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Co-remediation of Ni-contaminated soil by halloysite and Indian mustard (*Brassica juncea* L.)

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ABSTRACT: The effects of increasing nickel contamination of soil on the update of selected microelements by *Brassica juncea* L. in the presence of raw halloysite (RH) and halloysite modified by thermal treatment (calcination) at 650°C (MH) were investigated experimentally. Such treatment causes partial dehydroxylation and enhances mineral-adsorption properties towards cations. In a vegetative-pot experiment, four different levels of Ni contamination, *i.e.* 0 (control), 80, 160, 240 and 320 mg kg^{-1} were applied in the form of an analytical-grade $NiSO_4 \cdot 7H_2O$ solution mixed thoroughly with the soil. Among the minerals which were added to soil to alleviate the negative impact of Ni on plant biomass, MH had a particularly beneficial effect on the growth of *B. juncea* L. The amount of Ni, Zn, Cu, Mn, Pb and Cr in Indian mustard depended on the Ni dose and type of accompanying mineral structure. The average accumulation of trace elements in *B. juncea* L. grown in Ni-contaminated soil follow the decreasing order Mn > Zn > Cu > Ni > Pb > Cr.

KEYWORDS: halloysite, Indian mustard, Ni-contamination, remediation, stabilization.

The contamination of the environment with heavy metals, including Ni, is a very important issue as each year the number of substances which can lead to such contamination increases. Nickel in small amounts has a positive impact on the growth of plants; however, when taken up excessively, it stops transpiration and impairs the process of photosynthesis and ionic balance, as well as the absorption of other ions by plants. The toxicity of Ni becomes apparent as chlorosis and root damage, the effects of which can be restricted to absorption and transport of nutrients to the above-ground plant parts (Dąbrowski *et al.*, 2013; He & Van Gestel, 2015; Singh & Prasad, 2015).

Phytoremediation of heavy metals trapped in the soil environment is a low-cost, non-intrusive, and environmentally compatible alternative to other methods (Yang *et al.*, 2015). However, this method generally removes only a very small percentage of contaminants from the soil, and can only be applied in situations with a low level of heavy-metal contamination. More importantly, the low bioavailability of heavy metals in contaminated soil may also limit the efficiency of phytoremediation (Jiang *et al.*, 2008). Nevertheless, the sub-categories of phytoremediation are ever-expanding, *e.g.* phytodegradation – the destruction of organic pollutants by plants, phytoextraction – the

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removal of contaminants from the soil by plants, phytostabilization – the immobilization of contaminants in a confined area, phytovolatilization – the taking up of contaminants by plants and their release into the atmosphere through transpiration, rhizodegradation – the degradation of contaminants in the rhizosphere by root exudate and microbes (Ali *et al.*, 2013).

Using phytoremediation methods on a large scale in contaminated areas can lead to the hyperaccumulation of toxic chemical compounds in the organs of plants, which, as a result, can lead to the plant-to-animal transfer of heavy metals. This situation can lead to serious environmental risk because it facilitates the entry of heavy metals into the food chain (Wołejko *et al*. 2014; Jeong *et al*., 2015). The toxic effects of Ni on crop yield and the chemical composition of plants can be counteracted by applying commonly occurring mineral sorbents which restrict its phytoabsorbability.

TABLE 1. Physical and chemical parameters of the experimental soil.

Soil chemical parameters	
pH	4.80
Hydrolytic acidity (cmol(+)·kg^{-1})	33.75
Sum of exchangeable bases Ca^{2+}, Mg^{2+}, K^+, Na^+ (cmol(+)·kg^{-1})	62.20
Cation exchange capacity (cmol(+)·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
$N\text{-}NH_4^+$ (mg kg^{-1})	21.18
$N\text{-}NO_3^-$ (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
Trace metal (mg kg^{-1})	
Ni	4.05
Cu	8.49
Cr	10.95
Zn	24.21
Pb	16.33
Mn	210.9
Available forms (mg kg^{-1})	
P	46.6
K	8.20
Mg	33.9

