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Content of heavy metals in maize cultivated in soil amended with sewage sludge and its mixtures with peat

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A b s t r a c t. The experiment was aimed at an assessment of the effect of sewage sludge and its mixtures with peat on the content and uptake of chromium, copper, lead and nickel by maize cultivated in soils of different grain size composition. The concentrations of studied elements were assessed after plant material mineralization using the ICP-AES method. Fertilization with the sewage sludge, its mixtures with peat and with farmyard manure allowed to obtain significantly larger yields than on treatments fertilized exclusively with mineral salts. The experiment results indicate that the soil had a greater effect on trace element concentrations than the applied fertilization. Mean weighted average content of the analyzed elements in maize aboveground parts from the treatments where sewage sludge mixtures with peat were applied was generally smaller in comparison with the content determined in biomass from the treatments where only the sludge was used.

K e y w o r d s: maize, heavy metals, accumulation, sewage sludge

INTRODUCTION

Assessment of biological biomass in view of its fodder usability comprises not only determining the content of elements crucial for animal nutrition but also that of other ones which may be harmful. Absorption of mineral components, including heavy metals, by plants from the soil is conditioned by the physiological requirement for some of them, but may also result from environmental pollution or from the application of natural or artificial fertilization (Gondek, 2008a; Singh and Agrawal, 2007; Wiater and Furczak, 2004). Although the share of natural and artificial fertilizers in fulfilling plant nutritional needs is small and highly insufficient to generate the maximum crop yields possible to achieve under specific conditions, these fertilizers greatly increase the fertilizer effectiveness owing to their positive effect on the physical, chemical and biological soil properties (Furczak and Joniec, 2007; Gondek, 2008b; Hanč *et al*., 2008; Jezierska-Tys and Frąc, 2008).

In view of insufficient farmyard production and only just developing compost manufacturing there is a potential to use other materials, rich in organic matter and nutrients, for soil and plant fertilization, such as municipal sewage sludge. However, direct application of these materials to soils is limited by their physical, chemical and biological properties. Therefore, they should be subjected to a treatment, including composting with other materials, which would improve their chemical parameters and positively affect their physical properties.

The experiments were aimed at assessment of the effect of sewage sludge and its mixtures with peat on the content and uptake of chromium, copper, lead and nickel by maize cultivated in soils with different grain size composition.

MATERIAL AND METHODS

The effect of fertilization with sewage sludge and its mixtures with peat on the contents of chromium, copper, lead and nickel in maize was assessed in a two-factor (factors: soil and fertilization) three-year (2003-2005) pot experiment. The investigations were conducted on three soils and the experimental design, identical for each soil, comprized 7 treatments in four replications: without fertilization – 0; fertilization with chemically pure salts – NPK; farmyard manure – FYM; sewage sludge A – SSA; sewage sludge A mixture with peat – SSA + P; sewage sludge B – SSB; sewage sludge B mixture with peat – SSB + P. The experiment was conducted on the following soil material:

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weakly loamy sand (GI), sandy silt loam (GII) and medium silt loam (GIII) collected from the arable layer (0-20 cm) of arable fields in the vicinity of Cracow. The sewage sludges originated from two different mechanical-biological municipal sewage treatment plants. Mixtures of sewage sludge with peat were prepared in 1:1 weight ratio in conversion to the material dry matter. Apart from the treatment where mineral salt fertilization was applied, farmyard manure treatment was included in the experimental design as the reference point for the compared features. Peat with 408 g kg^{-1}dry matter content revealed the contents of 88 g ash, 34.4 g N , 0.91 g P , 1.14 g K kg^{-1} d.m. and 1.22 mg Cr, 4.64 mg Cu; 7.90 mg Pb and 1.20 mg Ni kg^{-1} d.m. The characteristics of chemical composition of the other organic materials and soil material (values per dry matter assessed at 105°C) are presented in Tables 1 and 2.

PVC pots used for the experiment contained 5.50 kg of air-dried soil material. Before the experiment outset the soils were gradually moistened, reaching a mixture corresponding to 30% of the maximum water capacity. After moistening, the sandy silt loam (GII) and medium silt loam (GIII) were limed to create conditions optimal for plant growth and development. The measurements were conducted separately in each pot. Liming was performed with a dose of chemically pure CaO determined on the basis of the soil hydrolytic acidity. Subsequently, the soils were left for 4 weeks and the water losses were supplemented periodically. Afterwards organic fertilization was introduced in the amount of 1.20 g N pot^{-1}. Phosphorus and potassium were supplemented with chemically pure salt solutions [P-$Ca(H_2PO_4)_2$ H_2O and K-KCl] to equalize the amounts of these elements introduced with the organic materials. Doses of nitrogen, phosphorus and potassium, identical to those applied in the treatments where organic materials were used, were supplied to the mineral (NPK) treatment. Doses of N, P and K were, respectively: 1.20 g N pot^{-1}as NH_4NO_3, 1.26 g P pot^{-1}as $Ca(H_2PO_4)_2$ H_2O and 1.48 g K pot^{-1}as KCl. Considering the residual fertilizer effect of the organic materials and the soil abundance in bioavailable phosphorus and potassium, fertilizer components were applied in amounts corresponding to 0.80 g N; 0.2 g P and 1.40 g pot^{-1} $year^{-1}$ as chemically pure salts, in the second and third year of the research.

