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EFFECT OF HEATING OIL AND NEUTRALIZING SUBSTANCES ON THE CONTENT OF SOME TRACE ELEMENTS IN MAIZE (*Zea mays* L.)

WPŁYW OLEJU OPAŁOWEGO I SUBSTANCJI NEUTRALIZUJĄCYCH NA ZAWARTOŚĆ WYBRANYCH PIERWIASTKÓW ŚLADOWYCH W KUKURYDZY (*Zea mays* L.)

Abstract: The purpose of the present experiment has been to determine the capability of maize (*Zea mays* L.) to uptake certain trace elements from soil contaminated with heating oil (0, 5, 10, 15 and 20 $g \cdot kg^{-1}$ soil) after soil amendment with neutralizing substances (nitrogen, compost, bentonite, zeolite and calcium oxide). The study relied on determination of the content of trace metals in plants. Incremental rates of heating oil caused depressed concentrations of copper and zinc, increased accumulation of nickel but did not induce unidirectional changes in the content of iron in maize. Bentonite was more effective than zeolite as a soil amending substance. Bentonite reduced the accumulation of three (copper, zinc, iron) and zeolite – just two (copper and nickel) of the analyzed elements in maize compared with the series without neutralizing substances. Application of calcium oxide and nitrogen to soil, in general, favoured the accumulation of the analyzed elements in aerial organs of maize.

Keywords: heating oil contamination, nitrogen, compost, bentonite, zeolite, calcium oxide, maize, trace elements

Contamination of the environment with petroleum substances affects the properties of soil, disrupts the cycling of elements [1–3] and affects the growth and development as well as accumulation of elements in plants [2, 4–5]. Plants are capable of accumulating pollutants, including heavy metals, in their organs and can therefore be used for rehabilitation of polluted soils. The method which employs plants to remove pollutants from soils, known as phytoremediation, became a more effective and economically viable tools once hyperaccumulators had been discovered [6]. The plants used for phytoremediation are the ones which produce large amounts of biomass and

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accumulate and transfer large quantities of metals to their aerial parts, which ensures that the metals will be removed with harvest [7]. Hyperaccumulator plants should accumulate at least 100 mg · kg^{-1} (0.01 % of dry matter) of cadmium and other trace metals, 1000 mg · kg^{-1} (0.1 % d.m.) of cobalt, copper, chromium, nickel and lead, and 10 000 mg · kg^{-1} (1 % d.m.) of manganese [6, 8]. Their phytoremediatory effect can be improved by introducing various substances to soil.

This study has been performed in order to determine the capability of maize (*Zea mays* L.) to uptake certain trace elements from soil contaminated with heating oil (0, 5, 10, 15 and 20 g · kg^{-1} soil) after soil amendment with neutralizing substances (nitrogen, compost, bentonite, zeolite and calcium oxide). The study relied on determination of the content of trace metals in maize.

Material and methods

A pot experiment was carried out in a greenhouse at the University of Warmia and Mazury in Olsztyn (Poland). The experiment was set up on soil of the texture corresponding to loamy sand (fractions in mm: < 0.002 – 1.89 %, 0.002–0.005 – 2.46 %, 0.005–0.010 – 2.87 %, 0.010–0.020 – 4.39 %, 0.020–0.050 – 8.89 %, 0.050–0.100 – 14.08 %, 0.100–0.250 – 36.90 %, 0.250–0.500 – 22.78 %, 0.500–1.000 – 5.74 %, 1.000–2.000 – 0.00 %). The pots were filled up with 9 kg of soil contaminated with incremental doses of heating oil: 0, 5, 10, 15 and 20 g · kg^{-1} d.m. of soil. The experiment was run with three replications and in five series: without the neutralizing substances and with the application of nitrogen (200 mgN · kg^{-1} of soil) as urea, compost (3 %), bentonite and zeolite (2 % relative to the soil mass) and 50 % calcium oxide in a dose corresponding to one full hydrolytic acidity. Additionally, all pots received aqueous solutions of macro- and micronutrients in the following quantities (in mg · kg^{-1} of soil): N – 100 $CO(NH_2)_2$, P – 30 (KH_2PO_4), K – 100 (KH_2PO_4 + KCl), 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 ($H_3BO_3$). Next, cv. Reduta maize (*Zea mays* L.) was sown. Aerial parts of the maize plants were harvested after 63 days of growing, during the intensive plant growth phase. The soil moisture was maintained at 60 % of water saturation throughout the whole experiment.

