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THE EFFECT OF ZEOLITES ON SELECTED HEAVY METAL FRACTIONS IN SOILS FERTILIZED WITH SEWAGE SLUDGE

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Summary. The aim of the work was the identification and quantitative determination of zinc, lead and copper fractions in soil fertilized with sewage sludge and examination of the effect of natural and synthetic zeolites on their contents in the determined fractions. In soils fertilized with sewage sludge, regardless the dose, Zn, Pb and Cu appeared in the examined fractions, arranged in the following quantitative sequence:

Zn: FIII(47%)>FII(25%)>FI(13%)>FV(12%)>FIV(3%),

Pb: FIII(52%)>FIV(22%)>FV(21%)>FII(4%)>FI(1%),

Cu: FIV(40%)>FIII(26%)>FV(23%)>FII(8%)>FI(3%).

The application of zeolites to soils fertilized with sewage sludge reduced the content of Zn, Pb, Cu to 68% in those fractions, which in the course of soil environment changes (pH, salinity, redox potential) may become an easily available source of these metals for plants.

Keywords: soil, sewage sludge, metal fractions.

INTRODUCTION

Sewage sludge belongs to a very controversial group of waste. It contains various valuable nutritional substances fit for natural use, however it may also contain significant amounts of harmful or even toxic substances, and their contents depends on the origin of the sewage and the treatment method used [1].

Excessive heavy metal loads are the most frequent causes limiting the natural use of sewage sludge. The determination of the trace element content itself does not give a full view of the threats arising from excessive accumulation of the examined metals. A more reliable evaluation of the heavy metal impact on the natural environment gives the knowledge on their existing forms and bindings, as well as reaction of plants. Such information may be obtained through sequential analysis.

The objective of the work was the identification and quantitative determination of zinc, lead and copper in soil fertilized with sewage sludge and examination of the effect of natural and synthetic zeolites on their contents in the determined fractions.

MATERIALS AND METHODS

To evaluate the effect of the use of varied doses of sewage sludge and zeolites on the contents of Zn, Cu and Pb fractions in soils surveys were carried out in a greenhouse in 2 kilogramme pots in a series of 4 repetitions.

Soil from a field in Chylice from an arable layer (0-20 cm) of a granulometric composition of low-clay content sand and pH of 5.8 was used in the experiment. Sewage sludge from the „Czajka" Treatment Plant in Warsaw was the source of heavy metals. The chemical composition of the sludge is shown in Table 1.

Table 1. Chemical composition of sewage sludge from the „Czajka" Sewage Treatment Plant in Warsaw

pH	d.w.	C_{org}	N	P	K	Ca	Mg	Mn	Zn	Pb	Cu
	%			$g \cdot kg^{-1}$ d.w.					$mg \cdot kg^{-1}$ d.w.		
7.2	25	54	26	22	4	9	5	1183	1997	84.5	399

The following zeolites were used in the experiment: natural and synthetic of 5A type. The natural zeolites used in the experiment was a zeolite-bearing rock with app. 90% of clinoptilolite content, of channels diameter 4.1-6.2 nm. Calcium and potassium were the dominating cations in this natural zeolite. Synthetic 5A zeolite was calcium and natrium concedered as the dominating cataions. The channels diameter of zeolite 5A is app. 4.9 nm. The soil with sewage sludge with no zeolites added played the role of a control sample. The following three levels of fertilization with sewage sludge were applied: 20%, 10% and 5% of fresh mass of sludge in relation to the soil mass. Zeolites were added in 1:1 weighted ratio in relation to the mass of the sludge.

Lettuce was grown repeatedly for 3 times on such a prepared soil substratum. The duration of the full vegetation period, starting from planting to harvesting, amounted up to 5 weeks. After this period soil samples were taken for analysis.

Identification and quantitative determination of different forms of the same element, according to the Tessier *et al.* [9] procedure, is presented in Table 2.

Table 2. Metal fractions in soils and ways of their determination using the sequential extraction by Tessier *at al.* [9] method

Fraction no.	Determined fraction of metals	Extraction reagent
I	present in soil solution + easily exchangeable (unspecifically bound)	1 M $MgCl_2$
II	bound to carbonates	1 M $CH_3COONa + CH_3COOH$
III	bound to Fe-Mn oxides	0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH
IV	specifically bound to organic matter	0.02 M $HNO_3 + H_2O_2$ i 3.2 M CH_3COONH_4 in 20% HNO_3
V	residual	$HCl + HNO_3$ (3:1)

