CHANGES IN THE AVAILABLE MAGNESIUM AND ZINC CONTENTS OF SOILS AFTER THE APPLICATION OF SEWAGE SLUDGES AND SEWAGE SLUDGE – PEAT MIXTURES

ZMIANY ZAWARTOŚCI DOSTĘPNEGO DLA ROŚLIN MAGNEZU I CYNKU W GLEBACH PO ZASTOSOWANIU OSADÓW ŚCIEKOWYCH I MIESZANIN OSADÓW ŚCIEKOWYCH Z TORFEM

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ABSTRACT

The main subject of our work was to evaluate the effects of applied organic fertilizers: farmyard manure, sewage sludges of various origin and the sludge-peat mixture on changes in the available magnesium and zinc content of two soils with different texture tested in an incubation experiment. Results of our experiment revealed that the contents of magnesium depended on the source and rate of fertilization whereas intensity of changes related with this element transformations was depending on the soil deposit. Zinc content was more dependent on soil properties than on the amounts of fertilization applied.

Key words: sewage sludge, peat, fertilization, zinc, magnesium

STRESZCZENIE

Celem badań było określenie wpływu zastosowanego nawożenia (obornik, osad ściekowy o zróżnicowanym pochodzeniu, oraz mieszaniny osadu ściekowego z torfem) na zmiany zawartości magnezu i cynku w dwóch typach gleb o różnym składzie granulometrycznym w doświadczeniu inkubacyjnym. Badania wykazały że zawartość magnezu zależała od zastosowanego nawożenia natomiast intensywność przemian była związana ze składem granulometrycznym gleb. Zawartość cynku była bardziej zależna od rodzaju gleby niż od zastosowanego nawożenia.

Słowa kluczowe: osad ściekowy, torf, nawożenie, cynk, magnez

DETAILED ABSTRACT

W pracy badano wpływ nawożenia osadami ściekowymi oraz mieszaninami osadów ściekowych i torfu na zawartość dostępnego dla roślin magnezu i cynku w glebach o różnym składzie granulometrycznym. Ocenę wpływu nawożenia osadami ściekowymi oraz mieszaninami osadów ściekowych z torfem na zawartość dostępnego dla roślin magnezu i cynku w glebach przeprowadzono w dwuczynnikowym doświadczeniu inkubacyjnym. Schemat doświadczenia obejmował następujące obiekty prowadzone w trzech powtórzeniach na dwóch glebach: bez nawożenia - (0); nawożenie czystymi chemicznie solami – (NPK); obornik – (FYM); osad ściekowy A (SSA); mieszanina osadu ściekowego A i torfu (SSAP); osad ściekowy B (SSB) oraz mieszanina osadu ściekowego B i torfu (SSBP). Do badań użyto następujący materiał glebowy: piasek słabo gliniasty (wls) oraz glinę średnią pylastą (msc), które zostały pobrane z warstwy ornej (0-20 cm) pól uprawnych okolic Krakowa. Osady ściekowe pochodziły z dwóch różnych komunalnych oczyszczalni mechaniczno-biologicznych, a ich mieszaniny z torfem sporządzono, w stosunku wagowym 1:1 w przeliczeniu na suchą masę materiałów. Glebę po zmieszaniu z materiałami organicznymi przeniesiono do pojemników PCV i umieszczono w inkubatorze. Okresowe analizy w materiale inkubowanym przeprowadzono po 3, 8, 16, 32 i 64 dniach od rozpoczęcia eksperymentu. Zastosowane nawożenie spowodowało istotne zróżnicowanie odczynu użytych w doświadczeniu gleb w obrębie poszczególnych terminów. Zawartość form dostępnych magnezu zależała od użytego nawozu, natomiast intensywność zmian związanych z przekształceniami tego pierwiastka od utworu glebowego. Zawartość cynku zależała bardziej od rodzaju gleby niż od zastosowanego nawożenia. Największe ilości tego pierwiastka oznaczono w obiektach nawożonych osadem ściekowym (SSB) oraz obiektach nawożonych mineralnie (NPK). Dodatek torfu do osadu ściekowego powodował zmniejszenie koncentracji cynku w glebie, jednak istotną zmianę odnotowano jedynie w przypadku osadu ściekowego (SSBB) w piasku słabo gliniastym.

