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Assessment of the effect of reactive materials on the content of selected elements in Indian mustard grown in Cu-contaminated soils

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Abstract

Zero-valent iron (ZVI) represent a promising agent for environmental remediation. The research was aimed to determine the influence of copper in doses of 0, 80, 150, 300, and 600 mg Cu·kg⁻¹ of soil as well as ZVI, and lignite additives on the content of macroelements in the Indian mustard (*Brassica juncea* (L.) Czern.). The average accumulation of analyzing elements in Indian mustard grown in copper contaminated soil were found to follow the decreasing order Mg > Na > P > Ca > K > N. Soil contamination at 600 mg Cu·kg⁻¹ of soil led to the highest increase in P, Mg, N, and Ca content. The application of ZVI had a positive influence on the average phosphorus and potassium content of Indian mustard. Moreover, the application of ZVI and lignite had a positive influence on the average Mg and Ca content in the above-ground parts of Indian mustard. From the analyzed reactive materials, the application of lignite was shown to be the most effective resulting in the decrease in the average nitrogen and calcium content when compared to the control crop. Calcium content in plants from the control group, without the addition of zero-valent iron, and powered lignite (control), was positively correlated with increasing doses of copper.

Key words: *Indian mustard, lignite, soil contamination, zero-valent iron (ZVI)*

INTRODUCTION

The contamination of soils with heavy metals, including copper (Cu), is a major problem for environmental quality worldwide [SANTANA *et al.* 2015]. In literature on the subject, the harmful effect of Cu has been well documented, especially in soils with a low pH [ZAHEER *et al.* 2015]. In Poland, the highest amounts of heavy metals released into the environment have been reported in the following voivode-

ships: Dolnośląskie, Śląskie, Małopolskie, Mazowieckie, Łódzkie, Wielkopolskie. It is in these regions that we can find so-called “hot spots”, characterized by the highest levels of heavy metal contamination in the country, which pose a huge danger to the environment.

According to the latest studies, the level of copper in the surface layers of soil in the protected zones fell within the range of 147 to 450 mg·kg⁻¹, which in the case of all trials exceeded the permissible level of

copper for heavy soils, i.e. $100 \text{ mg}\cdot\text{kg}^{-1}$. In terms of the level of soil contamination, as established by Institute of Soil Science and Plant Cultivation (IUNG) and accounting for the granulometric composition as well as the pH of soils, the 4th level of contamination was noted in 4 regions (Biała, Pawłowice, Jaszów – in the northern part of the zone as well as in Liniki – south of the foundry), which indicates severe contamination of soil with copper; only in the Smokowice region was level III, signifying a medium contamination of soil with Cu, reported. Despite recultivation processes, such as calcification or forestation, the problem of excessive copper mobility has still not been eliminated. This necessitates finding the most optimal methods of remediation based on the immobilization (stabilization) of Cu in soil.

Zero-valent iron (ZVI) is an environmentally benign material that has been widely used as a reducing agent to treat environmental pollutants, i.e. in wastewater, groundwater, and soils [FRONCZYK, PAWLUK 2014; FJORDBØGE *et al.* 2012]. Due to its large surface area and high number of active sites, zero-valent iron (ZVI) enhances the efficiency of remediation [CALDERON, FULLANA 2015]. Promising results of applying the sorption and reduction properties of zero-valent iron (ZVI) and products of its oxidation as an effective sorbent or material for the remediation waters or soils contaminated by heavy metals have been reported by authors, i.e. CUNDY *et al.* [2008], HWANG *et al.* [2016], ZHANG *et al.* [2003]. Iron nanoparticles (nZVI) are applied directly to the soil as a suspension or with the addition of a dispersant which prevents the agglomeration of particles and increases their reactivity [XU, ZHAO 2007]. Zero-valent iron (ZVI) is very effective in transforming and detoxicating many contaminants, e.g. chlorinated solvents, organochlorine pesticides and polychlorinated biphenyls. In soil, it binds cation contaminants, such as: Pb^{2+} , Cu^{2+} , Ni^{2+} , Cr^{6+} , and As^{3+} [ALOWITZ, SCHERER 2002]. Iron in the form of Fe^{+2} as well as metallic iron reduce and lower the toxicity of Cr(VI) in ground water and soil [PULS *et al.* 1999].

