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ZINC SPECIATION IN SOIL UNDER VARIOUS RATES OF SEWAGE SLUDGE AND LIMING

The influence of sewage sludge doses and liming on the speciation of zinc in the soil has been investigated. For the highest dose of sludge, 15 wt. %, more than twofold increase in zinc content compared with the control has been observed. Based on sequential analysis of zinc content in sewage sludge, it was found that its concentration in the easily soluble and exchangeable fractions was low while it was the highest in the organic fraction. The concentration of zinc in selected soil fractions was dependent on the sludge dose and liming. In the first year of the experiment, zinc was mainly bound to organic matter and residual, while in the second year – to organic matter. In limed soil, much more zinc was bound to the residual fraction compared with the soil without liming.

1. INTRODUCTION

Agricultural utilisation of sludge and its use in soil rehabilitation are highly feasible economically due to the possibility of taking advantage of substantial amounts of organic matter and biogenic components present in this kind of waste [1, 2]. Agricultural usage of sludge is strictly limited due to overrepresentation of toxic substances, i.e. heavy metals and sanitary contamination [3]. In soil, particularly acidic, heavy metals undergo processes changing their concentrations and chemical formulas. pH of soil is the decisive factor influencing the strength of bonds of heavy metals to an organic substance. Liming changes soil chemical and physical properties, maintaining a favourable structure and the optimal air-to-water ratio as well as reducing the content and uptake of heavy metals in plants. Zinc is thought to be the most mobile element in soil and its desorption decreases upon increasing pH. Its mobility depends on the redox potential, organic matter content, granulometric composition, and calcium and magnesium saturation of the soil adsorption complex [4]. Aluminum, iron and clay minerals bind zinc

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but in the process of weathering all zinc compounds are soluble, in particular in an acid environment, and the ions released form mineral and organic-mineral bonds of high mobility [5, 6].

The overall content of metals is not always a good indicator of their bio-assimilability [7, 8]. The speciation analysis allows specifying mobility of elements or possibility of their passing to the soil solution, and thus to the biogeochemical circulation. The widely used methods of sequential extraction of elements, including heavy metals, from soil is based on isolating or extracting a metal bound to other soil components by adding various extractant solutions. These methods make it possible to determine the concentration of heavy metals in soil and, at the same time, to assess their availability and toxicity to components of biotic factors at trophic levels [9]. Sequential extraction is more sensitive than single extraction because the order of sequences can be used to trace metal demobilization as an effect of the change in environmental conditions [10]. This technique is more and more commonly used and recommended for testing soils contaminated with heavy metals and for testing waste containing elevated content of these elements [11–13].

The aim of the study, done as an incubation experiment, was to evaluate the impact of applying various doses of sewage sludge and liming on the zinc speciation in soil.

2. MATERIALS AND METHODS

The incubation experiment was conducted over the period of two years in laboratory conditions and replicated three times. Containers were filled with 3 kg of soil (topsoil level) of the pH = 4.29, and with the granulometric content resembling loamy sand, according to the Polish Society of Soil Science [14]. The overall concentration of heavy metals in soil before the experiment was lower than that recommended in the Regulation of the Minister of the Environment concerning the use of municipal sludge on light soil [15], being equal to ($\text{mg}\cdot\text{kg}^{-1}$): Pb – 6.0, Cd – 0.12, Cr – 2.1, Cu – 2.2, Zn – 19.9, Ni – 1.6.

The soil, before filling the containers, was sieved through a sieve of a one-centimetre mesh and divided into two parts, with one part limed with CaCO_3 , equivalent to hydrolytic acidity $\text{Hh} = 1$, and left for a period of one month to bring it to the humidity of 50–60%, the maximum water capacity. Then 5, 10 and 15 wt. % of fresh sludge originating from the municipal mechanical-biological sewage sludge plant in Siedlce was added, and the components were thoroughly mixed. The heavy metal content in the sewage sludge was ($\text{mg}\cdot\text{kg}^{-1}$): Pb – 50.2, Cd – 0.17, Cr – 19.9, Cu – 85.0, Zn – 1120, Ni – 50.1. Nitrogen concentration was $40\text{ g}\cdot\text{kg}^{-1}$, with the dry matter content of 25%. Heavy metals concentration in the sludge tested did not exceed limits recommended in the Regulation of the Minister of the Environment on agricultural utilization of sewage sludge [16]. Two controls were established in the experiment: one without the sludge and without CaCO_3 , and the other without the sludge but with the addition of CaCO_3 .