INTRODUCTION

Macro- and microelements as well as organic matter contents in sludges may be instrumental in the improvement of physical, chemical and biological soil properties thus increasing its fertility, which undoubtedly determines the quality of obtained biomass [5,8,9,13,26]. Determining chemical composition of sewage sludges allows to assess usefulness of these substances for agriculture. However, the criteria does not comprise bioavailability of components in sewage sludge after it supplement to the soil. Determining the mobilisation rate of components from sewage sludges in soils is very important for agricultural practice since it allows to assess the rate of element passing into the soil solution and in result makes possible predicting their uptake by plants.

Application of sewage sludges leads to changes of physical, chemical and biological soil properties in time, which affects bioavailability of macro- and microelements in soil to a various degree (depending on soil texture). Our research aimed to assess the effect of fertilization with sewage sludges and sewage sludge-peat mixtures on the content of plant available magnesium and zinc in soils with different texture

MATERIAL AND METHODS

Assessment of the effect of fertilization with sewage sludges and sewage sludge-peat mixtures on the plant available magnesium and zinc content was conducted in a two-factor incubation experiment. The following treatments were applied in three replicates on two soils: unfertilized control – (0); fertilized with chemically pure salts – (NPK); farmyard manure –(FYM); sewage sludge A (SSA); mixture of sewage sludge A with peat (SSAP); sewage sludge B (SSB) and a mixture of sewage sludge B with peat (SSBP).

The following soils were used in our experiment: a sand (S) and a loam (L) [10], collected from the arable layer (0-20cm) of ploughlands situated in the vicinity of Krakow. The soil material collected was brought to an air-dry condition. In dried and sieved samples of initial soils granulometric composition was determined by the Casagrande method modified by Prószyński, pH value in KCl solution of 1 mol·dm-3 concentration – by the potentiometric method, the content of organic carbon after mineralization of samples in potassium dichromate(VI) by the Tiurin method, total nitrogen after sample mineralization in concentrated sulphuric acid(VI) in the open system by the Kjeldahl method using the automatic kit Kjeltec II Plus (Tecator), total sulphur after the oxidation of organic sulphur and its compounds to SO_4^{2-} with magnesium nitrate solution and mineralization in a muffle furnace for 8 hours at 500°C by the ICP-AES method, available forms of phosphorus and potassium by the Egner-Riehm method, and magnesium by the Schachtschabel method. The content of general forms of heavy metals after organic matter mineralization (500°C for 8 h) and solubilization the samples in concentrated acids – nitric(V) and chloric(VII) (2:1) [16]. The content of heavy metals was determined by the ICP-AES method using the apparatus Jobin Yvon 238 Ultarce, and mercury

Table 1. Main physical and chemical properties of experimental soils

Parameter			Soil	
			sand	loam
Particle size	1.0 – 0.1 mm	%	78	28
distribution ∅	0.1– 0.02 mm	%	13	29
	< 0.02 mm	%	9	43
pH_{KCl}			6.21	5.30
Hydrolitic acidity		mmol(+) · kg^{-1}	11.20	33.20
Organic C		g · kg^{-1}	9.37	17.70
Total N		g · kg^{-1}	0.96	1.72
Available forms				
P		mg · kg^{-1}	69.80	39.60
K		mg · kg^{-1}	160.80	128.60
Mg		mg · kg^{-1}	134.50	126.00
Total forms				
Cr		mg · kg^{-1}	5.93	17.30
Zn		mg · kg^{-1}	62.00	77.00
Pb		mg · kg^{-1}	29.80	36.00
Cu		mg · kg^{-1}	4.01	7.10
Cd		mg · kg^{-1}	0.68	0.78
Ni		mg · kg^{-1}	4.15	10.42
Hg		mg · kg^{-1}	0.33	0.38
Mn		mg · kg^{-1}	149.23	665.13