Phytoremediation methods may be combined with the use of reactive materials such as mineral sorbents. Research on the removal of heavy metals from contaminated soils by sorbents has been conducted for many years. Novel soil amendments for remediation can include halloysite, especially for slightly acidic soils, to reduce the availability of heavy metals in contaminated soils (Radziemska *et al.*, 2014). Halloysite was described for the first time by Berthier (1826) as a dioctahedral 1:1 layered clay mineral belonging to the kaolin group of minerals. A halloysite mine is found in the town of Dunino near Legnica (51°8′44″N, 16°4′31″E). The 'Dunino' halloysite deposit has resources of at least 10–12 million tons, and is characterized by an homogenous content, high clarity and trace amounts of heavy metals.

The objective of the present research was to investigate the effects of raw halloysite (RH) and a modified halloysite (MH) as adsorbents on the efficiency of the phytoremediation method involving the use of *Brassica juncea* L. for the removal of Ni from soils.

MATERIALS AND METHODS

Halloysite characterization

The raw halloysite (RH) used in the study was collected from the Dunino deposit located in SW Poland. The deposit is exploited by the Polish Intermark company. Kaolin group minerals dominate in the deposit with an average halloysite to kaolinite ratio of 60:40 (estimated by the formamide test of Churchman *et al*., 1984) without significant admixtures of other clay minerals (Matusik *et al*., 2009). The kaolin group minerals were formed by weathering of basaltic volcanic rocks. The mineral exhibiting tubular morphology is a dehydrated halloysite-(7 Å) of brownish colour due to co-existing Fe and Ti oxide minerals. The modified halloysite (MH) was produced from RH by the Intermark Company through thermal treatment (calcination) at 650°C. Such treatment causes partial dehydroxylation and enhances mineral adsorption properties towards cations. The RH and MH are efficient adsorbents mainly due to their large specific surface areas of 49.52 and 52.08 m^2 g^{-1}, respectively.

Plant material

Indian mustard was the crop of choice for the experiments because of its high biomass yields, heavy-metal tolerance, and the fact that it represents a commonly cultivated crop in the study area.

Seeds of *B. juncea* L. cv. Małopolska, were obtained from an authorized Seed Production Centre in Olsztyn, Poland (OLZNAS-CN Sp. z o.o.). Five seeds were planted per pot. Soil was fertilized with a macro- and micronutrient fertilizer mixture (g kg^{-1}) containing N-26%, K_2O-26%, B-0.013%, Cu-0.025%, Fe-0.05%, Mn-0.025% and Mo-0.20%. Indian mustard was harvested in the flowering phase and plant-material samples were collected for laboratory tests.

Experimental system

The co-remediation experiment was arranged in a randomized block design, with two factors and fourfold replication. The first factor was the addition of increased doses of Ni to soil (0, 80, 160, 240, and 320 mg kg^{-1}), introduced in the form of chemically pure aqueous solutions of Ni sulfate heptahydrate ($NiSO_4 \cdot 7H_2O$) (Sigma-Aldrich). The second factor consisted of the addition of two mineral adsorbents, *i.e.* raw halloysite (RH) and modified halloysite (MH) (3.0% w/w). Soils without Ni and mineral amendments (0.0%) were designated as the control. Non-polluted soils used for Indian mustard cultivation were collected at a depth of 0–20 cm from farmland in the vicinity of Olsztyn, Poland, (53°35′45″N, 19°51′06′E). The physicochemical properties of the soil are shown in Table 1. The soil was air-dried, passed through a 1 cm sieve and packed into experimental pots (10 kg of soil per pot); it was then used for physical and chemical analysis, as well as heavy-metal concentration analysis. The polyethylene pots were maintained under natural day/night conditions; during the day (14 h), the air temperature was 26 ± 3°C and ~10° lower (16 ± 2°C) at night (10 h), with a relative humidity of 75 ± 5%. The plants were watered every second day with distilled water to 60% of the maximum water holding capacity of the soil. The plants were harvested after 100 days. Afterwards, the soils and sorbents were collected.