RESULTS AND DISCUSSION

The content of zinc in the determined fractions of soil fertilized with sewage sludge, irrespective of the dose, formed the following quantitative sequence (Tab. 3.):

$$FIII > FII > FI > FV > FIV$$

Zinc from the fraction bound to iron and manganese oxides (FIII) can be mobilized the fastest way in the course of changes in the redox potential, and its decrease will cause an increase of the Zn availability for plants. Whereas zinc found in the carbonate fraction (FII) may be released as a result of a decrease in the pH value. Xian and Shokohifard [10] and Kuo *et al.* [5] stated that zinc in heavily polluted soils binds in significant quantities with Fe and Mn oxides, and its share in this fraction ranges from 35% to 57% of the total zinc. The presented studies also prove that the content of zinc in the exchangeable fraction increases together with a decrease in the carbonate fraction share, especially in low soil pH value conditions (Tab. 3).

Table 3. Zinc fractions in soil fertilized with sewage sludge with or without zeolites in $mg \cdot kg^{-1}$d.w.

Sludge and zeolite dose*	FI**	ID*** %	FII	ID %	FIII	ID %	FIV	ID %	FV	ID%	FI-FV
					Control						
20%	13.5		25.1		47.0		3.5		12.5		101.6
10%	16.8		13.0		26.4		2.9		10.3		69.4
5%	15.1		10.7		24.0		2.7		10.6		63.1
					Control + natural zeolite						
20%	9.3	31	18.3	27	34.3	27	4.1	-	13.2	-	79.2
10%	5.3	68	16.1	-	24.1	9	3.6	-	14.5	-	63.6
5%	6.2	59	10.7	-	10.2	58	2.8	-	12.1	-	42.0
					Control + 5A zeolite						
20%	12.0	11	16.6	34	31.9	32	3.0	14	13.1	-	76.6
10%	5.8	65	6.0	54	32.0	-	3.7	-	13.6	-	61.1
5%	5.2	65	5.9	45	30.0	-	3.4	-	13.9	-	58.4

* - weighted percentage values in relation to the soil mass

** - FI – V – as in Table 2

*** - ID - percentage decrease of elements content in relation to the control value with analogous treatment (without zeolites).

Taking into consideration the study results presented in Table 4, the lead content in the determined fractions may be arranged in the following order:

$$FIII > FIV \geq FV > FII > FI$$

On the basis of undertaken studies on lead fractionation Qian *et al.* [7] concluded that lead in fractions is found to be in the following order: FIII (Fe and Mn oxides) = FV (residual) > FII (carbonate) > FIV (organic) > FI (exchangeable).

Table 4. Lead fractions in soil fertilized with sewage sludge with or without zeolites in $mg \cdot kg^{-1}$d.w.

Sludge and zeolite dose	FI	ID %	FII	ID %	FIII	ID %	FIV	ID %	FV	ID %	FI - FV
Control											
20%	0.2		0.5		7.3		3.0		2.9		13.9
10%	0.2		0.5		7.7		1.9		2.0		12.3
5%	0.2		0.5		6.8		1.5		1.4		10.4
Control + natural zeolite											
20%	0.2	-	0.6	-	6.2	15	2.4	20	2.9	-	12.3
10%	0.2	-	0.4	20	6.1	21	1.8	5	1.9	5	10.4
5%	0.2	-	0.5	-	4.2	38	1.4	7	1.4	-	7.7
Control + 5A zeolite											
20%	0.2	-	0.4	20	4.2	42	2.0	33	2.9	-	9.7
10%	0.2	-	0.6	-	5.3	31	1.6	15	1.8	10	9.5
5%	0.2	-	0.5	-	4.2	38	0.9	40	1.4	-	7.2

Denotations as in Table 3.

The highest amounts of lead are found in fraction III and IV, which may be explained by the affinity to form bindings of lead with Fe and Mn oxides and organic matter. This means that this element may become more mobile in cases of the decrease in the redox potential or due to mineralization of the organic matter. The exchangeable fraction (FI) and the carbonate fraction (FII) are found to be in the smallest amounts compared with the others (1 to 4% of total content). These fractions among all the others can join the biological cycle in the fastest manner. The results of studies on the examination of lead fractions demonstrate that the highest amount of this element is found in the organic fraction, giving the value of 43% of its total contents [4,5,6]. According to Takenaga and Aso [8] the reason for this is the creation of very strong bindings between Pb^{+2} ions and humic acids, which are characterized by low solubility. In the accumulation horizons of the polluted soils from the Katowice Voivodeship area over 50% of total lead was bound to Fe and Mn oxides, and also a significant amount of it was found in the fraction bound to organic matter [7,11]. Also Karczewska [4] presents data on a high share of mobile forms of lead in heavily polluted soils, although this element is considered to be of low mobility [7,11].