by the cold steams method using the apparatus Philips PU 9100X equipped with a VP 90 countershaft (Unicam). Chemical analyses were made in accordance with the methodology elaborated by Ostrowska et al. [16] Main soil characteristics of experimental soils (values in conversion to dry mass assessed - at 105°C) are given in Table 1. The sewage sludges originated from two different municipal sewage mechanical-biological treatment plants and their mixtures with peat were prepared in 1:1 weight ratio in conversion to the material dry mass. Peat with 408 g · kg^{-1} of dry weight revealed the contents of 88 g ·$kg^{-1}$of ash; 34.4 g N · kg^{-1}, 0.91 g P · kg^{-1}, 1.14 g K · kg^{-1}, 0.74 g Mg · $kg^{-1}$and 13.2 mg Zn · kg^{-1} d.m. Prior to the experiment outset the soils were gradually moistened up to 30% of their maximum water capacity. After moistening loam (L) was subjected to liming to obtain pH as stated in the regulation [18]. The measure was conducted using chemically pure CaO according to total hydrolytic acidity value. Subsequently, both soils in PCV containers were left for about four weeks and protected against moisture loss. After that time weighted soil portions of 260 g each in conversion to dry mass were prepared separately for each soil to which organic materials and mineral salts were added. After mixing with organic materials the soil sample was transferred to PCV containers and placed in the incubator. A constant moisture of the incubated samples was maintained on the level of 45%±0.22 of maximum soil water capacity throughout the experiment at the temperature of 23.3°C ±0.03.

Nitrogen rate applied to the soils with organic materials was 0.217g N · kg^{-1} of soil dry mass. Phosphorus and potassium were applied to the equal level introduced with organic materials: P to 0.196 g and K to 0.230 g · kg^{-1} of soil dry mass. As NPK treatments, equivalent amounts of components were used as solutions of chemically pure salts: N – NH_4NO_3, P – $Ca(H_2PO_4)_2 \cdot H_2O$, K – KCl.

Organic matter characteristics are given in Table 2. Dry matter content was determined in fresh samples of organic materials (105° C for 12 h) and the total nitrogen content after sample mineralization in concentrated sulphuric acid(VI) by the Kjeldahl method. In dried and ground material were determined as follows: the total sulphur content after sample mineralization in nitric acid(V) and oxidation of organic sulphur and its compounds with magnesium nitrate by the ICP-AES method, and the content of ash components after sample mineralization in a muffle furnace (450° C for 5 h) and the ash solubilization in nitric acid(V) (1:2). The phosphorus content was determined by the vanadium-molybdenum method on the Beckman DU 640 spectrophotometer, potassium, sodium and calcium by the FES photometry method, magnesium by the atomic absorption spectrophotometry (AAS) method using the apparatus Philips PU 9100X. Heavy metals were determined by the ICP-AES method using the apparatus JY 238 Ultrace, and mercury by the cold steams method using the apparatus Philips PU 9100X

Table 2. Chemical composition of organic materials used in experiment

Parameters		FYM*	SSA*	MSSAP*	SSB*	MSSBP*
Dry matter $g \cdot kg^{-1}$		189.00	311.00	343.00	418.00	372.00
pH (H_2O)		6.22	6.12	5.57	5.73	5.20
Organic mater $g \cdot kg^{-1}$ d.m.		679.00	353.00	652.00	553.00	771.00
Total N	$g \cdot kg^{-1}$ d.m.	25.10	17.20	25.50	42.40	38.50
P		22.60	5.48	3.00	19.30	0.76
K		26.70	2.71	1.88	2.81	1.64
Ca		4.83	15.70	13.30	9.22	12.00
Mg		6.26	4.86	2.82	2.55	1.59
Cr	$mg \cdot kg^{-1}$ d.m.	6.07	19.70	10.30	37.90	17.50
Zn		531.00	899.00	488.00	1684.00	821.00
Pb		3.99	65.90	38.20	29.40	17.50
Cu		338.00	78.30	40.6	119.40	51.80
Cd		1.28	2.71	1.45	2.25	1.03
Ni		11.70	13.30	7.14	25.40	12.10
Hg		Trace	3.58	1.80	2.29	1.07

* see methodics

equipped with a VP 90 countershaft (Unicam).

