

Influence of Organic and Mineral Amendments on Accumulation of Selected Elements in Oat Cultivated on Soil Contaminated with Cr (III) and Cr (VI)

Maja Radziemska¹, Joanna Fronczyk², and Mirosław Wyszowski³

Abstract— Chromium is one of the most phytotoxic heavy metals found in soils, and its concentration is continuously increasing, mainly as a result of anthropogenic activities. The research aimed to determine the influence of Cr(III) and Cr(VI) in doses of 0, 25, 50, 100 and 150 mgCrkg⁻¹ of soil, as well as compost, zeolite and CaO amendments on the content of trace elements in the grain, shoot and roots of oat. Cr(VI) modified the content of heavy metals in oat more strongly than Cr(III). The highest levels of Cr were found in the treatments polluted with Cr(VI). All of the investigated heavy metal contents in the tested parts of oat were significantly different in the case of applying compost, zeolite, and CaO to the soil, as well as increasing concentrations of Cr(III) and Cr(VI). CaO reduced the content of Zn in oat more strongly than zeolite or compost. The substances introduced to the soil tended to favor the accumulation of Cu in plants, mainly in oat grain from pots polluted with Cr(VI). Negative relationships were determined in the grain of oat grown in soil polluted with Cr(III) and in the roots of oat plants from all test combinations.

Keywords— CaO, chromium, compost, contaminated soils, oat, zeolite.

I. INTRODUCTION

STUDIES on the effects of chromium, especially Cr(VI), on plants are important in every field of environmental protection. Chromium (chemical symbol Cr) is a member of a group of transition metals on the periodic table of elements - group VIA, with an atomic mass of 51.996, and atomic number of 24. As the tenth element in the Earth's crust, it is omnipresent component in nature; it is found in the air, water and soil, as well as in biological elements. Based on the diagrams of its state of oxidation, the most stable oxidation state is III. The biological activity of chromium depends on its valence state, with Cr(III) and Cr(VI) considered to be stable valence forms [1].

Chromium compounds are widely introduced into the

natural environment in form of various sources, e.g. waste [2], sewage [3], gas contaminants [4], steel slag [5], and products of the leather tanning industry [6] as well as inorganic and organic chemical manufacturing [7]. When passing through the natural environment, they affect all links of the trophic-chain [8].

Chromium can be found in all plant tissues, as an essential microelement responsible for many physiological processes, as well as the activation of certain enzymes, especially oxyreductases. The content of chromium in plants is connected with a set of chemical and geological properties of soil [9]. This means that the Cr content in plants is dependent on the abundance of this element in soil, as well as the plant species [10], [11], [12]. The chromium content of plants is a topic of interest mainly due to animal feed and dietary issues. In crops intended for consumption, large variation in the content of this element can be observed, e.g.: rapeseed - 1.0 mg·kg⁻¹ d.w., cucumbers - 0.02 mg·kg⁻¹ d.w., oats - 0.55 mg·kg⁻¹ d.w. [13].

The objectives of this study were to determine the effects of Cr(III) and Cr(VI) on the content of trace elements in the grain, shoot and roots of oat (*Avena sativa* L.) Moreover, an attempt was also made to determine the ability of organic and mineral amendments i.e., compost, zeolite and CaO, on the content of trace elements in the analyzed parts of oat.

II. MATERIAL AND METHODS

A. Plant Growth Experiment

The impact of zeolite as well as compost and CaO added to soil contaminated with Cr(III) and Cr(VI) on the content of Cr, Cu, Zn and Ni in oat (*Avena sativa* L.) was assessed under the conditions of a pot experiment in an acclimatized greenhouse at the University of Warmia and Mazury in Olsztyn (Poland). The experiment was set up in 9.5 kg polyethylene pots, 20 cm in diameter and 26 cm high. The pots were maintained in controlled conditions; during the day, the air temperature was 26-28°C, and approximately ten degrees lower (16-18°C) at night. Mineral fertilization was applied in the form of aqueous solutions of macro- and micronutrients (in milligrams per kilogram of soil): 110 - N, 50 - P, 110 - K, 50 - Mg, 0.33 - B, 5 - Mn, 5 - Mo. The soil was artificially polluted with aqueous solutions of Cr(III) in the form of KCr(SO₄)₂·12H₂O, and Cr(VI) in the form of K₂Cr₂O₇, in the following doses: 25, 50,