Once the plant material was mineralized in 65 % nitric acid(V), the content of trace metals was determined: copper (Cu^{2+}), zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{3+}) by the *flame atomic absorption spectrometric* (FAAS) method in a SpectrAA 240FS (VARIAN, Australia) atomic absorption spectrometer. The plant material was mineralized in a microwave oven type MARS 5 (CEM Corporation, USA), in HP500 Teflon vessels, according to the Mars 5 methodology [9].

The results were processed statistically using two-factor analysis of variance ANOVA from a software package Statistica [10]. The *least significant differences* (LSD) were determined at the levels of significance p = 0.01 and p = 0.05. In addition, Pearson's simple correlation coefficients (r) were calculated as well as regression equations and determination coefficients (R^2) between analyzed variables.

Results and discussion

Micronutrients, a very important component of soil, affect the volume and quality of crops. In excessive quantities, they turn into soil pollutants and pose a threat to plants, animals and people [11]. It is only in extreme cases that their deficit restrains the growth and development of plants [12]. Excessively high concentrations of copper, zinc and nickel in soil may inhibit the growth and development of plants, causing high yield loses [13].

In the present experiment, heating oil had a significant effect on the concentration of micronutrients in plants (Table 1). In the series without neutralizing substances, the relationship between the content of copper in maize and increasing rates of heating oil was reversely proportional and the decrease in its content was 32 % (r = –0.962). In the same series, the concentration of zinc in aerial parts of maize was reduced by 33 % under the influence of incremental doses of heating oil (r = –0.920) versus the control treatment (no heating oil). Positive correlations were found between the rising doses of heating oil and the concentration of nickel in maize (r = 0.974), but the maximum increase in the nickel content in that series was less than 20 %. Modifications in the concentration of iron induced by heating oil were relatively small.

The neutralizing substances added to unpolluted soil weakened the ability of maize to uptake copper and reduced the copper concentration in maize within the range of 13 % (compost) to 36 % (zeolite) compared with non-amended treatments (Table 1). The lowest concentrations of zinc in maize were determined in the series with bentonite. In fact, bentonite was the only alleviating substance that reduced the concentration of that element in maize. In contrast, the biggest increase in the zinc content versus the control was observed in the series with calcium oxide. The content of iron in maize plants grown on unpolluted soil demonstrated almost negligible modifications, which were series-dependent. Calcium oxide had a more stimulating effect on the content of iron in maize (+31 %) compared with the treatment without soil amending substances. It was also the most significant effect compared with the other applied soil improvement substances.

In soil contaminated with heating oil, the influence of alleviating substances on the concentration of copper in maize was significant (Fig. 1). Out of the tested substances, calcium oxide had the most stimulating effect on the increase in the content of copper (+54 % versus the series without neutralizing substances). Nitrogen also raised the content of copper in maize (+14 %). The effect of the other substances, especially bentonite and zeolite, was reducing and caused a decrease in the concentration of copper in maize compared with the series without contamination alleviating substances. In soil contaminated with heating oil, the content of zinc in maize declined under the influence of bentonite, by an average of 13 %, and was slightly lowered after soil had been amended with calcium oxide. The other substances proved to stimulate its plant content, for example nitrogen raised the accumulation of zinc in maize by an average 49 % versus the non-amended series. The average content of nickel in maize in particular series with soil amendments was similar to its content in treatments without such substances. The most significant effect was produced by compost, which caused an

Table 1

Content of some trace elements in maize (*Zea mays* L.) [$mg \cdot kg^{-1}$ d.m.]

