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Original Research

Zinc Content in Maize (*Zea mays* L.) and Soils Fertilized with Sewage Sludge and Sewage Sludge Mixed with Peat

K. Gondek

Department of Agricultural Chemistry, Agricultural University in Kraków,
al. Mickiewicza 21, 31-120 Kraków, Poland

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Abstract

This research aimed to assess the effect of fertilization with sewage sludge and their mixtures with peat on maize biomass yield and its zinc concentrations, as well as Zn contents in soils with various textures. The research was conducted as a two-factor (soil and fertilization), three-year pot experiment (2003-05). The soil material used for the experiment revealed the texture of weakly loamy sand (Soil I), sandy silt loam (Soil II) and medium silt loam (Soil III). The sewage sludge originated from two different municipal mechanic and biological treatment plants. The mixtures of sewage sludges with peat were prepared by mixing the organic material in weight ratio 1:1 in conversion to dry matter. Under the experimental conditions fertilization with sewage sludges and sludge mixtures with peat affected maize biomass yield more positively than fertilization with mineral salts. The smallest yield of biomass, irrespective of applied fertilization, was obtained when maize was cultivated in weakly loamy sand (Soil I). In comparison with organic materials and farmyard manure supplied to the soil, the greatest quantities of zinc were assessed in maize fertilized with mineral salts, irrespective of soil type. Sewage sludge mixtures with peat, as compared with sewage sludge used separately, affected maize biomass yields slightly better but had a similar effect on zinc concentrations in the plant biomass. The least of zinc mobile forms were determined in medium silt loam (Soil III). Following the application of organic materials but irrespective of the soil, the content of mobile zinc forms was significantly smaller than the content assessed in the soils from mineral salt treatments.

Keywords: sewage sludge, zinc, maize, soil, tolerance indices, contamination indices

Introduction

Environmental use of sewage sludges is often limited not only due to their pathogenic microorganism loading [1], but mainly because of the large content of heavy metals, which poses a hazard for soil environment, groundwater cleanliness and plant quality [2, 3]. Transformations and availability of heavy metals from sewage sludges are conditioned by soil properties [4, 5], and also by chemical properties of each element, which makes it difficult to predict heavy metal migration from soil to plant [6].

Zinc belongs among particularly active metals in soil, which is affected both by its exchangeable forms and combinations with organic matter. The application of sewage sludge, often containing considerable amounts of this element, may lead to an increase in the amount of its mobile forms in soil [7, 8]. It is the more dangerous, since usually

*e-mail: rrgondek@cyf-kr.edu.pl

plants absorb zinc proportionately to its concentration in the soil solution and do not reveal the symptoms of this element's toxicity. It leads to relatively easy translocation of zinc, through plants to further links of the food chain [9].

The investigations were conducted to assess the effect of fertilization with sewage sludge and sewage sludge mixed with peat on the yield of maize biomass, its zinc concentrations and Zn content in soils with different textures.

Methods

Experimental Design

The effect of fertilization with sewage sludges and sludge mixtures with peat on zinc content in maize was assessed in a two-factor, three-year pot experiment (2003-05). The investigations were conducted on three soils and the experimental design, identical for each soil, comprised 7 treatments (in four replications): without fertilization – (0); fertilization with chemically pure salts – (NPK); farmyard manure – (FYM); sewage sludge A – (SS A); sewage sludge A mixture with peat – (SS A + peat); sewage sludge B – (SS B); and sewage sludge B mixture with peat – (SS B + peat). The soil material used for the experiment was comprised of weakly loamy sand (Soil I), sandy silt loam (Soil II) and medium silt loam (Soil III) collected from the arable layer (0-20 cm) of ploughlands from the Kraków neighbourhood. The sewage sludge used for the experiment originated from two different mechanical-biological municipal sewage treatment plants. Sewage sludges were mixed with peat at a 1:1 weight ratio in conversion to material dry matter. Peat with 408 $g \cdot kg^{-1}$ of dry matter revealed the contents of 88 $g \cdot kg^{-1}$ of ash, 34.4 g $N \cdot kg^{-1}$, 0.91 g $P \cdot kg^{-1}$, 1.14 g $K \cdot kg^{-1}$ d.m. and 13.24 mg $Zn \cdot kg^{-1}$ d.m. The characteristics of chemical composition of the other organic materials and soil material (values converted to dry matter determined at 105ºC) were given in Tables 1 and 2.

Table 1. Chemical composition of materials used in the experiment.

Determination		FYM (FYM)	Sewage sludge A (SS A)	Sewage sludge A + peat (SS A + peat)	Sewage sludge B (SS B)	Sewage sludge B + peat (SS B + peat)
Dry matter $g \cdot kg^{-1}$		189±13.2[b]	310±21.7	343±22.2	418±29.2	372±12.2
pH (H_2O)		6.22±0.31	6.12±0.33	5.57±0.31	5.73±0.31	5.20±0.31
Organic matter $g \cdot kg^{-1}$ d.m.[a]		679±31.5	353±19.3	652±39.1	552±32.5	771±46.2
N_{tot}	$g \cdot kg^{-1}$ d.m.	21.6±0.64	17.0±0.69	24.7±1.23	37.4±1.87	35.1±1.71
P_{tot}		22.60±0.18	5.48±0.22	3.00±0.04	19.32±0.38	7.64±0.27
Ca_{tot}		4.83±0.10	15.66±0.20	13.31±0.10	9.22±0.10	11.95±0.30
Na_{tot}		4.60±0.04	0.54±0.02	0.40±0.01	0.70±0.20	0.44±0.10
Zn_{tot}	$mg \cdot kg^{-1}$ d.m.	531±9.15	899±2.43	488±5.00	1684±20.7	821±10.5

[a] data are based on 105ºC dry matter weight
[b] ± standard error of mean; n=3

Table 2. Some soil properties before the experiment.