Maja Radziemska¹ Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Joanna Fronczyk² Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Mirosław Wyszowski³ University of Warmia and Mazury in Olsztyn, Faculty of Environmental Management and Agriculture, Pl. Łódzki 4, 10-718 Olsztyn, Poland

100, and 150 mg·kg⁻¹ of soil. Control treatments were also established, where neither amendments nor Cr(III) or Cr(VI) compounds were introduced. The test plant was oat, which the US Environmental Protection Agency (US-EPA) recommends as a biomarker for chromium toxicity assessment. The seeds of *A. sativa* (L.) cv. Kasztan, were obtained from an authorized Seed Production Centre in Olsztyn, Poland (OLZNAS-CN Sp. z o.o.). Plant density was set at n=25 plants per pot. The plants were watered every other day with distilled water to 60% of the maximum water holding capacity of the soil by adding deionized water. Aerial (grain and shoot) and underground parts of plants (roots) were harvested for laboratory analyses when fully ripe.

B. Physicochemical Characteristics of Experimental Soil and Amendments

Non-polluted soils used for plant cultivation were collected at a depth of 0-20 cm from farmland in the vicinity of Olsztyn, Poland. The experimental soil was tested for its physicochemical and nutritional properties before sowing the seeds. It was found to be slightly acidic, with a pH of 5.5, and contained 7.87 g·kg⁻¹ Corg., 1.01 g·kg⁻¹ N, 21.29 mg·kg⁻¹ N-NH₄⁺, 2.95 mg·kg⁻¹ N-NO₃⁻, 90.2 P mg·kg⁻¹, 37.9 mg·kg⁻¹ K and 77.0 mg·kg⁻¹ Mg. Other metals (mg·kg⁻¹) present were Cr - 12.95, Cu - 9.01, Zn - 24.25 and Ni - 3.99. The grain size structure was that of light loamy sand (fractions in mm: <0.002 - 0.85%; 0.002-0.020 - 6.85%; 0.020-0.050 - 7.19%; 0.050-0.100 - 7.06%; 0.100-0.250 - 34.63%; 0.250-0.500 - 34.06%; 0.500-1.000 - 9.36%; 1.000-2.000 - 0%), and characterized by the following properties: hydrolytic acidity (HAC) - 26.6 mmol(H⁺)·kg⁻¹, total exchange bases (TEB) - 100.0 mmol·kg⁻¹, cation exchange capacity (CEC) -126.6 mmol·kg⁻¹ and base saturation (BS) -79.9%.

TABLE I
CHEMICAL COMPOSITION OF SUBSTANCES USED IN THE EXPERIMENT

Element	Unit	Compost	Zeolite	CaO
Phosphorous	g·kg ⁻¹	2.32	0.11	0.10
Potassium		1.33	23.2	0.77
Magnesium		1.47	0.31	2.65
Calcium		15.9	15.3	347
Sodium		0.12	16.1	0.07
Chromium	mg·kg ⁻¹	3.48	1.81	2.70
Copper		38.1	12.4	2.26
Zinc		31.8	14.7	5.14
Nickel		18.8	408	6.64

Three amendments were applied to the soil: compost and zeolite (2% of dry soil mass), and 50% CaO in a dose corresponding to one hydrolytic acidity (HAC), i.e. 1.25 g·kg⁻¹ of soil. The chemical composition of the substances applied to the soil has been provided in Table I.

C. Preparation And Analyses Of Plant And Soil Sample

In the laboratory plant samples were thoroughly rinsed, first with tap water and then with deionized water, to remove dust and soil particles. After oven drying (60°C, 48 h), the plants were weighed and powdered using an analytical mill (A 11 IKA, Germany), and kept at an ambient temperature prior to

the chemical analyses. The heavy metal concentrations (Cr, Cu, Zn and Ni) were determined using flame atomic absorption spectroscopy on a SpectrAA 240FS atomic absorption spectrophotometer (VARIAN, Australia) using a Sample Introduction Pump System in extracts obtained after the microwave digestion of plant samples in nitric acid (HNO₃ p.a.) with a concentration of 1.40 g·cm⁻¹, poured into HP500 Teflon vessels and placed in a MARS 5 microwave oven (CEM Corporation, USA). The mineralization conditions, i.e. the volume of an aliquot, the volume of nitrogen acid and mineralization temperature, were set as described in the methodology found in the Mars 5 Operation Manual.