Sample preparation and element content analysis

In the laboratory, the above-ground parts of *B. juncea* were rinsed thoroughly, 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 (DW) and powdered using an analytical mill (A 11 IKA, Germany) and kept at ambient temperature prior to the chemical analyses.

Samples were digested with nitric acid (Merck, 69% m/v) in a microwave oven (Milestone, Italy). Soil samples (1 g) were placed in inert Teflon microwave vessels and digested to assess the total concentrations of selected microelements after adding 10 mL of concentrated nitric acid (US-EPA Method 3051, 1994).

The Ni, Zn, Cu, Mn, Pb and Cr concentrations were determined using flame atomic absorption spectroscopy (AAS) on a SpecrtAA 240FS atomic absorption spectrophotometer (VARIAN, Australia), using a Sample Introduction Pump System (SIPS). Organic matter was determined according to Tiurin's method after the hot digestion of soil samples with $K_2Cr_2O_7$ and H_2SO_4 in the presence of Ag_2SO_4 as a catalyst and the titration of $K_2Cr_2O_7$ excess with $FeSO_4/(NH_4)2SO_4 \cdot 6H_2O$ (Mocek & Drzymała, 2010).

All reagents were of analytical reagent grade unless otherwise stated. Stock solutions of metals (1000 mg L^{-1}) were prepared from their nitrate salts. Ultra-pure (UP) water (Millipore System, USA) of 0.055 μS cm^{-1} resistivity was used in the preparation of the solutions and dilutions. All glass and polyethylene flaskware had been treated previously for 24 h in 5 mol L^{-1} HNO_3 and then rinsed with ultrapure water.

Statistical analysis

Statistical analysis was performed using the *Statistica* software. Differences of means between treatments were tested by ANOVA and comparisons of means using the LSD test, at $p = 0.05$. The means and standard deviations (±SD) of five replications are reported.

RESULTS AND DISCUSSION

Effect of co-remediation on Brassica juncea L. growth

Plant biomass production as well as the uptake of elements are two key indicators of the successful application of phytoremediation. The presence of small amounts of Ni in the soil has a favourable effect on the growth of many plant species (Brown *et al.*, 1987), whereas excessive amounts can lead to harmful effects in plant tissues (Rao & Sresty, 2000; Moreno *et al.*, 2003). The reaction of plants to the toxicity of Ni depends largely on the species as well as its variety (Guo *et al.*, 1995). The effects of different types of immobilizing agents and dosages of Ni-amendments

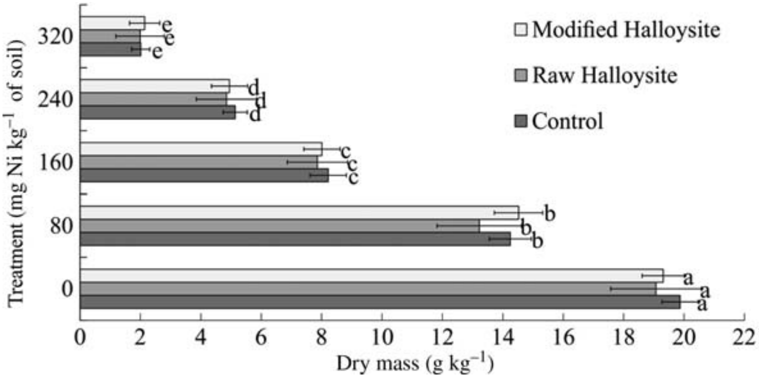

FIG. 1. Above-ground part of the biomass of *B. juncea* influenced by Ni or halloysite. Different letters indicate significant differences between members of the same set (Tukey test, $p < 0.05$).