Determination			Soil I (weakly loamy sand)	Soil II (sandy silt loam)	Soil III (medium silt loam)
Granulometric composition Ø	1.0 – 0.1 mm	%	78	42	28
	0.1 – 0.02 mm		13	33	29
	< 0.02 mm		9	25	43
pH KCl			6.21±0.43[b]	5.69±0.28	5.30±0.29
Hydrolitic acidity		$mmol(+) \cdot kg^{-1}$ d.m.[a]	11.2±0.44	23.4±1.17	33.2±1.93
Sum of alkaline cation			39.9±1.07	86.8±2.00	128.4±2.83
Organic C		$g \cdot kg^{-1}$ d.m.	9.37±0.26	13.36±0.57	17.68±1.06
Zn_{tot}		$mg \cdot kg^{-1}$ d.m.	62.0±3.10	78.2±4.00	77.0±3.85

[a] data are based on 105ºC dry matter weight
[b] ± standard error of mean; n=3

Table 3. Homogeneous groups according to the Tukey test for biomass yield of maize.

Objects[1]	Soil I (weakly loamy sand)			Soil II (sandy silt loam)			Soil III (medium silt loam)		
	PAG	R	Σ	PAG	R	Σ	PAG	R	Σ
0	a	a	a	c	bc	c	b	b	b
NPK	de	bcdef	de	gh	bcd	g	de	bcd	d
FYM	fg	cdefg	efg	ij	ghi	hi	de	ghij	defg
SS A	def	bcde	def	j	efgh	hi	d	defgh	d
SS A + peat	fg	bcdef	efg	ij	defgh	h	de	defgh	defg
SS B	fg	cdefg	fg	jk	ijk	ij	ef	hij	fg
SS B + peat	hi	fghi	h	k	jk	j	g	k	h

PAG – parts aboveground; R – roots; Σ – total biomass yield
Means followed by the same letters in columns did not differ significantly at $\alpha < 0.01$ according to the t-Tukey test, factors fertilization × soil.
[1] 0 – soil without fertilisation, NPK – soil with addition of mineral salts, FYM – soil with addition of farmyard manure, SS A – soil with addition of municipal sewage sludge A, SS A + peat – soil with addition of sewage sludge A mixture with peat, SS B – soil with addition of municipal sewage sludge B, SS B + peat – soil with addition of sewage sludge B mixture with peat.

Experimental Methodology

PVC pots used for the experiment contained 5.50 kg of air-dried soil material. Before the experiment outset the soils were gradually moistened to 30% of maximum water capacity. After moistening sandy silt loam (Soil II) and medium silt loam (Soil III), they were limed to obtain the conditions optimal for plant growth and development. The measure was applied separately in each pot. Chemically pure CaO was used in a dose calculated on the basis of soil hydrolytic acidity. Subsequently all soils were left for 4 weeks and water losses were supplemented occasionally. After this period fertilization in organic form was introduced in the amount corresponding to 1.20 g $N \cdot pot^{-1}$. Phosphorus and potassium quantities were supplemented with solutions of chemically pure salts [P-$Ca(H_2PO_4)_2 \cdot H_2O$ and K-KCl] to equalize the amounts of these components supplied with the organic materials. The identical nitrogen, phosphorus and potassium doses were used on mineral (NPK) treatment as on the treatments receiving organic materials. Doses of N, P and K were, respectively: 1.20 g $N \cdot pot^{-1}$ as NH_4NO_3, 1.26 g $P \cdot pot^{-1}$ as $Ca(H_2PO_4)_2 \cdot H_2O$ and 1.48 g $K \cdot pot^{-1}$ as KCl. Taking into consideration the residual fertilizer effect and the soil's abundance in bioavailable phosphorus and potassium (in the second and third year of the experiment) the following doses of fertilizer components were applied corresponding: 0.80 g N; 0.2 g P and 1.40 g $K \cdot pot^{-1} \cdot year^{-1}$ as chemically pure salts.

Each year, maize San, c.v. (FAO 240) was cultivated as a test plant and 5 pieces per pot were left. Maize (for green forage) was always harvested at the 7-9 leaves stage. The plant vegetation periods were 47 days in the first year, 66 days in the second and 54 days in the third. Throughout the experiment the plants were watered with distilled water to 50% of maximum water capacity.