Soil samples were digested and analyzed using the same reagents. Before setting up the experiment, the following soil properties were determined: the grain size composition of the soil by means of the laser method using a Mastersizer 2000 m, pH - determined by means of the potentiometric method using an aquatic solution of KCl at a concentration of 1M KCl·dm⁻³ with a glass electrode and a Handylab pH/LF 12 pH meter (Schott, Germany) hydrolytic acidity (HAC) by Kappen's method, with soil samples treated with 0.5 M/dm³ Ca-acetate solution adjusted to pH 8.2 in the ratio of 1:2.5) [14], total exchangeable bases (TEB-K⁺, Na⁺, Ca²⁺, and Mg²⁺) by Kappen's method, determining individual cations after extraction from the soil with CH₃COONH₄ [14], cation exchange capacity (CEC) from the formula: CEC=HAC+TEB, and percentage base saturation (V) from the formula: BS=100·TEB/CEC⁻¹. Organic matter was determined according to Tiurin's method, after the hot digestion of soil samples with K₂Cr₂O₇ and H₂SO₄ in the presence of Ag₂SO₄ as a catalyst and the titration of K₂Cr₂O₇ excess with FeSO₄/(NH₄)₂SO₄·6H₂O [15]. The contents of available phosphorus and potassium were established using the Egner-Riehm method [16], and magnesium using the Schachtschabel method [17].

All glass and polyethylene flaskware were previously soaked for 24 hours in 10% (v/v) HNO₃ and rinsed three times with ultra-pure water prior to use. Ultra-pure water (specific resistivity of 18.2 MΩcm) obtained from a Milli-Q system (Millipore, Bedford, USA) was employed to prepare all of the solutions and standards. The quality control of the heavy metal analyses was performed using certified reference material Sigma Aldrich Chemie GmbH, No. BCR142R. The solutions of metals were prepared by the dilution of certified standard solutions (Fluka, Sigma Aldrich). Stock solutions of metals (1000 mg·L⁻¹) were prepared from their nitrate salts.

D. Statistical Analysis

All statistical analyses were carried out with the Statistica 9.1 Statistical Package. The data were analyzed by three-factorial analysis of variance (ANOVA), considering the treatment as the independent variable. Significant statistical differences in all variables were established between the different treatments by Duncan's multiple range test, at p<0.05.

III. RESULTS AND DISCUSSION

A. Effect of Cr(III) and Cr(VI) on the Content of Trace Elements

The toxic effect of chromium on plants [18] depends on many factors, of which the most important are the degree to which the soil is polluted with this metal and other soil properties, e.g. the content of humus, acidity, sorptive properties, or the presence of certain elements [19]. Chromium accumulated in soil can be easily translocated to the aerial parts of plants and cause many morphological changes, e.g. decreased photosynthesis, chlorosis, necrotic spots, changes in colour, damage to roots, and finally, plant death [20]. Therefore, it is essential to search for effective methods for the neutralization of chromium in soil and the reduction of its influence on crops. The negative effect of chromium compounds on various plants has been widely investigated, e.g. *Brassica napus* var. *oleifera* [10], *Avena Sativa* L. [11], *Triticum aestivum* L. [18], *Solanum nigrum* L. and *Parthenium hysterophorus* L. [21], *Daucus carota* L. [23]. Cr(VI) has a stronger negative effect on plants than Cr(III) [Oliveira et al. 2015]. Fig. 1 shows the chromium (Cr) concentrations in the grain, shoot and root of *Avena Sativa* L. at the different doses of Cr(III) and Cr(VI) added to the soil. The highest value of Cr in the control series was found in the roots and ranged from 9.72 to 77.82 mg·kg⁻¹ d.w. (dry weight), with the lowest in grain, ranging from 0.52 to 2.28 mg·kg⁻¹ d.w. Cr(VI) in the amounts of 50 and 100 mg·kg⁻¹ d.w. of soil raised the content of chromium in the roots 18-fold as compared to the control. The content of this element in the shoot was positively correlated ($r=0.99$) with the increasing doses of Cr(VI), with the highest rate of this contaminant (150 mg·kg⁻¹ of soil) causing an over two-fold increase in the content of chromium in the shoot, compared to the control. According to Kabata-Pendias [13], very sensitive plants, e.g. oat, develop toxic symptoms in response to total chromium contents as low as 1-2 mgCrkg⁻¹ of soil, whereas maize can tolerate up to 8 mgCrkg⁻¹ of soil, and tobacco - up to 24 mgCrkg⁻¹ of soil. In the present study, the highest dose of Cr(III), i.e. 150 mg·kg⁻¹ of soil, caused an 8-fold increase in the concentration of Cr in the roots ($r=0.99$) as compared to the control treatment.