on Indian mustard growth are given in Fig. 1. The results showed that the growth of *Brassica juncea* L. was affected significantly by the dose of Ni-contaminant and the applied mineral amendments, *i.e.* RH and MH. In the series lacking neutralizing additives, only the dose of 80 mg Ni kg^{-1} in soil decreased the crop yield of Indian mustard to a small degree (28%) in relation to the control group; larger Ni doses restricted the crop yield of the analyzed plant significantly, however, by 74% under the influence of 240 mg Ni kg^{-1} soil. For example, when the concentration of Ni in soil remained at 320 mg kg^{-1}, it significantly decreased the biomass of *B. juncea,* from 19.87 to 2.01 g kg^{-1} dry mass (d. m.). The authors' research shows that increased Ni contents in the soil environment influence the reduction on the crop yield of plants, *e.g.* cabbage (*Brassica oleracea*) (Molas, 2002), wheat (*Triticum aestivum* L.) (Gajewska *et al*., 2006), *Halimione portulacoides* (Duatre *et al*., 2007), corn (Narwal *et al*., 1994). Brown *et al*. (1987) reported that the critical concentration of Ni in barley tissues is 90 µg g^{-1} d.m. Karimi *et al*. (2013) also observed a reduction in the biomass of fenugreek (*Trigonella corniculata*) grown under Ni stress.

The average yield of the aerial parts of *B. juncea* L. was greatest for those plants treated with modified halloysite (MH), in marked contrast to those not treated in this way. In pots containing soil with a Ni dose of of 80 mg Ni kg^{-1}, the application of modified halloysite (MH) turned out to be the most advantageous, causing an increase in the crop yield of *Brassica juncea* L. by 17% as compared to pots with raw halloysite (RH) and 2% as compared to the control series (without additives). For example, Chen & Wong (2006) showed that the lime-stabilization process facilitated the establishment of *Agropyron* in the Ni-contaminated soil, even at a concentration of 100 mg Ni kg^{-1} soil. Research carried out by Sun *et al*. (2014a) revealed brown rice biomass (*O. sativa* L.) to increase in bentonite-treated soil. Friesl *et al*. (2003) proved that the application of inorganic amendments to soil alleviates the toxic effect of heavy metals on soils and at same time influences crop yield. According to the results of the present study, in the case of the greatest doses of Ni contamination (240 and 320 mg kg^{-1}), modified halloysite (+4% and 6%), turned out to be the most successful, resulting in increased crop yields of Indian mustard as compared to the control group (without immobilizing additives).

Effects of adding mineral sorbents on the concentration of microelements in B. juncea L.

The application of mineral amendments to contaminated soils can immobilize heavy metals and may provide a sustainable solution for the phytoremediation of, *e.g.* Ni contaminants in soils (Wyszkowski & Radziemska, 2010; Radziemska *et al*., 2014; Sun *et al*., 2014b). Moreover, the immobilization of heavy metals in soils is one of the major methods of alleviating the phytotoxicity of heavy metals to plants. One of the common amendments used to decrease heavy metal availability is lime (Chen *et al*., 2003; Wyszkowski & Radziemska, 2009). Furthermore, rock phosphate (Geeblen *et al*., 2003), halloysite (Radziemska *et al*., 2013), zeolite (Putwattana *et al*., 2015), diatomite (Ye *et al*., 2015), sepiolite and palygorskite (Liang *et al*., 2014), as well as organoclays (Sarkar *et al*., 2012) have been shown to decrease heavy metals solubility and plant uptake in contaminated soils.

Concentration of Ni, Cu and Cr in B. juncea L.

In the present study, the concentration of Ni, Cu and Cr in the above-ground parts of Indian mustard (*Brassica juncea* L.) was closely correlated with the applied dose of the Ni contaminant and neutralizing minerals introduced into the soil (Fig. 2).