During the experiment, the soil humidity was kept at 50–60% of the maximum water capacity and temperature at 20–22 °C. Soil samples were collected four times in 30-day intervals (first year of the experiment). In the second year, the soil was sampled twice in 60-day intervals. In all soil samples, total zinc concentration was established after dry mineralisation at 450 °C by the atomic absorption spectroscopy method. Carbon concentration in organic compounds was determined by the oxidation-titration method and the zinc fractions by the 7-degree Zeien and Brümmer method [9] (Table 1).

Table 1

Sequential extraction of heavy metals by the Zeien and Brümmer method [9]^a

Fraction	Feature	Extraction reagent	Extraction time [h]	pH
F1	easily soluble	1 M NH ₄ NO ₃	24	natural
F2	exchangeable	1 M CH ₃ COONH ₄	24	6.0
F3	bound to MnO _x	1 M NH ₂ OH·HCl + 1 M CH ₃ COONH ₄	0.5	6.0
F4	F _{org} bound to organic matter	0.025 M C ₁₀ H ₂₂ N ₄ O ₈	1.5	4.6
F5	bound to amorphous FeO _x	0.2 M (NH ₄) ₂ C ₂ O ₄ + 0.2 M H ₂ C ₂ O ₄ · dm ⁻³	4	3.25
F6	bound to crystalline FeO _x	0.2 M (NH ₄) ₂ C ₂ O ₄ + 0.2 M H ₂ C ₂ O ₄ + 0.1 M C ₆ H ₈ O ₆	0.5	3.25
F7	F _{resid} residual	calculated as the difference between the total content of zinc and the sum of the above determined fractions		–

^aProportion of soil to solution: 1 g/10 cm³.

The zinc and carbon concentrations were processed statistically to analyse means with the analysis of variance (using the Statistica software, Version 10.0 StatSoft). Tukey's test was used to calculate the LSD_{0.05} value. The straight correlation coefficients between carbon content and zinc fractions in the soil were calculated.

3. RESULTS AND DISCUSSION

In the two-year incubation experiment, substantial differences were found in the concentration of zinc in the sludge fertilised soil (Table 2). Over the course of the entire experiment, with the highest dose of sludge in the soil (15 wt. %), the concentration of the tested metal at all dates was more than twofold higher than in the control. In all measurement periods, the concentration of zinc was much lower than the maximum concentration allowed for agricultural land [16] which in the top part of light soil should not exceed 150 mg·kg⁻¹ of soil dry matter [16]

Table 2

Total content of zinc [$\text{mg}\cdot\text{kg}^{-1}$] in soil in the incubation experiment

Days	Control object	5%	10%	15%	Mean	Control object	5%	10%	15%	Mean
	Without liming					After liming				
	First year of experiment									
30	19.8	41.9	45.2	58.0	41.2	23.1	45.6	42.7	57.6	42.2
60	21.7	37.2	45.6	63.8	42.1	20.8	39.9	46.9	57.5	41.3
90	19.9	32.1	70.8	63.7	46.6	22.7	56.0	47.3	51.2	44.3
120	32.7	38.5	55.9	66.4	48.4	22.3	43.7	53.2	62.6	45.4
mean	21.5	37.4	54.4	60.5	43.9	21.3	46.3	47.5	57.2	43.3
LSD _{0.05} for: $A = 2.38$, $B = \text{n.s.}$, $C = 2.38$, $A/B = 3.36$, $B/A = 2.55$, $A/C = 3.36$, $C/A = 3.36$, $B/C = \text{n.s.}$, $C/B = \text{n.s.}$										
Second year of experiment										
60	16.7	34.7	40.4	63.5	38.8	16.5	32.1	41.1	49.0	34.7
120	15.4	30.7	48.2	55.8	37.5	21.5	30.9	44.2	50.5	36.8
mean	16.0	32.7	44.4	59.6	38.2	18.9	31.5	42.6	49.8	35.7
LSD _{0.05} for: $A = 1.14$, $B = 0.61$, $C = \text{n.s.}$ $A/B = 1.61$, $B/A = 1.21$, $A/C = 1.61$, $C/A = 1.21$, $B/C = 0.86$, $C/B = 0.86$. n.s. – not significant, 5 wt. % , 10 wt. % , 15 wt. % of sewage sludge to dry mass of soil. A – fertilization, B – liming, C – days, A/B , B/A , A/C , C/A , B/C , C/B – interaction.										