The increasing concentrations of tri- and hexavalent chromium in soil in the series without amendments had a positive effect on the content of Cu in oat (Fig. 1). The highest value of Cu in the control series occurred in the grain and ranged from 40.70 to 54.58 mg·kg⁻¹ d.w., with the lowest observed in the shoot, ranging from 0.70 to 3.50 mg·kg⁻¹ d.w. In the series without amendments, the highest average content of Cu was found in the grain and roots of plants grown in soil contaminated with Cr(III). The increasing doses of tri- ($r=-0.99$) and hexavalent chromium ($r=-0.97$) contributed to a progressing decline in the concentration of Cu in the grain. The dose of Cr(VI) equal to 100 mg·kg⁻¹ of soil depressed the content of this element by 64% when compared to the control treatment. The accumulation of copper in the roots, determined

by Zheljazkov and Nielsen [24], was higher than in leaves or flowers of peppermint. This phenomenon can be explained by the defense mechanisms of plants, which protect themselves from the excessive accumulation of copper in aerial parts. In shoots harvested from the series without soil amending substances, Cr(III) caused a gradual decrease in the content of copper as the rates of contamination increased ($r=-0.89$). A reverse tendency occurred when Cr(VI) was applied, as the increasing rates of this contaminant contributed to increasing concentrations of Cu ($r=-0.84$) in relation to the control.

The concentrations of Zn in the grain, shoot and roots of oat were significantly shaped by the doses of Cr(III) and Cr(VI) (Fig. 1). Zinc demonstrates strong affinity to mineral colloids, and is characterized by a weak tendency to forming complex bonds with organic substance. It is also characterized by high mobility in soil and a high uptake by plants, owing to the fast solubility of compounds in which it appears, especially in an acidic environment [25]. In the present study, the highest values of Zn in the control series were noted in the grain and shoot, ranging from 91.08 to 112.4 mg·kg⁻¹ d.w. and 111.8 to 155.0 mg·kg⁻¹ d.w., respectively. The content of Zn in oat grain was positively correlated with increasing doses of Cr(III). A reverse dependency occurred in the treatments with Cr(VI). The tested organs of oat grown in the series without contamination and alleviating substances were characterized by a higher average content of Zn in the treatments with tri- rather than hexavalent chromium. Of the analyzed plant organs, the highest content of chromium in the series without soil amending substances was found in the roots. In the treatments contaminated with Cr(III) applied at a dose of 150 mg·kg⁻¹ of soil, a 22% higher content of Zn was observed than in the control treatment. A reverse tendency occurred in the treatments with Cr(VI), where increasing rates of this pollutant caused a decline in the content of Zn in oat grain by a maximum of 14% ($r=-0.98$) as compared to the control. Cr(VI) had a stronger effect than Cr(III) on the content of Zn in the oat shoot, depressing it by 27% ($r=-0.63$). Cr(III) raised the content of Zn in the shoot and roots of oat, but only when added in amounts of up to 50 mg·kg⁻¹ of soil. Chromium (VI) affected the content of Zn in the shoot and roots of oat more strongly than chromium (III).