Each year of the experiment maize, cv. San (FAO 240), was cultivated and 5 plants per pot were left. The maize (designed for green fodder) was always harvested at 7-9 leaves stage. The plant vegetation period in the consecutive years was 47 days in the first year, 66 days in the second and 54 days in the third. The plants were watered with distilled water throughout the experiment to 50% of the maximum soil water capacity.

After the harvest the plants were dried at 70°C to constant weight and the yield of aboveground parts and root dry matter was determined. Subsequently, the dry biomass was crushed in a laboratory mill and mineralized in a muffle furnace (at 450°C for 5 h). The remains were dissolved in

T a b l e 1. Chemical composition of materials used in the experiment

Properties	FYM	SSA	SSA+P	SSB	SSB+P
Dry matter content*	189	310	343	418	372
Organic matter content**	679	353	652	552	771
pH_{H_2O}	6.22	6.12	5.57	5.73	5.20
Total forms					
N**	21.6	17.0	24.7	37.4	35.1
S^{++}	7.24	8.81	6.23	14.62	7.85
P^{++}	22.60	5.48	3.00	19.32	7.64
K^{++}	26.69	2.71	1.88	2.81	1.64
Cr***	6.07	19.74	10.25	37.88	17.47
Cu^{+++}	338.0	78.3	40.6	119.4	51.8
Pb^{+++}	3.99	65.9	38.2	29.4	17.5
Ni^{+++}	11.74	13.32	7.14	25.36	12.07

*g kg^{-1}, **g kg^{-1} d.m., ***mg kg^{-1} d.m.

T a b l e 2. Some properties of soils before the establishment of the experiment

Properties		Soil		
		GI	GII	GIII
Grain size composition (%, dia in mm)	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	5.69	5.30
Hydrolytic acidity	mmol(+) kg^{-1} d.m.	11.2	23.4	33.2
Sum of alkaline cation		39.9	86.8	128.4
Total N	(g kg^{-1} d.m.)	0.96	1.25	1.72
Organic C		9.37	13.36	17.68
Total S		0.16	0.28	0.32
Total forms (mg kg^{-1} d.m.)				
Cr		5.93	19.20	17.28
Cu		4.00	6.55	7.10
Pb		29.8	30.3	36.0
Ni		4.15	9.50	10.38

diluted nitric acid 1:2 (v/v) (Ostrowska *et al*., 1991). The concentrations of the analyzed elements were assessed in the solutions using the ICP-AES method. A reference sample of plant material (NCS DC73448 China National Analysis Center for Iron and Steel) was added to the analyzed series.

The results of the analyses were verified statistically according to a fixed model where fertilization or the soil was the factor. Statistical computations comprized two factor ANOVA (factors: soil and fertilization) and the significance of differences was estimated at significance level $\alpha < 0.01$ using Tukey test.

RESULTS AND DISCUSSION

Organic materials used for the experiment differed in their chemical composition, including the content of the analyzed elements which in the sewage sludges, except copper, was higher than that determined in farmyard manure (Table 1). A peat supplement to the sewage sludge diminished the content of most elements in the mixture in comparison with the element concentrations in the sludges.
The soil material used for the investigations belonged to various granulometric groups and differed in chemical properties, including total content of chromium, copper, lead and nickel (Table 2).

ANOVA confirmed a significant effect of fertilization with organic materials on maize biomass yield (Fig. 1). Fertilization with sewage sludges or their mixtures with peat, as well as the farmyard manure treatment, allowed to obtain markedly higher yields than harvested on treatments with solely mineral salts. Greater yield was produced when sewage sludge mixtures with peat were used than sewage sludge alone (except SSA+P mixture on sandy silt loam GII). Fertilizer efficiency of organic materials is determined mainly by their nitrogen concentrations, particularly its mineral forms. On the other hand, disturbed relations between the other nutrients may directly affect mineral economy in plants and condition the biological value of the obtained yield. Over the three-year period of the experiment, applied fertilization with organic materials gave better results, expressed by the amount of maize biomass yields, than fertilization with mineral salts. This effect cannot be fully attributed to the activity of the applied sewage sludges or their mixtures with peat. It resulted from the residual effect of the organic materials and supplementary fertilization with mineral salts applied in the second and third years of the experiment. The factor determining plant yielding might be other elements, such as sulphur, magnesium or microelements supplied to the soil with organic materials, but whose amounts were not balanced. Application of natural or artificial fertilizers not always leads to an increase in crop yields under the influence of so-called residual effect. Drab and Derengowska (2003) proved a positive influence of sewage sludge fertilization on crop yielding, at the same time demonstrating that crop yield, irrespective of the soil, was conditioned by the amount of sewage sludge dose. Beside