In soils fertilized with sewage sludge copper formed the following quantitative sequence in the evaluated fractions (Tab. 5):

FIV > FIII > FV > FII > FI

Table 5. Copper fractions in soil fertilized with sewage sludge with or without zeolites in $mg \cdot kg^{-1}$d.w.

Sludge and zeolite dose	FI	ID %	FII	ID %	FIII	ID %	FIV	ID %	FV	ID %	FI - FV
					Control						
20%	0.6		1.8		5.8		9.3		5.1		22.6
10%	0.7		1.1		4.0		4.9		4.1		14.8
5%	1.2		0.7		2.9		3.8		3.3		11.9
					Control + natural zeolite						
20%	0.6	-	1.9	-	5.2	10	7.4	20	4.4	14	19.5
10%	0.6	14	1.3	-	2.2	45	3.7	24	2.8	45	10.6
5%	0.8	33	0.6	14	1.8	38	3.0	21	2.6	21	8.8
					Control + 5A zeolite						
20%	0.2	67	2.2	-	4.6	21	4.3	54	3.6	29	14.9
10%	0.2	71	2.2	-	2.8	30	3.9	20	2.6	37	11.7
5%	0.3	75	2.3	-	1.5	48	3.3	13	2.1	36	9.5

Denotations as in Table 3.

Such an order shows that this element may become available, mainly in the course of the mineralization process of the organic matter or due to the decrease of the redox potential. Copper in fractions easily joining the biological cycle, meaning the exchangeable fraction (FI) and the carbonate fraction (FII), is found in small quantities (3 do 8%).

A similar sequence for the copper fractions was obtained by the authors examining soils around the „Glogow" Smelter [4,6]. These authors obtained the highest amounts of this element in bindings with organic matter. Copper bound to Fe and Mn oxides and hydroxides was the following fraction with respect to the quantitative level [4].

Different results were obtained by Kuo *et al.* [5] examining surface horizons of soils located in the vicinity of copper smelters, concluding that the highest quantities of copper were found in the fraction bound to Fe and Mn oxides i.e. from 69% to 83%.

Introducing zeolites to soils fertilized with sewage sludge indicates the possibility of reducing examined heavy metal fractions content (Tab. 3-5). Similar conclusions were obtained in the earlier studies regarding heavy metal content in anthropogenic soils before and after adding synthetic zeolites [2,3]. The present study demonstrates that adding zeolites to soils polluted with heavy metals, in the course of using sewage sludge, reduces the amounts of Zn, Pb and Cu in fractions most sensitive to environmental changes (exchangeable (FI), carbonate (FII), Fe and Mn oxide (FIII)).

The 20% dose of natural zeolite proved to be least effective in the reduction of zinc content in the exchangeable fraction as the amounts decreased only by 31% in relation to the control value. But using the proportion of doses for zeolite: sludge = 10:10 the zinc content dropped by 68%. On the other hand the lowest dose of sludge : zeolite reduced the zinc content in the exchangeable fraction by 59%. This means that the lowest dose of zeolite : sludge, the amount of 5% by weight, caused a decrease in the zinc content in the exchangeable fraction.

Reduction levels of the contents of zinc bound to iron and manganese oxides, depending on the dose, are as follows: the highest reduction of zinc in this fraction took place using a 5% natural zeolite dose (by 58% in relation to the control value); next with regard to the effectiveness was a 20% dose, which caused a drop in the zinc content by 27% compared to the control value. A dose of 10% proved to be least effective, reducing the contents of this element in the fraction III only by 9%.

No effects of adding natural zeolites on the zinc content in the organic and residual fraction were observed. This is reflected by a small percentage share of zinc in the mentioned fractions, being 3% and 12%, respectively in relation to its total contents.

The effect of the 5A synthetic zeolite on different zinc fractions may be presented as follows: a 20% dose of this zeolite caused reduction only by 11% of zinc in the exchangeable fraction (FI), a 10% dose by 65% in relation to the control value, and the smallest dose of 5% even up to 66% in relation to the control value. Alike natural zeolite, the synthetic one also proved to be effective with the use of the lowest dose.

The introduction of the 5A type zeolite to soils fertilized with sewage sludge caused reduction of the zinc content in the carbonate fraction; with a 20% dose of this zeolite it decreased by 34% compared to the control treatment, and with a dose of 10% - by 54% in relation to the control value. Adding the smallest dose of the 5A zeolite (5% by weight of sewage sludge) caused a decrease in the FII zinc contents by 45% in relation to the control value. The above data demonstrate that a 10% weighted dose of sludge and zeolite proved to be most effective. No effect was observed of the 5A zeolite on the zinc content in fractions: FIII (bound to iron and manganese oxides), FIV (organic) and FV (residual).

