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INFLUENCE OF ALKALIZING AND COMPOSTING OF SEWAGE SLUDGE ON COPPER AND ZINC CONTENT IN PLANTS AND SOIL

The three-year pot experiment was aimed to show the influence of such fertilizers as fresh and composted sewage sludge (from Siedlce and Łuków), manure, and their mixtures with calcium oxide and brown coal ash on copper and zinc contents in plants and soil. Copper and zinc concentrations were lower in plants fertilized with sewage sludge and manure mixed with CaO and ash than in plants treated with these substances with no additives. Content of heavy metals in maize and sunflower fertilized with sludge and manure mixtures with brown coal ash was higher as compared to their mixtures with calcium oxide. The composting of sewage sludge, manure, and their mixtures with CaO and ash reduced the copper content and increased the zinc content in both test plants. The content of these metals in the soil similarly increased after its fertilization with the same sewage sludge and its mixtures with calcium oxide and brown coal ash.

1. INTRODUCTION

The utilization of sewage sludge being abundant in organic matter and nutrients for agricultural production improves physicochemical properties of soils, but at the same time often leads to an increase in mineral and organic contaminants in soil [1]. In general, the content of heavy metals in sewage sludge does not exceed obligatory standards in an aspect of its agricultural utilization and is a principle criterion of its use for fertilizing. Excessive concentrations of chromium and zinc are most often observed, while these of cadmium and nickel occur rarely [2], [3]. This fact is most frequently associated with the origin of the sludge, whether it is produced in large cities or in smaller agglomerations in more industrialized areas with a specific type of pollution. Heavy metals are the subject of a special interest, because they can be accumulated both in soil and plants, and be a serious threat to the entire environment [4]. Determining the forms in which

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these elements occur is a reliable indicator of their release from the sludge. Only a small quantity of total heavy metals in sewage sludge occurs in the form of mobile fractions, but most often they are bounded to organic and aluminosilicate fractions. Zinc can be found mainly in the fractions associated with iron and manganese oxides, while copper is predominantly bounded to organic matter [5]. Due to a sludge stabilization using lime, the concentration of heavy metals in ion-exchangeable fraction can be increased along with an increase in the rate of organic matter mineralization, which leads to the formation of mobile fractions [6]. Brown coal ash added to sewage sludge decreases copper and zinc content in the forms that are easily available for plants, and at the same time it increases carbonate content [7].

The aim of this study was to evaluate the influence of CaO and brown coal ash addition to sewage sludge and the composting of these mixtures on copper and zinc contents in test plants and soil.

2. MATERIAL AND METHODS

Both sewage sludge from wastewater treatment plants in Siedlce and Łuków and manure as a standard fertilizer were mixed with CaO and brown coal ash in 2:1 proportion, adjusted to a dry matter basis. Thus prepared mixtures as well as sewage and manure without additives were composted for 3 months (from February till May) at ambient temperature. Then 1 kg of this compost was added to each pot containing 9 kg of soil, so that the manure percentage was 10% of total medium weight. At the same time sewage sludge from Siedlce and Łuków as well as manure were prepared once more by mixing them with CaO and brown coal ash in such a way as to obtain the ratio of the components of dry matter equal to 2:1. One kilogram of fresh mixtures, sewage sludge and manure without additives were introduced into the soil. Control objects were not fertilized with organic compounds. The plants grew on unfertilized soil and on the soil fertilized with CaO and brown coal ash in the amount corresponding to the mean weight introduced to fresh mixtures (105 $g \cdot pot^{-1}$). The pot experiment was carried out in a greenhouse in the years 2000–2002.

The soil used in the experiment, of granulometric composition at Ap level – dusty light loamy sand, showed acidic reaction (pH_{KCl} 4.0). The contents of carbon in organic compounds, total nitrogen [$g \cdot kg^{-1}$] as well as copper and zinc [$mg \cdot kg^{-1}$] were 10.3 and 0.98 as well as 4.69 and 34.7, respectively.

Organic materials were applied only once in the 1st year (10 days before seed sowing), the after-effects were examined in the 2nd and 3rd years. Due to the low content of potassium in sewage sludge and its mixtures as well as the possibility of phosphorus retarding in the pots with CaO, complementary phosphorus and potassium fertilization in the amounts of 0.44 g $P \cdot pot^{-1}$(granulated triple superphosphate – 20% P) and 1.25 g $K \cdot pot^{-1}$ (potassium sulphate – 49.8% K) was applied every year before seed sowing.

