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POSSIBLE USE OF HALLOYSITE IN PHYTOREMEDIATION OF SOILS CONTAMINATED WITH HEAVY METALS

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Abstract

The impact of adding a natural clay sorbent such as halloysite on the content of selected heavy metals in the biomass of common orchardgrass (*Dactylis glomerata* L.) was studied in a pot experiment. The study was conducted on mucky soil enriched anthropogenically with heavy metals, whose values exceeded permissible standards of soil quality and values of the geological background. The experiment included three variants with differentiated percentage of halloysite, i.e. 10%, 30% and 50%, as well as two control cultivations. The results confirm the impact of halloysite on the physicochemical properties of soil, consisting in increased soil pH and sorption capacity. Addition of halloysite to soil also differentiated the quantity of crop yield and concentration of heavy metals in the plant and soil. Halloysite was found to have an inconsistent impact on the concentration of heavy metals in the biomass of common orchardgrass, which was proven by some elevation in the level of heavy metals and a higher bioaccumulation factor (BAF). Halloysite constituting 50% of the mass of substrate substantially increased the consumption of Pb and reduced the sorption of Cr. Addition of halloysite stabilised Zn and Cu in soil. The results of our preliminary investigation indicate that addition of halloysite to soils with excessive concentrations of heavy metals influences the level of soil sorption to the extent which may be effective for soil remediation.

Keywords: halloysite, common orchardgrass *Dactylis glomerata* L., phytoremediation, heavy metals.

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INTRODUCTION

High concentrations of heavy metals in soils is considered to be a major global problem in ecology (Jiang et al. 2010, Wei, Yang 2010).

Contamination of soils with heavy metals forces us to seek for alternative methods that would allow removal or complete stabilisation of these elements. One option is to apply phytoremediation, which uses the natural adaptation of plant organisms to absorb heavy metals from soils, and therefore immobilises them in plant tissues (Wuana, Okieimen 2011, Banach et al. 2012). Some species of grass, including common orchardgrass used in the experiment, have well-defined mechanisms for absorption of increased amounts of heavy metals from soils, which is why they are widely used in phytoremediation (Alkorta et al. 2004, Gratao et al. 2005, Aydin, Cakir 2009). Clay minerals are primarily used for purification of parent rocks contaminated with heavy metals (Cr, Cu, Zn, Pb) by means of phytostabilisation. Moreover, they are successfully applied to the phytoremediation of soils, as they improve the effectiveness of this process (Abollino et al. 2008, Gupta, Bhattacharyga 2008).

The aim of this study was to make a preliminary assessment of a possible use of halloysite, a natural clay mineral which is the weathering product of volcanic rock, in the process of phytoremediation of soils contaminated with heavy metals and seeded with common orchardgrass (*Dactylis glomerata* L.). Simultaneously, the impact of halloysite on the removal and/or stabilisation of Zn, Pb, Cu and Cr by the above species of grass was assessed through an analysis of the total content of these metals in the biomass and halloysite amended soil.

MATERIAL AND METHODS

The study on the impact of halloysite added to soil contaminated with heavy metals on the growth and development of common orchardgrass (*Dactylis glomerata* L.) was based on a pot experiment maintained in a KK 350/FIT 700S phytotrone chamber by the POL-EKO-APARATURA GP. The experiment included four replicates and two eight-week cycles of growing grass plants while preserving identical circadian parameters of the plant growth, i.e. light, temperature and humidity (Table 1).

During the plant growing cycle, the substrate humidity was maintained at the average level of 60% of field water capacity.

The pots with a capacity of 5 dm^3 were filled with a mix of halloysite and soil in predefined proportions, to the total weight of 2000 g. The following experimental variants were designed:

Table 1

Circadian parameters for the growth of common orchardgrass in pot cultivation

Section/parameter	S1	S2	S3	S4
Duration (hrs)	3	9	3	9
Temperature (°C)	18	24	20	16
Air humidity (%)	70	75	60	60
Light intensity (%)	70	100	70	10

Z – mineral and organic soil contaminated with heavy metals,

0 – (mucky) mineral and organic soil with the natural content of heavy metals,

I – soil Z with a 10% addition of halloysite,

II – soil Z with a 30% addition of halloysite,

III – soil Z with a 50% addition of halloysite.