Analytical Methods

Assessment of Chemical Properties of Farmyard Manure, Sewage Sludges and their Mixtures with Peat Used for the Experiments

In fresh samples of organic materials dry matter content was assessed (at 105ºC for 12 hrs), pH by potentiometer and total nitrogen content after sample mineralization in concentrated sulphuric acid (VI) using the Kjeldahl method. The following were determined in dried and ground material: organic matter content after sample calcination in a muffle furnace at 600ºC, mineral contents after sample mineralization in a muffle furnace at 450ºC for 5hrs and ash was disssolved in a diluted nitric acid (v/v) (1:2). Phosphorus content was assessed by colorimetry using a Backman DU 640 spectrophotometer, calcium and sodium using flame photometry (FES) and zinc by means of ICP-AES method on a JY 238 Ultrace apparatus.

Determining Physical and Chemical Properties in Soils Used in the Experiment

In dried and sifted samples of initial soils I determined granulometric structure using Casagrande method in Prószyński's modification, pH by potentiometer in 1 mol dm^{-3} KCl solution, organic carbon content after sample mineralization in potassium dichromate using Tiurin method, hydrolytic acidity in 1 mol dm^{-3} CH_3COONa using Kappen method and the contents of exchangeable base cations after extraction with 0.1 dm^{-3} HCl solution. Concentration of total zinc forms in soils was assessed after organic matter mineralization (at 500ºC for 8 hrs) and sample solving in concentrated nitric and chlorous acids (2:1) using ICP-AES method on Jobin Yvon 238 Ultrace apparatus [10].

Table 4. Homogeneous groups according to the Tukey test for average weighted content of zinc in biomass of maize.

Objects[1]	Soil I (weakly loamy sand)		Soil II (sandy silt loam)		Soil III (medium silt loam)	
	PAG	R	PAG	R	PAG	R
0	ab	def	a	ab	a	ab
NPK	fg	g	fg	d	ef	ab
FYM	ab	de	ab	ab	bc	a
SS A	def	g	bcd	abc	de	abc
SS A + peat	bcd	de	ab	ab	bcd	ab
SS B	de	fg	bcd	cd	cde	bc
SS B + peat	ab	efg	ab	bc	bc	ab

PAG – parts aboveground; R – roots; Σ – total biomass yield
Means followed by the same letters in columns did not differ significantly at $\alpha < 0.01$ according to the t-Tukey test, factors fertilization x soil.
[1] see Table 3 for symbols

Determining Contents of Zinc in Plant and Soil Material from Pot Experiment

After the harvest the plants were dried (at 70ºC) to constant weight and the yield of dry mass of shoots and roots was determined. Subsequently, the dried biomass was crushed in a laboratory mill and mineralized in a muffle furnace (at 450ºC for 5 hours). The remains were dissolved in diluted nitric acid 1:2 (v/v) [10]. The soil material collected each year after completed vegetation period was analyzed with reference to the changes of physicochemical properties occurring as a result of the applied fertilization. In the material, dried and sifted through a sieve with 1mm mesh, pH was assessed in 1 mol·dm^{-3} KCl solution [9] and zinc content after extraction with 1 mol·dm^{-3} NH_4NO_3 solution [11]. Zinc was determined in the obtained plant material solutions and soil extracts using ICP-AES method on JY 238 Ultrace apparatus. Reference material: NCS DC73348 (China National Analysis Center for Iron &Steel) for plants or AG-2 (*Agro*MAT) for soils was attached to each analyzed series and the result was considered reliable if RSD error did not exceed 5%.

Calculations and Statistics

On the basis of aggregate maize biomass yields tolerance index (Ti) was computed as a quotient of dry mass of plant yield on treatments fertilized with organic and mineral materials. The contamination index (C) was calculated on the basis of arithmetic average-weighed zinc content in the shoots as a quotient of zinc content in the plant fertilized with organic and mineral materials [12]. The results were verified statistically using a fixed model, where fertilization and soil were the factors. The statistical computations considered two-way ANOVA (factors: soil and fertilization) and the significance of differences was estimated using t-Tukey test at significance level $\alpha <$ 0.01 [13].

Results and Discussion

Organic materials used for the experiments differed with their chemical composition, including zinc content, which was higher in sewage sludges than in farmyard manure (Table 1). Peat supplement diminished the contents of most elements in the mixture in comparison with component content in the sludges.

The soil material applied in the experiments belonged to various texture groups but also differed considerably by its chemical properties, including total zinc content (Table 2).

Analysis of variance confirmed a significant effect of fertilization with organic materials on maize biomass yield (Fig. 1). Fertilization with sewage sludges or their mixtures with peat and farmyard manure treatment enabled significantly greater yields on treatments received exclusively with mineral compounds. Greater yields were obtained when sewage sludge mixtures with peat were used (except SS A + peat on sandy silt loam – Soil II) than when solely sewage sludge was applied. Fertilized effectiveness of organic materials is mainly determined by their concentrations of nitrogen, particularly its mineral forms [14]. However, disturbed relationships between the other nutrients may directly influence plant mineral economy and condition biological value of the obtained yield. Over the three-year period of investigations the applied fertilization with organic materials produced better effects expressed by the quantity of maize biomass yield than fertilization with mineral salts. This effect cannot be fully ascribed to the activity of applied sewage sludges or their mixtures with peat. It resulted from the residual effect of organic materials and supplementary fertilization with mineral salts in the second and third year of the experiment. The factor determining plant yielding might have been other elements supplied to the soil with organic materials, such as sulphur, magnesium or microelements, whose amounts were not balanced. Application of natural or organic fertilizers do not always ensure increased yields as a result of the so-called residual effect. Drab and Derengowska [15] demonstrated the advantageous effect of sewage sludge fertilization on plant yield, at the same time revealing that crop yield, irrespective of the soil, was conditioned by the dose of sewage sludge. On the other hand Wiater et al. [16] obtained worse direct effect of sewage sludge granulate on maize yield in comparison with mineral fertilization, but the residual fertilizer effect of the sewage sludge was better.