The Ni content in the above-ground parts of Indian mustard was determined by the dose of soil contamination, as well as the applied mineral sorbents (RH and MH). Alloway (1990) claimed that the Ni content

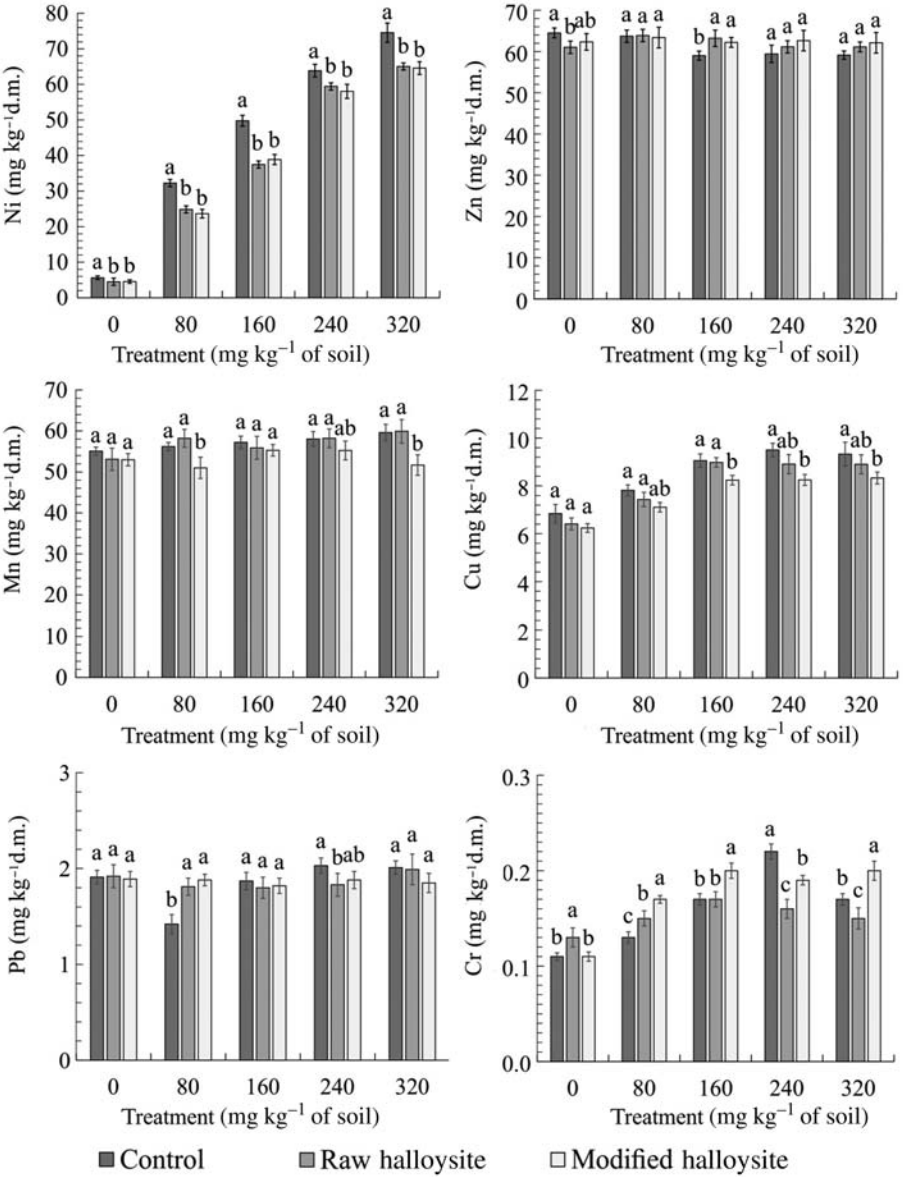

FIG. 2. Plant chemical characteristics obtained with the different amendments tested: Ni, Zn, Cu, Mn, Pb and Cr (mean ± SD, $n = 3$). Columns marked with different letters indicate significant differences between members of the same set (Tukey test, $p < 0.05$); d.m. = dry mass.

