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CHANGES IN ZINC COMBINATIONS IN SEWAGE SLUDGE COMPOSTED WITH AND WITHOUT AN ADDITION OF LIME

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ABSTRACT

The share of zinc in fractions is not constant and changes under the influence of different factors. Taking it into consideration relevant studies were conducted. Their aim was to explain the influence of time factor and addition of calcium oxide into the sewage sludge on the quantitative changes of zinc in particular chemical fractions of sludge. The experiment was carried out in incubation conditions in time of six months.

It has been proved, among other things, that composting had an influence on changes in the amount of zinc in most fractions, not only in sludge itself but also in sludge with added calcium oxide. What is characteristic for the sludge is a 40% increase in zinc content in organic combinations (Fr. IV) in comparison to the quantity showed on the initial day of experiment, and a decrease in the element content in other fractions except fraction I.

On the other hand, in combination with calcium oxide after six months of composting appeared a decrease in the quantity of zinc, mostly in organic fractions (10%), and also a significant increase (by about 87%) in residual fraction (Fr. VII), in comparison to the initial day of experiment. What is worth pointing is a 4-5 fold increase in zinc content in fraction I under the influence of liming in comparison to the quantity noticed in the sludge itself.

Key words: zinc, sewage sludge, incubation, sequential extraction

INTRODUCTION

The agricultural use of sewage sludge at the present level of its production has become a necessity, especially that it is a good source of nutrients and organic matter [6]. However, the amounts of sludge utilized by agriculture in Poland in comparison to other countries remain low [3]. Reasons for such a situation stem from the quality of the sludge, which frequently fails to meet standards defined by the Polish legislation concerning the contents of heavy metals and sanitary conditions. These negative properties may be changed as a result of the employed process of composting of sewage sludge or its stabilization using calcium oxide. The addition of lime, apart from the sanitation of sludge, affects also the changes in the mobility and bioavailability of elements contained in the sludge, similarly to the effect of composting [8]. The amounts of elements released to the environment, as well as the rate of this process may determine agricultural usability of sewage sludge. The attention is focused on the quantitative changes between the combinations of readily and sparingly soluble metals, which occur as a result of long-term use of sewage sludge of various origin [7].

In the light of this fact, knowledge on the combinations in which they occur in sludge, with special consideration given to the type of these combinations, is gaining more significance than the determination of the total amounts of heavy metals.

In order to perform this task on the basis of the sequence chemical extraction method, the combinations of zinc were analyzed in sludge composted with and without an addition of calcium.

MATERIALS AND METHODS

Sewage sludge used in the study came from mechanical biological sewage treatment plants located in Gniezno (the Wielkopolska province). Sludge samples were taken from a heap from various places in the pile, using an auger. After 6 – 10 individual samples were taken from one heap, they were all mixed together and one average sample was compiled for an incubation experiment. The basic characteristics of sewage sludge are presented in table 1.

Table 1. Characteristics of sewage sludge used in experiment

PARAMETER	UNIT	CONTENT
pH		7.9
dry matter	$g \cdot kg^{-1}$	345.9
organic matter		505.0
Organic C		280.0
Total N	$g \cdot kg^{-1}$	22.0
C:N		12.7:1
P	$g \cdot kg^{-1}$	22.4
K		3.3
Ca		33.4
Mg		9.54
S		12.5

The experiment was conducted in the period of 6-month long incubation at room temperature and at the 50-60% moisture content of composted mass. Calcium oxide was added in the amount of 50 g to 1 kg of fresh mass of sewage sludge. After thorough mixing, the material was placed in plastic containers of the capacity of 1.5 kg. Each of the combinations was performed in two replications. Samples of the composted material were collected on the day the experiment was set up and after it was completed, i.e. after 6 months. The collected material was dried and ground to pass through a 0.5 mm stainless steel sieve, and then analysed for basic physico-chemical properties using standard procedures:

dry matter – the samples were heated up to 105°C overnight to dry,
pH – was measured with a glass electrode in 1 $mol \cdot L^{-1}$KCl (1:2.5 ratio),
organic matter (OM) – weighed samples were ignited in 550°C for 8 h, weight loss representing the loss of organic material, organic carbon – by wet dichromate oxidation with sulphuric acid,
Ca^{2+} and K^{+} - by flame atomic absorption following burned to ash at 450°C and then the residual was dissolved in 6 $mol \cdot L^{-1}$HCl,
S – by turbidimetric method with $BaCl_2$ according to Butters and Chenery [4],
Sequential chemical extraction of zinc was undertaken using a sequential extraction procedure described by Zeien and Brümmer [17].