Values of tolerance index computed for aggregate yield of maize biomass were bigger than one, both on farmyard manure treatments and objects receiving organic materials (Fig. 2). Values of the discussed parameter higher than assessed on treatments fertilized with sewage sludge were registered after the application of sewage sludge mixtures with peat. It may testify better fertilizer parameters of the mixtures and at the same time may point to the presence of a factor limiting growth and development of plants in the case of sewage sludge application without peat. In previous investigations Gondek and Filipek-Mazur [17] observed an inhibition of maize shoots and roots in result of direct fertilizer effect of vermicomposts produced from tannery sludge. In the opinion of Gondek and Filipek-Mazur [17] the quoted research results do not necessarily demonstrate a toxic effect of the applied materials but rather a potential deficiency of nitrogen, which as a whole was supplied with vermicomposts. The highest values of tolerance index (Ti), irrespective of applied fertilization, were registered on sandy silt loam (Soil II).

Irrespective of applied fertilization or soil, greater quantities of zinc were assessed in maize roots than in its shoots (Fig. 3, Table 4). The biggest content of zinc was assessed in shoots and roots of plants from the treatment fertilized with mineral salts (NPK). Considering the potential use for forage, weighed average zinc content in maize shoots for three years on this treatment was 36.3 mg Zn·kg^{-1} d.m. and on average was over 30% bigger than this element content determined in maize shoots fertilized with farmyard manure and mixtures of sewage sludges and peat, and by over 20% higher than the content in maize shoots fertilized with sewage sludge. With respect to forage value, zinc concentrations in maize shoots on all treatments ranged within the optimal values [18]. Significant diversification in zinc content depending on the soil was noted only for maize root biomass (Fig. 4). Roots of plants cultivated in weakly loamy sand (Soil I) contained the greatest amounts of this element. Also, the yield of this plant part biomass was the smallest.

Values of zinc contamination index (C) for maize shoots cultivated on farmyard manure (FYM) treatments and on treatments with sewage sludges (SS A, SS B) and sludge mixtures with peat (SS A + peat, SS B + peat) shown in Fig. 5 were diversified and depended on soil kind. Generally, values of computed parameter (C), irrespective of applied fertilization were smaller than one. The highest values of zinc contamination index (C) of shoots were determined when maize was cultivated in soil of medium silt loam texture (Soil III).

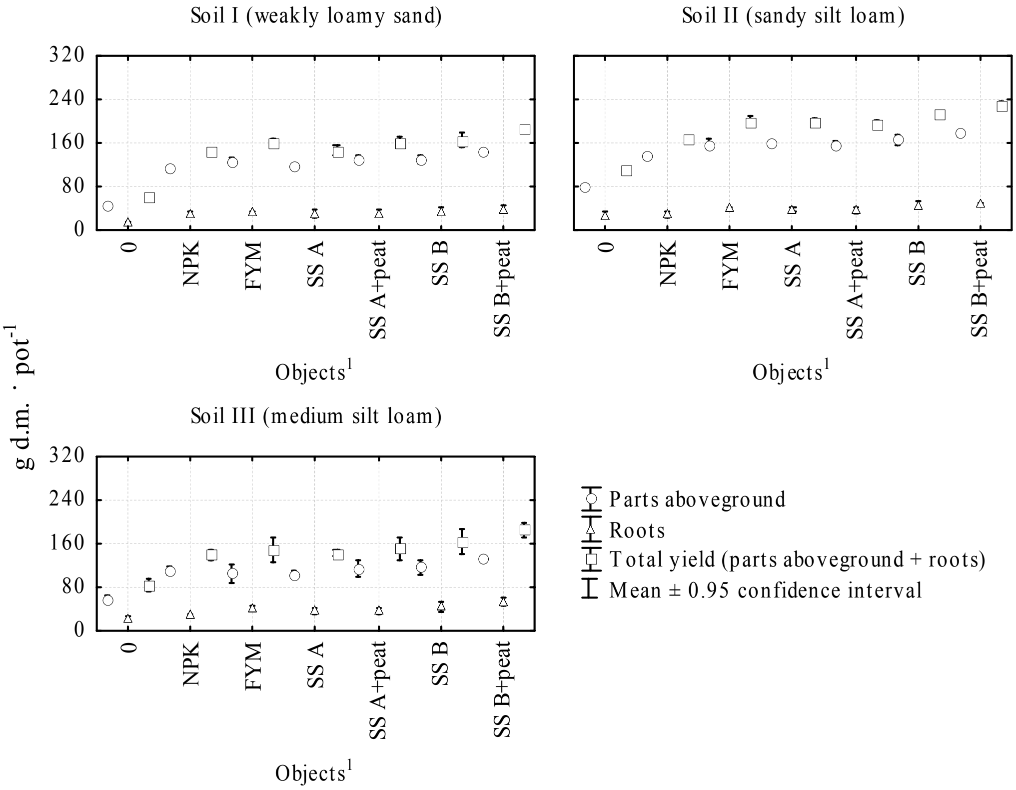

Fig. 1. Biomass yield (parts aboveground and roots) of maize in each soil.