Table 3

The content of carbon [$\text{g}\cdot\text{kg}^{-1}$] in soil in the incubation experiment

Days	Control object	5%	10%	15%	Mean	Control object	5%	10%	15%	Mean
	Without liming					After liming				
	First year of experiment									
30	10.1	10.9	12.4	13.8	11.8	10.3	11.0	13.1	14.0	12.1
60	10.0	11.2	12.9	13.9	12.0	10.2	12.2	13.5	15.0	12.7
90	10.0	12.8	13.9	14.8	12.9	10.5	12.6	14.1	15.1	13.1
120	10.9	12.6	14.3	14.5	13.1	10.6	13.5	13.6	14.5	13.1
mean	10.3	11.9	13.4	14.3	12.4	10.4	12.3	13.6	14.7	12.7
LSD _{0.05} for: $A = 0.49$, $B = 0.27$, $C = 0.49$. A/B – n.s., B/A – n.s., $A/C = 0.70$, $C/A = 0.70$, B/C , C/B – n.s.										
Second year of experiment										
60	10.5	12.3	13.8	15.0	12.9	10.6	12.8	14.0	15.2	13.1
120	10.8	12.4	13.9	14.8	13.0	10.8	12.7	14.1	15.0	13.2
mean	10.7	12.4	13.9	14.9	12.9	10.7	12.8	14.1	15.1	13.2
LSD _{0.05} for: $A = 1.02$, $B = \text{n.s.}$, $C = \text{n.s.}$ A/B , B/A , A/C , C/A , B/C , C/B – n.s. n.s. – not significant, 5 wt. % , 10 wt. % , 15 wt. % of sewage sludge to dry mass of soil. A – fertilization, B – liming, C – days, A/B , B/A , A/C , C/A , B/C , C/B – interaction.										

In the first year of the experiment, the liming of the soil did not have any substantial impact on the total zinc concentration. In the second year, substantial differences were found in the Zn content in the limed soil with doses of sludge added.

During the experiment, the application of sewage sludge caused an increase in carbon concentration in soil organic compounds compared to the control object (Table 3).

A key role of sludge in restoring the stock of organic matter in soils is confirmed by the research of Maćkowiak [17]. The doses of sludge and liming made a substantial difference in the content of organic carbon. In the second year of the experiment, an increased concentration of organic carbon was reported after the application of higher doses of sludge, on average $14.9 \text{ g} \cdot \text{kg}^{-1}$ in non-limed soil and $15.1 \text{ g} \cdot \text{kg}^{-1}$ in limed soil. In the soil of the controls, carbon content was slightly over $10 \text{ g} \cdot \text{kg}^{-1}$.

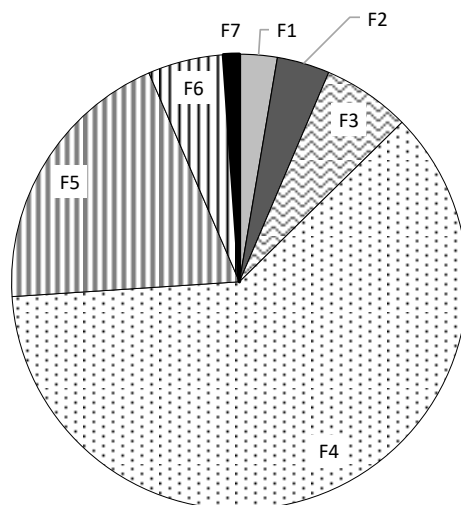


Fig. 1. Percentage share of zinc fractions in its total content in sewage sludge:

F1 – easily soluble, F2 – exchangeable, F3 – bound to MnO_x ,
 F4 – bound to organic matter, F5 – bound to amorphous FeO_x ,
 F6 – bound to crystalline FeO_x , F7 – residual

Sequential analysis of zinc in the sludge, determined by the Zeien and Brümmner method [9] showed the highest content of Zn (61.3%) in the organic fraction F4 (Fig. 1). The dominance of this fraction is typical of most kinds of sludge [18]. On the other hand, zinc in the tested sludge was found to be only slightly bio-accessible. The total of F1 and F2 fractions amounted to 6.41%. The similarly low amount of absorbable zinc in plants growing on soil with sludge was reported by Shrivastava and Banerjee [19]. Zinc bound to MnO_x (F3) made up 6.23%, bound to amorphous FeO_x (F5) 19.53 %, bound to crystalline FeO_x (F6) 5.38%. The lowest content of Zn was reported in the residual fraction (F_{resid} residual – F7), slightly over 1%.

Sequential analysis of zinc concentration in soil proved a great differentiation in its content depending on the dose of the sludge and liming (Figs. 2–7). The difference in the mobility of zinc in soil fertilised with sludge is confirmed by the research of Hlavay et al. [20] and Patorczyk-Pytlik [21].

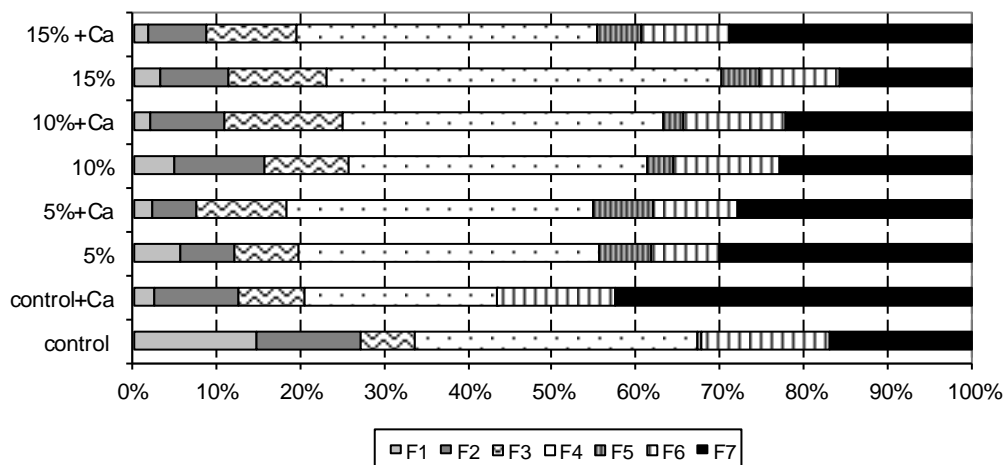


Fig. 2. Percentage share of zinc fractions in its total content in the soil after 30 days

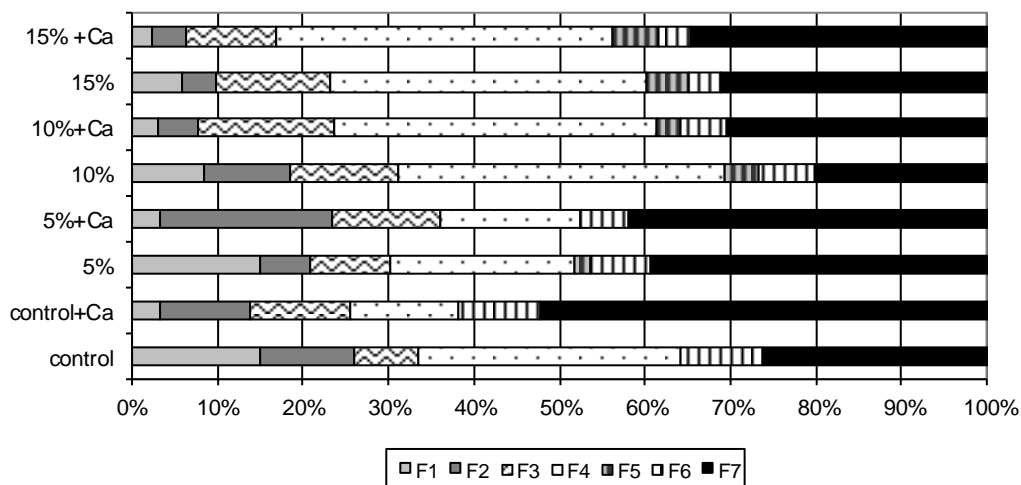


Fig. 3. Percentage share of zinc fractions in its total content in the soil after 60 days