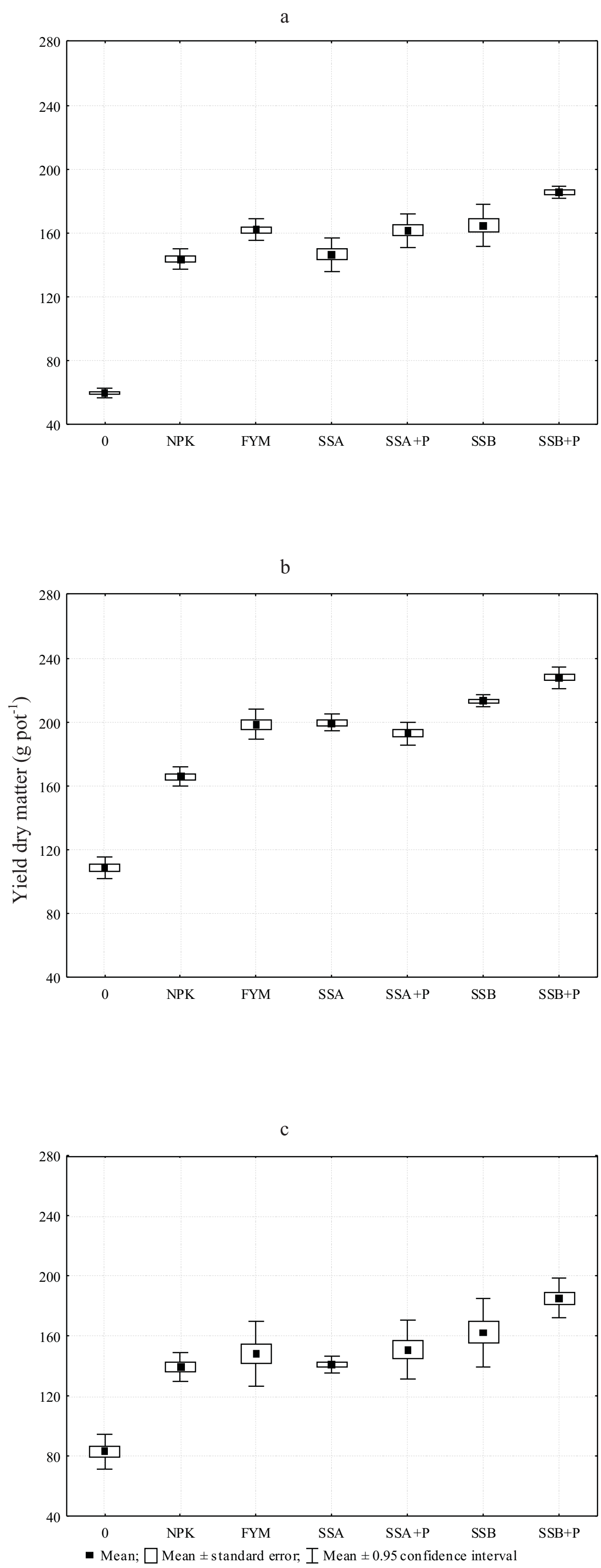

Fig. 1. Total yield (from three years) of maize biomass: a – GI, b – GII, c – GIII.

sewage sludge dose, the date of fertilization with these materials may be equally important, as well as heavy metal concentrations and soil properties, mainly pH (Sanders *et al*., 2006). On the other hand, Wiater *et al*. (2004) 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.

Due to potential destination for animal feeds, the content of analyzed heavy metals was presented for maize aboveground parts, whereas the taken up element quantities were computed for the aboveground parts and roots and presented as the total uptake.

Chromium concentrations in maize aboveground parts generally did not differ between the biomass from an individual treatment within the soils (Fig. 2). Bigger differences in chromium content were detected between maize aboveground parts biomass from the individual soil treatments fertilized identically. The greatest chromium quantities, no matter which fertilization was used, were assessed in the aboveground parts of plants cultivated in weakly loamy sand GI. Chromium content determined in the analyzed biomass was within the range of normal content (Gorlach and Gambuś, 2000). No significant effect of peat supplement to sewage sludge on chromium content in maize aboveground parts was detected in comparison with sewage sludge used separately.

