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Influence of Applying Halloysite and Zeolite to Soil Contaminated with Nickel on the Content of Selected Elements in Maize (*Zea mays* L.)

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Soil contaminated with heavy metals, including nickel is one of the consequences of an intensively developing civilization is the contamination of the natural environment. The purpose of the conducted research was to determine the influence of nickel applied in doses of 0, 80, 160, 240 i 230 mg Ni · kg^{-1} soil and additives in the form of zeolite as well as natural and dried halloysite on the content of mineral elements in maize (*Zea mays L.*). The doses of the nickel as well as a type of neutralizing substance used both influenced phosphorus, potassium, sodium, calcium, and magnesium content. Contamination of soil in the amount of 240 mg Ni · kg^{-1} resulted in the highest increase of phosphorus in maize. Modified halloysite added to soil with doses of 160 and 240 mg Ni · kg^{-1} soil caused almost a twofold increase in phosphorus content of maize when compared to plants without the addition of neutralizing substances. Modified halloysite also had a positive effect on the accumulation of potassium in the above-ground parts of maize, especially in plants exposed to the lowest analyzed dose of nickel (80 mg · kg^{-1} soil). Among the substances applied to neutralize nickel contamination, the application of modified halloysite was shown to be the most effective and increased the average calcium content by 29 %. Plants in the group without neutralizing additives and doses of nickel of 160 and 240 mg · kg^{-1} soil respectively were characterized by the highest Mg content in the above-ground parts of the plant. The application of sorption substances had a positive effect on the average content of magnesium in the above-ground parts of maize. The addition of modified halloysite led to the highest increase in the average level of magnesium in the tested plant when compared to the control group. Zeolite and natural halloysite also had a positive effect, although to a smaller degree.

1. Introduction

One of the consequences of an intensively developing civilization is the contamination of the natural environment. The soil, as the external layer of the lithosphere, is especially prone to the negative influence of these disadvantageous factors. Heavy metals, including nickel, constitute a specific group of such contaminants. Protecting the soil from them is of extreme importance, especially considering the longevity of such compounds and their negative effects. Soil contaminated with heavy metals is most often recultivated by the addition of sorption materials. Zeolites are characterized by a well-developed specific surface area, greater than that of humus and other fine-grain minerals known as particle or molecular sieves. They are characterized by selective sorption properties, ion exchanging ability and an optimal geometry of chambers and canals within the crystals. Many studies describe the positive results obtained by adding zeolites to polluted soils (Stefanovic et al. 2007, Belviso et al. 2010, Fronczyk et al. 2012). Because of the characteristics of their structures and their adsorbent properties, zeolites have been applied as adsorbents in contaminated soils (Hui et al. 2005). Halloysite is a loamy mineral material which

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possesses the ability to adsorb organic contaminants as well as the ions of heavy metals (Zhao and Liu 2008). This aluminosilicate clay mineral is mined in countries such as the U.S.A., Brazil, China, France, Japan, South Korea, Turkey, and Poland (Levis and Deasy 2002). The fact that sorption materials don't undergo biochemical degradation when introduced into the soil and can be removed at any time along with the adsorbed contaminants are some additional reasons for applying such substances.

Taking the above into consideration, studies aimed at determining the reaction of maize, an important crop to Polish agriculture which has recently been suggested as a candidate species for Ni phytoextraction (Maksimovic´ et al. 2007). The content of selected macroelements in the above-ground parts of maize (*Zea Mays L.*) following application of zeolite and natural as well as modified halloysite to soil contaminated with nickel compounds.