Maize ("Nimba") and root sunflower sown after maize harvest in the same pots were test plants in every year of experiment. Five seeds of maize or sunflower were sown in each pot, and after their germination only three of them were left in every pot. The overground parts of plants were harvested after 75 days of cultivation at the stage of flowering.

The contents of copper and zinc in sewage sludge, manure and their mixtures with CaO and ash as well as harvested plant material were determined by means of ICP-AES in a basic solution achieved after sample ashing at 450 °C.

The study results were subjected to statistical processing using variance analysis, in which the significance of the factors studied was confirmed by the Fisher–Snedecor distribution. The values of $LSD_{0.05}$ for a detailed comparison of the average data were calculated using Tukey's test.

3. RESULTS AND DISCUSSION

The contents of copper and zinc in fresh and composted sewage sludge from Siedlce and Łuków as well as in all mixtures (table 1) met the standards which allowed their use in agriculture [8]. The types of sewage sludge tested contained several times more copper and zinc than manure.

Table 1

Copper and zinc content in fresh and composted sewage sludge, farmyard manure (FYM) and their mixtures with CaO or brown coal ash (mg·kg^{-1} of D.M.)

Specification		Kind of additive mixed with sewage sludge and manure											
		Without additives				CaO				Ash			
		Cu		Zn		Cu		Zn		Cu (39.1)*		Zn (81.3)*	
		II[1]	V[2]	II[1]	V[2]	II[1]	V[2]	II[1]	V[2]	II[1]	V[2]	II[1]	V[2]
Sludge from Siedlce	fresh	108.7	111.2	730.7	1325.4	67,76	69.46	457.9	822.1	83.35	86.88	522.4	914.6
	composted	116.1	–	760.6	–	70.91	–	479.9	–	87.45	–	556.0	–
Sludge from Łuków	fresh	71.24	84.89	715.6	792.5	43.09	53.07	447.1	482.4	57.81	69.30	498.1	542.7
	composted	79.62	–	792.1	–	47.35	–	497.3	–	63.91	–	560.2	–
Farmyard manure	fresh	7.50	8.12	77.7	192.6	4.54	5.14	47.2	122.7	21.29	19.34	77.8	158.0
	composted	8.29	–	83.6	–	5.03	–	50.1	–	23.72	–	86.1	–

* The content of Cu and Zn in brown coal ash.

II[1] The content of Cu and Zn in fresh and composted sewage sludge, FYM and their mixtures with CaO and brown coal ash prepared in February.

V[2] The content of Cu and Zn in fresh sewage sludge, FYM and their mixtures with CaO and brown coal ash prepared in May.

Copper and zinc contents in maize and sunflower grown in the soil fertilized with sewage sludge and manure with no additives were most often significantly higher compared with plants grown on these organic materials mixed with CaO and brown coal ash (tables 2 and 3). The plants grown in the soil fertilized with sludge and manure mixtures with CaO accumulated most frequently considerably less copper and zinc as compared to those treated with ash mixtures. The results obtained confirm the thesis about a lack of a higher threat from heavy metals as an effect of adding ash from power plants to the sewage sludge. In view of the literature data, the quantitative and qualitative evaluation of heavy metals' contents indicates no significant effects of such sludge sanitation on the contamination of biomass by heavy metals, and the elements under investigation occur in sludge–ash mixtures mainly in forms that are scarcely available for plants [9]. No tendency to accumulate heavy metals in the plants fertilized with sewage sludge mixed with CaO should be attributed to the effect of soil deacidification and the decrease of their availability as a result of hardly available metal hydroxides formation [10].

Table 2

Copper content in test plants (mg·kg^{-1} of D.M.)

