances alleviating soil chromium contamination, zeolite in pots with Cr(III) and compost in pots with Cr(VI) had the strongest effect on the content of zinc in soil. The application of zeolite contributed to decreasing the content of zinc by 10% in pots with chromium (III), while compost increased it by 10% as compared to the series without additives. In an experiment by Radziemska and Mazur (2016) where natural zeolite was applied to the soil, a significant decrease in the zinc content was observed in soil contaminated with nickel compounds.

The addition of alleviating substances in the form of compost, zeolite and calcium oxide significantly influenced nickel contents in soil following the harvest of oat (Tab. 3, Fig. 1). The neutralizing additives had a much stronger influence on Ni content in soil following the harvest of oat in the case of adding Cr(III) as opposed to Cr(VI). The accumulation of Ni in the analyzed soil with Cr(III) was most severely limited by the addition of zeolite (-48%) and, to a lesser extent, CaO (-41%) and compost (-27%). In pots with Cr(VI), the application of CaO reduced Ni content by 38% as compared to the control series. In research carried out by Herwijnen *et al*. (2007), zeolite-amended composts were found to be more effective than un-amended ones in the remediation of heavy metal polluted soils in a leaching experiment.

Compost, zeolite and calcium oxide significantly shaped the content of cobalt in soil after harvesting oat (Tab. 3, Fig. 1). Neutralizing additives significantly affected the content of cobalt in soil, both in pots with Cr(III) as well as Cr(VI). Compost, zeolite and especially CaO limited the content of cobalt in the variants containing trivalent chromium. The opposite situation was observed in pots with Cr(VI) upon applying zeolite and, to a lesser degree, compost.

CONCLUSIONS

The content of chromium, manganese, copper, zinc, nickel, and cobalt in soil was dependant on the dosage of Cr(III) and Cr(VI), as well as the addition of compost, zeolite and calcium oxide. An increase of chromium in soil was observed in response to the increased contamination of soil with Cr(III) and Cr(VI), as well as manganese, zinc and nickel when dealing with the highest doses of the contaminants. The contents of copper and cobalt in the analyzed soil were negatively correlated with increasing Cr(III) and Cr(VI) contamination. In pots with Cr(VI), the addition of compost significantly increased the copper, zinc, and cobalt content of the analyzed soil as compared to the control. The application of calcium oxide significantly reduced the copper content of soil from pots with Cr(III), and nickel content in its Cr(VI) contaminated counterpart, as well as influencing an increase in the chromium and copper contents of soil subjected to Cr(VI) contamination.

ACKNOWLEDGEMENTS

The work was supported by grants No N N305 1059 33 from the Polish Ministry of Science and Higher Education.

REFERENCES

[1] Adamcová, D., Vaverková, M., Břoušková, E., 2016. *Emission assessment at the Štěpánovice municipal solid waste landfill focusing on CH_4 emissions*. Journal of Ecological Engineering, 17, 3: 9–17.

[2] Antoniadis, V., Polyzois, T., Golia, E.E., Petropoulos, S.A., 2017. *Hexavalent chromium availability and phytoremediation potential of Cichorium spinosum as affect by manure, zeolite and soil ageing*. Chemosphere, 171: 729–734.

[3] Arshad, M., Khan, A.H.A., Hussain, I., Zaman, B., Anees, M., Iqbal, M., Soja, G., Linde, C., Yousaf, S., 2017. *The reduction of chromium (VI) phytotoxicity and phytoavailability to wheat (Triticum aestivum L.) using biochar and bacteria*. Applied Soil Ecology, 114: 90–98.

[4] Banks, M.K., Schwab, A.P., Henderson, C., 2006. *Leaching and reduction of chromium in soil as affected by soil organic content and plants*. Chemosphere, 62: 255–264.

[5] Dumoulin, D., Billon, G., Proix, N., Frérot, H., Pauwels, M., Saumitou-Laprade, P. 2017. *Impact of a zinc processing factory on surrounding surficial soil contamination.* Journal of Geochemical Exploration, 172: 142–150.

[6] Grzywnowicz, I., 1997. *Zawartość i rozmieszczenie niklu w glebach różnych regionów Polski*. Zeszyty Problemowe Postępów Nauk Rolniczych, 448a: 147–153.