Total (for three years) amounts of chromium absorbed by maize (aboveground parts and roots) were diversified mainly depending on the soil, which was connected with the yield and chromium content in the biomass (Table 3). Irrespective of the applied fertilization maize took up the greatest chromium quantities (beside the plants cultivated on the treatment receiving mineral fertilizers) when cultivated in medium silt loam GIII. In comparison with the chromium amounts absorbed by maize on mineral (NPK) treatment and irrespective of the soil, the plants fertilized with farmyard manure and organic materials took up greater amounts of this element.

Applied fertilization notably diversified copper content in maize aboveground parts. The greatest quantities of this element, no matter which fertilization was applied, were assessed in maize aboveground parts cultivated in medium silt loam GIII (Fig. 3). The assessment of maize aboveground parts in view of its fodder quality revealed that copper quantities were smaller than 6 mg kg^{-1} of dry mass (Gorlach, 1991), irrespective of the soil and fertilization, therefore they did not meet the nutritional requirements for animals. Maize aboveground parts from treatments fertilized with sewage sludge mixtures with peat contained less copper in comparison with the plant aboveground parts fertilized only with sewage sludge. No significantly higher content of copper was found in the aboveground parts biomass of plants fertilized with farmyard manure, which contained the biggest quantities of this element.

Total (for three years) amounts of copper taken up by maize (aboveground parts and roots) were diversified mainly between the soils (Table 4). Significantly the biggest amounts

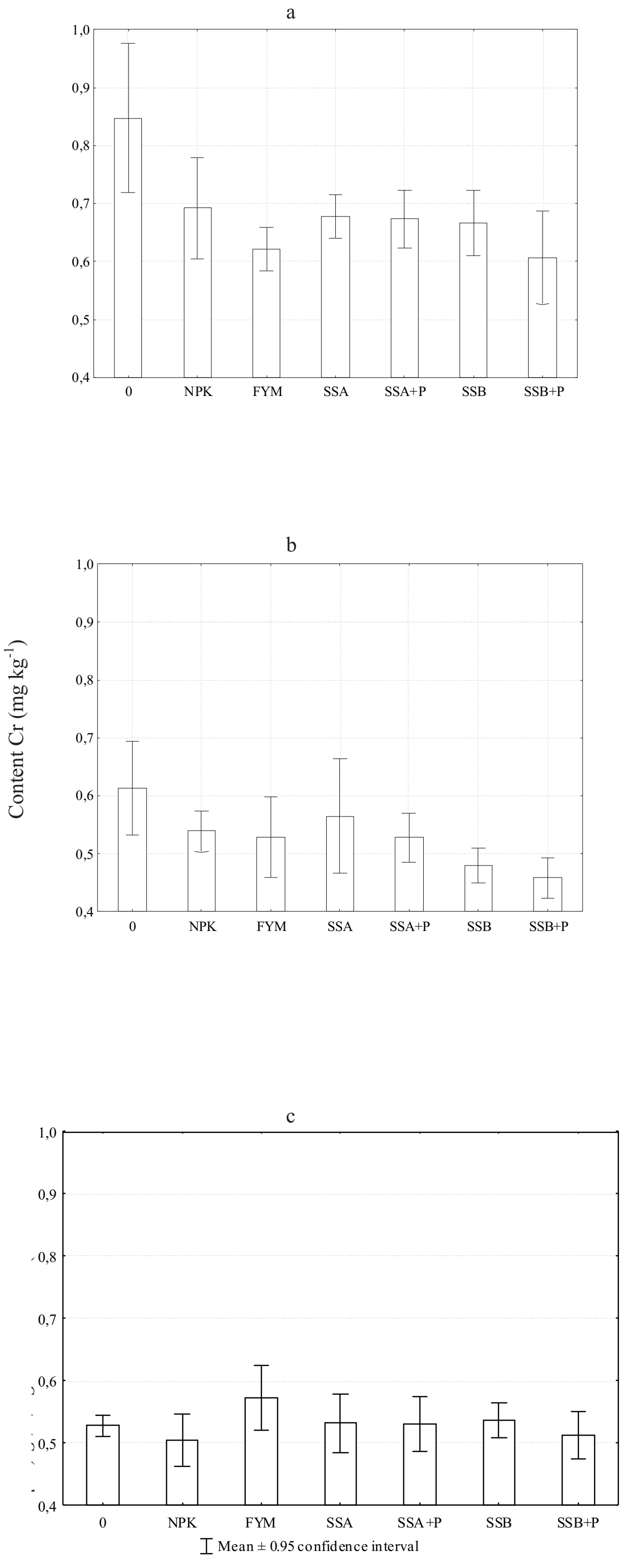

Fig. 2. Mean weighted content of chromium in aboveground parts of maize: a – GI, b – GII, c – GIII.