Fertilizers	1st year		2nd year		3rd year	
	Maize	Sunflower	Maize	Sunflower	Maize	Sunflower
Mean values for fertilizers with sewage sludge and farmyard manure mixed with different additives						
Without additives	11.29	18.46	8.61	16.19	8.28	17.27
With CaO additive	6.41	14.84	6.30	13.35	7.07	15.39
With ash additive	8.72	15.34	7.73	14.00	7.25	16.22
$LSD_{0.05}$	0.74	0.47	0.40	0.43	0.49	0.40
Mean values for organic fertilizers						
Without organic fertilizers	7.04	13.36	6.10	10.87	8.40	11.38
Fresh sewage sludge from Siedlce	11.45	20.25	9.01	17.38	8.85	18.42
Fresh sewage sludge from Łuków	8.83	17.92	7.59	16.19	7.21	15.97
Fresh farmyard manure	8.18	15.48	6.58	12.30	7.24	19.44
Composted sewage sludge from Siedlce	10.92	16.68	8.01	15.89	6.71	15.85
Composted sewage sludge from Łuków	7.27	16.04	8.18	16.13	6.28	18.61
Composted farmyard manure	7.96	13.76	7.38	12.83	8.03	14.38
$LSD_{0.05}$	1.43	0.91	0.78	0.84	0.95	0.77

Mean values of copper and zinc content (for three years of experiment) in the plants fertilized with the sludge and manure without additives were higher than these in the plants treated with these substances mixed with CaO and brown coal ash. Less copper and zinc (by 21.3% and 46.8%, respectively) were found in the plants harvested from the soil fertilized with sludge and manure mixtures with CaO than in the plants grown in these organic materials with no additives. The plants fertilized with

mixtures containing ash accumulated less copper and zinc by 13.7% and 28.0%, respectively, as compared to those harvested from the soil treated with the sludge and manure with no additives.

T a b l e 3

Zinc content in test plants (mg·kg^{-1} of D.M.)

Fertilizers	1st year		2nd year		3rd year	
	Maize	Sunflower	Maize	Sunflower	Maize	Sunflower
Mean values for fertilizers with sewage sludge and farmyard manure mixed with different additives						
Without additives	53.5	139.4	34.3	163.6	68.1	115.6
With CaO additive	38.7	54.0	26.1	62.7	49.5	77.6
With ash additive	48.0	77.6	37.3	100.5	66.0	90.6
$LSD_{0.05}$	3.3	16.8	1.6	23.8	n.i.	94.6
Mean values for organic fertilizers						
Without organic fertilization	28.8	56.0	27.5	55.2	25.7	79.2
Fresh sewage sludge from Siedlce	38.1	97.8	28.9	131.1	44.7	145.6
Fresh sewage sludge from Łuków	38.0	100.5	24.6	174.2	68.2	92.7
Fresh farmyard manure	53.4	65.4	35.6	100.2	57.5	84.9
Composted sewage sludge from Siedlce	53.3	164.0	41.3	120.5	36.4	95.7
Composted sewage sludge from Łuków	64.0	84.7	34.5	116.1	53.5	96.5
Composted farmyard manure	51.6	63.8	35.6	65.3	142.2	67.7
$LSD_{0.05}$	6.5	32.8	3.1	46.2	40.2	38.7

n.i. – differences between unimportant averages.

Most often, the content of copper in maize and sunflower fertilized with fresh sewage sludge from Siedlce and Łuków as well as with manure (mean for pots with no additives and after CaO and ash addition) was higher than that after using composts made of these organic and organic-mineral materials (tables 2 and 3). The concentration of zinc determined in the plants harvested from the soil fertilized with fresh sewage sludge, manure, and their mixtures with CaO and brown coal ash was most frequently lower in comparison to that found in the plants grown on the soil fertilized with composts made of these materials.

Copper and zinc contents in the plants fertilized with sewage sludge were by 14.5% and 18.1% higher (mean values for soil with no additives and with CaO and ash additives) than in the plants cultivated on manure.

Maize and sunflower fertilized with fresh and composted sewage sludge and manure as well as their mixtures with CaO and ash accumulated more copper and zinc by 28.0% and 69.4%, respectively, as compared with those grown in control soil.

Besides heavy metals accumulation by the plants fertilized with sewage sludge, the soil contamination with those elements is also interesting. Excessive concentration of heavy metals in the soil is observed in the case of low sludge doses with high contents of

heavy metals [11]. High doses of sewage sludge and its mixtures with CaO and brown coal ash were used in the present experiment, making 10% of the soil weight. The increase the copper concentration in the soil (see table 4) after applying either the sewage sludge only or its mixtures with CaO and brown coal ash, in relation to its content before the experiment, amounted to 29.6%, 27.2%, and 35.6%, respectively (mean values for the fresh and composted sludge from Siedlce and Łuków). The amount of zinc in the soil fertilized with sewage sludge was by 45.5% higher after the three years of experiment than before sludge application, whereas after using their mixtures with CaO and brown coal ash, its content increased by 41.4% and 40.7%, respectively.