The soil material (Z) used in the experiment was collected from the surface layer (to a depth of 25 cm) of mucky soil with the AM-Amu-Gr structure (muck on non-skeletal loamy sand) originating from an area with confirmed high heavy-metal contamination, which was Białogoński Pond located in the industrial district of Kielce, near disused metal steelworks (Świercz, Prażak 2014). It was decided that soil uncontaminated with heavy metals would consist of mucky meadow organic and mineral soil collected from the village of Wymysłów (0) located beyond the reach of industrial pollution (Cisowsko-Orłowiński Landscape Park).

The experiment involved the clay mineral halloysite collected from the Dunino open-pit mine. Halloysite is broadly applicable in environmental protection, including the remediation of soils contaminated with heavy metals (Słomkiewicz, Świercz 2011). Halloysite [$Al_2Si_2O_5(OH)_4$ (H_2O)] is a natural aluminosilicate, which is characterised by high porosity, ion exchange and specific surface area (Prashantha et al. 2011, Słomkiewicz, Świercz 2011, Cholewa, Kozakiewicz 2012, Rawtani, Agrawal 2012). The specific elemental composition of raw halloysite demonstrated that the main constituents are Al (19.57%), Si (18.51%) and Fe (11.38%), while the following elements occur in small proportions: Ti (1.37%), Ca (0.51%), Mn (0.22%), and P (0.23%). The chemical analysis showed a negligible content of heavy metals (Ni – 0.05%, Cr – 0.04%, Cu – 0.01%, and Zn – 0.01%). The presence of Pb in halloysite was undetected (Banaś et al. 2013). Raw halloysite was initially ground in a mortar, sieved through a 2 mm mesh sieve, washed with distilled water, and dried to the air-dry state. Before setting up the experiment and after harvesting the plants, basic properties of soils (contaminated and uncontaminated with heavy metals) were determined: pH in 0.1 n KCl dm^{-3}, cation exchange capacity (CEC) by the Kappen's method, as well as content of heavy metals, content of total nitrogen (C_{TN}) by the Kjeldahl's method, and content of total organic carbon (C_{TOC}) by the Tiurin's method. The total content of Pb, Zn, Cu, and Cr was determined in the soil material after mineralisation in *aqua regia* (HCl-HNO_3 – 3:1) by the ICP-AES method (Ostrowska et al. 1991).

Seeds of common orchardgrass (*Dactylis glomerata* L.) were sown in an amount of 1g per pot. The elongation growth of plants in all variants of the experiment was measured every 48 hours since emergence.

The total content of Pb, Zn, Cu, and Cr was determined after mineralisation of plants by using the ICP-AES method (Ostrowska et al. 1991). Absorption (elevation) (B) of the analysed heavy metals (in mg pot^{-1}) was calculated by multiplying the crop yield P_c (g d.m. pot^{-1}) by the content of a given heavy metal C_g (mg kg^{-1} d.m.) (Kalembasa, Malinowska 2008, Kuziemska et al. 2014).

$$B = P_c C_g.$$

Content of heavy metals in the analysed plant was expressed as mean values from two swaths. The data were compiled statistically, and the correlation coefficients were calculated for the analysed characteristics, the variability of which was presented graphically. Moreover, bioaccumulation factors (BAF), which correspond to the ratio of the content of an analysed heavy metal in the plant's dry mass C_x (mg kg^{-1} d.m.) to its total content in the soil C_g (mg kg^{-1} d.m.), were determined in order to specify the sorption level of heavy metals (Skorbiłowicz 2008).