T a b l e 3. Total uptake (from three years) of chromium with maize biomass (aboveground parts and roots)

Treatment	Soil		
	GI	GII	GIII
	mg pot^{-1}		
0	0.074a	0.124b	0.135bcd
NPK	0.132bc	0.178defg	0.156bcde
FYM	0.140bcd	0.186efgh	0.216ghi
SSA	0.130bc	0.179defg	0.205fghi
SSA+P	0.136bcd	0.170cdef	0.207fghi
SSB	0.146bcde	0.209fghi	0.233ij
SSB+P	0.157bcde	0.228hij	0.267j

Means followed by the same letters in columns do not differ significantly at $p < 0.01$ according to the Tukey test; factors: fertilization × soil.

T a b l e 4. Total uptake (from three years) of copper with maize biomass (aboveground parts and roots)

Treatment	Soil		
	GI	GII	GIII
	mg pot^{-1}		
0	0.135a	0.250ab	0.304bc
NPK	0.319bcd	0.366bcdef	0.409cdefg
FYM	0.470fghi	0.500ghi	0.577i
SSA	0.358bcdef	0.411cdefgh	0.501ghi
SSA+P	0.324bcde	0.450efghi	0.452efghi
SSB	0.406cdefg	0.442defgh	0.539hi
SSB+P	0.355bcdef	0.414cdefgh	0.523ghi

Explanations as in Table 3.

of this element were absorbed by maize cultivated in medium silt loam GIII, irrespective of applied fertilization. Treatment with farmyard manure and with the other organic materials did not cause any increase in copper amount absorbed by maize.

Generally, fertilization did not diversify significantly nickel content in maize aboveground parts in the soils (Fig. 4). Bigger differences in nickel concentrations were assessed between maize aboveground parts biomass from individual soils of treatments receiving identical fertilizers. The smallest amounts of nickel, no matter which fertilization was used, were determined in maize aboveground parts cultivated in medium silt loam GIII. Nickel concentrations determined in the analyzed biomass ranged within the normal contents and proved only trace values considering fodder assessment (Gorlach and Gambuś, 2000). No significant effect of peat