Table 4

Copper and zinc content in soil after 3-year experiment (mg·kg^{-1} D.M.)

Fertilizers	Kind of additive					
	Without additives		CaO		Ash	
	Cu	Zn	Cu	Zn	Cu	Zn
Control object	4.43	33.3	4.63	33.3	4.95	34.7
Fresh sewage sludge from Siedlce	6.23	58.8	6.23	56.4	6.70	57.8
Fresh sewage sludge from Łuków	5.49	46.7	5.58	45.5	5.94	43.3
Fresh farmyard manure	4.13	34.8	4.31	35.7	4.73	38.9
Composted sewage sludge from Siedlce	6.95	47.7	6.36	46.0	6.80	48.8
Composted sewage sludge from Łuków	5.65	48.7	5.69	48.3	6.00	45.4
Composted farmyard manure	4.21	33.0	4.25	33.2	4.89	33.4

Reducing soil contamination by heavy metals due to sewage sludge application can be achieved by adding the substances with their lower concentrations [12]. Our own studies revealed that copper content in the soil fertilized with the sludge without additives was most often slightly lower, while that of zinc – slightly higher than after applying their mixtures with CaO and brown coal ash.

The influence of fertilization on the content of heavy metals in soil, besides their concentration changes, can be completed with its comparison with standards defining such extent of the soil contamination (e.g. with heavy metals) at which soil functions are not disturbed. The areas considered as arable lands (excluding the area under ponds and ditches) should contain (in kg of DM) in 0–30 cm soil layer not more than 150 mg of copper and 300 mg of zinc [13]. The contents of heavy metals in the soil fertilized with sludge, manure as well as their mixtures with CaO and brown coal ash proved to be much lower than the above mentioned concentrations after the 3-year experiment.

4. CONCLUSIONS

1. Calcium oxide and brown coal ash added to sewage sludge decreased copper and zinc content as a result of their “dissolving”. The sewage sludge mixtures with

ash contained higher concentration of both elements as compared to those with CaO additive. Composting only slightly increased the content of copper and zinc both in sewage sludge and in its mixtures with these composts.

2. Copper and zinc contents in maize and sunflower grown on sewage sludge and manure mixed with calcium oxide and brown coal ash additives were lower compared with those contents in plants grown on these organic materials with no additives. Concentrations of both heavy metals were found to be higher in the test plants fertilized with sludge–ash mixtures than in those treated with sewage sludge with CaO additive.

3. Composting the sewage sludge, manure, and their mixtures with CaO and ash most often decreased copper content, while increasing the zinc amount in the test plants.

4. The sewage sludge applied either with no additives or with the addition of CaO or brown coal ash similarly increased copper and zinc concentration in the soil.

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WPŁYW ALKALIZOWANIA I KOMPOSTOWANIA OSADÓW ŚCIEKOWYCH NA ZAWARTOŚĆ MIEDZI I CYNKU W ROŚLINACH I GLEBIE

W trzyletnim doświadczeniu wazonowym badano wpływ nawożenia świeżymi i kompostowanymi osadami ściekowymi (z Siedlec i Łukowa), obornikiem oraz ich mieszaninami z tlenkiem wapnia i popiołem z węgla brunatnego na zawartość miedzi i cynku w testowych roślinach i w glebie. W roślinach (kukurydza i słonecznik) nawożonych osadami ściekowymi i obornikiem z dodatkiem tlenku wapnia i popiołu z węgla brunatnego stwierdzono mniejsze stężenia miedzi i cynku niż w roślinach nawożonych tymi substancjami bez dodatków. Zawartość badanych metali ciężkich w kukurydzy i słoneczniku nawożonych mieszaninami osadów i obornika z popiołem była większa niż w roślinach rosnących w ich mieszaninach z tlenkiem wapnia. Proces kompostowania osadów ściekowych, obornika oraz ich mieszanin z tlenkiem wapnia i popiołem z węgla brunatnego najczęściej zmniejszał zawartość miedzi oraz zwiększał ilość cynku w roślinach testowych. Stężenia tych metali w glebie w podobnym stopniu zwiększyły się, gdy stosowano same osady ściekowe oraz ich mieszaniny z tlenkiem wapnia i popiołem z węgla brunatnego.