A treatment of a 20% dose of the natural zeolite and sewage sludge caused a decrease in the content of lead in the fraction bound to iron and manganese oxides (FIII) by 15% in relation to the control value. A reduction of lead by 21% in relation to the control value took place with a 10:10 combination. A combination of a 5% dose of natural zeolite and 5% of sludge proved to be most effective, resulting with a 38% reduction of the content of the examined element in relation to the control value. Applying a 20% dose of sludge and zeolite caused reduction of the lead content in the fraction bound to organic matter by 20% in relation to the control value, applying a 10% dose - by 5%, whereas the smallest dose - by 7%.

Analysis of the effect of a synthetic zeolite on the lead content in individual fractions provides evidence that it proved that it can cause the reduction of the contents of this metal in relation to the control value in individual fractions. Adding a 20% dose of this zeolite with the same sludge dose caused reduction of the lead content in the fraction bound to iron and manganese oxides by 42%, with 10:10 doses the lead content reduced by 31% in relation to the control value, whereas with a 5% dose of the 5A zeolite and a 5% dose of sludge - by 38%.

Introducing the 5A type zeolite did not affect the lead content in the following fractions: the exchangeable (FI), the carbonate (FII) and the residual (FV) one. This is demonstrated by low percentage shares of lead in these fractions: 1% in the exchangeable fraction, 4% - in the carbonate and 21% - in the residual one.

Adding natural zeolite changed the contents of copper in individual fractions. The introduction of natural zeolite to soils fertilized with sewage sludge caused reduction of the copper content, depending on the dose in the following fractions: bound to iron and manganese oxides, bound to organic matter and the residual one. Adding a 20% dose of natural zeolite with a 20% weighted dose of sludge caused reduction of the contents of this metal in the fraction bound to organic matter by 20% in relation to the control value. Applying the sludge dose: to the natural zeolite dose of 10% weighted each caused reduction of the copper content in this fraction by

24% in relation to the control value, whereas, adding the smallest doses of 5% each for the natural zeolite and the sludge caused reduction of the copper content in the fraction bound to organic matter by 21% in relation to the control value.

Reduction of the copper content in the fraction bound to iron and manganese oxides took place while applying the highest doses. It was demonstrated by the reduction of the contents of this element in the mentioned fraction by 10% in relation to the control value, whereas using 10% doses of natural zeolite and the sludge - by 45% compared to the control. In a treatment with the lowest doses of sludge: natural zeolite the copper content in the examined fraction decreased by 38% in relation to the control value. Doses of 10% for natural zeolite and 10% for sewage sludge proved to be the most effective doses affecting reduction of the copper content in the mentioned fraction.

Introducing natural zeolite to soils fertilized with sewage sludge did not affect the contents of copper in the exchangeable fraction (FI) and in the carbonate one (FII). A low copper amount in these fractions as compared to the total content: FI (exchangeable) - 3% and FII (carbonate) - 8% may serve as an explanation to this. Stated reduction of copper bound to iron and manganese fractions (FIII), bound to organic matter (FIV) and to the residual fraction (FV) may reflect the selective properties of the mentioned iron and manganese compounds and organic matter in creating specific compounds with these elements.

The synthetic type 5A zeolite in terms of distribution, of copper into separate fractions, it may reduce the copper content in the examined fractions. Doses of 20% both for this zeolite and sewage sludge caused reduction of the copper content in fraction bound to iron and manganese oxides by 21% in relation to the control value, and with 10:10 doses - by 30%, whereas with 5:5 doses by 48%. Analyzing the copper fraction bound to organic matter (FIV) it was noticed that in a 20:20 combination of doses, a copper content reduction took place in this fraction by 54% in relation to the control value, and with 10:10 doses - by 20%, whereas with 5:5 - by 13%.

Reduction of the copper content in the residual fraction was also observed in a combination with synthetic zeolite. Doses of 20:20 of 5A zeolite and sewage sludge reduced the copper content in this fraction by 29% in relation to the control value. Applying 10:10 doses caused reduction of copper by 37%, whereas 5:5 doses - by 36% in relation to the control value.

Summarizing the above results it can be noticed that specific properties of zeolites, both the natural and the synthetic ones, may be applied in reducing the contents of heavy metals found in fractions, which can be mobilized in the course of environmental changes.