$$BAF = C_x / C_g.$$

RESULTS AND DISCUSSION

The soil used in the experiment was rich in C_{TOC} and C_{TN} (Table 2), and was characterised by a high content of heavy metals, above permissible standards of quality (for Pb and Zn) or the geological background values (*Ordinance*... 2002, Świercz, Prażak 2014). In all variants of the experiment (except for the 0 control cultivation), the soils were classified either as neutral or slightly alkaline (pH in 0.1 n KCl), which substantially reduced the sorption of heavy metals by common orchardgrass. Solubility of heavy metals, conditioned by the processes of exchangeable sorption, is low under neutral and alkaline reaction (Szatanik-Kloc 2004, Dąbkowska-Naskręt, Różanki 2009). Addition of halloysite influenced the initial value of pH in the soils used in the experiment. After finishing the experiment, it was reported to increase (from 0.2 to 0.3 unit), proportionately in each variant of grass cultivation, not only in the soils enriched with halloysite, but also in the control cultivations.

One of the factors influencing the retention of metal ions and their migration into the soil solution is a share of clay minerals (Szatnik-Kloc 2004, Jiang et al. 2010). Addition of halloysite increased the cation exchange

Table 2

Physicochemical properties of soil substrates in the pot experiment

Parameter		Object/Variant of experiment				
		I	II	III	Z	**0**
		(mg kg^{-1} d.m.)				
Pb*		603.3	285.6	187.1	910.5	42.5
Zn*		759.6	543.6	377.0	1140	49.6
Cu*		91.0	78.8	68.5	121.3	16.2
Cr*		187.1	308.4	377.9	120.2	8.29
pH KCl	before experiment	7.07	7.13	7.14	6.90	4.68
	after experiment	7.37	7.44	7.50	7.33	4.90
		(g kg^{-1} d.m.)				
C_{TOC}	before experiment	7.21	7.01	4.86	11.07	15.9
	after experiment	6.71	5.74	3.53	10.07	14.4
C_{TN}	before experiment	0.68	0.61	0.57	0.81	0.75
	after experiment	0.62	0.55	0.51	0.73	0.52
		(cmol kg^{-1} d.m.)				
CEC	before experiment	42.2	42.6	42.8	42.2	39.6
	after experiment	42.4	42.8	43.0	43.0	38.8

* permissible content according to soil quality standards (mg kg^{-1} d.m.): Pb = 100, Zn = 300, Cu = 150, Cr =150 (*Ordinance*... 2002).

capacity of the analysed substrates in the range of 0.2 to 0.8 cmol kg^{-1} d.m. (Table 2). The studies conducted by Sipos (2010) involving another clay mineral, montmorillonite, showed a significant role of organic matter in the retention of Cu and Pb.

Small changes were observed for C_{TN}, corresponding to the variability in the control cultivations. Addition of halloysite to the soil decreased C_{TN} in the soils of control cultivations and those enriched in the clay mineral.

A reduction of all the analysed heavy metals was observed in the contaminated soil. Even a small, 10% addition of halloysite reduced the content of heavy metals in the range of about 1/4 (Cu) ÷ 1/3 (Pb, Zn). An opposite trend was observed for Cr. A significant increase in its content was determined in the soil substrates enriched with halloysite. It may be due to a slightly higher content of Cr in halloysite, which is 0.04%, and according to most studies, it remains in forms inaccessible to plants (Banaś et al. 2013).

The addition of halloysite differentiated the rate of absorption of heavy metals by common orchardgrass (Table 3). A significant increase of their content in the biomass of orchargrass plants grown in soil enriched with halloysite was reported for Pb, which is weakly accumulated in aerial parts of plants under natural conditions (Ciurzyńska, Gawroński 2002, Rączka, Gawroński 2004). The experiment showed that halloysite in soil increased the

Table 3

Content of heavy metals in the biomass of *Dactylis glomerata* L. – mean values from two growth cycles (swath 1 and 2) of the pot experiment