in plants depends mostly on its concentration and forms available in the soil. According to Kabata-Pendias & Pendias (2011), the typical levels of Ni in plant tissues are between 24 and 308 mg kg^{-1} d.m. In the present study, concentrations of Ni in the tested plants ranged from 3.35 to 74.55 mg kg^{-1} d.m. (Fig. 2). At a Ni soil concentration of 80 mg Ni kg^{-1}, modified halloysite (MH), caused a decrease (27%) in the average amount of Ni in the aerial parts of Indian mustard plant compared to the control series (without soil-amending substances). The greatest reductions in Ni content, *i.e.* by 25% and 22%, were observed in the above-ground parts of mustard grown in soil to which 160 mg of Ni per kg of soil had been added and contained raw or modified halloysite (MH), respectively, as compared to the uncontaminated soil. In addition, previous studies by Yang (1996) showed that Ni causes visible phytotoxic symptoms in maize at a concentration of 26 mg g^{-1}, while in rye grass, 50 mg g^{-1} (d.m.) leads to slight chlorosis. A recent paper by Bharagava *et al*. (2008) reported significantly greater accumulations of heavy metals in various parts of the mustard plant (*Brassica nigra* L.) when plants were grown in soil irrigated with distillery effluent. Increased Ni contents in plant tissues following the application of Ni to soil were also noted by Wadhawan (1995) in pearl millet and spinach, as well as Gupta *et al*. (1996) in mustard, lentil and chick pea.

The present study indicates a strong relationship between the application of mineral amendments and increasing Ni concentrations of soil on the Cu content of Indian mustard (Fig. 2). Schöne *et al*. (1992) reported that Cu concentrations can range from 4.5 to 21.1 mg kg^{-1} d.m. among grass species grown on the same soil. In the authors' experiment, the mean Cu concentration in mustard plants was significantly lower than the critical concentrations of Cu content in plant tissues (15–20 mg kg^{-1}) (Kabata-Pendias & Pendias, 2011), irrespective of treatments. The lower concentration observed might be due to the small concentration of bioavaliable Cu in soil. Concentrations of Cu in Indian mustard ranged from 5.51 to 9.33 mg kg^{-1} d.m. The increasing concentrations of Ni in soil in the series without any alleviating substances had a negative effect on the average Cu content in the above-ground parts of *Brassica juncea* L. relative to the control. In the same series, larger doses of Ni (320 mg Ni kg^{-1} of soil) led to increased Cu accumulation in the plant tested, with a maximum of 27%. Modified halloysite (MH) added to objects containing increased doses of Ni reduced the average amount of Cu in mustard plants by 12%, when compared to plants to which neutralizing substances had not been added. An analogous situation was observed in when RH was added, although its influence was weaker. By changing the properties of the soil environment, the availability of Cu can be modified with the liming of soil (Kabata-Pendias & Pendias 2011). Wyszkowski & Radziemska (2013a,b) also reported that *Avena sativa* L. accumulated maximum amounts of minerals and microelements when plants were cultivated with mineral amendments. Patel *et al.* (1976), on the other hand, could not find any definite relationship between Ni and Cu in plants.

The Cr content in the above-ground parts of Indian mustard was influenced significantly by the Ni dose contaminating the soil and the neutralizing substances applied in the form of RH and MH (Fig. 2). The Cr concentration in particular plant organs is related to its concentration in the soil (Mishra *et al*., 1995). Nayek *et al*. (2010) also demonstrated that Cr accumulation in the above-ground part of *Phaseolus vulgaris* was higher when the plants were irrigated with metal-contaminated wastewater. In the presented study, concentrations of Cr in mustard plant ranged from 0.11 to 0.22 mg kg^{-1} d.m. In the non-amended soil (no additives), the increasing rates of Ni had an explicitly positive effect on the content of Cr in *B. juncea* L. The greatest reductions in Cr content, *i.e.* by 28% and 14%, respectively, were observed in the above-ground parts of Indian mustard grown in soil to which 240 mg of Ni kg^{-1} of soil had been added and containing raw (RH) or modified halloysite (MH), as compared to the uncontaminated soil.

Concentration of Zn, Mn and Pb in B. juncea L.