The efficiency of the sorption of contaminants is dependent on the composition of the liquid phase of the soil-solution system, as well as the presence of ions competing with organic matter [JIN *et al.* 2015]. A decrease of copper mobility can be achieved by applying organic materials characterized by high sorption capacity, such as compost and lignite, to the soil. Studies presented by KWIATKOWSKA *et al.* [2006] have shown that the fertilization of soils with lignite causes remarkable enrichment of soil in organic matter, as well as increasing the sorption and water capacity of soils. However, not all aspects nor long-term effects of applying metallic iron to soil are fully known, which stems from the complexity of chemical

and microbiological processes [MASCANGIOLI, ZHANG 2003].

The research objective of this work was to investigate the effect of zero-valent iron (ZVI) and lignite on the efficiency of the applied phytoremediation technique for the removal of copper from soils involving the use of Indian mustard (Fig. 1).



Fig. 1. Concept of co-remediation of Cu-polluted soils with ZVI and lignite; source: own elaboration

MATERIAL AND METHODS

The impact of adding zero-valent iron (ZVI) and lignite to soil contaminated with copper (Cu) on the content of selected elements in Indian mustard (*Brassica juncea* (L.) Czern.) was assessed under the conditions of a pot experiment in an acclimatized greenhouse. The experiment was arranged in a randomized block design, with two factors and fourfold replication. The first factor was the addition of increased doses of copper to soil (0, 80, 150, 300, and $600 \text{ mg}\cdot\text{kg}^{-1}$) introduced in the form of chemically pure aqueous solutions of copper(II) chloride dihydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$). The second factor consisted the addition of two reactive materials, i.e. ZVI, lignite, and the mixture of ZVI/lignite (3.0% w/w). Soils without copper and reactive materials (0.0%) were designated as the control. Uncontaminated soil for the experiment was collected from the humic horizon from the arable layer (0–20 cm) of farmland in the vicinity of Olsztyn, Poland, ($53^\circ 35' 45'' \text{N}$, $19^\circ 51' 06'' \text{E}$). The selected properties of the soil are shown in Table 1.

Polyethylene pots were filled with 9.5 kg of the air-dried soil sieved to $<1 \text{ cm}$, and were maintained under natural day/night conditions; during the day (14 h), the air temperature was $26\pm 3^\circ \text{C}$ and approximately ten degrees lower ($16\pm 2^\circ \text{C}$) at night (10 h). Soil was fertilized with a macro- and micronutrient fertilizer mixture ($\text{g}\cdot\text{kg}^{-1}$) containing N – 26%, K_2O – 26%, B – 0.013%, Cu – 0.025%, Fe – 0.05%, Mn – 0.025%, and Mo – 0.20%. 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.

Nano zero-valent iron (ZVI) was purchased from iPutec GmbH & Co. KG, Rheinfelden, Germany. Moreover, a surface area and porosity analyzer (ASAP 2020M Micromeritics, USA), scanning elect-

Table 1. Physicochemical parameters of the experimental soil

Parameter	Value
Soil chemical parameters	
– pH	4.80
– hydrolytic acidity, mmol·kg ⁻¹	33.75
– sum of exchangeable bases, mmol·kg ⁻¹	62.20
– cation exchange capacity, mmol·kg ⁻¹	95.95
– base saturation, %	64.80
Organic matter	
– organic carbon, g·kg ⁻¹	7.13
– total N, g·kg ⁻¹	1.04
– carbon : nitrogen	6.85
– N-NH ₄ ⁺ , mg·kg ⁻¹	21.18
– N-NO ₃ ⁻ , mg·kg ⁻¹	9.88
Grain size distribution, %	
– fractions 2.0–0.05 mm	86.6
– fractions 0.05–0.002 mm	11.2
– fractions 0.002 mm	2.2
Available forms, mg·kg ⁻¹	
– phosphorous	46.6
– potassium	8.2
– magnesium	33.9

Source: own study.

ron microscope (SEM) images (FEG Quanta 250, USA), and X-ray diffraction (Philips X'Pert APD, Netherlands) spectra were used to detailed characterization of zero-valent iron (ZVI). Lignite sample came from Konin Brown Coal Basins (Poland). Scanning electron microscope (SEM) images of zero-valent iron (ZVI) and lignite are shown in Fig. 2.