CONCLUSIONS

1. In soils fertilized with sewage sludge, regardless the dose, Zn, Pb and Cu appeared in the examined fractions, forming the following quantitative sequences:

   Zn: FIII(47%)>FII(25%)>FI(13%)>FV(12%)>FIV(3%),

   Pb: FIII(52%)>FIV(22%)>FV(21%)>FII(4%)>FI(1%),

   Cu: FIV(40%)>FIII(26%)>FV(23%)>FII(8%)>FI(3%).
2. Among the examined elements, introduced with sewage sludge, zinc was found to be the most mobile one, which is reflected by the percentage share of this element in the exchangeable fraction, amounting to 13% in relation to its total contents; next is copper with 3% and lead - 1%.
3. Introducing zeolites to soils fertilized with sewage sludge has reduced the contents of Zn, Pb, Cu to 68% in those fractions, which, in the course of soil environment changes (pH, salinity, redox potential), may become easily available sources of these metals for plants.

REFERENCES

1. **Baran S., Turski R.:** Selected waste management aspects (in Polish). Wydawnictwo AR, Lublin, 1999.
2. **Borowiak M., Czarnowska K., Lewandowski W., Kot Z.:** Dynamic of changes in heavy metal levels in anthropogenic soils in the presence of zeolites (in Polish). Rocz. Glebozn. XXXVII, 3/4, 67-83, 1986.
3. **Gworek B., Brogowski Z., Jeske K.:** Effects of synthetic zeolites on the soil up-take of heavy metals by lettuce fertilized with sewage sludge (in Polish). Rocz. Glebozn. XLVII, 1/2, 47-53, 1996.
4. **Karczewska A.:** Forms of selected metals in surface horizons of soils polluted by emissions from copper smelters (in Polish). Zesz. Probl. Post. Nauk Roln., 418, 481-485, 1995.
5. **Kuo S., Heilman P.E., Baker A.S.:** Distribution and forms of copper, zinc, cadmium, iron and manganese in soils near a copper smelter. Soil Sci., 135, 101-109, 1983.
6. **Mocek A.:** Possibilities of rational management of soils chemically contaminated in the industrial sanitary protection zones (in Polish). Rocz. AR in Poznań, Rozprawy naukowe, 1- 97, 1989.
7. **Qian J., Wang Z., Shan X., Tu Q., Wen B., Chen B.:** Evaluation of plant availability of soil trace metals by chemical fractionation and multiple regression analysis. Environ. Poll., 91, 3, 309-315, 1996.
8. **Takenaga H., Aso S.:** Studies on the physiological effect of humic acid (part 9). Stability constants of cation-nitrohumic acid chelats. J. Soil Sci. Plant Nutri., 46, 349-354, 1975.

9. **Tessier A., Campbell P.G.C., Bisson M.:** Sequential extraction procedure for the speciation of particular trace metals, Anal. Chem., 5, 844-850, 1979.
10. **Xian X., Shokohifard G.:** Effect of pH on chemical forms and plant availability of cadmium, zinc and lead in polluted soil. Water, Air, Soil Poll., 45, 265-273, 1989.
11. **Zhang M.:** Chemical association of Cu, Zn, Mn and Pb in selected sandy citrus soils, Soil Sci., 162, 3,181-188, 1997.

WPŁYW ZEOLITÓW NA FRAKCJE WYBRANYCH METALI CIĘŻKICH W GLEBACH NAWOŻONYCH OSADEM ŚCIEKOWYM

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S t r e s z c z e n i e. Celem pracy było identyfikacja i ilościowe oznaczenie frakcji cynku, ołowiu i miedzi w glebie nawożonej osadem ściekowym oraz zbadanie wpływu naturalnych i syntetycznych zeolitów na ich zawartość w oznaczonych frakcjach.
W glebach nawożonych osadem ściekowym, niezależnie od dawki, Zn, Pb i Cu występowały w analizowanych frakcjach, tworząc następujące szeregi ilościowe:

Zn: FIII(47%)>FII(25%)>FI(13%)>FV(12%)>FIV(3%),
Pb: FIII(52%)>FIV(22%)>FV(21%)>FII(4%)>FI(1%),
Cu: FIV(40%)>FIII(26%)>FV(23%)>FII(8%)>FI(3%).

Wprowadzenie zeolitów do gleb nawożonych osadem ściekowym obniżyło zawartość Zn, Pb, Cu do 68% w tych frakcjach, które w wyniku zmian w środowisku glebowym (pH, zasolenie, potencjał redox) mogą stać się ich łatwo dostępnym źródłem dla roślin.

S ł o w a k l u c z o w e: gleba, osady ściekowe, frakcje metali.