[7] Guimarães, M.M, Carvalho, A.C.M.S., Silva, M.S., 2016. *Effect of chromium supplementation on the glucose homeostasis and anthropometry of type 2 diabetic patients: Double blind, randomized clinical trial: Chromium, glucose homeostasis and anthropometry*. Journal of Trace Elements in Medicine and Biology, 36: 65–72.

[8] Hao, Q., Jiang, C., 2015. *Heavy metal concentrations in soils and plants in Rongxi Manganese mine of chongqing, southwest of China*. Acta Ecologica Sinica, 35(1): 46–51.

[9] Herwijnen, R., Hutchings, T.R., Ai-Tabbaa, A., Moffat, A.J., Johns, M.L., Ouki, S.K., 2007. *Remediation of metal contaminated soil with mineral-amended composts*. Environmental Pollution, 150: 347–354.

[10] Hewelke, E., Szatyłowicz, J., Gnatowski, T., Oleszczuk, R., 2014. *Zmienność przestrzenna uwilgotnienia hydrofobowej gleby organicznej w warunkach przepływu preferencyjnego*. Rocznik Ochrona Środowiska, 16*,* 1: 580–607.

[11] Hewelke, P., Gnatowski, T., Hewelke, E., Tyszka, J., Zakowicz, S., 2015. *Analysis of water retention capacity for select forest soils in Poland.* Polish Journal of Environmental Studies, 24, 3: 1013–1019.

[12] Jalali, M., Majeri, M., 2016. *Cobalt sorption–desorption behavior of calcareous soils from some Iranian soils*. Chemie der Erde – Geochemistry, 76, 1: 95–102.

[13] Kabata-Pendias, A., Pendias, H., 2011. *Trace Elements in Soil and Plants*, 4th ed.; CRC Press: Boca Raton, FL, USA, pp. 365.

[14] Klute, A., 1996. *Methods of soil analysis. Madison*: American Society of Agronomy. Agronomy Monograph, 9.

[15] Król, M., Mikuła, A., 2017. *Synthesis of the zeolite granulate for potential sorption application.* Microporous and Mesoporous Materials, 243: 201–205.

[16] Liu, H., 2016. *Relationship between organic matter humification and bioavailability of sludge-borne copper and cadmium during long-term sludge amendment to soil*. Science of the Tototal Environment, 566–567: 8–14.

[17] Lukina, A.O., Boutin, C., Rowland, O., Carpenter, D.J., 2016. *Evaluating trivalent chromium toxicity on wild terrestrial and wetland plants.* Chemosphere, 162: 355–364.

[18] Mathebula, M.W., Mandiwana, K., Panichev, N., 2017. *Speciation of chromium in bread and breakfast cereals.* Food Chemistry, 217: 655–659.

[19] Mazur, Z., Radziemska, M., Fronczyk, J., Jeznach, J., 2015. *Heavy metal accumulation in bioindicators of pollution in urban areas of northeastern Poland.* Fresenius Environmental Bulletin, 24, 1a: 216–223.

[20] Mocek, A., Drzymała, S., 2010.*Genesis, Analysis and Soil Classification*. Poznań University of Life Sciences (in Polish).

[21] Otabbong, E., 1990. *Chemistry of Cr in some Swedish soils. Interreaction between* CrO_3 *and* $Si(OH)_4$ *ant its impact on Cr toxicity and elemental contents in ryegrass (Lolium perenne*). Plant Soil, 123: 89–93.

[22] Pils, J.R.V., Karathanasis, A.D., Mueller, T.G., 2004. *Concentration and distribution of six trace metals in nothern Kentucky soils*. Soil Sediment Contamination, 13(1): 37–51.

[23] Radziemska, M., Mazur, Z., 2016. *Content of selected heavy metals in Ni-contaminated soil following the application of halloysite and zeolite.* Journal of Ecological Engineering, 17, 3: 125–133.

[24] Radziemska, M., Mazur, Z., Jeznach, J., 2013. *Influence of applying halloysite and zeolite to soil contaminated with nickel on the content of selected elements in Maize (Zea mays L.*). Chemical Engineering Transactions, 32: 301–306.