Dose of heating oil [$g \cdot kg^{-1}$ of soil]	Kind of substance neutralizing effect of heating oil						
	without additions	nitrogen	compost	bentonite	zeolite	CaO	average
Copper							
0	1.90	1.62	1.66	1.46	1.21	1.54	1.56
5	1.70	1.86	1.66	1.17	1.21	2.10	1.62
10	1.46	1.94	1.33	1.05	1.38	2.10	1.54
15	1.29	1.54	1.17	0.93	0.73	2.22	1.31
20	1.29	1.21	1.09	0.73	0.81	2.43	1.26
Average	1.53	1.63	1.38	1.07	1.07	2.08	1.46
r	-0.962^{**}	-0.621^{*}	-0.962^{**}	-0.987^{**}	-0.724^{*}	0.909^{**}	-0.962^{**}
LSD	a – 0.14^{**}, b – 0.15^{**}, a · b – 0.34^{**}						
Zinc							
0	74.2	88.1	81.9	50.4	90.3	83.1	78.0
5	70.7	83.3	85.8	50.1	69.9	59.7	69.9
10	59.6	109.9	51.1	51.7	74.8	50.4	66.2
15	44.4	76.6	51.6	42.5	42.9	49.6	51.3
20	50.0	64.0	48.5	51.2	42.4	49.4	50.9
Average	59.8	84.4	63.8	49.2	64.1	58.4	63.3
r	-0.920^{**}	-0.514	-0.868^{**}	-0.250	-0.927^{**}	-0.849^{**}	-0.967^{**}
LSD	a – 4.1^{**}, b – 4.5^{**}, a · b – 10.1^{**}						
Nickel							
0	0.47	0.63	0.62	0.60	0.63	0.80	0.62
5	0.55	0.64	0.54	0.59	0.51	0.59	0.57
10	0.56	0.63	0.66	0.57	0.59	0.65	0.61
15	0.50	0.51	0.74	0.53	0.44	0.65	0.56
20	0.56	0.47	0.57	0.53	0.44	0.45	0.50
Average	0.53	0.58	0.62	0.56	0.52	0.63	0.57
r	0.974^{**}	0.804^{**}	0.929^{**}	-0.673^{*}	0.585	-0.557	0.788^{**}
LSD	a – 0.05^{**}, b – 0.06^{**}, a · b – 0.13^{*}						
Iron							
0	95.8	107.2	99.0	99.5	93.4	125.7	103.4
5	92.4	108.8	108.3	92.7	106.8	122.0	105.2
10	99.8	135.8	96.7	95.3	107.4	116.9	108.6
15	104.0	109.3	107.1	93.1	120.3	114.4	108.0
20	93.6	96.3	94.2	92.9	100.7	107.0	97.5
Average	97.1	111.5	101.0	94.7	105.7	117.2	104.5
r	0.238	-0.231	-0.271	-0.705^{*}	0.448	-0.989^{**}	-0.320
LSD	a – 3.4^{**}, b – 3.7^{**}, a · b – 8.2^{**}						

LSD (least squares deviation) for: a – heating oil dose, b – kind of neutralizing substance, a · b – interaction; significant for: ** – P = 0.01, * – P = 0.05, n.s. non-significant; r – correlation coefficient.