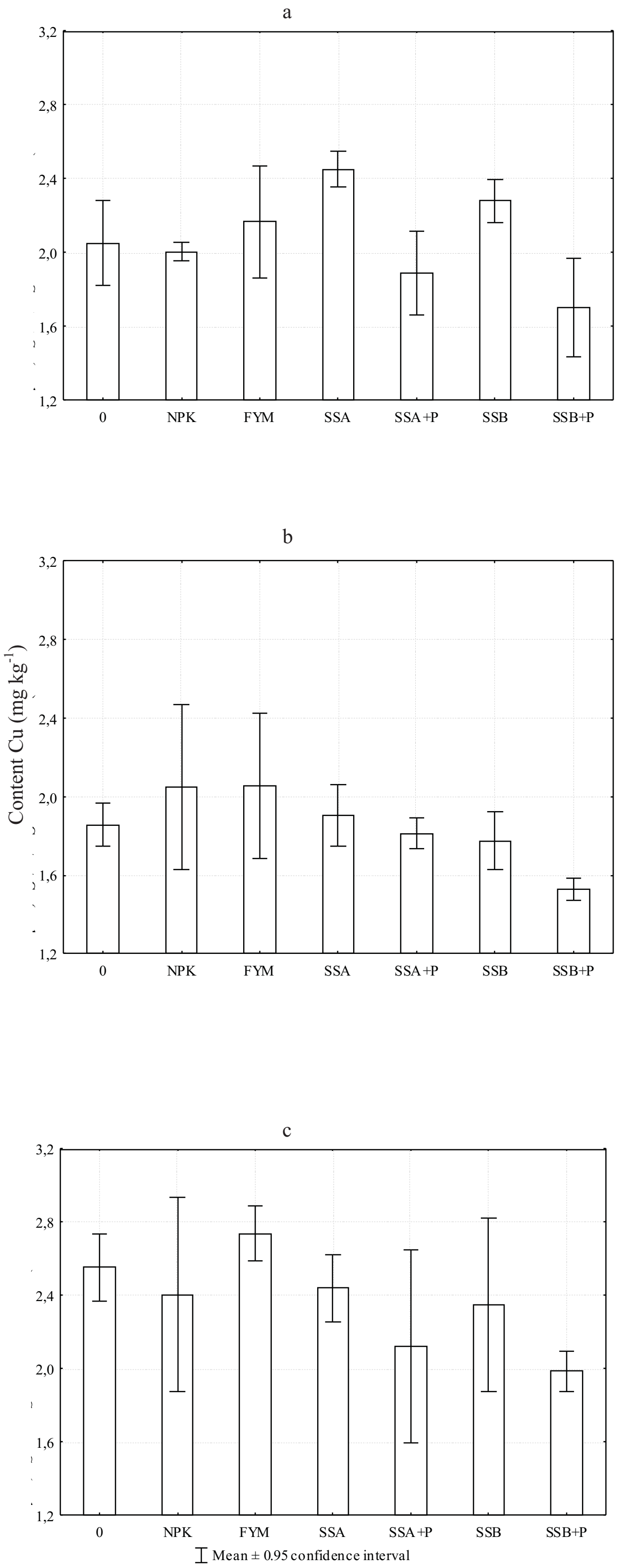

Fig. 3. Mean weighted content of copper in aboveground parts of maize: a – GI, b – GII, c – GIII.

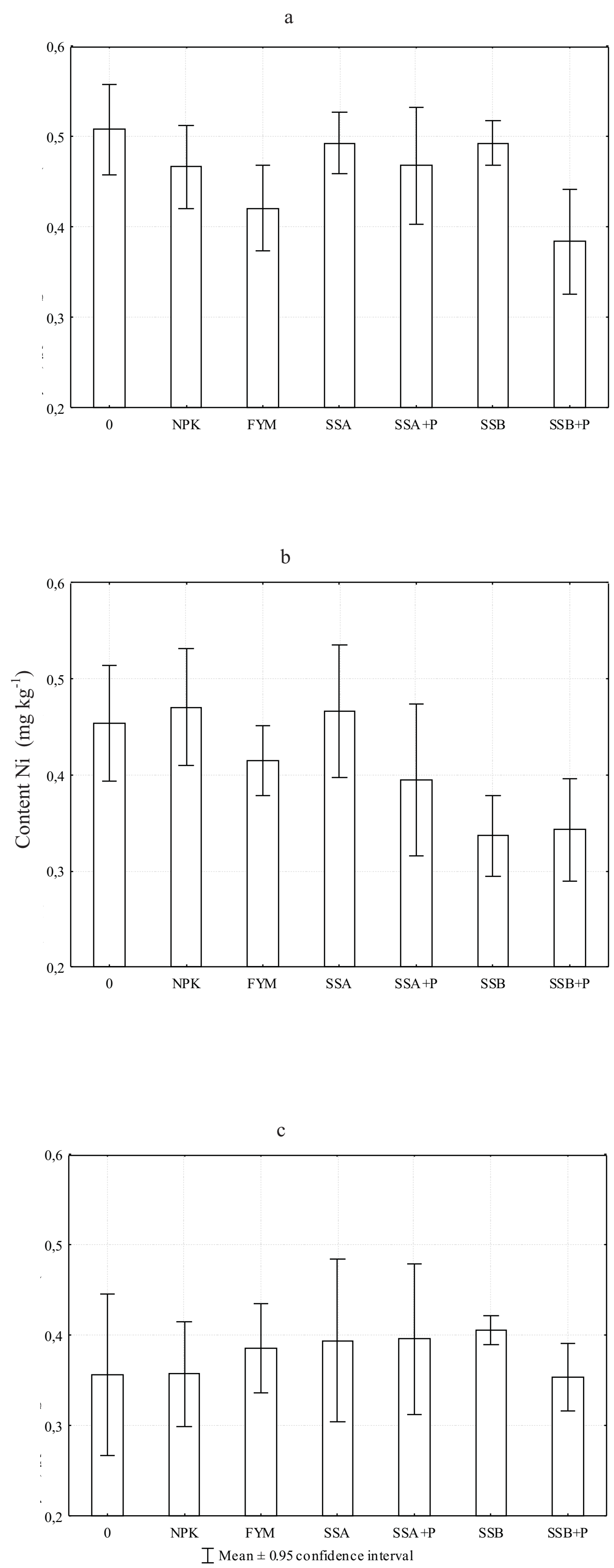

Fig. 4. Mean weighted content of nickel in aboveground parts of maize: a – GI, b – GII, c – GIII.

supplement to sewage sludge was noticed on nickel content in maize aboveground parts as compared with fertilization with sewage sludge alone.

Total (for three years) nickel quantities absorbed by maize (aboveground parts and roots) were diversified mainly with regard to on the soil agronomic category, and were affected by the crop yield and nickel concentrations in the yield (Table 5). No matter which fertilization was applied, notably the smallest amounts of nickel were taken up by maize cultivated in weakly loamy sand GI. In comparison with nickel amounts absorbed by maize on farmyard manure treatment and irrespective of the soil, plants fertilized with sewage sludge B (SSB) and its mixture with peat (SSB+P) took up greater amounts of this element.