Total content of zinc and its content in fractions obtained in the sequence analysis were determined using the method of atomic absorption spectrophotometry (AAS). Samples in which total content of zinc was to be determined were incinerated at the temperature of 450°C, dissolved in hydrofluoric acid and evaporated. The dry residue was transferred quantitatively with the 2 mol·L^{-1} solution of HNO_3. In case of all the fractions obtained in the sequence analysis the produced extracts were evaporated, then incinerated at the temperature of 450°C and next, the residue was dissolved in the 2 mol·L^{-1} solution of HNO_3.

On the day the experiment was set up, reaction of the sludge was pH=7.4, whereas that of the sludge + CaO was pH=12.1. After the incubation was completed, pH was 6.8 for the sludge itself and 10.3 for the mixture with lime.

RESULTS

The analysis of the total contents of zinc showed that the addition of lime applied to the sludge resulted in their decrease from 1024 to 995 mg · kg^{-1} (Table 2). On the other hand, the 6-month long period of incubation did not have the same effect. In case of sludge stabilized with calcium oxide no changes in total contents of this element were observed, whereas for the sludge itself there was a slight increase (by 7.8%) in the content of zinc.

Table 2. Content of zinc in chemical fractions of investigated materials (mg·kg^{-1})

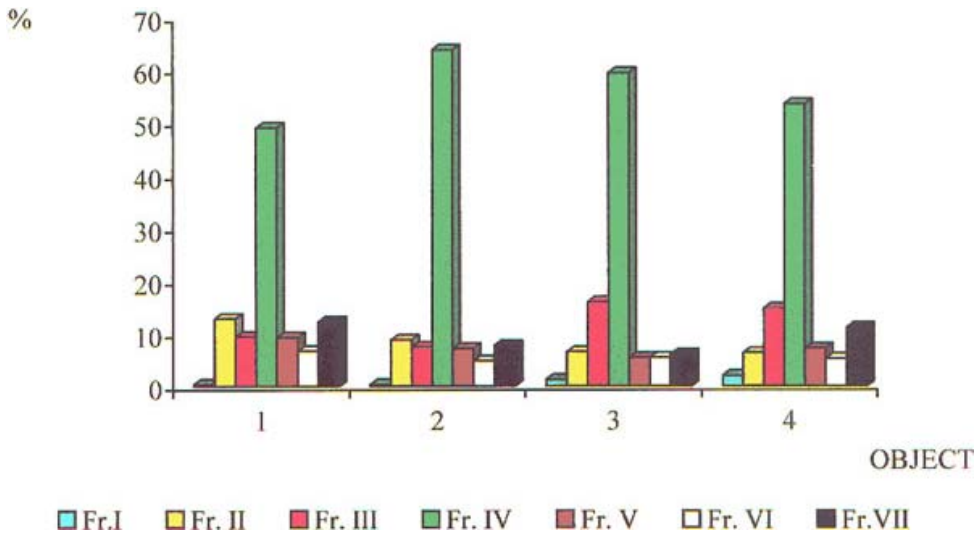
Experiment object	Fractions							Total content
	I**	II	III	IV	V	VI	VII	
1*	4.6	132.5	96.0	501.3	95.0	68.6	126.0	1024.0
2	4.5	97.6	82.1	704.0	78.0	53.4	84.4	1104.0
3	12.8	64.7	159.5	591.0	54.0	53.6	59.4	995.0
4	20.0	62.7	147.0	531.5	71.4	51.6	111.0	995.0