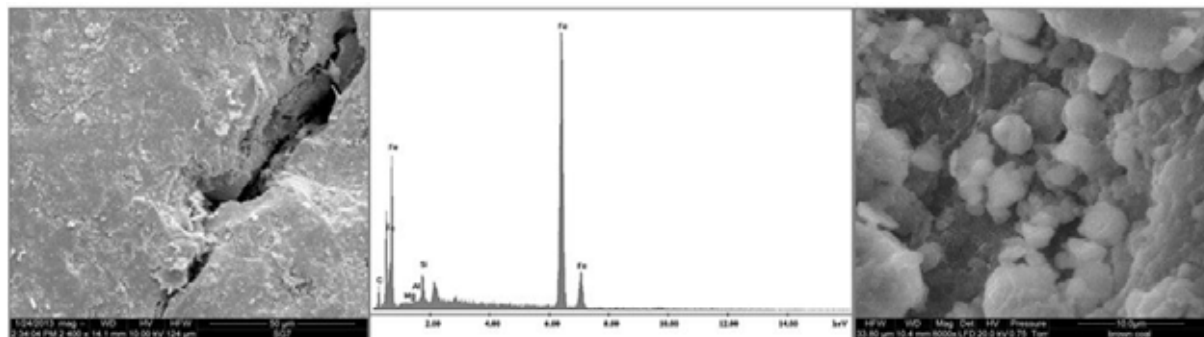


Fig. 2. The SEM images and EDX pattern of ZVI; SEM of lignite samples; source: own elaboration

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), Standard Methods; hydrolytic acidity (HAC) by Kappen's method, the soil samples were treated with 0.5 M·dm⁻³ Ca-acetate solution adjusted to pH 8.2 in the ratio of 1:2.5) [KLUTE 1996], total exchangeable bases (TEB-K⁺, Na⁺, Ca²⁺, and Mg²⁺) by Kappen's method through determining individual cations after extraction from the soil with CH₃COONH₄ [KLUTE 1996], cation exchange capacity (CEC) from the formula: CEC = HAC + TEB and percentage base saturation (V) from the formula: BS = 100TEB/CEC⁻¹. Organic matter was determined according to Tiurin's method after the hot digestion of

Indian mustard of the Małopolska variety was the plant of choice for the experiment. The seeds of Indian mustard were obtained from an authorized Seed Production Centre in Olsztyn, Poland (OLZNAS-CN Sp. z o.o.). The plant density was set at 5 plants per pot and was picked following 98 days of vegetation in the flowering phase. In the laboratory, aboveground parts of Indian mustard were thoroughly rinsed first with tap water and then with deionized water to remove dust and soil particles. After oven drying (60°C, 48h), the plants were weighed and before being powdered using an analytical mill (A 11 IKA, Germany), preceding the chemical analyses.

The plant samples were subjected to mineralization in condensed sulphuric acid (VI) with hydrogen peroxide. The content of the following elements was determined in the obtained extracts: total nitrogen content by Kjeldahl's distillation method [BREMNER 1965] after mineralization in concentrated sulphuric (VI) acid with hydrogen peroxide added as a catalyst; phosphorus (P) – colorimetric analysis using the vanadium-molybdenum method [CAVELL 1955]; sodium (Na), calcium (Ca), potassium (K) – atomic emission spectrometry – AES method [SZYSZKO 1982]; magnesium (Mg) – atomic absorption spectrometry – AAS method [SZYSZKO 1982].

Before setting up the experiment, the following soil properties were determined: the grain size composition of the soil with the laser method using a Mastersizer 2000 m, pH – determined by means of the

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 [MOCEK, DRZYMAŁA 2010]. Deionized water with a specific conductance of 0.055 μS·cm⁻¹ was used for the analyses.

Statistical analysis was performed using the software Statistica ver 10.0. Differences of means between treatments were tested by ANOVA and comparisons of means using Least Significant Difference (LSD) test, at $p = 0.05$. The means and standard deviations ($\pm SD$) of five replications are reported. Pearson's simple correlation coefficient (r) was also calculated between the heavy metal content indicated in the soil with the level of significance set at $p < 0.001$, $p < 0.01$ and $p < 0.05$.