Lead concentrations in maize aboveground parts did not differ significantly either between soils or fertilization treatments within the soils (Fig. 5). The biggest quantities of this element, irrespective of the soil, were assessed in maize aboveground parts from the treatments without fertilization. Lead concentrations determined in maize aboveground parts were visibly below the lower limit of this element concentrations permissible in fodders (Gorlach and Gambuś, 2000). The biomass of maize saboveground parts from treatments fertilized with sewage sludge mixtures with peat was characterized by comparable or lower lead content in relation to the aboveground parts of plants fertilized only with sewage sludge. No marked difference was registered in lead content in maize aboveground parts biomass fertilized with farmyard manure and sewage sludge.

The amounts of lead absorbed by maize (aboveground parts and roots) generally did not differ markedly either with relation to the soil or to the applied fertilization (Table 6).

According to Gorlach (1991), either excess or deficiency of trace elements is dangerous for animals. The content and availability of trace elements in soils are conditioned by many factors including, among others, the soil pH, organic

T a b l e 5. Total (from three years) uptake of nickel with maize biomass (aboveground parts and roots)

Treatment	Soil		
	GI	GII	GIII
	Ni (mg pot^{-1})		
0	0.045a	0.089b	0.086b
NPK	0.095b	0.160ef	0.134cde
FYM	0.104bc	0.152ef	0.150ef
SSA	0.100b	0.151ef	0.150ef
SSA+P	0.102b	0.136de	0.152ef
SSB	0.116bcd	0.162ef	0.175fg
SSB+P	0.114bcd	0.180fg	0.193g

Explanations as in Table 3.

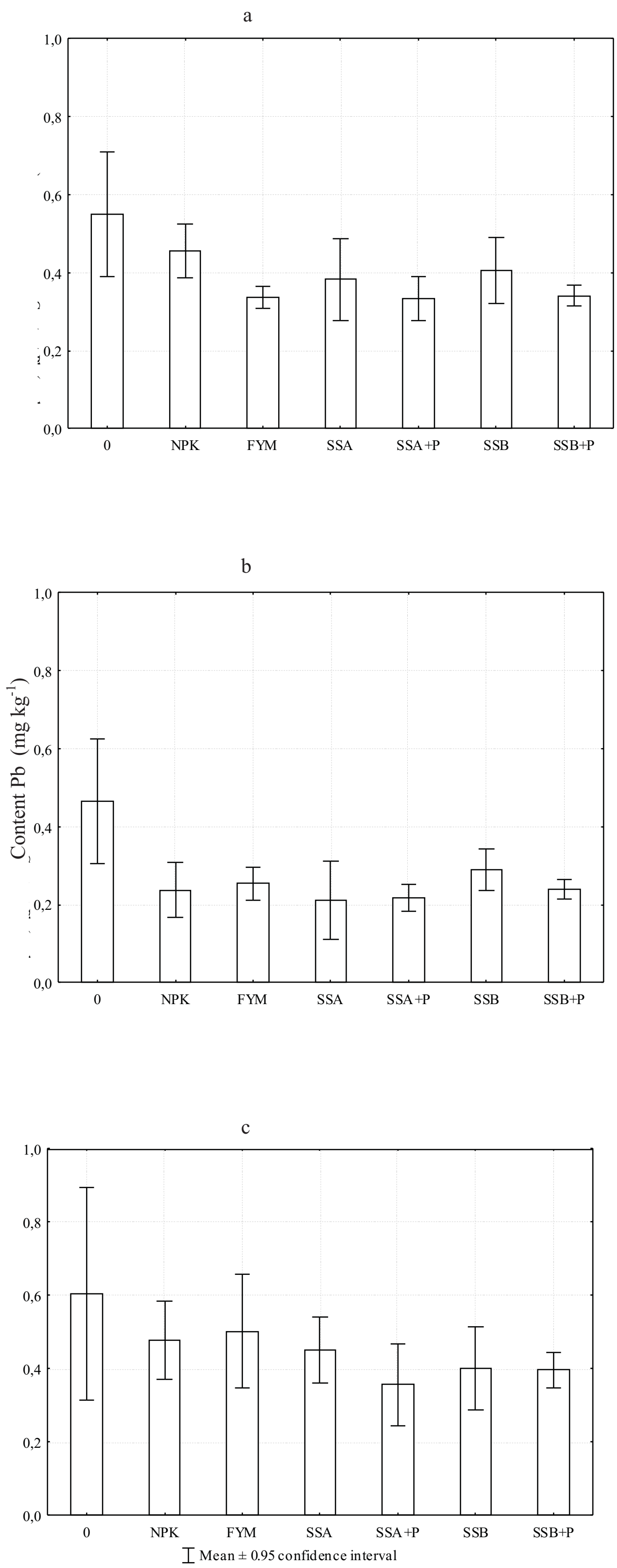

Fig. 5. Mean weighted content of lead in aboveground parts of maizee: a – GI, b – GII, c – GIII.