[1] 0 – soil without fertilisation, NPK – soil with addition of mineral salts, FYM – soil with addition of farmyard manure, SS A – soil with addition of municipal sewage sludge A, SS A + peat – soil with addition of sewage sludge A mixture with peat, SS B – soil with addition of municipal sewage sludge B, SS B + peat – soil with addition of sewage sludge B mixture with peat.

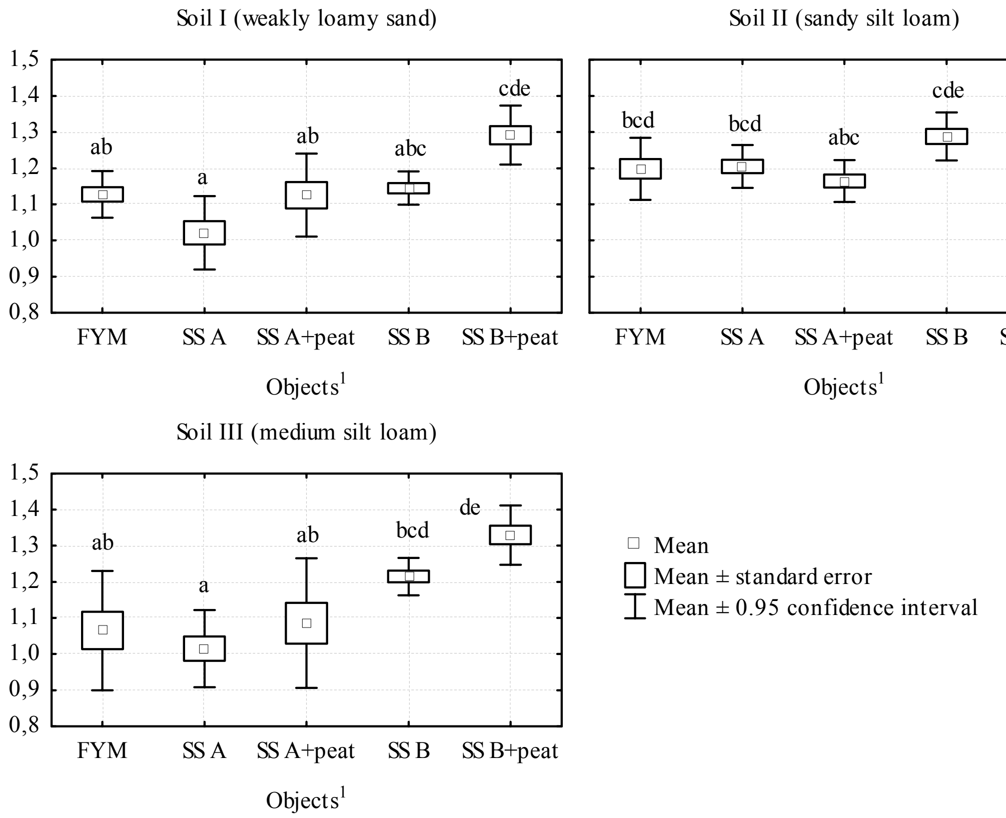

Fig. 2. Values and statistic parameters of tolerance indices (Ti) on each soil.
Means followed by the same letters did not differ significantly at α < 0.01 according to the t-Tukey test, factors fertilization x soil
[1] see Fig. 1 for symbols.