Periodical analyses were conducted on the incubated material after 3, 8, 16, 32 and 64 days from the experiment outset. In the soil material (dried at 105°C for 12hrs) magnesium and zinc contents were assessed after extraction with 0.01mol· dm^{-3} $CaCl_2$ according to the methodology of Houba et al. for two hours and the soil-solution ratio maintained at 1:10 [11].

Magnesium concentrations were determined in the extracts using AAS method on Philips PU 9100X spectrophotometer and zinc content was determined with ICP-AES method on JY 238 Ultrace apparatus. pH was determined in the soils by potentiometer in 1 mol · dm^{-3} KCl solution [16].

Analyses on the experimental soil were conducted in three replicates. Statistical evaluation was based on two-way ANOVA (i.e. soils and fertilization were considered as the two factors) and the significant differences between means was estimated using Tukey test at the significance level $p<0.05$ [23]. The changes of pH value and contents of Mg and Zn were evaluated from regression equation.

RESULTS AND DISCUSSION

Fertilization resulted in a marked diversification of the pH of the soils used for the experiment within the individual dates (Fig.1, Tab.3). During the early period of the experiment (until the eighth day), a mild decline of pH value was observed in the sand (S) on all objects. A more serious pH regression (until the eighth day of the experiment) was detected in loam (L). Until the 64th day of the experiment a progressive acidification of sand (S) was registered. Loam responded differently, as increased pH values were observed there since the 32nd day. In both soils the lowest pH values were noted in effect of fertilization with mineral salts (NPK). According to Koncius [13] fertilizing with physiologically acid mineral fertilizers significantly speeded up acidification process. In the present study the decline was statistically significant in comparison with the soils of organic treatments. In the soils used for the experiments pH was decreasing successively, irrespective of the applied fertilization or liming. Values of pH were relatively higher in soils of farmyard manure and sewage sludge (A) treatments, which may suggest a slower rate of acidification in comparison with other organic material treatments. According to Whalen et al. [25] acid soil reaction may be amended not only by liming, abut also by organic fertilization with farmyard manure.

These authors applied cattle manure for soil fertilization in an incubation experiment, registered its advantageous effect not only on the soil reaction, but also on improvement of the soil buffer properties. Our experiment did not reveal any such beneficial influence of farmyard manure fertilization on the soil pH, although acidification rate in the soils from farmyard manure treatments was slower than after the application of sewage sludge (B) and sludge mixtures with peat. Sienkiewicz [20,21] demonstrated that farmyard manure applied once in two years considerably raised pH values but decreased the soil hydrolytic acidity. Wiater [26] published different results, stating that organic fertilizers, including farmyard manure, caused significant increase in hydrolytic acidity of fertilized soil in comparison with the object without fertilization.

Table 3. . Homogeneus groups according to the Tukey test for the mean soil pH during incubation (factors: soil and fertilization)

Objects*	Soil (sand)					Soil (loam)				
	Days									
	3	8	16	32	64	3	8	16	32	64
0	f	g	g	f	i	b	bc	cd	c	cd
NPK	d	e	cd	c	bc	a	a	a	a	a
FYM	f	g	g	g	h	c	d	d	c	e
SSA	g	g	h	g	j	bc	cd	d	c	de
SSAP	e	f	f	e	g	a	bc	bc	b	bc
SSB	e	f	ef	d	fg	a	b	b	b	b
SSBP	d	ef	e	d	ef	a	b	b	b	b