2. Materials and test method

Experiment Description

The impact of adding zeolite and halloysite to soil contaminated with nickel on the content of selected macroelements in maize (Zea mays L.) was assessed under the conditions of a pot experiment at a greenhouse facility of the Warmińsko-Mazurski Universtiy in Olsztyn (Poland). The experiment was conducted in three repetitions, using random assignment. The soil, with a granulometric composition of light clay sand, was placed in pots with a capacity of 9.5 kg and characterized by a: pH_{KCl} – 4.8, hydrolytic acidity (Hh) - 33.75 mmol(H^+) · kg^{-1} soil, sum of exchangeable base cations (S) – 62.20 mmol · kg^{-1}, cation exchange capacity (T) – 95.95 mmol · kg^{-1}, base cation saturation of sorption complex (V) - 64.8 %, C_{org} content – 7.13 g · kg^{-1}, and content of absorbable: phosphorus – 46.6 mg · kg^{-1}, potassium – 8.2 mg · kg^{-1}, and magnesium – 33.9 mg · kg^{-1}.

In addition to the control group (without the addition of halloysite, zeolite, and Ni), the experimental design included crops the soil of which mineral sorbents: zeolite, natural and modified (roasted in a stream of hot gases in order to evaporate water from the outside and from in between the crystals) were added in what amounted to 3 % of the soil mass.

Doses of nickel in the amount of 0 (control), 80, 160, 240, 320 mg·kg^{-1} soil were introduced in the form of chemically pure aqueous solutions $NiSO_4 \cdot 7H_2O$. The plants were watered with distilled water to 60 % of the maximum water holding capacity of the soil. In order to ensure the nutritional needs of plants, aqueous mineral fertilizer solutions were applied.

Maize (*Zea Mays* L.) of the San variety was the plant of choice for the experiment. The plant density was set at 8 plants per pot. The maize was picked following 69 days of vegetation, during the phase of intense stalk growth.

Laboratory Analysis

The above-ground plant yield was determined in the collected material. The plant samples were then dried at a temperature of 60 ^oC, ground, and subjected to mineralization in condensed sulphuric acid (VI) with hydrogen peroxide. The content of the following elements was determined in the obtained extracts: 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). Deionized water with a specific conductance of 0,055 µS · cm^{-1} was used for the analyses.

The following parameters were determined in soil samples prior to setting up the experiment: pH - potentiometric method in 1M KCl·dm^{-1} (ISO 10390. Soil quality-Determination of pH 2005), hydrolitic acidity (Hh) and sum of exchangeable cations (S) - Kappen method, organic carbon content (C_{org}) - Tiurin method (Lityński et al.1976), phosphorus and potassium content - Egner-Riehm method (Lityński et al. 1976), and magnesium content - atomic absorption spectrometry method following extraction using the Schachtschabel method (Lityński et al. 1976). Based on the hydrolytic acidity and exchangeable cation bases, the cation exchange capacity (CEC) and base saturation (BS) were caluculated using the following formulas: $CEC = ECB + HA$, $BS = (ECB/CEC)\cdot 100$.

Statistical Analysis

Statistical analyses of results was performed using the Statistica StatSoft, Inc. 2010 programme, applying the analysis of variance (ANOVA). Correlation coefficients between the doses of nickel and phosphorus, potassium, sodium, calcium and magnesium content of plants were also calculated.

3. Results and discussion

Heavy metals, including nickel, can initiate a series of morphological changes in plants which, among others, include chlorosis, necrotic spots, changes in colour, the curling up of leaves, sugar transport, and water relations (Kahle 1993, Seregin and Kozhevnikova 2006); a further consequence can be a decrease in the biomass of above-ground plant parts (Yang 1996, Redjala et al. 2010). By introducing substances that are capable of increasing the sorption capacity of soil, such as zeolites, halloysites, or other compounds which exhibit sorption properties, the amount of absorbable forms of heavy metals in soil can be decreased.

Crops differ in terms of their ability to absorb nickel, although it is usually taken up easily and in amounts that are proportional to its concentration in soil, up to a certain level of toxicity. The content of macroelements in the biomass of plants is subjected to specific changes which can be affected by the heavy metal content in soil. In the presented studies, phosphorus content in the above-ground biomass of maize was influenced by the nickel dose as well as the addition of zeolite as well as natural and modified halloysite to the soil (Table 1). In the control series (no additives), the differences in phosphorus content were positively correlated with the increasing doses of the above mentioned element. Soil contamination at 240 mg Ni $\cdot$ kg^{-1} soil led to the highest increase in phosphorus content in the analyzed plant. The application of zeolite and modified halloysite had a positive influence on the average phosphorus content of maize.