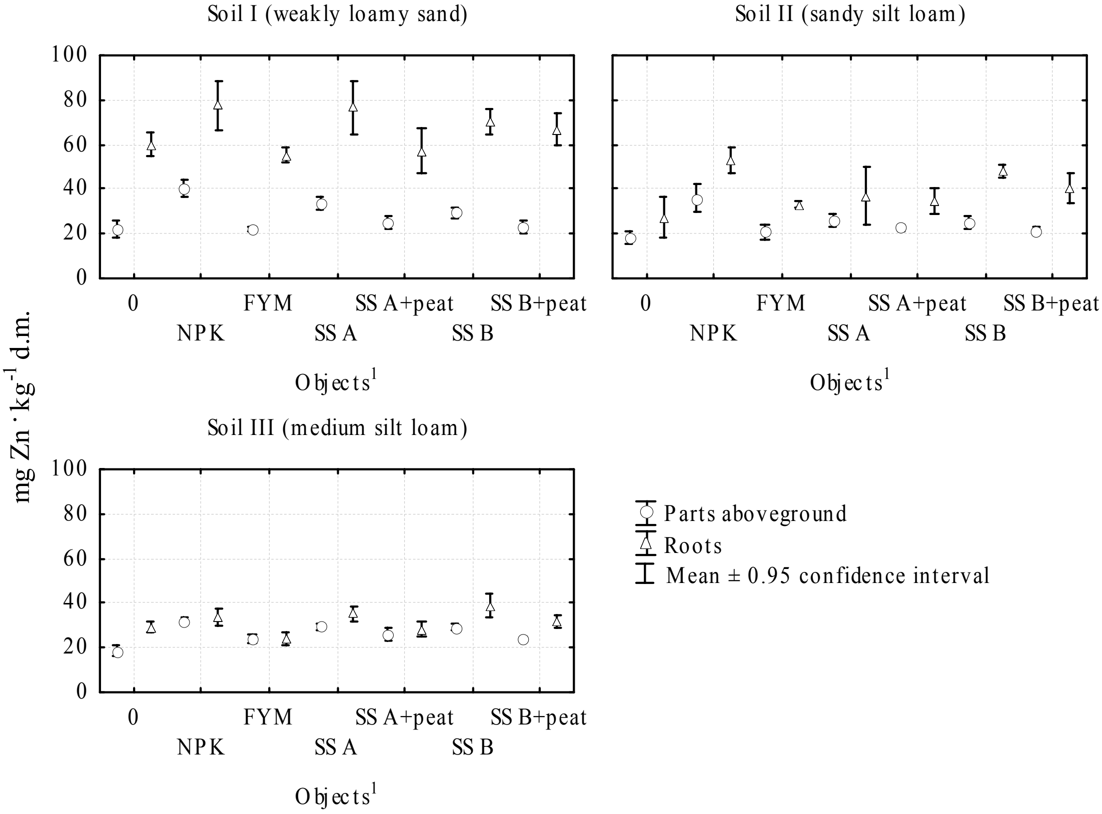

Fig. 3. Average weighted content of zinc in biomass (aboveground parts and roots) of maize in each soil.
[1] see Fig. 1 for symbols.

The content of heavy metals in plants depends on many factors, including soil properties (organic matter content, bioavailable forms of the element and soil pH) [6, 19, 20], but also on fertilization, especially when waste substances are used [21]. Patorczyk-Pytlik [22] revealed that an excessive accumulation of heavy metals in plants takes place when large doses of sewage sludges, heavily loaded with these elements, are used for fertilization. The author's own results show that zinc concentration in plant biomass at moderate doses of sewage sludges or their adequate preparation (in this case peat addition), irrespective of soil, was smaller than that determined in plant biomass fertilized solely with mineral salts (NPK). Also Krzywy et al. [23] demonstrated that plant fertilization with sewage sludge with low content of heavy metals does not pose a hazard of excessive cumulation among other zinc in plant biomass. Diversified physical and chemical properties of soil material used for the experiments suggested significant differentiation of zinc contents in maize biomass, irrespective of the applied treatment. However, the Author's own research results did not corroborate the significant diversification of zinc content in shoots depending on the soil kind, as was revealed by King and Dunlop [24]. Significant diversification in zinc content depending on soil type was found in maize roots. It might have resulted from zinc cumulation in a relatively small amount of root biomass, although a definitely larger zinc amount in maize roots suggests the existence of biological barriers efficiently limiting zinc translocation to plant shoots [25].

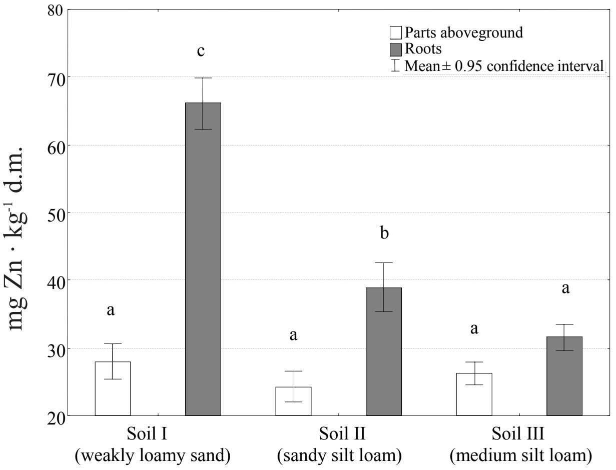

Fig. 4. Average weighted content of zinc in biomass of maize for soils.
Means followed by the same letters in columns did not differ significantly at α < 0.01 according to the t-Tukey test, factor soil.

Mean content of mobile zinc forms, irrespective of the applied fertilization, was the smallest in soil belonging to heavy soil agronomic category (Soil III) (Fig. 6). A significant relationship was revealed between the contents of mobile zinc forms in soil and soil pH (Fig. 7). The content of mobile zinc forms in soil after the application of organic materials and farmyard manure was generally smaller than