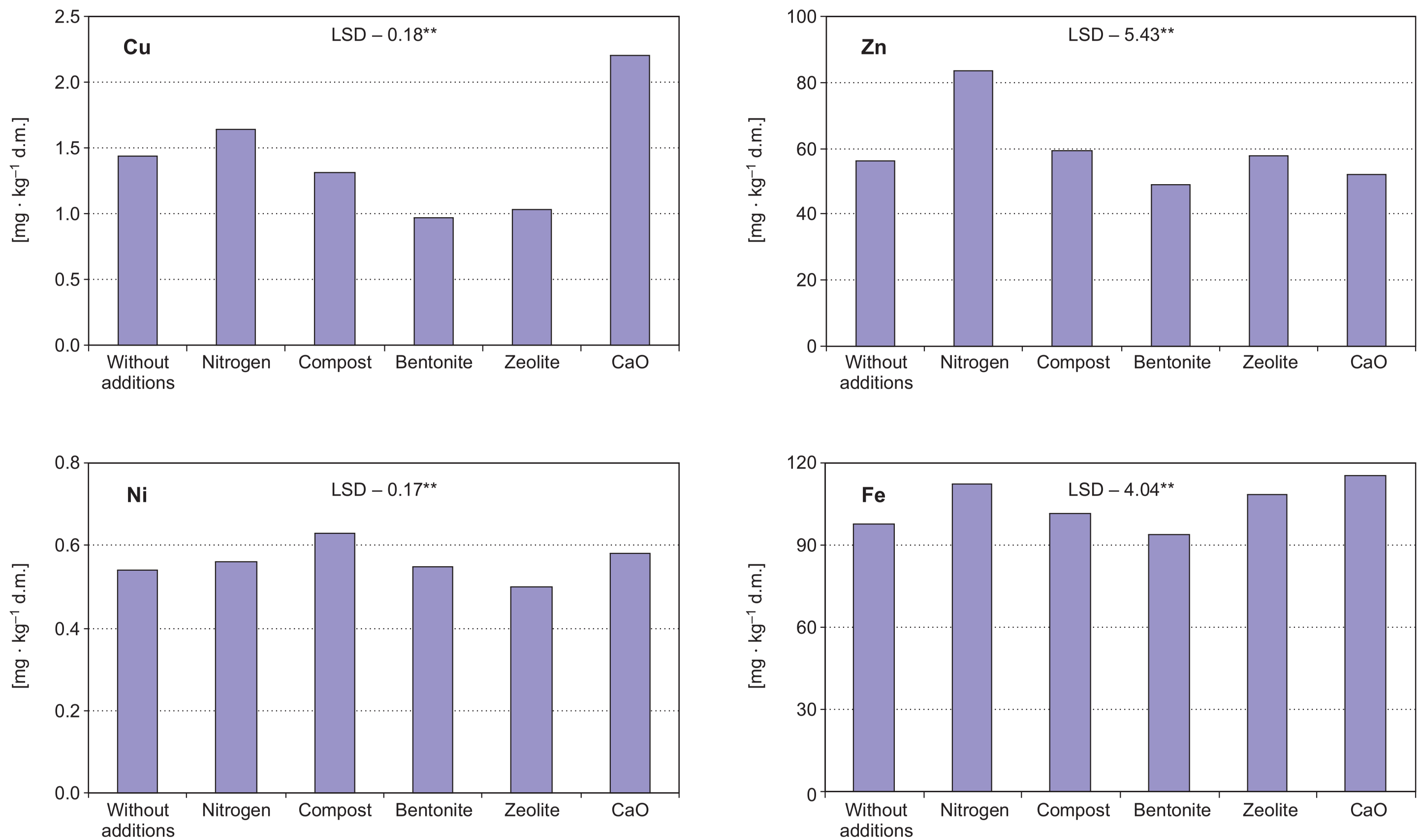

Fig. 1. Content of some trace elements in maize (*Zea mays* L.) (average from series contaminated with 5–20 g heating oil per kg of soil), in dependence on applied neutralizing substances. Differences significant for: ** – P = 0.01, * – P = 0.05

average 16 % increase in the content of nickel compared with the non-amended series. All the neutralizing substances, except bentonite, slightly stimulated the increase in the iron content in aerial maize organs. Its biggest increase, versus the series without alleviating substances, was caused by the following amendments: calcium oxide (+18 %), nitrogen (+15 %) and zeolite (+12 %).

Maize is recognized to be a good hyperaccumulator of heavy metals. It takes up heavy metals and transports them from roots to vegetative organs, which can be removed from a field [14]. Mizera [15] and Jasiewicz et al [16] noticed elevated accumulation of zinc and copper in maize. This finding proves that zinc and copper are more mobile than other elements and can be relatively easily absorbed by plants [16, 17]. As the content of metals in soil increases, maize tends to accumulate larger quantities of these elements in its green matter [11].

In their research, Sady and Smolen [18] observed that mineral fertilizers can depress or contribute to the rise in quantities of available metals as they themselves are a source of metals. Alkaline nitrogen fertilizers (sodium nitrate, calcium nitrate) inhibit the uptake of heavy metals by plants. Urea, which contains reduced forms of nitrogen, raises quantities of available metals and reduces the soil reaction. Both effects were confirmed in the authors' own study. Sady and Smolen [18] found out that increasing doses of nitrogen led to improved accumulation of zinc and nickel but had no effect on the concentration of copper in carrot.

Organic matter, both originally present in soil and added with organic fertilizers, contributes to reduced availability of metals to plants. The plant yield harvested under such conditions contains less metals [18]. In another experiment, conducted by Jasiewicz et al [16], benthic sediments significantly depressed the content of zinc in plant roots. This is most probably a consequence of the effect the sediments had on soil reaction, *ie* higher pH depresses plant availability of zinc, whereas lower pH favoures the uptake of zinc by plants. Jasiewicz et al [17] point to a higher content of nickel and inferior accumulation of zinc and copper in maize in series with benthic sediments, a finding partly confirmed by the authors' own studies. Nezdoyminov and Chernysheva [11] observed that organic fertilization (sewage sludge) contributed to a slight increase in the accumulation of metals in plants.