The opposite situation was observed in the case of adding natural halloysite, which had an adverse effect causing the average phosphorus content to decrease in the analyzed plant in relation to plants in the control group. Modified halloysite added to objects containing 160 and 240 mg Ni $\cdot$ kg^{-1} soil doses of nickel almost doubled the amount of phosphorus in the maize when compared to plants to which neutralizing substances had not been added.

The potassium content in above-ground parts of maize was significantly influenced by: the contamination of soil by nickel (dose) and neutralizing substances in the form of zeolite as well as natural and modified halloysite (Table. 1).

In general, applying nickel to soil contributed to increased levels of potassium in plants as compared to the control series - without neutralizing additives. An exception to this were the above-ground parts of maize grown in soil with the highest dose (320 mg $\cdot$ kg^{-1} soil) of nickel.The potassium content in these plants was 2.5 % lower than in the uncontaminated variant. Polocis et al. (1998) noted higher potassium contents in tomatoes which had been exposed to nickel contamination. The addition of modified halloysite, which caused a 24 % increase in the average content of the above mentioned element in maize as compared to the control series, was shown to be the most successful from the assortment of neutralizing substances added to the soil. An analogical situation was observed in the case of adding zeolite and natural halloysite, although their influence was weaker. Modified halloysite had a positive effect on the storage of potassium in the above-ground parts of maize, especially evident in the group of plants with a lowest dose of nickel (80 mg $\cdot$ kg^{-1} soil).

The nickel dose and application of zeolite as well as natural and modified halloysite had a significant effect on the sodium content of maize (Table 1) In the control series (without additives) a positive correlation between the sodium content and the increasing contamination of soil with Ni occurred. The neutralizing substances used in the experiment had a positive effect on the average sodium content in the analyzed plant. Only the addition of natural halloysite led to a decrease in the average sodium content of 6 % when compared to the control group.

The applied doses of nickel as well as neutralizing substances had a significant effect on the calcium content of maize (Table 1). In the series without additives (control), calcium content was positively correlated with increasing nickel contamination. In objects contaminated with 160 and 240 mg Ni $\cdot$ kg^{-1}, the content of the analyzed element was over twice higher in relation to objects which had not been contaminated. Similar dependencies in the increase of calcium content in the biomass of oats under the influence of Ni doses were noted in studies conducted by Crooke (1955) and Polocis et al. (1998). The present research reveals that the application of neutralizing substances (zeolite, natural and modified halloysite) to soil contaminated with nickel had a significant effect on the calcium content in the above-ground biomass of maize. The listed additives most significantly influenced plants exposed to the highest doses of nickel. From the analyzed substances neutralizing the effects of nickel contamination, the application of modified halloysite was shown to be the most effective resulting in a 29 % increase in the average calcium content when compared to the control crop.

Table 1: Effect of nickel contamination on phosphorus, potassium, sodium, calcium and magnesium content in above ground parts of maize (Zea mays L.) (g · kg^{-1} d.m.)