RESULTS AND DISCUSSION

The content of macroelements in the biomass of plants is subjected to specific changes which can be affected by the heavy metal content of soil. The research of other authors, including COLLIN *et al.* [2014], KABATA-PENDIAS, PENDIAS [2001], WYSZKOWSKI, RADZIEMSKA [2010; 2013] and LEMBERKOVICS *et al.* [2002], reveals that trace elements have a strong and varied influence on the content of macroelements in plants, which was confirmed by our studies. The analysis of results shows that the content of phosphorous (P), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and nitrogen (N) in the Indian mustard is influenced by the dose of copper, as well as the addition of zero-valent iron and lignite.

In the control series (no additives), the differences in phosphorus content were positively correlated with the increasing doses of copper (Fig. 3). Indian mustard from this experiment was characterized by phosphorus concentrations ranging from 1.61 to 2.55 g·kg⁻¹. Soil contamination at 600 mg Cu·kg⁻¹ of soil led to the highest increase in the phosphorus content of Indian mustard. The application of zero-valent iron (ZVI) had a positive influence on the average phosphorus content of Indian mustard. This reactive material has high surface reactivity, and the introduction of zero-valent iron (ZVI) could shift the redox condition of the local environment and affect the oxygen release rate of plant roots [KIRSCHLING *et al.* 2010; ZHANG 2003]. The opposite situation was observed in the case of adding lignite, which had an adverse effect causing the average phosphorus content to decrease in the analyzed plant in relation to plants in the control group. The addition of a ZVI/lignite mixture, which caused a 13% increase in the average content of the above-mentioned element in Indian mustard as compared to the control series, was shown to be the most successful among the assortment of reactive material added to the soil. The results are in agreement with the research of KALEMBASA and WYSOKIŃSKI [2002], in which the addition of brown coal ash caused a de-

crease in the contents of phosphorus in plants. Our earlier investigation showed that the application of mineral reactive materials to Ni-contaminated soil led to a positive influence on the average phosphorus content of maize [RADZIEMSKA *et al.* 2013].

The contamination of soil with copper, as well as the application of zero-valent iron (ZVI) and lignite, had a significant effect on the content of potassium in Indian mustard (Fig. 4). Indian mustard from the present experiment was characterized by potassium concentrations ranging from 13.27 to 16.88 g·kg⁻¹. In the control series (without additives), a positive correlation between the potassium content and the increasing contamination of soil with Cu occurred. Zero-valent iron (ZVI) had a positive effect on the storage of potassium in the above-ground parts of Indian mustard, which was especially evident in the group of plants with the lowest dose of copper (150 and 300 mg·kg⁻¹ soil). When compared to the control series, zero-valent iron (ZVI) was shown to have the most beneficial effect on the average potassium content in the analyzed plant. Lignite as well as the ZVI/lignite mixture also had a positive effect, although not as pronounced. LESZCZYŃSKA and KWIATKOWSKA-MALINA [2011] reported data revealing that potassium contents in the roots of rye significantly decreased in comparison with the control object as a result of adding lignite. According to KOZERA *et al.* [2006], copper may decrease potassium content in potato tubers.

Calcium has been found to impede the negative effects of abiotic stress through the regulation of water relations and antioxidant metabolism [ZORRIG *et al.* 2012]. According to KABATA-PENDIAS and PENDIAS [2001], there is an antagonism between copper and calcium. Calcium concentrations of Indian mustard in the above experiment ranged from 4.96 to 7.05 g·kg⁻¹. In the present study, calcium content in the Indian mustard was significantly influenced by the dose of copper as well as the reactive materials added to the soil (Fig. 5). Calcium content in plants from the control group, i.e. without the addition of zero-valent iron (ZVI) or lignite, was positively correlated with

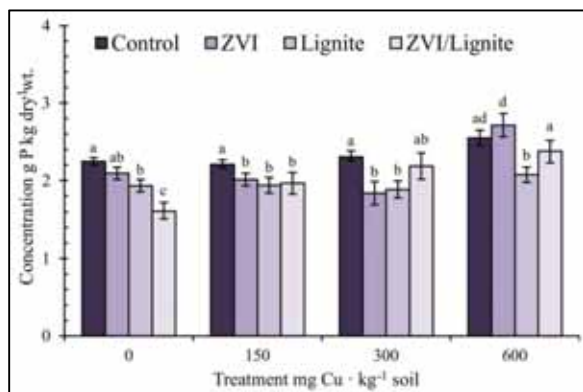


Fig. 3. Effect of copper (Cu) contamination on phosphorus (P) content in Indian mustard (g·kg⁻¹ dry mass); mean ± SD, n = 3; columns marked with different letter indicate significant differences between members of the same set (Tukey test, p < 0.05); source: own study