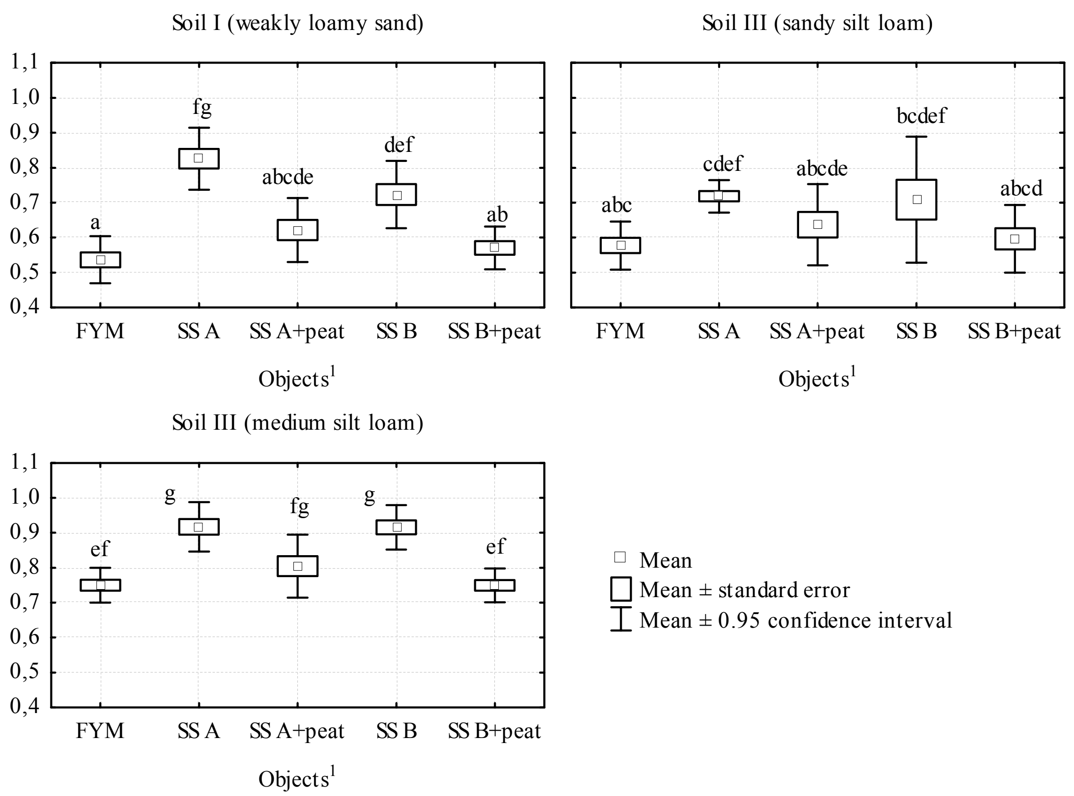

Fig. 5. Values and statistical parameters of contamination degree indices (C) on each soil.
Means followed by the same letters did not differ significantly at α < 0.01 according to the t-Tukey test, factor fertilization x soil
[1] see Fig. 1 for symbols.

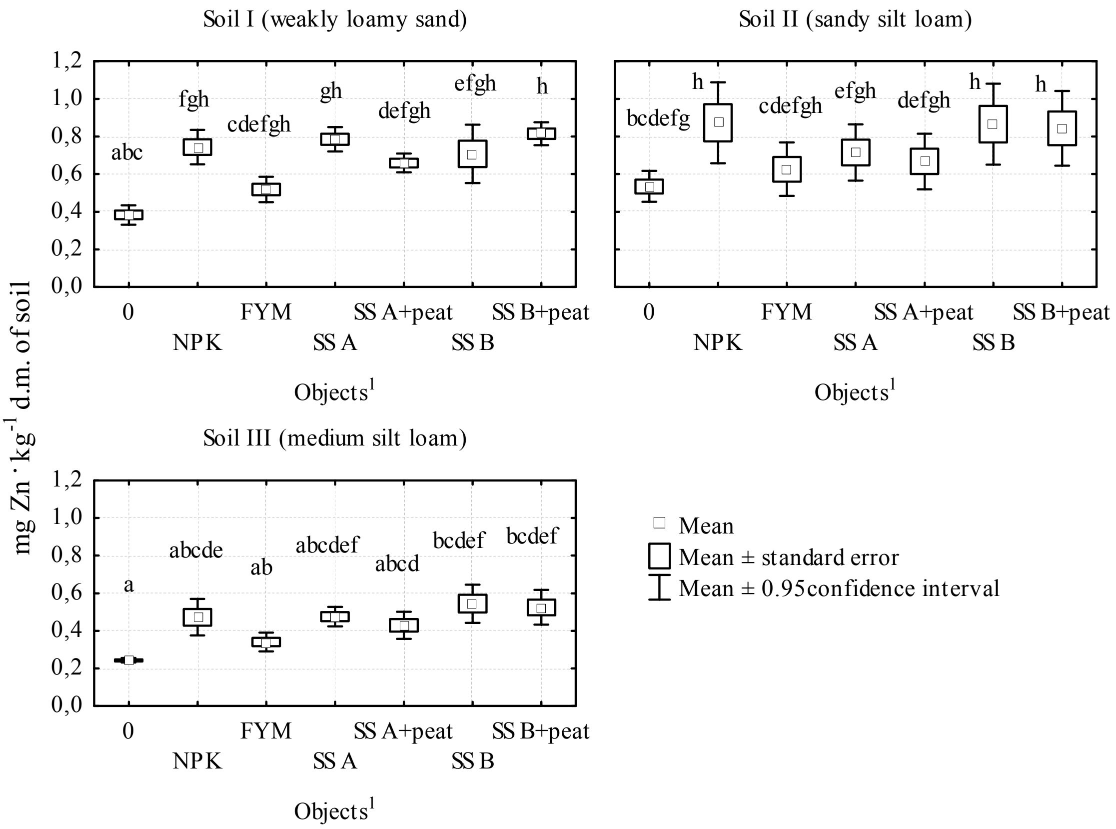

Fig. 6. Mean and statistic parameters of zinc mobile form content in soils.
Means followed by the same letters did not differ significantly at α < 0.01 according to the t-Tukey test, factors fertilization x soil
[1] see Fig. 1 for symbols.

