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PHYTOAVAILABILITY OF COPPER AND ZINC FROM SOIL RECLAIMED BY LIME-TREATED SEWAGE SLUDGE AND OTHER WASTE

The research was undertaken in order to find the way of utilizing in agriculture lime-treated sewage sludge (biosolid) and its mixture with sugar beet washing earth and ash from straw-fired boilers. It has been shown that large amount of sewage sludge increases plant biomass, does not increase copper and zinc levels in soil and improves their levels in maize. The addition of sugar beet washing earth and ash still increases the crop-enhancing property of the soil, but simultaneously it lowers the level of copper and zinc in the plants tested. Agricultural utilization of the wastes mentioned increases yields and limits the use of mineral fertilizers, which are not environmentally neutral. Hence this is the best way to dispose these wastes.

1. INTRODUCTION

The loss of soil organic matter (SOM) observed in Europe [15] is a destructive process because of ecological, agronomical and even climatological reasons. Therefore it is advisable not only to rationally use humus, but also to circulate again all organic compounds, which do not damage the environment, e.g., sewage sludge. According to the present decree issued by the Minister of the Environment [11], sewage sludge can be used as fertilizer (up to 10 Mg DM ha^{-1}) or for reclamation of arable land (up to 200 Mg DM ha^{-1}), provided that its content of heavy metals and sanitary conditions meet standards.

Sewage sludge treated with quicklime, slaked lime or cement kiln dust is of particular value. Although its crop-increasing properties are slightly lower compared to those of sludge without any addition of calcium compounds (one of the reasons is the loss of nitrogen during treatment with lime [5]), such sludge has a very positive impact on other properties of the soil, particularly acid soils [1], [2], [9]. However it is not

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clear how high doses of alkalized sludge can affect soil, because their pH is high and simultaneously they contain large amounts of non-stabilized SOM.

The aim of this study, which is part of a larger project, was to assess the effect of lime-treated sewage sludge and its mixtures with other kinds of waste on the content of zinc and copper (metals strongly bounded with SOM [3]) in light soils and in maize.

2. MATERIALS AND METHODS

A pot experiment was carried out in 1996–1998. Light, acid soil was used (pH_{KCl} 5.1). Such a soil has a limitted cation exchange capacity (CEC) (5 cmol(+)kg^{-1}), is poor in humus (6 g C kg^{-1}) and its particle-size distribution corresponds to light loamy sand. The content of heavy metals is much below a typical natural level [4], i.e., it contains 3 mg Cu kg^{-1} and 17 mg Zn kg^{-1}. Two doses of lime-treated sludge (LS) were used: 2 percentage by weight (corresponding to 56 Mg DM·ha^{-1}) and 5 percentage by weight (corresponding to 140 Mg DM ha^{-1}), which are further called 2% LS and 5% LS. Both doses were later enriched with sugar beet washing earth (equivalent of 280 Mg DM·ha^{-1}) and ash from a straw-fired boiler (equivalent of 9 Mg·ha^{-1}), which are later called waste (W). Sugar plant flumes (sugar beet washing earth from sugar plant sediment tanks in Werbkowice) were treated as a source of fine soil particles, whereas ash was used to supplement sludge, typically being poor in potassium. The control consisted of pots with maize which was fertilized by mineral fertilizer in the standard way. Combinations of soil and waste were also tested. Maize was grown indoors and was watered with deionized water. The crop was harvested at the milky-wax ripeness stage.

Sewage sludge came from the mechanical-biological municipal sewage plant in Zamość. It was dehydrated and then treated with quicklime, hence it fulfilled all the standards [11]. In 1 kg of sludge dry matter the concentration of copper was 103 mg, and that of zinc – 1 300 mg, which is much less than permissible levels (800 and 2 500 mg kg^{-1} DM, respectively). If grain composition is taken into account, washing earth belongs to loamy silt and has natural levels of heavy metals (Cu – 7 mg kg^{-1}, Zn – 26 mg kg^{-1}) [4], in the ash also low concentration of these elements is found (Cu – 10 mg kg^{-1}, Zn – 40 mg kg^{-1}).