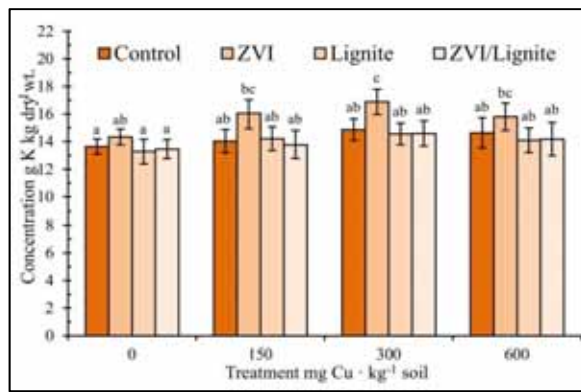


Fig. 4. Effect of copper (Cu) contamination on potassium (K) content in Indian mustard (g·kg⁻¹ dry mass); mean ± SD, n = 3; columns marked with different letter indicate significant differences between members of the same set (Tukey test, p < 0.05); source: own study

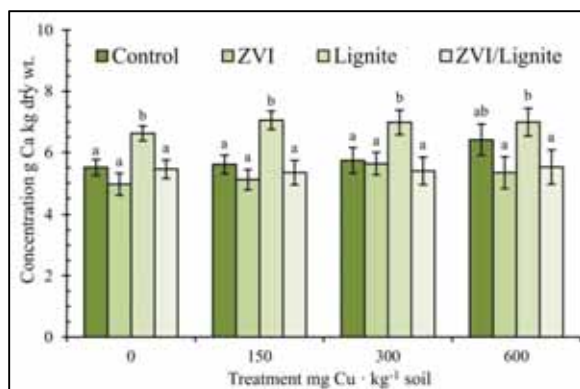


Fig. 5. Effect of copper (Cu) contamination on calcium (Ca) content in Indian mustard ($\text{g}\cdot\text{kg}^{-1}$ dry mass); mean \pm *SD*, $n = 3$; columns marked with different letter indicate significant differences between members of the same set (Tukey test, $p < 0.05$); source: own study

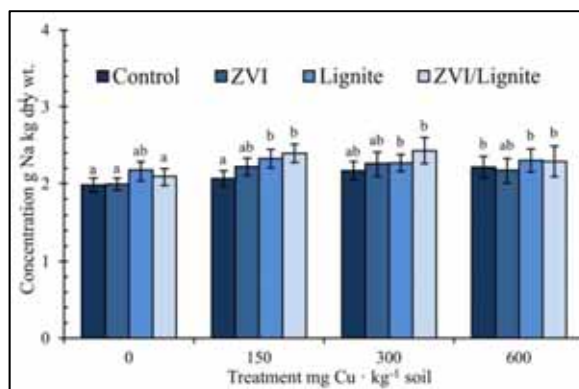


Fig. 6. Effect of copper (Cu) contamination on sodium (Na) content in Indian mustard ($\text{g}\cdot\text{kg}^{-1}$ dry mass); mean \pm *SD*, $n = 3$; columns marked with different letter indicate significant differences between members of the same set (Tukey test, $p < 0.05$); source: own study

increasing doses of copper. Soil contamination at 600 $\text{mg}\cdot\text{kg}^{-1}$ of soil led to the highest increase in calcium content in the analyzed plant. From the analyzed substances neutralizing the effects of copper contamination, the application of lignite was shown to be the most effective, resulting in a 19% increase in the average calcium content when compared to the control crop. LESZCZYŃSKA and KWIATKOWSKA-MALINA [2011] demonstrated that the addition of lignite to soil causes a higher content of calcium in all parts of rye.