Dose of Ni in mg·kg^{-1} of soil	Kind of substance neutralizing effect of Ni				
	without additives	zeolite	natural halloysite	modified halloysite	Av.
	Phosphorus (P) in g kg^{-1} d.m.				
0	2.36	2.26	2.08	1.77	2.12
80	2.57	2.81	2.33	2.79	2.63
160	2.60	2.76	2.45	3.39	2.80
240	2.97	2.42	2.64	3.24	2.82
320	2.33	2.79	2.40	2.73	2.56
Av.	2.57	2.61	2.38	2.78	2.58
r	0.206	0.426*	0.739**	0.590**	
LSD	a - 0,199**, b - 0,178**, a · b - 0,397**				
	Potassium (K) in g kg^{-1} d.m.				
0	32.51	36.58	41.13	48.74	39.74
80	34.13	36.82	39.93	51.18	40.52
160	33.08	35.14	32.51	44.72	36.36
240	32.99	33.47	35.38	36.10	34.49
320	31.07	30.31	33.70	35.14	32.56
Av.	32.76	34.46	36.53	43.18	36.73
r	-0.571**	-0.937**	-0.804**	-0.918**	
LSD	a - 1,195**, b - 1,069**, a · b - 2,390**				
	Sodium (Na) in g kg^{-1} d.m.				
0	0.56	0.60	0.64	0.66	0.62
80	0.55	0.80	0.67	0.71	0.68
160	0.83	0.87	0.64	0.75	0.77
240	0.89	0.87	0.67	0.67	0.78
320	0.62	0.80	0.66	0.73	0.70
Av.	0.69	0.79	0.65	0.70	0.71
r	0.450*	0.680**	0.489*	0.385*	
LSD	a – 0,033**, b – 0,030**, a · b - 0,067**				
	Calcium (Ca) in g kg^{-1} d.m.				
0	3.16	3.84	4.26	5.01	4.07
80	5.01	7.09	7.75	8.75	7.15
160	7.92	9.00	8.84	11.50	9.32
240	8.50	8.00	10.17	10.58	9.31
320	7.92	7.42	8.67	10.00	8.50
Av.	6.50	7.07	7.94	9.17	7.67
r	0.889**	0.656**	0.797**	0.738**	
LSD	a – 0,231**, b – 0,207**, a · b - 0,462**				
	Magnesium (Mg) in g kg^{-1} d.m.				
0	2.70	3.05	2.69	2.92	2.84
80	2.98	3.67	3.52	3.79	3.49
160	3.25	3.99	3.59	4.35	3.80
240	3.46	3.39	3.76	3.41	3.51
320	3.27	3.46	3.51	3.87	3.53
Av.	3.13	3.51	3.41	3.67	3.43
r	0.867**	0.249	0.712**	0.451*	
LSD	a – 0,083**, b – 0,074**, a · b - 0,166**				

LSD for: a – nickel dose, b - kind of neutralizing substance
** - significant for p=0.01, * - significant for p=0.05, r - correlation coefficient

Zeolite, natural and modified halloysite, as well as the increasing doses of nickel significantly influenced the magnesium content of maize (Table 1). Magnesium content in plants from the control group, without the addition of neutralizing substances, was positively correlated with increasing doses of nickel. A similar dependency was observed in studies conducted by Matraszek et al. (2002) in which increasing doses of nickel the magnesium content in spinach leaves increased.

On the other hand, in research carried out by Palocis et al. (1998), the content of magnesium in oats was negatively correlated exposure to increasing doses of nickel. Crops in the study group without neutralizing additives and exposed to nickel doses of 160 and 240 · kg^{-1} soil were found to have the highest Mg content in their above ground parts. The application of neutralizing substances had a positive influence on the average magnesium content in the above-ground parts of maize.

When compared to the control series, modified halloysite was shown to have the most beneficial effect on magnesium content in the analyzed plant. Zeolite as well as natural halloysite also had a positive effect, although not as pronounced.

4. Conclusions

The content of macroelements including phosphorus (P), potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg) in maize (*Zea mays* L.) depended on the dose of nickel as well as type of neutralizing substance applied. The contamination of soil with 240 mg Ni · kg^{-1} soil resulted in the highest increase of phosphorus content in the analyzed plant. Modified halloysite in crops subjected to doses of 160 and 240 mg Ni · kg^{-1} soil led to a nearly twofold increase in the phosphorus content of maize in relation to plants without the addition of neutralizing substances. From the three analyzed substances applied to neutralize the nickel contamination of soil, the addition of modified halloysite was determined to be the most effective and resulted in a 24 % increase in the average content of the above mentioned element in maize when compared to the control group.

The addition of halloysite caused an insignificant decrease in the average sodium content in relation to the control. In the case of average calcium (Ca) and magnesium (Mg) contents, the application of modified halloysite proved to be most effective.

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