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Research Article

CHEMICAL COMPOSITION OF SPRING RAPESEED GROWN IN COPPER-CONTAMINATED SOIL AMENDED WITH HALLOYSITE AND ZEOLITE

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ABSTRACT

The purpose of this study was to determine the effect of soil contamination with copper doses of 0, 150, 300, and 450 $mg \cdot kg^{-1}$ of soil and the application of zeolite, raw and modified halloysite on the biomass of spring rapeseed and the content of nitrogen compounds and macronutrients in the above-ground parts of the tested plants. The content of macronutrients in plants was determined spectrophotometrically. The applied soil amendments and copper doses led to significant variations in the concentrations of the analyzed nutrients in spring rapeseed. Zeolite and halloysite were most effective in increasing the average above-ground biomass of the tested plants. Zeolite had a beneficial effect on the content of total nitrogen, ammonia nitrogen and phosphorus in the above-ground parts of spring rapeseed. Raw halloysite increased the content of sodium and calcium, whereas modified halloysite contributed to an increase in the nitrogen, potassium, sodium, calcium and magnesium content of the tested plants.

Keywords: halloysite, macronutrients, Cu-contamination, spring rapeseed, zeolite

INTRODUCTION

Expansive human activities lead to environmental pollution, and the main causes and effects of contamination have recently attracted considerable scientific interest [Mazur et al., 2013; Goretti et al., 2016; Parviainen et al., 2016]. The main pollutants in the soil environment are pesticide residues and heavy metal compounds, including copper compounds [Adlassnig et al., 2016]. Water-soluble compounds can penetrate deeper into the soil and contaminate ground water [Fronczyk et al., 2015].

Phytoremediation is a highly promising method of reducing contamination levels in the soil environment [Dhiman et al., 2016]. It relies on the phytostabilization potential of plants which immobilize harmful xenobiotics in soil [Saadani et al., 2016]. One of the greatest advantages of phytoremediation is that it can be applied directly in the polluted site. Heavy metals are easily transferred from contaminated substrates into the food chain, therefore, the chemical composition of crops growing in polluted areas has to be determined to minimize health risks for humans and animals.

Contaminated soil can be treated with amendments which improve the soil structure, increase its sorption capacity, maximize the availability of essential nutrients for plant growth, and immobilize heavy metals. Zeolite and halloysite have unique physicochemical properties, and they can be effectively used to minimize the adverse effects of heavy metal contamination in soils [Radziemska et al., 2013; Radziemska and Mazur, 2016c].

Zeolites are porous aluminosilicates composed of metal oxides and alkaline earth metals with crystalline structure. Their exceptional sorption properties can be attributed to a large specific surface area and high cation exchange capacity [Lee and Valla, 2017]. Halloysite is also characterized by a significantly larger specific surface area and higher cation exchange capacity than other aluminosilicate clay materials. Halloysite occurs naturally in the form of layered cylindrical tubes. It is composed of a tetrahedral sheet of silicon oxide and an octahedral sheet of hydrated aluminum oxide [Cravero et al., 2016]. Zeolites and halloysite are widely used in engineering and environmental protection, including in the chemical industry, microelectronics, medicine, construction and agriculture [Bellussi et al., 2015; Li et al., 2016].

The aim of this study was to determine the yield and chemical composition of spring rapeseed (*Brassica napus* L. var. *Napus*) plants grown in soil contaminated with copper and amended with halloysite (raw and modified) and zeolite by measuring the content of total N, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, P, K, Na, Ca and Mg in the above-ground parts of the tested plants.

MATERIAL AND METHODS

A greenhouse experiment was performed on samples of topsoil (0–20 cm) collected in an arable field. The analyzed soil samples had the following granulometric composition: sand – 86.6% (2.0–0.05 mm), silt – 11.2% (0.05–0.002 mm) and clay – 2.2% (<0.002 mm). Before the experiment, the pH_{KCl} of soil was determined at 6.2, the content of available nutrients was determined at 58.5 mg K, 75.9 mg Mg and 80.3 mg $P \cdot kg^{-1}$ soil, and the content of available organic carbon and total nitrogen was determined at 6.1 $g \cdot kg^{-1}$and 1.02 $g \cdot kg^{-1}$ of soil, respectively. The analyzed soil samples had sorption capacity of 87.3 $mmol(+) \cdot kg^{-1}$ and base saturation of 71.27%.

The experiment was carried out in three replications, in pots filled with 5 kg of air-dry soil each. All treatments were supplied with the same macronutrient and micronutrient fertilizer mix ($g \cdot kg^{-1}$) containing N – 26%, K_2O – 26%, B – 0.013%, Cu – 0.025%, Fe – 0.05%, Mn – 0.25% and Mo – 0.20%. Experimental treatments were contaminated with copper ($CuSO_4 \cdot 5H_2O$) in three different doses (150, 300 and 450 $mg \cdot kg^{-1}$). The control treatment consisted of soil without the addition of copper or mineral amendments.