1* - sewage sludge (ss) in 1st day of experiment
2 - ss after 6 months of composting
3 - ss + CaO in 1st day of experiment
4- - ss + CaO after 6 months of composting
I** - mobile; II – easily available bonds III – bonds with Mn oxides; IV- organic bonds; V – bonds with amorphous Fe oxides; VI – bonds with crystalline Fe oxides; VII - residual

However, bigger changes were found in the investigated fractions. Irrespective of the applied addition and the duration of the composting process, the highest amount of zinc was observed in the combinations with manganese oxides (Fr. III) – from 82.1 to 147.0 mg · kg^{-1}, with organic matter (Fr. IV) from 501.3 to 704.0 mg · kg^{-1} and the insoluble combinations defined by the residual fraction (Fr. VII) – from 59.4 to 126.0 mg · kg^{-1} (Table 2).

A confirmation of the above distribution of zinc in fractions is its percentage in the total content. A very high percentage of the metal in the organic fraction, ranging from 49 to 63.8%, needs to be emphasized here (Fig. 1). At the same time, the lowest values (0.4 – 2.0%) in case of fraction I, representing combinations soluble in water and readily soluble metal – organic complexes of zinc, should be mentioned here.

Fig. 1. Percentage share of zinc in chemical fraction of investigated materials (descriptions of figure see at table 2)



The factors of the experiment including the 6-month period of composting, as well as the addition of CaO, affected the dynamics of changes in the analyzed fractions of the investigated materials. It manifested itself most clearly in case of fraction I, where the addition of CaO to sludge after 6 months of incubation (object 4) resulted in the increase in the amount of Zn almost 4.5 times in comparison to the sludge composted with no additive (object 2) (Table 2). These observations were not confirmed by the analysis of the amounts of zinc in the combinations easily available for plants expressed in the total of the content of this element in fractions I and II. On the basis of the total mentioned above, a decrease in the amount of this element was found from 102.1 (object 2) to 82.7 mg · kg^{-1} (object 4) (Table 2). It was properly expressed by the total percentage of zinc in fractions I and II, taking the value of 9.2% for sludge (object 2) and 8.3% for the combination with lime (object 4).

The increasing tendency of the content of this metal under the influence of liming and composting was also evident in the combinations with manganese oxides (Fr. III) with the change from 82.1 to 147.0 mg · kg^{-1}, i.e. by 77.8%, and for the residual fraction (Fr. VII) - from 84.4 to 111.0, i.e. by 31.7%, respectively.

In case of the other fractions, the direction of changes occurring under the influence of the addition and the 6-month long incubation was the opposite and manifested itself most profoundly in fractions II and IV, which was expressed in the decrease by 1.5 times in the amount of the element in relation to that found in sludge alone.

The analysis of the effect of the duration of composting on the distribution of zinc in the fractions of the investigated materials indicates that in sludge alone there was generally a decrease in the amount of the metal after the 6-month long period of incubation. An exception to the rule was the fraction of organic combinations, for which a 40% increase was observed in the content of zinc in comparison to the amount found on the day the experiment was set up. Such a definite direction of changes in the fractions, as in case of sludge composted with no additive, was not observed for the combination with CaO after 6 months of composting. The significant increase should be noted in the amount of the metal - by 87% in fraction VII, by 56.3% in fraction I and by 32.5% in fraction V in comparison to the content observed on the 1st day of incubation. In the other fractions of the investigated mixture of sludge with lime a decrease in the content of zinc was found on the day the experiment was completed.

DISCUSSION

Sewage sludge as an unconventional organic fertilizer enriches the soil environment not only in organic matter, but also in elements, among which there are both nutrients and heavy metals toxic for the natural environment. The decision to use sludge in agriculture is taken on the basis of the total amounts of the latter, which in practice does not reflect the availability of elements for plants or determine the nature of combinations in which they occur [9]. Special attention is paid to these compounds which are readily soluble, becoming mobile in the soil environment.