* see methodics

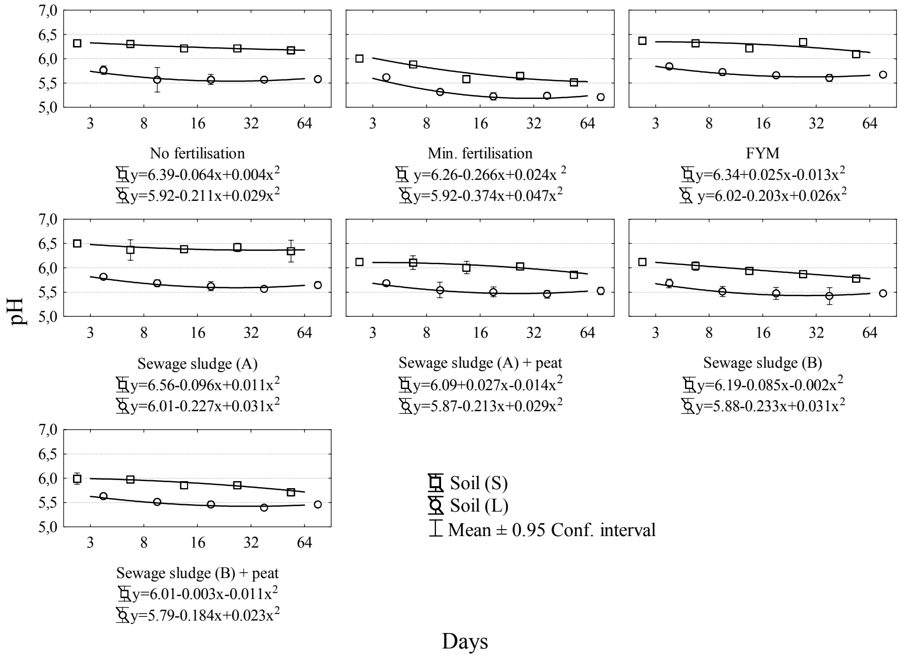

Figure 1. soil pH during incubation

Irrespective of the applied fertilization, the plant available magnesium content was higher in sand (S) after 3 days of incubation. (Fig.2, Tab.4). After eighth days of incubation, the contents of available magnesium diminished significantly in the sand (S) on all objects in comparison with the earlier date. During the same period the contents of available magnesium in loam (L) did not reveal any greater changes. After 16 days of incubation, available magnesium content was successively increasing in sand (S), in each treatment. Such tendency was registered until the 64th day of incubation. The situation was opposite for changes in magnesium content in loam (L), where after 64 days of incubation, an increase in available magnesium was observed. Although differences were not significant, in comparison with this component quantities assessed in the same soil at earlier dates, only in the soil of the farmyard manure (FYM) and mineral salt treatment. Among the organic materials used, farmyard manure treatment (FYM) positively influenced the content of available magnesium in both soils.

Favourable effect of farmyard manure fertilization on the available magnesium amount in soil was revealed also by other authors [15,17]. In the other organic treatments, lower contents in available magnesium forms were observed compared to the control. Skowrońska et al.[22] demonstrated that application of organic wastes for light soil fertilization caused a between 10 and 29% decrease in the content of available Mg forms. The use of sewage sludges in her experiments did not affect significantly the changes in the soil magnesium concentrations during the

Table 4. Homogeneus groups according to the Tukey test for the average magnesium content in soils during incubation (factors: soil and fertilization)

Treatments*	Soil (sand)					Soil (loam)				
	Days									
	3	8	16	32	64	3	8	16	32	64
0	de	abc	def	de	e	a	ab	a	a	a
NPK	de	bcd	f	f	f	ab	abcd	bc	b	bc
FYM	f	f	g	g	f	de	e	f	c	c
SSA	bcd	a	cd	d	d	abc	cd	ab	ab	ab
SSAP	cde	abc	de	de	d	a	bcd	ab	ab	ab
SSB	de	bcd	def	e	de	abc	d	bc	ab	ab
SSBP	e	d	ef	de	d	ab	d	bc	ab	ab