Nickel is an essential micronutrient for plants, but in high doses, it reduces the growth of roots and results in disorders in nutrient uptake, nitrogen metabolism and photosynthesis [26]. Alloway [27] claims that the content of nickel in plants depends largely on its concentration and forms available in the soil. Among the analyzed oat organs, the highest average content of nickel was found in the roots, both in the treatments with tri- and hexavalent chromium (Fig. 1). This can be explained by the fact that the roots are the main pathway for trace elements to enter the plant. Increasing doses of Cr(III) had a negative effect on the content of Ni in oat grain: -52% ($r=-0.97$). A reverse tendency was observed in the treatments contaminated with chromium (VI), where, under the influence of its increasing rates, the content of Ni increased by 53%

($r=0.96$). Hexavalent chromium had a stronger effect on the content of nickel in oat shoots than Cr(III). In the series without soil amending substances, the highest rate of this contaminant (150 mg kg^{-1} of soil) caused a 52% decline ($r=-0.73$) in the content of the above element as compared to the control (no contamination). Under the influence of increasing doses of Cr(VI), increased Ni concentration in oat roots was noted ($r=0.96$).

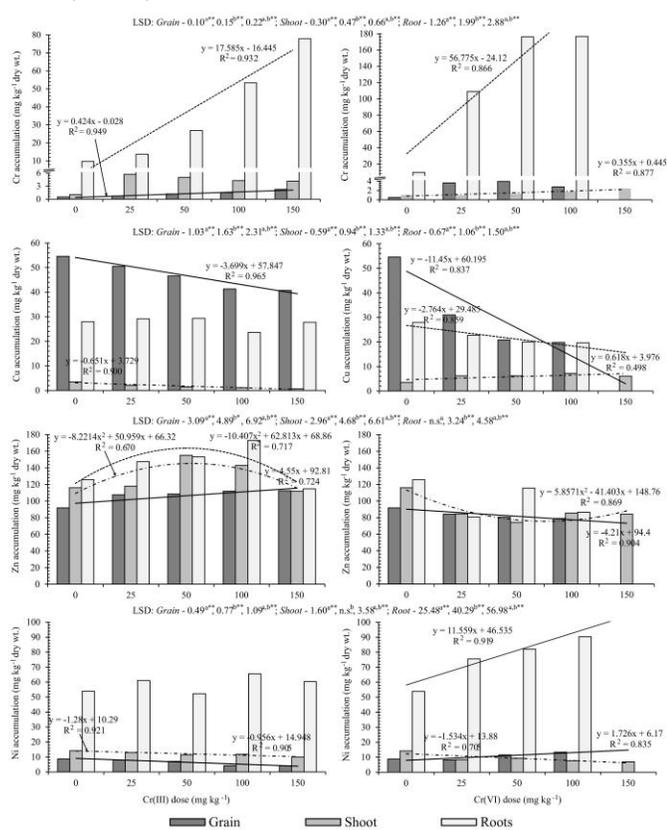


Fig. 1 Effect of Cr(III) and Cr(VI) on the content of Cr, Cu, Zn, and Ni in oat (*A. sativa* L.), in mg dry weight per kg. LSD for: a - type of chromium, b - Cr dose; c - type of amendments; n.s. - insignificant differences; **significant for $p=0.01$; *significant for $p=0.05$

B. Effect of Compost, Zeolite and CaO on the Content of Trace Elements

The application of organic and mineral amendments to contaminated soils can immobilize heavy metals and may provide a sustainable solution for the phytoremediation of, i.a. Cr-contaminants in soils [28]. Numerous studies have shown that the application of rock phosphate [29], halloysite [30], zeolite [31], and diatomite [32], decreased heavy metal solubility and plant uptake in contaminated soils. The present study indicates a strong relationship between the application of compost, zeolite and CaO and increasing Cr(III) and Cr(VI) concentrations of soil on the chromium content of oat (Fig. 2).