The stabilization of sludge with the use of calcium oxide may facilitate the reduction of excessive mobility and in this way – also the availability of metals for plants [15]. The authors cited above observed that under the influence of lime added to sludge there was not only a drop by 400% in the total amounts of Zn, but also the formation of $Zn(OH)_2$, a compound slightly soluble in water. Data obtained as a result of investigations conducted by the authors of this study also indicates a decrease in the total amounts of Zn as a result of the added Ca, although the order of magnitude of this drop was much lower and reached 11% in the composted objects and 3% in non-composted objects, respectively.

From the point of view of agriculture and ecology it is of more importance to analyze the combinations of an element, which are easily available for plants, in this study reflected in the total zinc contents in fractions I and II. The results show that this amount was considerably reduced due to the application of lime to sludge, which confirms the data reported by the authors mentioned above only indirectly. The content of zinc in the water soluble combinations and readily soluble metal-organic complexes described by fraction I rose significantly under the influence of the stabilization of CaO, irrespective of the duration of incubation. This phenomenon is a consequence of the increased pH value in the composted material, which promoted increased solubility of organic matter, primarily low molecular weight compounds, forming organic-metal complexes affecting bigger solubility of metals [1,13]. Shuman [16] reported an increase in the amounts of Zn in the solution. While interpreting the obtained results that author referred also to the effect of the increased dispersion of organic matter at pH above 7, which either complexed the metal or supplied chelating agents.

Irrespective of the relationships presented above, the fact of the stable fixation of zinc by organic matter was presented in the studies conducted by this author, as well as data found in literature [10, 11, 14]. Shuman [16] emphasized the action of the reaction within the pH range 5-7 on the strong adsorption of zinc by humic acids in the fraction of organic matter in the municipal and industrial sewage sludge. This finding is reflected in the results presented in this study, reporting higher amounts of zinc bounded with the organic fraction of the sludge composted for the period of 6 months with no addition of calcium oxide, which had the pH value of 6.8.

Duration of the incubation process is of significance for the changes of elements as indicated by Han et al. [8], who in soil conditions at high pH found an increase in the amounts of Zn in the combinations with organic matter. Moreover, they observed that at pH > 6 the sorption of zinc on manganese oxides increases significantly. Model studies conducted earlier by

Brümmer et al. [5], in which manganese oxides were found to be compounds strongly absorbing zinc, confirmed this phenomenon. High bonding of zinc by manganese oxides, especially at high reaction, was also confirmed in this study.

On the basis of the conducted sequence analysis of chemical extraction of zinc, significant amounts of this element were found in slightly soluble compounds. Moreover, the data in literature concerning the fractionation of heavy metals in the soil [2, 12] and in sludge [10, 14] also indicates a high accumulation of this element, primarily in the residual fraction.

Commonly applied procedures of composting and liming of sewage sludge are not only to produce a stable material with some value as a fertilizer, but also to improve the physical and sanitary properties of sludge. As indicated by the results obtained by this author and by data reported in literature, it is also of considerable importance that the above mentioned processes affect changes in the chemical properties of sludge, primarily in terms of changes in the solubility of heavy metals found in sludge.

Undoubtedly, the increase in the amounts of this element in slightly soluble combinations, as a result of composting and liming of sludge, is beneficial from the environmental point of view. On the other hand, the interaction of these two factors facilitated also an increase in the content of zinc in readily soluble compounds. Taking into consideration the fact that zinc is a microelement indispensable for plants, the release of its bigger amounts to the soil solution may have an advantageous effect, especially in case of soils deficient in this element and for plants with high zinc requirements. However, in view of the long-term application of sewage sludge the possible negative consequences need to be considered, of the effect on the soil environment, expressed in the high concentrations of the element in the soil environment and its leaching and excessive accumulation in the lower layers of soil [13].

CONCLUSIONS

1. Irrespective of the experimental factors, the highest percentage of zinc was found in organic combinations, with manganese oxides and slightly soluble compounds.
2. Composting of sludge with the addition of calcium oxide resulted in an increase in the amounts of zinc in the water-soluble combinations (Fr. I), combinations with manganese oxides (Fr. III) and in the residual fraction (Fr. VII).
3. Under the influence of the 6-month period of incubation the amounts of zinc generally decreased, primarily in the fraction of sludge.

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