The tested plant was spring rapeseed cv. Feliks. The plants were harvested after 65 days in the early flowering stage. The harvested plants were dried, and biomass yield was calculated. The plants were ground in a laboratory mill (Retsch type ZM 300, Hann, Germany) and mineralized. Total nitrogen content was determined by Kjeldahl's method after mineralization in concentrated sulfuric (VI) acid with hydrogen peroxide as a catalyst [Bremner, 1965]. The content of $N\text{-}NH_4^+$ was determined with Nessler's reagent [Ostrowska et al., 1991], and the content of $N\text{-}NO_3^-$ – with phenoldisulphonic acid [Ostrowska et al., 1991]. Phosphorus concentration was assessed by colorimetric analysis using the vanadium-molybdenum method [Cavell, 1955]. Sodium, calcium and potassium levels were determined by atomic emission spectrometry (AES) [Szyszko, 1982], and magnesium concentrations – by atomic absorption spectrometry (AAS) [Szyszko, 1982]. Five-point calibration was performed with standard solutions. Every sample was analyzed in triplicate. Ultra-pure water with 0.055 $\mu S \cdot cm^{-1}$ resistivity was used for preparing the solutions and dilutions.

The results were processed statistically in Statistica 9.1 software (StatSoft, Inc. 2010) by ANOVA and the LSD test at a significance level of $p<0.05$. Boxplots were developed in the XLStat (Addinsoft) application.

RESULTS AND DISCUSSION

The results of this study and published data suggest that copper's adverse influence on crop yield is determined not only by copper concentration in soil, but also by the applied soil amendments [Yan et al., 2013; Zhang et al., 2014; Radziemska et al., 2016b]. In our study, the above-ground biomass of plants in the control series (without the addition of zeolite or halloysite to copper-contaminated soil) decreased by 9% in the treatment with the lowest Cu dose (150 mg Cu kg^{-1} soil) to 62% in the treatment with the highest Cu dose (450 mg Cu kg^{-1} soil) (Figure 1). Copper is an essential micronutrient that participates in electron transfer reactions, but it can be toxic for plants and humans at high concentrations [Fernández-Calviño and Bååth, 2016]. The availability of copper is influenced mostly by the organic matter content of soil and soil pH [Conway and Keller, 2016]. In a study by Kubicka and Jaroń [2011], the growth of rye seedlings, in particular the above-ground parts of the analyzed plants, was also stilted under exposure to increasing doses of copper. In our experiment, the addition of mineral adsorbents to soil limited copper's negative influence on plant yield, but the applied minerals differed in their remediation capacity. Both zeolite and halloysite increased the average above-ground biomass of spring rapeseed plants in comparison with control (without the addition

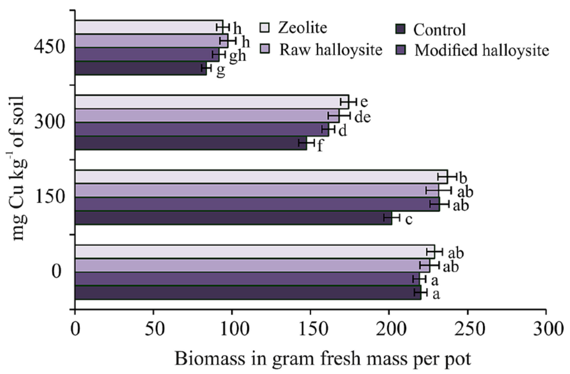

Figure 1. The effect of copper and the tested mineral amendments on the above-ground biomass of spring rapeseed in grams of fresh weight per pot. Error bars represent ± standard error (n=3). Bars marked with different letters differ significantly ($P<0.05$) according to Duncan's test

of mineral adsorbents). Zeolite and raw halloysite contributed to the highest increase in average biomass yield at 13% and 11%, respectively. In the work of Wyszkowski and Radziemska [2013a, 2013b, 2010], zeolite increased the average yield of aerial parts of oats, spring barley and maize grown in soil polluted with hexavalent chromium. The application of halloysite to nickel-contaminated soil increased the yield of *Brassica juncea* (L.) [Radziemska et al., 2016d].