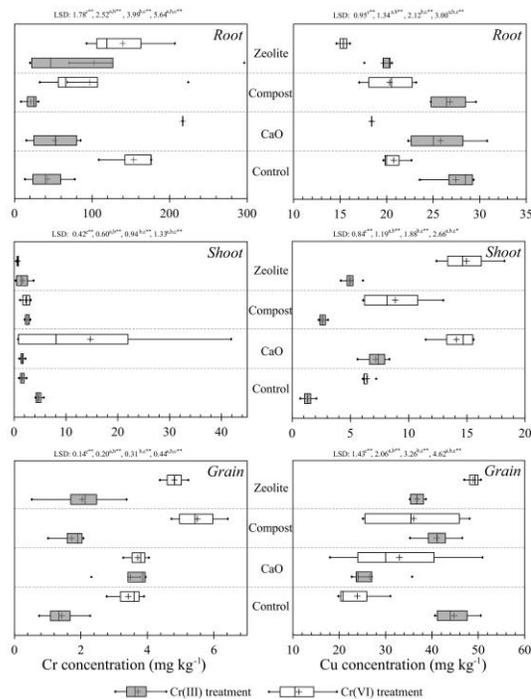


Fig. 2 Boxplots showing the median, quartiles, and minimum and maximum values of Cr and Cu in the individual plant organs depending on the type of additive. LSD for: a - type of chromium, b - Cr dose; c - type of amendments; n.s. - insignificant differences; **significant for $p=0.01$; *significant for $p=0.05$.

As regards Cr(III), calcium oxide had the strongest effect, although the other neutralizing substances also caused a decrease in the content of chromium in oat grain. In the treatments with Cr(III), zeolite and calcium oxide reduced the content of the analyzed element by 65%, and in the pots with Cr(VI), zeolite reduced its content by 60% in comparison to the control series. Liming materials, including CaO, are the typical amendment used for in-situ immobilization and to transform soluble metals into residual ones, and to reduce the metal concentration in plant tissues [33]. In another experiment conducted by Radziemska et al. [34], zeolite and halloysite influenced the average content of selected elements in the aerial parts of maize grown on soil contaminated with nickel. In the present study, the influence of compost and CaO on the content of chromium in the oat shoot in pots with Cr(VI) was not favorable. A positive effect, that is a reduction in the content of chromium in the oat roots, was determined only after the application of zeolite and CaO to soil in the Cr(VI) treatments; compost added to soil polluted with Cr(III) resulted in an even better effect. However, it should be mentioned that, due to an insufficient amount of plant material, the content of chromium was not determined in oat grain and roots collected from some of the treatments. Heavy metals can be stabilized by mixing inorganic and organic amending agents with, or injecting them into the soil, which decreases their bioavailability. Organic waste, such as sewage sludge and domestic refuse or manure compost, can be used as soil amendments to lower metal availability.

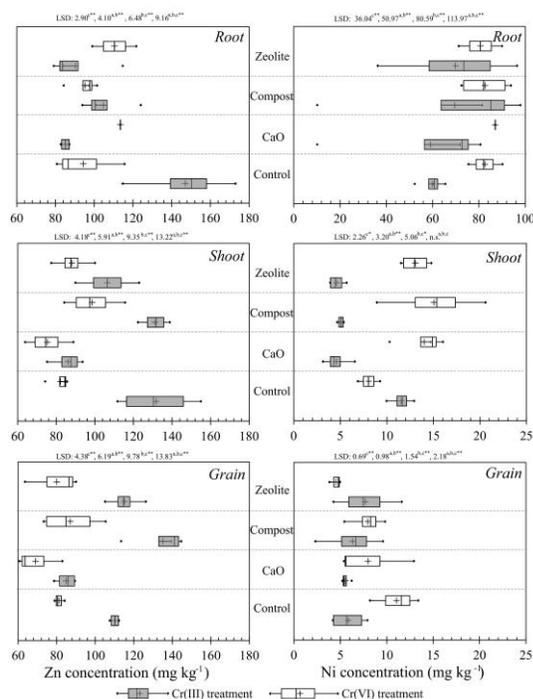


Fig. 3 Boxplots showing the median, quartiles, and minimum and maximum values of Zn and Ni in the individual plant organs depending on the type of additive. LSD for: a - type of chromium, b - Cr dose; c - type of amendments; n.s. - insignificant differences; ** significant for $p=0.01$; * significant for $p=0.05$.