Object/ Variant of experiment	Pb		Zn		Cu		Cr		Biomass crop yield	
	(mg kg^{-1} d.m.)								(g d.m pot^{-1})	
	swath 1	swath 2	swath 1	swath 2	swath 1	swath 2	swath 1	swath 2	swath 1	swath 2
I	32.16	31.12	128.0	111.8	33.88	34.09	21.05	20.11	1.34	1.40
II	32.08	32.87	156.5	160.1	31.00	30.90	10.37	8.67	0.88	0.82
III	65.38	67.22	176.1	180.00	34.95	36.11	6.84	6.07	0.66	0.70
Z	28.17	27.90	177.6	169.5	41.68	41.09	20.18	19.70	0.33	0.27
0	6.41	5.55	74.40	70.21	67.07	65.11	2.06	2.11	1.92	2.01

sorption of this heavy metal by common orchardgrass. Interestingly, Pb was most strongly absorbed by the plants in the soil with the 50% addition of halloysite, where there was over a twofold increase of its value in each of the swaths.

The highest concentration of Zn was found in the biomass of common orchardgrass growing in the substrate enriched with the 50% of halloysite (176.06 and 180.00 mg kg^{-1} d.m., respectively). These results are comparable to the content of this heavy metal in the biomass obtained from the Z control cultivation. Reducing the share of halloysite in soil resulted in the inhibition of Zn sorption. The biomass of common orchardgrass from variant I contained 30.9% less Zn than in the control cultivation. It is noteworthy that Zn belongs to heavy metals which have the highest level of mobility. Addition of halloysite at a high C_{TOC} may result in forming complex compounds of different durability (Kwiatkowska-Malina, Maciejewska 2011).

Cu belongs to heavy metals easily absorbed by common orchardgrass (Vangronsveld et al. 2009, Krems et al. 2013). Addition of halloysite to the substrate decreased the bioaccessibility of Cu for the analysed plant. The research results indicated that the variant most favourable for reducing the phytoaccessibility of this heavy metal comprised the 30% addition of halloysite. This variant led to a reduction in the sorption of Cu by 14.1% and 46.2% in the Z and 0 control cultivation treatments, respectively.

The level of Cr sorption by orchardgrass plants was characterised by significant variation. The content of this heavy metal in the biomass was increasing parallel to the increase of its concentration in the soil, which was confirmed by the results from the control cultivations. Halloysite added to the substrate increased the content of Cr in the initial cultivation substrates (Table 2). Nevertheless, the sorption of Cr was the lowest (variants II and III) or comparable (I variant) to the level of its sorption by the plant in the Z control cultivation being highly contaminated with heavy metals. It was confirmed that Cr included in halloysite had reduced phytoaccessibility.

The increase in fresh mass of plants depends on many factors, such as the type of contaminated soils, degree of contamination, as well as plant species and varieties. Additionally, studies conducted with the use of plants indicate that high concentrations of heavy metals in soils reduce crop yields (Gontarz, Dmowski 2004). The increase in fresh mass of common orchardgrass from the Z control cultivation was by 1/3 lower than that in the 0 control cultivation. Soil addition of halloysite influenced the growth rate of the plant and its final crop yield. Variant I was the most effective as the biomass weight was nearly fourfold higher in each swath in comparison to that obtained in the Z control cultivation (Table 3). No clear correlations were found between the quantity of biomass and the time of plant's growth (Figure 1). The most intensive increase in fresh mass of the plant was observed in the 0 control cultivation. The lowest increase in the biomass was in turn reported for variant III.