The availability of trace elements for plants is determined mainly by the soil environment, mostly soil pH, and the content of humus and mineral colloids [Likar et al., 2015]. Soil contamination with copper has a varied effect on macronutrient and micronutrient concentrations in plants, thus

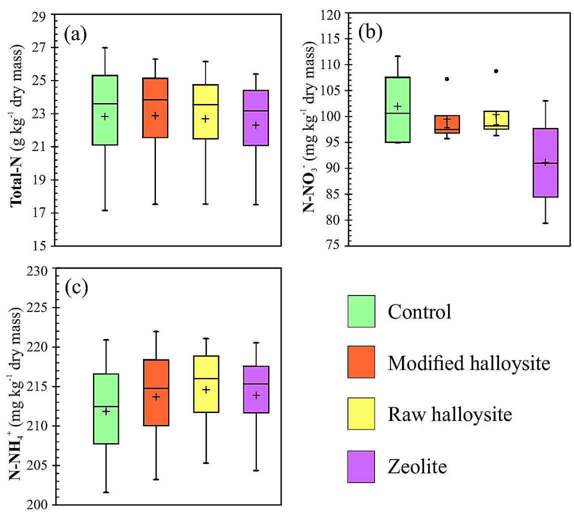

Figure 2. Boxplots showing the median, quartiles, and minimum and maximum values of total N (a), $N\text{-}NO_3^-$(b) and $N\text{-}NH_4^+$(c) content of spring rapeseed

influencing their suitability for processing and consumption [Radziemska et al., 2016b]. In this study, exposure to growing doses of copper led to a 36% increase in the total nitrogen content of spring rapeseed relative to the control treatment without copper contamination (Figure 2). The tested mineral adsorbents (zeolite, raw and modified halloysite) increased the total nitrogen content of plants, and the highest increase was noted in zeolite treatments. Wyszkowski and Radziemska [2013a] demonstrated that zeolite applied to chromium-contaminated soil had the most profound effect on the nitrogen content of oat grain. In our experiment, both copper and the applied amendments significantly influenced mineral nitrogen levels in spring rapeseed (Figure 2). In treatments without mineral amendments, a negative correlation was observed between increasing copper doses and the content of ammonia nitrogen in the aerial parts of plants. Zeolite as well as raw and modified halloysite increased the concentration of ammonia nitrogen in the above-ground parts of the tested plants, and the greatest increase was noted in treatments supplied with raw and modified halloysite. The accumulation of $N\text{-}NO_3^-$ in the aerial parts of spring rapeseed plants grown without the addition of mineral adsorbents was negatively correlated with increasing copper doses. The applied mineral amendments influenced the content of nitrate nitrogen (V) in the aerial parts of the plants (Figure 2). All of the tested mineral adsorbents reduced $N\text{-}NO_3^-$ concentrations in the above-ground parts of spring rapeseed plants. The application of zeolite to copper-contaminated soil decreased the content of $N\text{-}NO_3^-$ in the aerial parts of the tested plants by 11% relative to control (without soil amendments).

Phosphorus is found in many organic compounds, and it plays a very important role in plants [Arora et al., 2016]. The main source of phosphorus for plants are soluble orthophosphates in the soil solution, including H_2PO_4 and, to a lesser degree, HPO_4 [Egli et al., 2012]. In plant cells, inorganic phosphorus is accessible from the metabolic pool [Gomes et al., 2014]. In our experiment, the addition of copper and mineral adsorbents to soil significantly influenced the phosphorus content of the aerial parts of spring rapeseed plants (Figure 3). In non-amended treatments, increasing levels of copper contamination increased phosphorus levels in the above-ground parts of the tested plants, and the highest increase of 13% was observed in the treatment with the highest copper dose (450 $mg \cdot kg^{-1}$ soil). The addition of zeolite led to a 9% increase in the average phosphorus content of plants relative to control. Raw and modified halloysite also increased phosphorus concentrations in plants, but they were less effective than zeolite.

Potassium regulates the water balance in plants, it influences enzyme activity and has a minor influence on biomass yield [Blanch et al., 2014]. The potassium content of the aerial parts of spring rapeseed plants was influenced by the copper dose and the application of mineral adsorbents (Figure 3). In non-amended treatments, potassium concentration in the above-ground parts of the tested plants was positively correlated with increasing copper doses. Mineral amendments increased the average content of potassium in the aerial parts of spring rapeseed plants, and modified halloysite was the most effective adsorbent which led to a 6% increase in potassium concentrations relative to control.

Plants absorb sodium in the form of Na^+ ions from the soil solution and the soil sorption complex. Sodium concentrations vary considerably in plants. Sodium and potassium have similar properties, and they exert complementary effects on crop yield [Böhm et al., 2016]. In this experiment, the addition of copper and mineral adsorbents had a minor influence on the sodium content of the aerial parts of spring rapeseed plants (Figure 3). In a non-amended treatment exposed to the highest copper dose, sodium concentrations in the above-ground parts of the tested plant increased by 20%. The highest average sodium content was noted in pots treated with raw and modified halloysite. In the studies conducted by of Radziemska et al. [2013], the addition of modified halloysite and zeolite to nickel-contaminated soil also contributed to the accumulation of sodium in the maize.