[25] Radziemska, M., Mazur, Z., Fronczyk, J., Jeznach, J., 2016. *Effect of reactive materials on the content of selected elements in Indian mustard grown in Cr(VI)-contaminated soils*. Journal of Ecological Engineering, 17, 2: 141–147.

[26] Radziemska, M., Fronczyk, J., 2015. *Level and Contamination Assessment of Soil along an Expressway in an Ecologically Valuable Area, Central Poland*. International Journal of Environmental Research and Public Health, 12: 13372–13387.

[27] Riehm, H., 1958. *Die ammoniumlaktatessigsaure-methode zur bestimmung der leichtloeslichen phosphosaure in karbonathaltigen boden*. Agrochimica, 3: 49–65.

[28] Sas, W., Głuchowski, A., Radziemska, M., Dzięcioł, J., Szymański, A., 2015. *Environmental and geotechnical assessment of the steel slags as a material for road structure*. Materials, 8: 4857–4875.

[29] Sasso, A.F., Schlosser, P.M., 2015. *An evaluation of in vivo models for toxicokinetics of hexavalent chromium in the stomach.* Toxicology and Applied Pharmacology, 287(3): 293–298.

[30] Silva, B., Figueiredo, H., Quintelas, C., Neves, I.C., Tavares, T., 2008. *Zeolites as supports for biorecovery od hexavalent chromium and trivalent chromium.* Microporous and Mesoporous Materials, 116: 550–560.

[31] Thacher, R., Hsu, L., Ravindran, V., Nealson, K.H., Pirbazari, M., 2015. *Modeling the transport and bioreduction of hexavalent chromium in aquifers: Influence of natural organic matter.* Chemical Engineering Science, 138: 552–565.

[32] Vareda, J.P., Valente, A.J.M, Durães, L., 2016. *Heavy metals in Iberian soils: Removal by current adsorbents/amendments and prospective for aerogels.* Advances in Colloid and Interface Science, 237: 28–42.

[33] Wyszkowski, M., Radziemska, M., 2009a. *The effect of chromium content in soil on the concentration of some mineral elements in plants.* Fresenius Environmental Bulletin, 18, 7: 1039–1045.

[34] Wyszkowski, M., Radziemska, M., 2009b. *Content of nitrogen compounds in soil polluted with chromium (III), chromium (VI) after application of compost, zeolite and calcium oxide*. Ecological Chemistry and Engineering A, 16(8): 1039–1046.

[35] Wyszkowski, M., Radziemska, M., 2009c. *Oddziaływanie kompostu, zeolitu i tlenku wapnia na zawartość węgla organicznego i składników mineralnych w glebie zanieczyszczonej chromem.* Zeszyty Problemowe Postępów Nauk Rolniczych, 537: 413–420.

[36] Wyszkowski, M., Radziemska, M., 2010. *Effects of chromium (III and VI) on spring barley and maize biomass yield and content if nitrogenous compounds*. Journal of Toxicology and Environmental Health, Part A, 73(17–18): 1274–1282.

[37] Wyszkowski, M., Radziemska, M., 2013a. *Influence of chromium (III) and (VI) on the concentration of mineral elements in oat (Avena sativa L.).* Fresenius Environmental Bulletin, 22, 4: 979–986.

[38] Wyszkowski, M., Radziemska, M., 2013b. *Assessment of tri- and hexavalent chromium phytotoxicity on Oats (Avena sativa L.) biomass and content of nitrogen compounds*. Water, Air, & Soil Pollution, 244: 1619–1632.

[39] Yilmaz, E., Soylak, M., 2016. *Ultrasound assisted-deep eutectic solvent based on emulsification liquid phase microextraction combined with microsample injection flame atomic absorption spectrometry for valence speciation of chromium (III/VI) in environmental samples*. Talanta, 60: 680–685.

[40] Yoo, J., Shim, T., Hur, J., Jung, J., 2016. *Role of polarity fractions of effluent organic matter in binding and toxicity of silver and copper.* Journal of Hazardous Materials, 317: 344–351.

[41] Yu, C.H., Huang, L., Shin, J.Y., Artigas, F., Fan, Z.T., 2014. *Characterization of concentration, particle size distribution, and contributing factors to ambient hexavalent chromium in an area with multiple emission sources.* Atmospheric Environment, 94: 701–708.