The greatest share of mobile zinc forms was observed in non-limed soil in the control. The total content of easily soluble (F1) and exchangeable (F2) fractions is normally over 20%, while in the control with CaCO_3 , the total content of these fractions does not

exceed 15%, except for the second year of the experiment. Compared to other doses, the lowest dose of sludge (5 wt. %) caused the highest mobility of zinc in the soil. The percentage share of zinc in the soluble fraction was more than twofold higher in the non-limed soil and constituted more than 10% of its total content in the soil, except for the first test period.

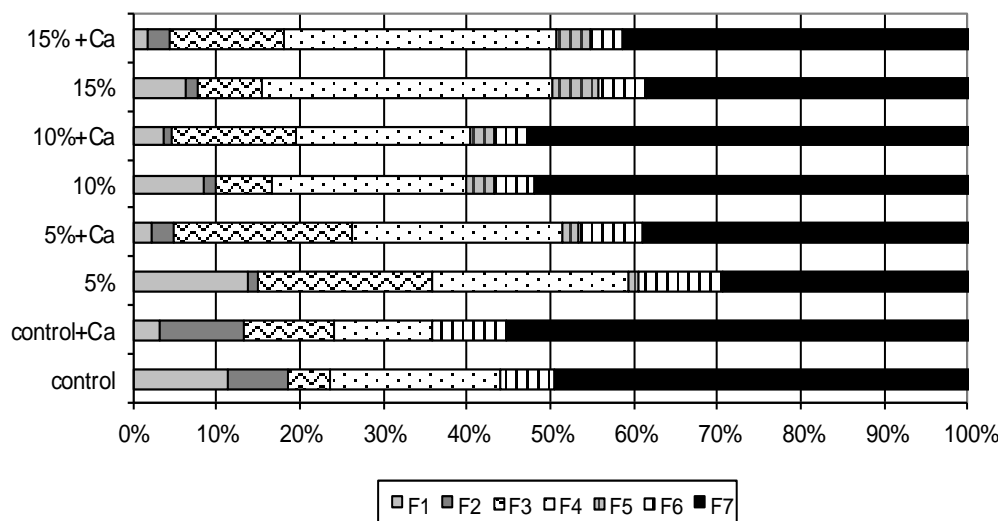


Fig. 4. Percentage share of zinc fractions in total content in the soil after 90 days

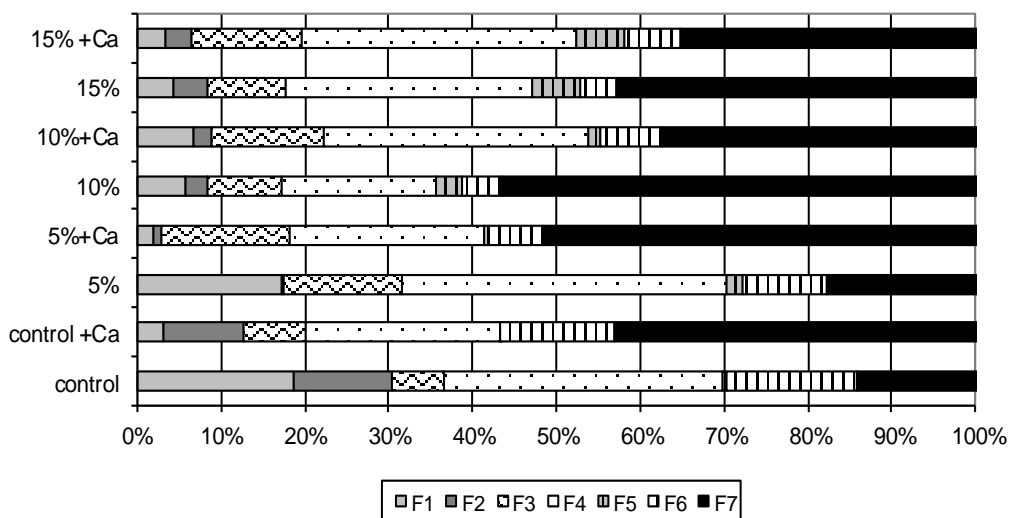


Fig. 5. Percentage share of zinc fractions in total content in the soil after 120 days