A total content of copper and zinc in soils was measured at the beginning and end of the study, using the samples digested in aqua-regia, whereas their soluble forms were extracted in spring, using HCl (1 mol·dm^{-3}). Every year these elements were measured in the above ground plant parts, after mineralizing them in a mixture of acids (H_2SO_4, HNO_3, $HClO_4$). In all the samples, the concentration of elements was measured using atomic absorption spectrometry AAS-3 (Carl-Zeiss Jena).

The analysis of variance was used in the statistical analysis. The differences between individual means were tested using an LSD at 0.05 significance level. Linear correlation coefficients were calculated for the variables measured, the tables show only the type of relationship (negative/positive) and significance level.

3. RESULTS AND DISCUSSION

In our previous studies it was shown that sewage sludge from the plant in Zamość applied once improved pH and increased the amount of SOM, CEC and the concentration of all nutrients [9]. This enabled higher yields of maize to be produced, and their quality was better compared to mineral fertilization [10]. Moreover, simultaneous application of waste that enriched soil with <0.02 mm particles proved to be better for yield (tables 1 and 2).

Table 1

Selected soil properties after the application of sewage sludge and waste (the beginning of experiment)

Treatment	pH in H_2O	$C_{organic}$ (g kg^{-1})	CEC* (cmol(+) kg^{-1})	Fractions of <0.02 mm (%)	Cu_{total} (mg kg^{-1})	Zn_{total}
Soil	5.2	6.1	4.9	13	2.9	15.3
+ W	7.1	6.4	8.1	20	3.4	18.0
+ 2% LS	7.1	10.1	8.0	17	4.6	37.2
+ 2% LS + W	7.0	10.0	8.8	20	4.8	33.8
+ 5% LS	7.3	15.5	10.5	20	6.9	58.5
+ 5% LS + W	7.3	16.3	11.7	20	8.2	59.7
LSD	0.2	1.7	1.2	–	0.5	2.8

W – waste; LS – limed sewage sludge; CEC – cation exchange capacity.

As expected, due to applying of the above mentioned substances, a general concentration of copper and zinc in the soil increased (table 1). Although higher concentration of these metals was observed throughout the year in all variants of the experiment, except for the control (figure 1), it did not exceed the permissible levels [12].

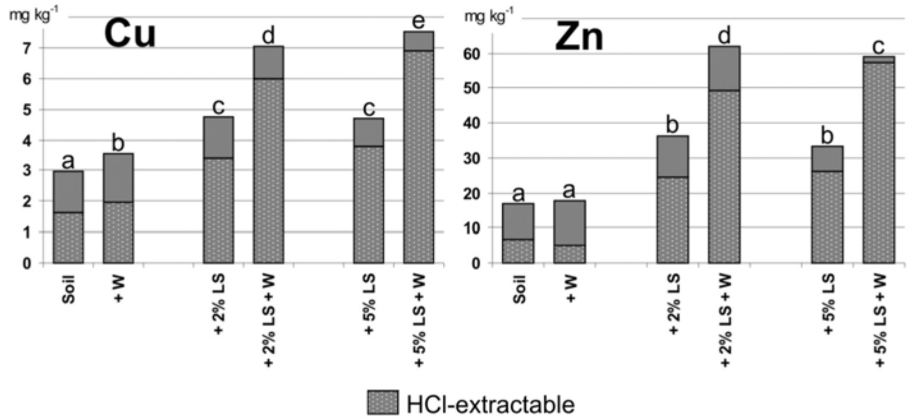
The content of HCl-extractable forms of copper and zinc also increased proportionally to the dose of sewage sludge (the figure). The waste introduced into soil increased total content of copper at 5% dose and slightly decreased zinc content in both variants with sewage sludge. However, the solubility of the compounds of these metals improved, particularly in zinc compounds at a higher dose of sludge. Both the total and HCl-extractable content of Cu and Zn were positively and highly correlated ($p < 0.001$) with CEC, organic carbon content, fractions of <0.02 mm, and clay, which confirms the importance of organic matter and clay minerals for binding metals [3]. However, according to BROWN et al. [2] greater mobility of metal ions in the soil with lime-stabilized biosolid may be caused by a better of solubility of the complexes of metals and fulvic acids, observed with an increase in soil pH. It is highly probable since, as previously shown [8], the correlation between the amount of these metals and the concentration of fulvic acids was found to be stronger than that between the amount of these metals and the concentration of humic acids.