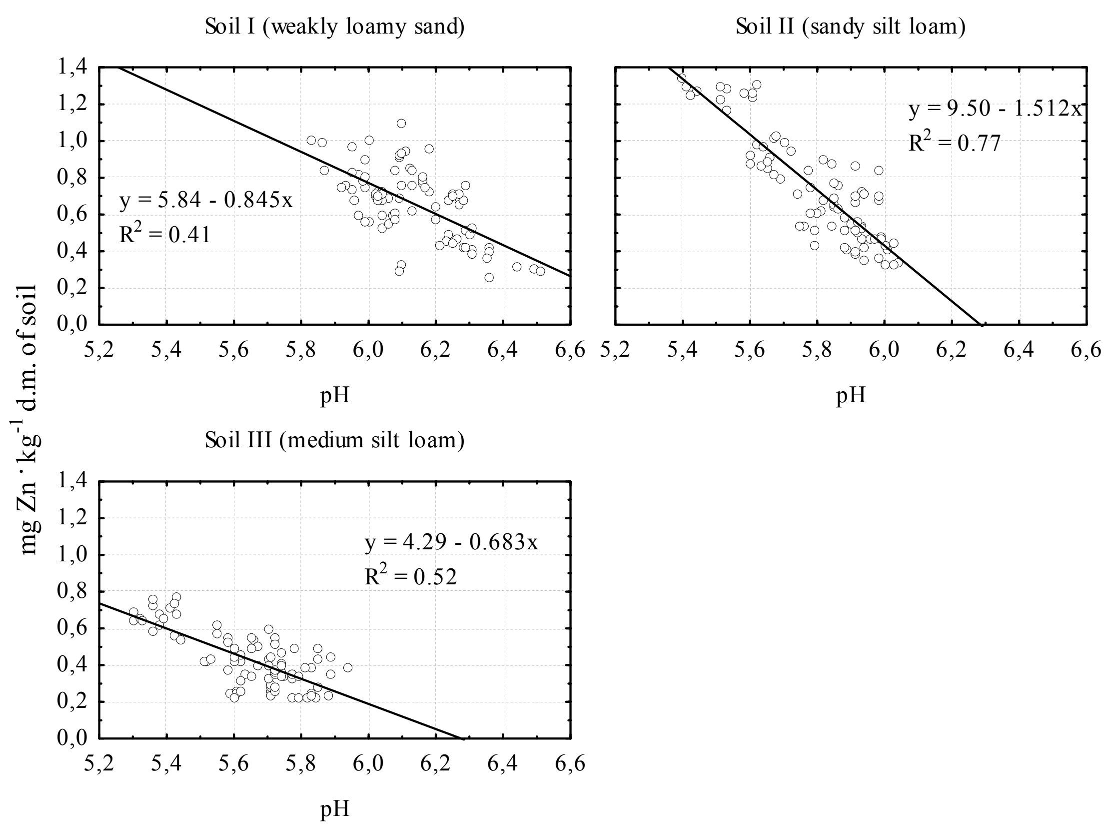

Fig. 7. Relationship between soils pH and content of zinc mobile forms in soils (I, II III).

the content determined in soil from treatments fertilized with mineral salts (NPK). Heavy metal bioavailability in soil is not the same for all elements [6]. Heavy metal release into the soil solution depends on chemical properties of each element and is strongly determined by the soil properties [26]. In my own investigations the lowest pH values were registered in all soils fertilized exclusively with mineral salts, which contributed to improving zinc bioavailability [4, 6]. Also, Jakubus et al. [27] revealed that soil reaction has a noticeable influence on the contents of, among others, zinc in water soluble fraction. Moreover, the authors quoted above found that farmyard manure fertilization caused a decrease in the share of zinc forms in readily soluble fractions, whereas mineral fertilization increased this share, which the same authors ascribe to greater soil acidification.

Conclusions

1. Under conditions of the conducted experiment fertilization with sewage sludge and sludge mixtures with peat affected maize biomass yields better than treatment with mineral salts. Irrespective of the applied fertilization, the smallest biomass yield was obtained when maize was cultivated in weakly loamy sand (Soil I).
2. Irrespective of the kind of soil, maize fertilized with mineral salts contained the greatest quantities of zinc, in comparison with organic materials and farmyard manure added to the soil.
3. Sewage sludge mixtures with peat, as compared with separately used sewage sludge, slightly better affected maize biomass yield, but had a similar influence on zinc content in the plant biomass.
4. The smallest quantity of mobile zinc forms was assessed in medium silt loam (Soil III). Following the application of organic materials, irrespective of the soil, the content of zinc mobile forms was significantly smaller than the content determined in the soil from treatments fertilized with mineral salts.

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