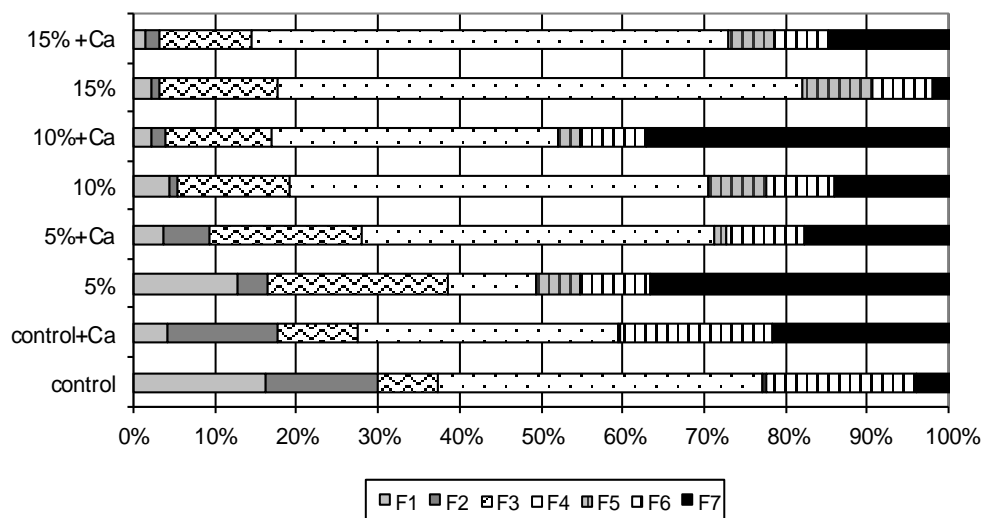


Fig. 6. Percentage share of zinc fractions in total content in the soil after 60 days in the second year

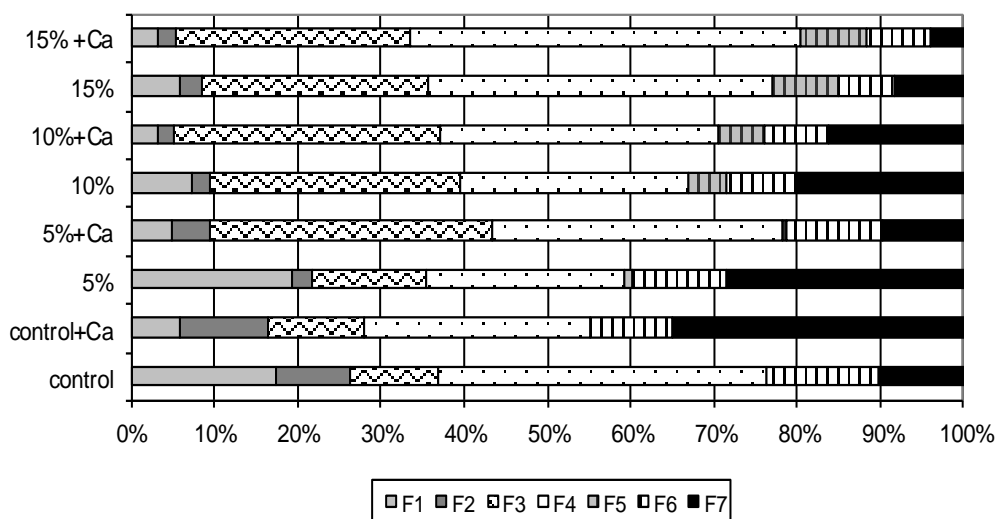


Fig. 7. Percentage share of zinc fractions in total content in the soil after 120 days in the second year