The study results indicate that the Zn content in Indian mustard varied and was affected by the amount of Ni added and the type of amendments used (Fig. 2). The normal range of Zn concentration in plant tissues is 27–150 mg kg^{-1} (Kabata-Pendias & Pendias, 2011). Zinc demonstrates a strong affinity for mineral colloids and is characterized by high mobility in soil and a significant uptake by plants, especially in acidic environments (McBride, 1994). Concentrations of Zn in *Brassica juncea* L. ranged from 59.09 to 65.12 mg kg^{-1} d.m. In the control treatments (without alleviating substances), the average Zn content was less than in plants grown in pots with neutralizing substances. Doses of 160, 240 and 320 mg Ni kg^{-1} of soil without the addition of neutralizing agents decreased Zn concentration in Indian mustard as compared to the control (no contamination). Novo &

González (2013) found that technosols made of waste can be used successfully to increase the growth and the uptake of Zn by mustards in mine soils. On the other hand, Feng *et al*. (2007) demonstrated that soil amended with minerals, *i.e.* bentonite, clays and zeolite, effectively restrained the action of Zn on *Lupinus arboreus* L.

The concentration of Mn in *B. juncea* L. was closely correlated to the extent of Ni contamination and type of reactive materials introduced into the soil (Fig. 2). However, several studies have demonstrated that Mn is a micronutrient that is essential throughout all stages of plant development and has become an important factor limiting crop growth and yield (Ali *et al*., 2008). Concentrations of Mn in the mustard plant ranged from 50.99 to 59.92 mg kg^{-1} d.m. In the control treatments (without alleviating substances), the largest Ni dose caused an increase in the Mn content of up to 8% as compared to the control. Crops in the series with modified halloysite (MH), exposed to Ni doses of 240 and 320 mg kg^{-1} soil, were found to have the greatest reduction in Mn content in their above-ground parts. Modified halloysite (MH) added to soils containing increased Ni doses reduced the average amount of Mn in *B. juncea* L. by 9% when compared to plants to which neutralizing substances had not been added. An analogous situation was observed when RH was added, although its influence was less.

Both the Ni contamination of soil and the application of the substances analysed (halloysite) to the soil modified the Pb content in the aerial parts of *Brassica juncea* L. (Fig. 2). Pb is not an essential nutrient for plants, but is easily taken up by them from contaminated soils (Patra *et al*., 2004). According to Chlopecka & Adriano (1996), the addition of 0.4 wt.% of apatite to metal-contaminated soil led to a reduced Pb content in three-week-old maize plants. Epstein *et al*. (1999) demonstrated that *B. juncea* (cv. Rohini and 426308) was characterized by larger Pb concentrations in the roots of plants when they were grown in soil with this metal. The present study has revealed that the application of neutralizing substances had a positive influence on the average Pb content in mustard plants. Concentrations of Pb in these plants ranged from 1.42 to 2.03 mg kg^{-1} d.m. The largest reductions in Pb content, *i.e.* by 9% and 8%, were observed in the above-ground parts of *B. juncea* L. grown in soil to which 240 mg of Ni per kg of soil had been added and containing raw halloysite (RH) or modified halloysite (MH), as compared with the uncontaminated soil. In another experiment conducted by Radziemska *et al*. (2014), the average Pb content in the above-ground parts of maize (cv. San) after the application of modified halloysite added to Ni-polluted soil was reduced, by an average of 41%.

CONCLUSIONS

The trace elements contents (Ni, Zn, Pb, Cr, Cu and Mn) and growth of Indian mustard (*Brassica juncea* L.) depended on the dose of the Ni contaminant and the application of alleviating mineral substances incorporated into the soil. In the series without neutralizing substances, Ni had a negative effect on the growth of Indian mustard. The phytotoxic effect occurred in response to a dose of 160 mg Ni kg^{-1} of soil. Among the substances added to soil in order to alleviate the negative impact of Ni on mass of plants, halloysite modified by calcination at 650°C had a particularly beneficial effect on the growth of *B. juncea* L. In the control series (with no added halloysite), the differences in Ni, Cr and Cu content were correlated positively with the increasing doses of Ni contamination. Soil with 320 mg of Ni kg^{-1} of soil led to the largest increase in Ni, Cu and Mn content in the above-ground parts of *Brassica juncea* L. On the other hand, mustard plants showed the maximum accumulation of Zn in the series without the addition of mineral sorbents.

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