T a b l e 6. Total uptake (from three years) of lead with maize biomass (aboveground parts and roots)

Treatment	Soil		
	GI	GII	GIII
	mg pot^{-1}		
0	0.068a	0.079abc	0.112cdefg
NPK	0.132fgh	0.069ab	0.104abcdef
FYM	0.123defgh	0.095abcdef	0.134fgh
SSA	0.115cdefg	0.088abcde	0.126efgh
SSA+P	0.110bcdefg	0.083abcd	0.118cdefg
SSB	0.125defgh	0.131fgh	0.131fgh
SSB+P	0.146gh	0.127efgh	0.164h

Explanations as in Table 3.

matter content, sorption capacity, but also by plant ability for their uptake (Basta *et al*., 2005; Gorlach and Gambuś, 2000). Obligatory control of trace element content concentrations in plant biomass becomes particularly important when plants are fertilized with waste organic materials. This results mainly from these materials abundance in trace elements, although as such the element content in organic materials does not determine the rate of their migration to the soil solution.

Research conducted by Czekała (1997) shows that plant response to chromium depends to a considerable degree on the level of the element oxidation, the fact having also been indicated by Filipek-Mazur and Gondek (2000). The effect of hexa-valent chromium on plant is limited by the presence of organic substance and calcium in soil. Diversified effect of three- and hexa-valent chromium on plants is also caused by different biological properties of both element forms (Czekała, 1997). In sewage sludge chromium occurs mainly in less bioavailable combinations (Gondek and Filipek-Mazur, 2003). Moreover, after introduction into the soil, chromium becomes oxidized, which significantly limits its bioavailability. Chromium occurring on +3 oxidization level reveals considerable affinity to form complexes and chelates with cell membrane components. It limits chromium penetration into the cell and translocation to the aboveground organs. In the presented experiments, but also in research conducted by other authors (Singh and Agrawal, 2007), chromium was accumulated primarily in plant root system.

Copper content in the investigated plant material proved deficient in view of fodder quality (Gorlach, 1991). Copper was retained mainly in maize root system. The relatively small amount of this element in maize aboveground parts biomass might also indirectly determine the crop yield, the more so as copper participates in specific metabolic processes. As results from the research conducted, a relatively big amount of copper in farmyard manure was reflected in higher concentrations of this metal in plant root system, which indicates the existence of efficient mechanisms limiting copper transport to plant aboveground parts. Also Sanders *et al*. (2006) demonstrated a significant dependence between the content of copper forms extracted with calcium chloride, EDTA and DTPA from soil fertilized with sewage sludge and copper concentrations in plant roots.

Nickel, although it does not fulfil any metabolic functions, is easily absorbed by plants. The element is taken up generally proportionately to its soil concentrations, however the intensity of nickel absorption depends to the same extent on plant properties as on the soil properties (Sengar *et al*., 2008). According to Kuziemska and Kalembasa (1997), also the dose and content of nickel in sewage sludge do not have any marked influence on this element content in plants. The results of the Author's own investigations show that soil had a bigger influence on nickel concentrations in maize aboveground parts yield than the fertilization applied, which might have resulted from diversified properties of the soil materials used in the experiment, mainly the content of organic matter and the soil pH.

Lead uptake by plants is a passive process, therefore lead content in plant biomass depends on its concentrations in the substratum. Lead, like chromium and copper, became arrested in maize roots, which might have resulted from forming poorly soluble forms of this element in this plant part. Dudka *et al*. (1991), while investigating trace element contents in oat and maize fertilized with municipal- industrial sewage sludge, found that lead concentrations in these plants did not differ notably under the influence of fertilization with these materials, however, maize contained more lead than oat did.

CONCLUSIONS

1. Fertilization with sewage sludges, mixtures of sewage sludges and peat, and farmyard manure treatment allowed to obtain significantly bigger yields than those harvested on treatments fertilized solely with mineral salts.

2. The research results indicate that the soil had a more serious influence on trace element concentrations than the fertilization applied.

3. Mean weighted content of the analyzed elements in maize aboveground parts from the treatments where mixtures of sewage sludges with peat were used was generally lower than the content assessed in the biomass from the treatments where the sludges were used separately.

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