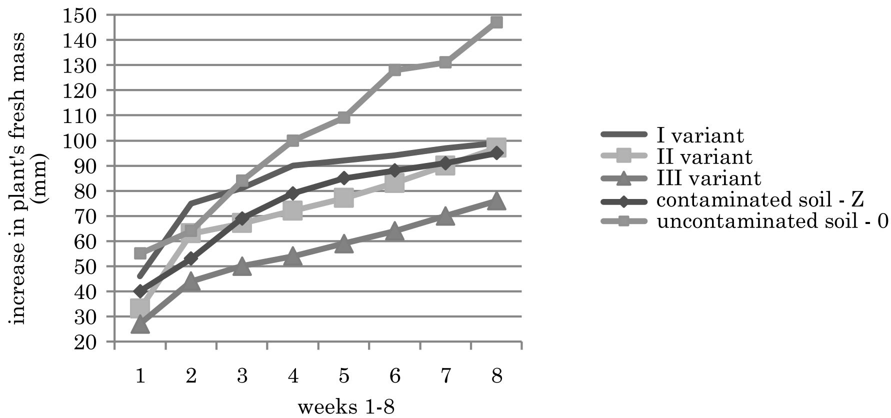

Fig. 1. Growth rate of common orchardgrass fresh mass in the pot cultivation

Rączka and Gawroński (2004) indicate that the biomass growth is limited as metabolic pathways are weakened by the toxic activity of heavy metals, or else other pathways are activated, which allows plants to survive under adverse environmental conditions. The biomass of common orchardgrass in the 0 control cultivation was characterised by a significantly lower content of the heavy metals in comparison to the Z control cultivation. Copper was an exception because its content in the 0 control cultivation was high.

One of the indicators in assessment of the extent and direction of heavy metal transport within the soil-plant system is the bioaccumulation factor, BAF (Jasiewicz et al. 2010). Addition of halloysite differentiated the values of BAF for each of the analysed heavy metals.

Under natural conditions, Pb is hardly mobile and forms chelates with metallothioneins as well as phytochelatins, and is not easily accessible to plants (Ciurzyńska, Gawroński 2002, Baran, Kołton 2008). With regard to the soil excessively contaminated with Pb in the Z control cultivation, the addition of halloysite caused an increase of this heavy metal in the plant, proportionally to the share of halloysite in the substrate (BAF_{Pb} in the range from 0.031 to 0.349). An identical trend was observed for Cu and Zn, and the opposite one for Cr. Reduction of the bioaccessibility of heavy metals indicates that halloysite limits the mobility of heavy metals in soils through increasing pH values and sorption capacity.

The highest values of BAF_{Cu} were found in the uncontaminated soil cultivation treatment (0). This factor was high there, reaching 4.132. As reported by Kwiatkowska-Malina, Maciejewska (2011), it may indicate a significant bioaccessibility of Cu for the analysed plant species under conditions that include a natural content of this heavy metal in soil. The value of BAF_{Cu} for the Z control cultivation was 0.344 and tended to increase as the proportion of halloysite in the substrate increased. Its highest value was noted for variant III (BAF_{Cu} = 0.511).

The plant absorbed Zn most readily in the soil contaminated with heavy metals (Z). The value of BAF_{Zn} for the Z control cultivation was nine-fold higher than that for the 0 control cultivation. Halloysite added to the substrate decreased the value of BAF_{Zn} in the range between 60% and 80% when compared to the Z control cultivation.

Despite its high content in the substrates enriched with halloysite, Cr assumed a form hardly accessible to plants. The use of halloysite limited the accumulation of Cr in the plant (BAF_{Cr} in the range from 0.017 to 0.110) in relation to both control cultivations, i.e. Z (BAF_{Cr} 0.166) and 0 (BAF_{Cr} 0.252) – Table 4.

The concentration factors of heavy metals in the biomass of common orchardgrass (BAF_{Cu}, BAF_{Pb}, $BAF_{Zn,}$ BAF_{Cr}) growing in the soil enriched with halloysite were lower than the value 1, which may indicate their limited bioaccessibility for the analysed plant or its ability to metabolise contamination (Ciurzyńska, Gawroński 2002).