Sarbak [19] confirms that bentonite effectively stimulates sorption of zinc. Bentonite reduces availability of zinc and copper to wheat and improves yields of this cereal [20]. Changes in the soil environment, such as higher organic matter content, soil solution pH modifications, etc., can enhance the mobility of metals and impair the ability of loamy minerals to immobilize these elements. The presence of Ca^{2+} or Al^{3+} ions lowers the effectiveness of the sorption of metals by minerals [21].

In another experiment, by Rehakova et al [22], the lowest concentration of heavy metals was observed in plants grown on soil with zeolite. Zeolite is characterized by strong affinity to $Zn^{2+}$and Cu^{2+} ions but weaker to Ni^{2+} [23, 24]. According to Ulmanu et al [24], the content of copper and zinc in biomass of three analyzed species of plants was drastically reduced as the rates of zeolite introduced to soil increased. Prasad and Freitas [6] confirm the effective action of zeolites, which prevent the uptake of metals by plants. The research conducted by Castaldi et al [25] proves that zeolite can induce an increase in the fraction of heavy metals in soil, but lowers their uptake by plants.

Many metal cations are available to plants in soil solution of low pH (less than 5.5), including Cu^{2+}, Ni^{2+} and Zn^{2+} [6]. Sady and Smolen [18] concluded that sometimes the mobility of heavy metals can increase in alkaline soil. The reason is the formation of mobile metal-organic complexes. These metal + organic substance complexes are easily absorbed by plants. Thus, on soils rich in organic matter liming can contribute to elevated amounts of heavy metals available to plants. Alekseev and Vyalushkina [26] observed the following dependence: the accumulation of nickel in plants is lower when calcium is present in soil.

With respect of iron deficit in plants, plant roots release phytosidorephores into soil, which convert insoluble into soluble iron forms. Phytosidorephores also contribute to better accumulation of copper and zinc in plants. Availability of metals to plants is improved by reductase in plant root cellular membranes. Roots of some plants (*eg* bean) respond to iron deficit by raising the acidity of soil, which causes conversion of iron from insoluble into soluble forms [27].

Conclusions

1. Incremental rates of heating oil caused depressed concentrations of copper and zinc, increased accumulation of nickel but did not induce unidirectional changes in the content of iron in maize.

2. Bentonite was more effective than zeolite as a soil amending substance. Bentonite reduced the accumulation of three (copper, zinc, iron) and zeolite – just two (copper and nickel) of the analyzed elements in maize compared with the series without neutralizing substances.

3. Application of calcium oxide and nitrogen to soil, in general, favoured the accumulation of the analyzed elements in aerial organs of maize.

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WPŁYW OLEJU OPAŁOWEGO I SUBSTANCJI NEUTRALIZUJĄCYCH NA ZAWARTOŚĆ WYBRANYCH PIERWIASTKÓW ŚLADOWYCH W KUKURYDZY (*Zea mays* L.)

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Abstrakt: Celem badań było określenie zdolności kukurydzy (*Zea mays* L.) do pobierania niektórych pierwiastków śladowych z gleby zanieczyszczonej olejem opałowym (0, 5, 10, 15 i 20 g $\cdot$ kg^{-1} gleby) po aplikacji do niej substancji neutralizujących (azotu, kompostu, bentonitu, zeolitu i tlenku wapnia), którą określono na podstawie badań ich zawartości w roślinach. Wzrastające dawki oleju opałowego przyczyniły się do obniżenia zawartości miedzi i cynku, wzrostu nagromadzania niklu i nie wywołały ukierunkowanych zmian w zawartości żelaza w kukurydzy. Bentonit był dodatkiem działającym bardziej korzystnie niż zeolit, gdyż ograniczał akumulację trzech (miedzi, cynku i żelaza) z badanych pierwiastków w kukurydzy, a zeolit tylko dwóch (miedzi i niklu), w porównaniu do serii bez dodatków. Aplikacja tlenku wapnia i azotu do gleby na ogół sprzyjała zwiększeniu nagromadzania badanych pierwiastków w częściach nadziemnych kukurydzy.

Słowa kluczowe: zanieczyszczenie olejem opałowym, azot, kompost, bentonit, zeolit, tlenek wapnia, kukurydza, pierwiastki śladowe