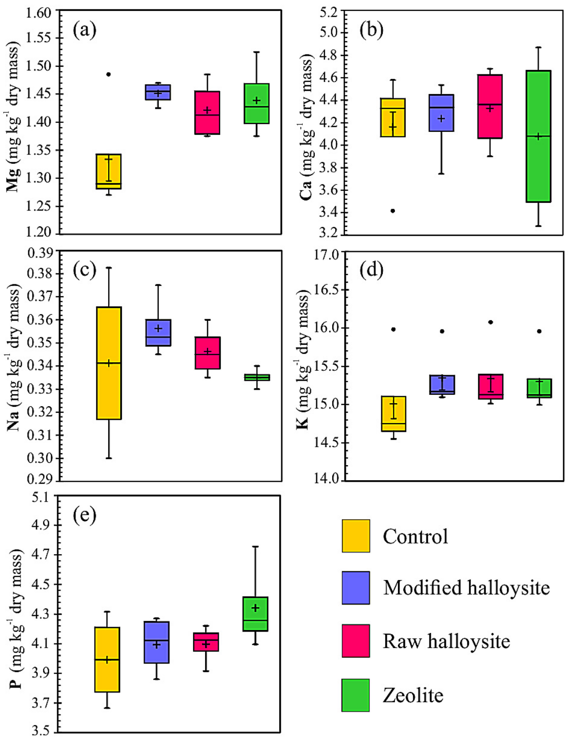

Figure 3. Boxplots showing the median, quartiles, and minimum and maximum values of magnesium (a), calcium (b), sodium (c), potassium (d) and phosphorous (e) concentrations in spring rapeseed

Calcium ions in the walls of plant cells are balanced with Ca^{2+} ions in the soil solution [Picard and Chaouki, 2016], whereas roots take up calcium in the form of Ca^{2+} ions or chelate [Zhang et al., 2016]. The calcium content of the aerial parts of spring rapeseed plants was significantly influenced by the copper dose and the applied mineral adsorbents (Figure 3). In the control series, the exposure to increasing copper doses increased calcium concentrations in the above-ground parts of the tested plants. The application of raw and modified halloysite increased the average calcium content of plants relative to control (without mineral amendments). In a study by Radziemska et al. [2016a, 2016b], sodium concentration in the aerial parts of Indian mustard plants grown in soil with the addition of reactive materials (zero-valent iron, lignite) was generally negatively correlated with increasing levels of chromium (VI) and copper contamination. In the work of Tlustoš et al. [2006], the use of CaO for soil amendment increased calcium levels in spring wheat plants grown in soil contaminated with heavy metals.

Magnesium is the central element in chlorophyll, which determines the effectiveness of photosynthesis [Zhou et al., 2012]. Magnesium stimulates root growth and nutrient uptake from soil [Jin et al., 2016]. It is a key determinant of root function and cell wall quality, and it directly contributes to plant resistance to adverse environmental conditions [Guo et al., 2016]. In this study, increasing copper doses were positively correlated with the magnesium content of the aerial parts of spring rapeseed plants in non-amended treatments (Figure 3). Magnesium concentration in plants increased by 14% under exposure to the highest copper dose of 450 mg Cu·kg^{-1} soil. The average content of magnesium in plants was also influenced by the applied mineral amendments (zeolite, raw and modified halloysite). Modified halloysite and zeolite induced the greatest increase in magnesium levels in the above-ground parts of spring rapeseed plants at 8% and 9%, respectively. In a study of soil contaminated with zinc, lead and cadmium, the application of dolomite increased the magnesium content of winter wheat grain and straw [Leszczyńska and Kwiatkowska-Malina, 2012]. In the work of Radziemska et al. [2013], the addition of zeolite and modified halloysite to nickel-contaminated soil also contributed to the accumulation of magnesium in the tested plants.

CONCLUSIONS

The amendments applied in the experiment (zeolite, raw and modified halloysite) significantly influenced the total nitrogen content, concentrations of ammonia nitrogen, nitrate nitrogen, phosphorus, potassium, sodium, calcium and magnesium, and the above-ground biomass of spring rapeseed plants. The addition of zeolite, raw and modified halloysite to soil minimized copper's adverse effects on the yield of spring rapeseed, but the tested mineral amendments differed in their effectiveness. In comparison with control, zeolite and halloysite had the most beneficial effect on the average biomass yield of spring rapeseed. Modified halloysite contributed to an increase in the average concentrations of ammonia nitrogen, potassium, sodium, calcium and magnesium in spring rapeseed. Raw halloysite increased the content of sodium and calcium in the tested plants. The greatest increase in the phosphorus content of spring rapeseed was observed in treatments amended with zeolite. Zeolite also exerted a beneficial effect on the content of total nitrogen and ammonia nitrogen in the above-ground parts of spring rapeseed plants.

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