Much higher amounts of absorbable zinc in soil fertilised with compost from sludge have been reported by Patorczyk-Pytlik [21]. In the soil with the addition of sludge, a greater share of zinc bound to MnO_x (F3) was recorded as compared to the soil in the control. The amount of this fraction increased in proportion to the progressive mineralization of sludge and in the second year of the experiment ranged from 10 to 35%. The greatest share of the total zinc pool in soil was the metal-organic (F_{org} bound to organic

matter – F4) and residual fractions (F_{resid} residual – F7), mainly in the first year. The mineralization of sludge triggered the occurrence of this element in the soil due to significant reduction in the amount of zinc in the post-extraction residues (F7). After the application of sludge, the share of zinc in the residual fraction was even above 50% in non-limed soil. In the second year of the experiment (Fig. 7) in non-limed soil the content of zinc in this fraction was up to 28%, while in limed objects it was up to 35% of its total content in the soil. The dominating role of extremely durable organic and mineral compounds of zinc in soil was established by Kalembasa and Pakuła [22, 23]. Zinc was also present in large amounts in compounds with iron oxides, particularly crystalline ones, with the total of F5 and F6 slightly over 10%. McBride [24] reports that zinc is strongly bound with iron and manganese oxides.

The control systems of environmental pollution should primarily include the first link in the food chain, namely the soil. Usually, such assessment is only carried out basing on the total or close-to-total content of heavy metals in the soil. It is an imprecise assessment due to a significant variability of soil factors, which may substantially impact the bio-absorption of heavy metals. The recognition of mobility, i.e. the possibility of the elements to transfer into the soil solution and thus to the biogeochemical circulation, is necessary for the assessment of the condition of the environment [25].

Table 4

Simple correlation coefficients between carbon content and zinc fractions in the soil in the two-year experiment

Fraction	First year		Second year	
	Without liming	After liming	Without liming	After liming
F1	0.084	0.595*	-0.240	0.235
F2	-0.085	-0.155	-0.598	-0.909*
F3	0.749*	0.794*	0.778*	0.633
F4	0.755*	0.817*	0.850*	0.927*
F5	0.784*	0.628*	0.889*	0.860*
F6	0.135	0.109	0.833*	0.746*
F7	0.698*	0.585*	0.527	0.173

$p < 0.05$, critical value $r = 0.482$ for the first year, $r = 0.666$ for the second year.

Based on the statistical analysis in non-limed soil, in the first and second years of the experiment, a significant positive relation was established between the content of carbon in organic compounds and the content of zinc in the fraction bound to MnO_x (F3). A similar relation was between carbon concentration and the organic fraction (F_{org} bound to organic matter – F4) or zinc normally bound to amorphous FeO_x (F5). There was also a positive correlation between carbon content and the concentration of zinc in residues (F_{resid} residual – F7) in the first year of the experiment (Table 4). The content of organic carbon in limed soil was significantly positively correlated with the

content of Zn in fractions F1, F3, F4, F5 and F7. In the second year, in limed soil, a negative relation was found between the contents of the carbon and the appearance of zinc in the exchangeable fraction (F2), along with a positive correlation between fractions F4, F5 and F6.

4. CONCLUSIONS

In the incubation experiment testing, the effect of sewage sludge doses and soil liming substantial differences were established in the contents of zinc in the soil with sewage sludge applied. The highest dose of the sludge (15 wt. %) caused more than twofold increase in zinc, compared with the control.

- In the soil samples taken every 30 days in the first year and every 60 days in the second year of the experiment, a significant relation between doses of sewage sludge and a content of carbon in organic compounds was found. The highest carbon content was found in the second year of the experiment in limed soil with the highest dose of sludge. Sequential analysis of zinc in municipal sludge showed a low content of Zn in bio-accessible compounds, with the highest in the organic fraction.

- In isolated fractions of the soil from individual objects, the percentage share of zinc in its overall content was dependent on the dose of sludge and liming. In the first year what dominated was zinc F_{org} bound to organic matter and F_{resid} residual, and in the second year zinc F_{org} bound to organic matter. In limed soil, much more zinc was bound to the residual fraction compared to the soil without liming.

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