Table 2

The concentration of Cu and Zn in above ground parts of maize and availability indices, 3-year mean

Soil	Yield (g DM per pot)	Content in the plant ($mg\ kg^{-1}$ DM)		Availability indices*	
		Cu	Zn	Cu	Zn
+ NPK	142	2.0	43.0	1.24	6.54
+ W	78	1.8	21.1	0.93	4.01
+ 2% LS	157	3.4	39.9	1.01	1.62
+ 2% LS+ W	171	3.0	32.3	0.80	1.22
+ 5% LS	131	5.7	76.2	0.95	1.55
+ 5% LS + W	195	3.4	54.8	0.50	0.96
LSD	11	0.2	4.9	0.06	0.39

* The ratio of metal content in the plant to their HCl-extractable amount in soil.



A total content of Cu and Zn in the soil and their HCl-extractable proportion (3-year mean). Means followed by different letters are significantly different at the 0.05 probability level

Copper content increased in maize proportionally to the sewage sludge dose applied, whereas the level of zinc was increased only by the 5% LS dose and as a result the concentration of both elements approached the optimum, typical of animals [7]. It must be emphasized that under Polish conditions the defficiency of these minerals (especially of copper) often occurs in fodder plants. Waste added to soil made absorption of Cu and Zn less effective (table 2).

Phytoavailability of metals is affected by many factors. That is why, depending on the properties of soil and sewage sludge, its dose, the kind and the amount of alkalizing substance, plant species and even the part of the plant, the results obtained can vary and can contradict each other. They prove that such biosolids do not affect the bioaccumulation of copper and zinc, or they decrease it, or, more rarely, increase it [1], [6], [13], [14], [16], [17]. It was noticed however that phytoavailability of elements from alkalized sediments is always lower than phytoavailability of elements from dehydrated ones [1], [13], [14], [16].

As mentioned, the addition of waste significantly reduced the copper and zinc uptake by maize (table 2), which is also corroborated by the levels of availability indices (calculated as the ratio of their content in the plant to their HCl-extractable amount in the soil). The plants from pots treated with sewage sludge and waste were the largest, which might have occurred as a result of the dilution effect. This is corroborated by a negative correlation ($p > 0.001$) between the mass of plants and their metal content. The waste also reduced the rate of degradation of organic matter in the sludge [8], and increased cation exchange capacity (table 1), which decreased the amount of these elements in the soil solution [3].

Moreover, a very high negative correlation ($p < 0.001$) was found between copper and zinc availability indices and some soil properties (pH, CEC, SOM content, clay content). Significant differences between the absolute values of correlation coefficients and pH ($r_{Zn} = -0.85$, $r_{Cu} = -0.69$) and clay content ($r_{Zn} = -0.93$, $r_{Cu} = -0.57$) indicate that pH increase and clay content have greater effect on the availability of zinc than on availability of copper, whereas soil organic matter reduces bioaccumulation of both these elements in a similar way.

4. CONCLUSION

A great variability of the content of sewage sludge and other waste does not allow us to make far reaching generalizations. However, it can be concluded that:

1. The lime-treated sewage sludge with heavy metal levels not exceeding permissible standards, even in soil-reclamation doses (54 and 140 Mg DM$\cdot$ha^{-1}), does not cause the standards of copper and zinc content in the soil to be exceeded, and, used together with sugar beet washing earth with ash, improves the uptake of copper and zinc by maize.

2. An increase in pH and in clay content is more important for a decrease in the availability of zinc than that of copper, whereas soil organic matter reduces the bioaccumulation of both elements in a similar way.

3. Agricultural use of lime-treated sewage sludge, washing earth and ash from straw-fired boilers enables us to raise the plant crop and to reduce the use of mineral fertilizers, which can be harmful to the environment. Hence such an application of waste is the best way of utilizing it.

REFERENCES

[1] BASTA N.T., SLOAN J.J., *Bioavailability of heavy metals in strongly acidic soils treated with exceptional quality biosolids*, J. Environ. Qual., 1999, 28, 633–638.

[2] BROWN S., CHANEY R., ANGEL J.S., *Subsurface liming and metal movement in soil amended with lime-stabilized biosolids*, J. Environ. Qual., 1997, 26, 724–732.