Laboratory and pot trial experiments have clearly demonstrated that the concentration of Cu in oat was closely correlated with the type of amendments introduced into the soil (Fig. 2). All of the tested substances reduced the content of Cu in the treatments with trivalent chromium, but a reverse tendency occurred in the analogous series with chromium (VI). In the series with Cr(III) and Cr(VI), CaO, zeolite and, to a lesser degree, compost, caused an increase in the average content of copper in the oat shoots as compared to the control series. The strongest effect on the content of Cu in the oat roots in the case of chromium (VI) polluted treatments was observed when soil was enriched with CaO or zeolite. These substances reduced the content of Cu in oat roots by 24-25% in relation to the control (no soil amending substances). A weaker, albeit significant, effect of these substances occurred in the treatments with Cr(III), where the average content of Cu in oat roots was 14% (CaO) and 28% (zeolite) lower than in the series without neutralizing substances.

A stronger effect of the contamination alleviating substances on the content of Zn in oat grain was observed in the treatments with Cr(III) than Cr(VI) (Fig. 3). In the pots with Cr(III), compost and zeolite raised the content of zinc in oat grain by 23% and 9%, respectively, as compared to the control (no neutralizing substances). Calcium oxide reduced the content of copper by 24%. The same dependencies appeared in the treatments with Cr(VI), but the range of differences was much smaller. With respect to the oat shoot, the content of Zn was most strongly affected by soil supplementation with CaO and, even more so, zeolite in the treatments with chromium

(III), and CaO in pots with Cr(VI). By changing the acidity of the soil environment, the availability of Zn can be modified when the soil is limed [13]. Novo et al. [35] reached the conclusion that technosols made of wastes can be successfully used to increase the growth and the uptake of Zn by mustards in reclaimed mine soils. In the present series, CaO reduced the content of Zn by 36% - Cr(III), and 16% - Cr(VI). Zeolite and CaO raised the content of zinc in the roots, but only some of the analyses were performed for these treatments due to insufficient amounts of plant material.

The effect of the neutralizing substances used in the experiment was reflected in the Ni content of the grain, shoot and roots of oat (Fig. 3). Compost, zeolite and CaO in the treatments with Cr(VI) had a negative effect on the mean content of nickel in oat grain. In this series, zeolite decreased the average content of nickel by as much as 57% when compared to the series without neutralizing substances (control). In another trial by Radziemska et al. [30], zeolite caused the highest (of the analyzed additives) reduction of nickel content in the above-ground parts of maize grown in soil with $240 \text{ mg Ni kg}^{-1}$ of soil. The influence of the tested neutralizers was weaker in the treatments with Cr(III) but, in respect to compost and CaO, analogous to that found in the Cr(VI) contaminated treatments.

The content of Ni in the oat shoot in the Cr(VI) contaminated treatments was positively affected by all of the tested neutralizing substances. The strongest effect was attributed to compost, which increased the average content of nickel by 50% in the shoot compared to the control series. Organic amendments such as biochar can be used to improve the quality of metal-polluted reclaimed mine soils. Reverse dependencies were found in the pots with Cr(III). The strongest effect on the average Ni content in the roots of oat grown in Cr(III) contaminated soil was produced by compost and CaO, while zeolite had a weaker impact. In the pots polluted with Cr(VI), zeolite and compost were more effective.

IV. CONCLUSIONS

Heavy metals concentrations followed the decreasing orders of: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cr}$ in grain, and $\text{Zn} > \text{Ni} > \text{Cr} > \text{Cu}$ in the shoot and roots. In addition, the content of chromium in oat was higher when the soil contamination with this metal was stronger. Cr(VI) modified the content of heavy metals in oat more strongly than Cr(III). The highest levels of Cr were found in the treatments polluted with Cr(VI). The content of chromium was particularly high in oat roots, as compared to the grain or shoot. Compost reduced the negative influence of Cr(III) most significantly, causing a significant decrease in the content of Cr in the oat shoot and roots. The effects of calcium oxide and zeolite, albeit beneficial, were weaker than that of compost. The highest rates of Cr(VI) caused an increase in the content of chromium in the grain, shoot and roots of oat, but depressed that of Cu and Zn. The effects influenced by both forms of chromium on the content of Ni in oat were less consistent, and depended on the plant organ and dosage of

chromium. All of the investigated heavy metals in the tested parts of oat differed significantly on application of compost, zeolite, and calcium oxide to the soil, as well as increasing concentrations of Cr(III) and Cr(VI). CaO reduced the content of Zn in oat more strongly than zeolite or compost.

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