Zero-valent iron (ZVI) and lignite, as well as increasing doses of copper significantly influenced the sodium content of Indian mustard (Fig. 6). The above-ground parts of Indian mustard from the present experiment had sodium concentrations ranging from 1.98 to 2.39 $\text{g}\cdot\text{kg}^{-1}$. Applying copper to soil contributed to increased levels of sodium in plants as compared to the control series – without additives. Crops in the study group without reactive materials, exposed to copper doses of 150 and 300 $\text{mg}\cdot\text{kg}^{-1}$ soil were found to have the highest sodium content in their above-ground parts. The addition of zero-valent iron (ZVI) with lignite (ZVI/lignite), which caused a 9% increase in the average content of the above-mentioned element in Indian mustard as compared to the control series, was shown to be the most successful from the assortment of reactive materials added to the soil. An analogical situation was observed in the case of adding zero-valent iron (ZVI), and lignite, although their influence was weaker. Data presented by LESZCZYŃSKA and KWIATKOWSKA-MALINA [2011] showed that organic matter from different sources did not have an effect on the content of sodium in some parts of rye in variants of soil contaminated with, or without the addition of heavy metals. Indian mustard from the present experiment had sodium concentrations ranging from 4.96 to 7.05 $\text{g}\cdot\text{kg}^{-1}$.

Magnesium has a number of key functions in plants. Moreover, the uptake of Mg is strongly influenced by the availability of other cations, i.e. Ca, K, and NH_4^+ [RÖMHELD, KIRKBY 2007]. Magnesium content in Indian mustard was influenced by the dose

of copper, as well as the addition of reactive materials (Fig. 7). Indian mustard from the present experiment was found to have magnesium concentrations ranging from 0.91 to 1.25 $\text{g}\cdot\text{kg}^{-1}$. Crops in the study group without reactive materials and exposed to a copper dose of 600 $\text{mg}\cdot\text{kg}^{-1}$ soil were found to have the highest magnesium content in their above-ground parts. The application of zero-valent iron (ZVI) and lignite had a positive influence on the average magnesium content in the above-ground parts of Indian mustard. When compared to the control series, lignite was shown to have the most beneficial effect on magnesium content in the analyzed plant. Zero valent-iron (ZVI), as well as mixture of ZVI and lignite also had a positive effect, although not as pronounced.

An analysis of the results showed that the content of nitrogen in the Indian mustard was influenced by the dose of copper, as well as the addition of zero valent-iron (ZVI) and lignite (Fig. 8). Indian mustard in the present experiment had nitrogen concentrations ranging from 9.34 to 18.30 $\text{g}\cdot\text{kg}^{-1}$. Nitrogen content in plants from the control group (without the addition of reactive materials) was positively correlated with in-

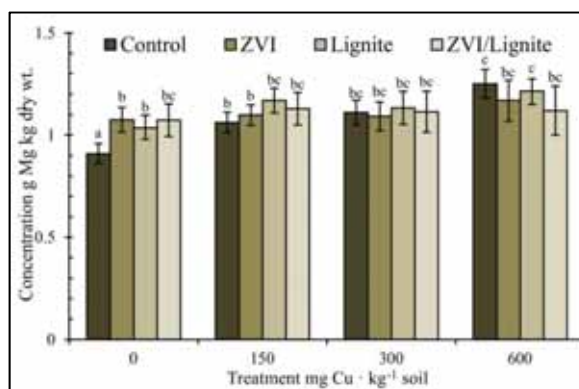


Fig. 7. Effect of copper (Cu) contamination on magnesium (Mg) content in Indian mustard ($\text{g}\cdot\text{kg}^{-1}$ dry mass); mean \pm *SD*, $n = 3$; columns marked with different letter indicate significant differences between members of the same set (Tukey test, $p < 0.05$); source: own study

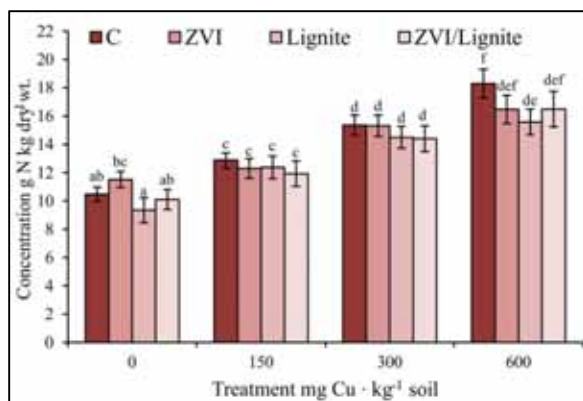


Fig. 8. Effect of copper (Cu) contamination on nitrogen (N) content in Indian mustard ($\text{g}\cdot\text{kg}^{-1}$ dry mass); mean \pm SD, $n = 3$; columns marked with different letter indicate significant differences between members of the same set (Tukey test, $p < 0.05$); source: own study