[3] KABATA-PENDIAS A., PENDIAS H., *Biogeochemia pierwiastków śladowych*, PWN, Warszawa, 1999.

[4] KABATA-PENDIAS A., PIOTROWSKA M., MOTOWICKA-TERELAK T., MALISZEWSKA-KORDYBACH B., FILIPIAK K., KRAKOWIAK A., PIETRUCH C., *Podstawy oceny chemicznego zanieczyszczenia gleb*, Biblioteka Monitoringu Środowiska, Warszawa, 1995, 141.

[5] KALEMBASA S., WYSOKIŃSKI A., *The influence of fertilization with composted mixtures of waste activated sludges with CaO and brown coal ash on the yield of tested plants and effectiveness of nitrogen* (in Polish), Annales UMCS, Sectio E, 59, 4, 1899–1904.

[6] LITTLE D.A., RENEAU R.B., MARTENS D.C., *Lime-stabilized and chemically-fixed sewage sludges as lime amendments*, Bioresource Technology, 1991, 37, 93–102.

[7] PREŚ J., KINAL S., *New approach to the supply animals with trace elements* (in Polish), Zesz. Probl. Post. Nauk. Roln., 1996, 434, 1043–1061.

[8] RESZEL R., RESZEL H., GŁOWACKA A., *Changes in the contents of organic carbon in the light soil fertilised with sewage sludge, sugar-beet washing earth, and straw ash*, Acta Agrophysica, 2001, 52, 209–217.

[9] RESZEL R., RESZEL H., GŁOWACKA A., *Altered properties of light soils improved with lime-treated sewage sludge or its mixture with sugar beet flume washing earth and straw ash*, EJPAU, series Environ. Develop., 2003, 6(2), http://www.ejpau.media.pl.

[10] RESZEL R., RESZEL H., GŁOWACKA A., *The reaction of maize to fertilizing light soils with lime-treated sewage sludge, its mixtures with sugar-beet washing earth from a sugar plant sediment tanks and with ash from straw burning stations* (in Polish), Annales UMCS, Sectio E, 2004, 59, 2, 697–703.

[11] Rozporządzenie Ministra Środowiska z dnia 1 sierpnia 2002 r. w sprawie komunalnych osadów ściekowych. Dz. U. Nr 134, poz. 1140.

[12] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości ziemi. Dz. U. Nr 165, poz. 1359.

[13] SEYHAN D., ERDINCLER A., *Plant availability of heavy metals and phosphorus in the agricultural reuse of biological sludges*, J. Environ. Sci. Health, Part A, 2003, 38, 10, 2413–2423.

[14] STĘPIEŃ W., MERCIK S., SZULC W., *Influence of crude and composted sewage sludge on the uptake of heavy metals by red beet plants* (in Polish), Zesz. Probl. Post. Nauk Roln., 2000, 472, 611–618.

[15] Strategia ochrony gleb, komunikat Komisji Europejskiej COM 179, Bruksela, 16.04.2002.

[16] SU D.C., WONG J.W.C., *Chemical speciation and phytoavailability of Zn, Cu, Ni and Cd in soil amended with ash-stabilised sewage sludge*, Environ. International, 2003, 29, 895–900.

[17] VASSEUR L., FORTIN M.J., CYR J., *Clover and cress as indicator species of impact from limed sewage sludge and landfill wastewater land application*, Sci. Total Environ., 1998, 217, 231–239.

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Prezentowane badania są próbą zastosowania w rolnictwie wapnowanego osadu ściekowego oraz jego mieszanki z ziemią spławiakową i popiołem z pieca na słomę. Wykazują, że duże dawki osadu zwiększają masę roślin, nie powodują przekroczenia zawartości miedzi i cynku w glebie, a poprawiają ich poziom w kukurydzy. Dodatek ziemi spławiakowej i popiołu jeszcze bardziej podwyższa wartość plono-

twórczą podłoży, choć obniża stężenie badanych pierwiastków w roślinach. Rolnicze wykorzystanie tych odpadów pozwala zwiększyć plony roślin i ograniczyć zużycie, nieobojętnych dla środowiska, nawozów mineralnych, stąd też jest najwłaściwszym sposobem pozbycia się tych odpadów.