The content of the analysed heavy metals absorbed by common orchardgrass in all experimental variants was dependent on the biomass quantity and the content of heavy metals in the plant's dry mass (Tables 3 and 5). The values of elevations of the heavy metals observed along with crop yields (Table 5) showed that Zn and Pb were the most effectively absorbed not only

Table 4

Heavy metal bioaccumulation factors (BAF) in common orchardgrass

No.	Variant	Pb	Cu	Zn	Cr
		BAF			
1.	I	0.053	0.372	0.288	0.110
2.	II	0.112	0.394	0.467	0.031
3.	III	0.349	0.511	0.643	0.017
4.	Z	0.031	0.344	1.501	0.166
5.	0	0.151	4.132	0.169	0.252

Table 5

Average absorption of heavy metals (μg pot^{-1}) by common orchardgrass in relation to the biomass (basing on two swaths)

No.	Variant	Pb	Cu	Zn	Cr
		(μg pot^{-1})			
1.	I	86.66	93.13	328.1	56.36
2.	II	55.19	52.62	269.0	16.26
3.	III	90.21	48.34	242.2	8.763
4.	Z	16.83	24.85	104.4	11.98
5.	0	23.47	259.6	284.0	8.20

in the variants with the halloysite addition (I, II, III), but also in the Z control cultivation. The content of heavy metals can be arranged in the following order of decreasing values: Zn>Pb>Cu>Cr. In the 0 control cultivation, the elevation of heavy metals along with crop yields followed the order: Zn>Cu>Pb>Cr. The elevation in the content of heavy metals mentioned above is similar to that reported by other authors (Baran, Kołton 2008).

The calculated correlation coefficients (Table 6) indicated significant relationships for the substrate's physicochemical properties (after finishing the

Table 6

Significant correlation coefficients between the analysed characteristics, with $p < 0.05$

Pair of variables	Significant correlation coefficient value $p < 0.05$
Cr – C_{TOC}	-0.967
Pb – pH	0.535
Zn – pH	0.676
Cu – pH	0.828
Cr – pH	0.768
Pb – C_{TN}	0.975
Zn – C_{TOT}	0.927
Cu – C_{TOT}	0.816
Pb – CEC	0.570
Zn – CEC	0.712
Cu – CEC	0.856
Cr – CEC	0.745
Pb – biomass	-0.602
Zn – biomass	-0.967
Cu – biomass	0.666
Pb – mass increase	-0.896
Zn – mass increase	-0.919
Cu – mass increase	0.892
BAF_{Zn} – elevation	-0.965
BAF_{Cu} – elevation	0.965

experiment) and also for the correlations between crop yields and heavy metal content in the biomass.

A positive correlation was reported for both soil pH and content of heavy metals in the cultivation substrates. A positive correlation was also noted for such heavy metals as Pb, Zn and Cu, and for values of C_{TN} and CEC. The values of CEC were significantly correlating with the values of Cr (positive correlation). In the case of C_{TOC}, a negative correlation was found for Cr. The above differences among the relationships indicate that there are different chemical mechanisms which govern the concentration of Cr in relation to other analysed heavy metals.

The biomass or increase of plant fresh mass were negatively correlated with the content of Pb and Zn. A positive correlation was verified for Cu. In the case of Pb and Zn, the elevation of heavy metals was significantly dependent on the bioaccumulation factor.

CONCLUSIONS

1. Halloysite added to soil influenced its physicochemical properties by increasing soil pH and sorption capacity.

2. Increase of Pb, and decrease of Zn, Cu and Cr were observed in the biomass of common orchardgrass growing in the substrate enriched with halloysite. In addition, halloysite increased the quantity of biomass in comparison to the control cultivation, in which soil was contaminated with heavy metals.

3. Bioaccumulation factors indicate that the analysed plant absorbs Zn and Cu more intensively than Pb and Cr. An increase in the value of BAF_{Pb} was noted for Pb – the highest in variant III (50% addition of halloysite). The stabilisation of Cu and Zn in soils occurred most effectively with the 10% addition of halloysite, and for Cr – with the 50% addition of halloysite.

4. The pot experiment results seem to suggest that halloysite can be as used as a factor supporting the phytoremediation of soils contaminated with heavy metals. In order to confirm the above, more studies should be conducted with the use of different species of plants and environmental conditions.

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