* see methodics

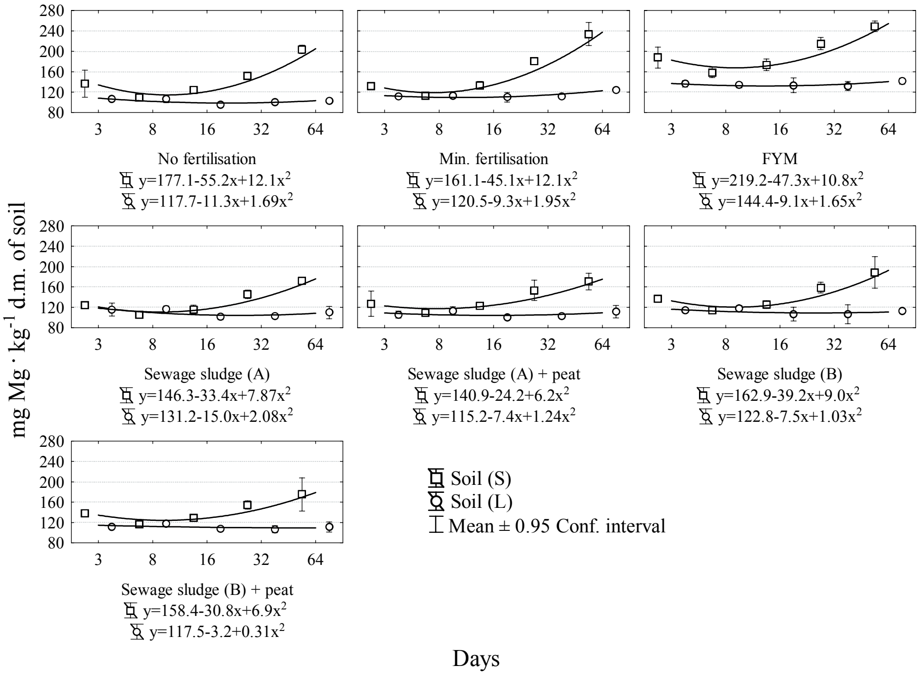

Figure 2. The content of magnesium in soils during incubation

period of investigations. However, a noticeable tendency to increase this magnesium form under the influence of the experimental factor i.e. the duration of the experiment was noticed. Other authors [2,3,4] reported similar regularities in their research. In the presented experiments, mineral (NPK) fertilization caused elevated content of mobile magnesium forms, which might have resulted from decreasing soil pH. In their investigations Stępień and Adamiak [24] also found an increase in bioavailable magnesium amount under the influence of mineral fertilization.

The content of zinc extracted from soil with calcium chloride was very low, irrespective of the applied rate of fertilization, while the changes occurring during the period of the experiment were dynamic (Fig.3,Tab.5). On the basis of obtained results a more serious effect of soil properties, mainly pH on the content of mobile zinc forms may be seen than the applied fertilization. Higher content of this element mobile forms was found in the soil having sand (S) texture. Despite the lowest pH values assessed in the soils of mineral treatments, amounts of mobile zinc forms were markedly higher after 64 days of incubation only in the sand (S) in comparison with the treatment where organic materials were used. Shuman [19] presented the action of the reaction within the pH range 5-7 on the strong adsorption of zinc by humic acids in the fraction

Table 5 Homogeneus groups according to the Tukey test for the mean zinc content in soils during incubation (factors: soil and fertilization)

Objects*	Soil (sand)					Soil (loam)				
	Days									
	3	8	16	32	64	3	8	16	32	64
0	cd	a	abcd	ab	ab	a	ab	a	a	a
NPK	g	cd	h	e	e	ab	abc	bcde	abc	b
FYM	de	ab	cde	abc	cd	ab	a	ab	ab	ab
SSA	ef	bcd	def	c	c	bcd	abc	abc	abc	ab
SSAP	fg	abcd	ef	c	cd	abc	abcd	abc	ab	ab
SSB	g	e	g	de	e	abc	de	bcde	abc	ab
SSBP	fg	cde	f	d	d	abc	cde	abcd	bc	ab