creasing doses of copper. In objects contaminated with 300 and 600 $\text{mg Cu}\cdot\text{kg}^{-1}$, the content of the analyzed element was higher (44% and 61%) in relation to objects which had not been contaminated. From the analyzed reactive materials, the application of lignite was shown to be the most effective, resulting in a 9% decrease in the average nitrogen content when compared to the control crop. The application of organic matter to soil usually leads to a higher accumulation of nitrogen in plants [EGHBALL *et al.* 2002]. Lignite can be a good source of supplementing soils with organic matter. This substance delivers material with a high degree of humification and is relatively resistant to mineralization [LOPAREVA-POHU *et al.* 2011]. In regards to soil enrichment with organic matter, increased contents of nitrogen have been observed in the organs of many plant species, i.e. spring barley and maize [WYSZKOWSKI, RADZIEMSKA 2010], and triticale grain and straw [CIEĆKO *et al.* 2001]. In an experiment conducted by ELEIWA [2004], copper strongly affected nitrogen assimilation in wheat and lupine.

CONCLUSIONS

The reactive materials applied in the experiment, i.e. zero-valent iron (ZVI) and lignite, significantly shaped the content of phosphorus, calcium, sodium, magnesium, potassium, and nitrogen in the above-ground parts of Indian mustard cv. Małopolska. The average accumulation of macronutrients in Indian mustard grown in Cu-contaminated soil was found to follow the decreasing order of $\text{Mg} > \text{Na} > \text{P} > \text{Ca} > \text{K} > \text{N}$.

Soil contamination at 600 $\text{mg Cu}\cdot\text{kg}^{-1}$ of soil led to the highest increase in phosphorous, magnesium, nitrogen, and calcium content in Indian mustard. The application of zero-valent iron (ZVI) had a positive influence on the average phosphorus and potassium content of this plant species. Moreover, the application of zero-valent iron (ZVI) and lignite had a posi-

tive influence on the average magnesium and calcium content in the above-ground parts of the studied plant. In the non-amended treatments (no reactive materials), the increasing rates of copper had an explicitly positive effect on the content of calcium in Indian mustard. From the analyzed reactive materials, the application of lignite was shown to be the most effective, resulting in a decrease in the average nitrogen and calcium content as compared to the control crop.

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Ocena wpływu materiałów reaktywnych na zawartość wybranych pierwiastków w gorczycy sarepskiej uprawianej na glebie zanieczyszczonej miedzią

STRESZCZENIE

Słowa kluczowe: gorczyca sarepska, węgiel brunatny, zanieczyszczenie gleby, żelazo elementarne

Zakres badań obejmował określenie wpływu zanieczyszczenia gleby miedzią (0, 80, 150, 300 i 600 mg Cu·kg⁻¹) oraz dodatku żelaza elementarnego (ZVI) i węgla brunatnego na zawartość wybranych makroelementów w gorczycy sarepskiej (*Brassica juncea* (L.) Czern.). Średnia zawartość analizowanych makroskładników w gorczycy rosnącej na glebie zanieczyszczonej miedzią kształtowała się następująco: Mg > Na > P > Ca > K > N. Gleba zanieczyszczona w dawce 600 mg Cu·kg⁻¹ spowodowała zwiększenie zawartości P, Mg, N i Ca. Dodatek żelaza elementarnego (ZVI) wywarł pozytywny wpływ na średnią zawartość fosforu i potasu w *Brassica juncea*. Ponadto ZVI i węgiel brunatny wpływały pozytywnie na średnią zawartość Mg i Ca w częściach nadziemnych analizowanej rośliny. Spośród dodawanych do gleby analizowanych materiałów reaktywnych węgiel brunatny spowodował największy wzrost zawartości azotu i wapnia w częściach nadziemnych analizowanej rośliny. Zawartość wapnia w roślinach rosnących w grupie kontrolnej (bez dodatku żelaza elementarnego i węgla brunatnego) była dodatnio skorelowana ze wrastającym zanieczyszczeniem gleby miedzią.