* see methodics

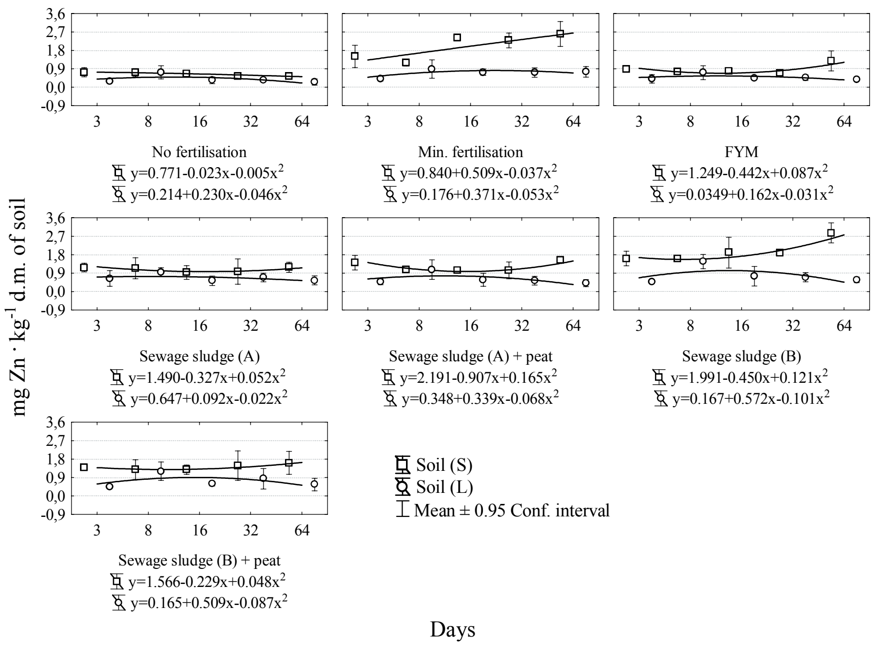

Figure. 3. The content of zinc in soils during incubat

of organic matter. The solubility of zinc compounds is affected mainly by soil reaction, organic matter and clayey particles content [1,6]. A cooperation of both factors in shaping zinc compounds solubility is mentioned. A higher content of organic substance in heavy soil (L) and considerably greater content of clayey particles in comparison with the light soil (S) might effectively limit the contents of this element mobile forms, irrespective of decreasing soil pH. The research conducted by Jakubus et al. [10] on the effect of long-term fertilization on the mobile forms of soil zinc confirmed a significant effect of soil pH on the amount of this zinc fraction. Fertilization with farmyard manure led to a diminished percentage of readily soluble zinc fractions in its total content, whereas mineral fertilization increased the ratio. In weakly loamy sand such relationship was noticed until the 32^{nd} day of the experiment, whereas at later dates the contents of this zinc form in the soil from the treatments fertilized with organic materials originating from wastes was increasing at a greater rate.

CONCLUSIONS

1. During the incubation, a decrease in the soil pH was proceeding whereas the applied fertilizers, except sewage sludge (A) and farmyard manure resulted in an increase in acidification.

2. Amounts of available magnesium forms depended

on the applied fertilizer (the greatest quantities were registered on farmyard manure and mineral treatments), whereas intensity of changes related with this element transformations depending on the soil used in experiment. In the sand a significantly greater increase in magnesium content was observed than in the loam.

3. Zinc content was more dependent on soil properties than on the amounts of fertilization applied. Higher amounts of this element were obtained in sewage sludge (B) treatments than in treatments receiving mineral forms.

4. Peat supplement to sewage sludge caused a diminishing of zinc concentration in soil, however a notable change was registered only for sewage sludge (B) in the sand soil.

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