
CONTENT OF AVAILABLE Cu, Zn AND Mn IN SOIL AMENDED WITH MUNICIPAL SEWAGE SLUDGE

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Abstract

Municipal sewage sludge is an unavoidable byproduct of the contemporary live and business activities of people. Proper handling and utilization of sewage sludge continue to create serious problems in Poland although this waste product is a source of both organic carbon and macronutrients. The present study has been carried out in order to assess the influence of municipal sewage sludge on the content of available forms of Cu, Zn and Mn in soil. A microplot experiment set up according to the random sub-block method was conducted in 2005-2008. The experiment was established on anthropogenic, humic urban soil developed from loamy sand rich in phosphorus and magnesium, but poor in potassium, and alkaline in reaction. The design of the trials comprised 5 doses of municipal sewage sludge from the Lyna Municipal Wastewater Treatment Plant in Olsztyn: 0, 70, 140, 210 and 280 Mg ha⁻¹ of fresh matter. The tests have demonstrated that a dose of sewage sludge had a significant effect on the content of available forms of Cu, Zn and Mn in soil. In alkaline soil, however, the observed increase in the content of available forms of Cu, Zn and Mn was not hazardous to the environment, but could improve the plant nutrition with these elements. It is highly probable that the availability of Cu may increase in the second and third year after the application of sewage sludge. The accumulation of soluble Zn in soil started to decrease in the second year, but did not become significantly limited until four years after sewage sludge application. Sewage sludge raised the amount of soluble manganese in soil during the first three years, but in the final year of the experiment the quantity of soluble Mn in soil did not undergo any significant fluctuations.

Key words: sewage sludge, available forms of Cu, Zn and Mn.

ZAWARTOŚĆ PRZYSWAJALNYCH FORM Cu, Zn I Mn W GLEBIE UŻYŻNIONEJ KOMUNALNYM OSADYM ŚCIEKOWYM

Komunalne osady ściekowe są nieodzownym produktem działalności bytowo-gospodarczej współczesnego człowieka, a ich zagospodarowanie to wciąż poważny problem w Polsce. Odpad ten jest nie tylko źródłem węgla organicznego i makroelementów, ale także mikroelementów. Celem badań była ocena wpływu komunalnego osadu ściekowego na zawartość przyswajalnych form Cu, Zn i Mn w glebie. Mikropletkowe doświadczenie prowadzono w latach 2005-2008 metodą losowanych podbłoków na glebie antropogenicznej urbanoziemnej próchnicznej wytworzonej z piasku gliniastego o wysokiej zawartości fosforu i magnezu oraz niskiej potasu i o odczynie zasadowym. Schemat doświadczenia obejmował 5 dawek komunalnego osadu ściekowego z Miejskiej Oczyszczalni Ścieków „Lyna” w Olsztynie: 0, 70, 140, 210 i 280 Mg ha⁻¹ świeżej masy. W badaniach udowodniono istotny wpływ dawki osadu ściekowego na zawartość przyswajalnych form miedzi, cynku i manganu w glebie. W warunkach gleby zasadowej wzrost zawartości przyswajalnych form Cu, Zn i Mn w glebie nie stwarzał zagrożenia dla środowiska, a jedynie mógł poprawić odżywienie roślin tymi mikroelementami. Z dużym prawdopodobieństwem można oczekiwać wzrostu dostępności Cu przyswajalnej w glebie w 2. i 3. roku po zastosowaniu osadu ściekowego. Nagromadzenie rozpuszczalnego Zn w glebie zmniejszyło się od 2. roku, ale istotne ograniczenie wystąpiło dopiero w 4. roku po zastosowaniu osadu ściekowego. Osad ściekowy miał wpływ na zwiększenie ilości rozpuszczalnego manganu w glebie w pierwszych trzech latach, a w ostatnim roku ilość rozpuszczalnego manganu w glebie nie uległa już znaczącym zmianom.

Słowa kluczowe: osad ściekowy, przyswajalne formy Cu, Zn i Mn.

INTRODUCTION

Waste containing organic matter and biogenic elements should be managed – as long as possible – so as to return it to the environment (SRREN et al. 2003, SPEIR et al. 2003, CASADO-VELA et al. 2006, SPYCHAJ-FABISIAK et al. 2007, CZEKAŁA 2009, MAZUR, SIENKIEWICZ 2009). In the contemporary world, municipal sewage sludge is an unavoidable byproduct of our live and business activities, but its proper handling and utilization continue to create problems in Poland. It is the organic carbon contained in sewage sludge that draws most attention as an element which should be reintroduced into the soil-plant cycle. The positive effect of sewage sludge on soil properties has been evidenced in numerous papers by Polish and foreign researchers (STĘPIEŃ et al. 2000, JAKUBUS 2006, SADEJ et al. 2007, DELIBACAK ET AL. 2009, SINGH and AGRAWAL 2008, KLASA et al. 2007). Municipal sewage sludge is also a source of micronutrients (KALEMBASA et al. 1999, SPIAK, KULCZYCKI 2004, IŻEWSKA et al. 2006). However, special care should be taken with respect to micronutrients so as not to introduce excessive amounts of these elements, which could have an adverse effect on the environment, especially when soil is acidic (MERCİK et al. 2003, PASCUAL et al. 2004, DELIBACAK et al. 2009). The purpose of this work has been to evaluate the effect of municipal sewage sludge on the content of available forms of Cu, Zn and Mn in soil.

METHODS

A microplot experiment (1m x 1m) was carried out in 2005-2008. The experiment was set up on anthropogenic, humic urban soil developed from loamy sand in a random sub-block design. Prior to the experiment, the soil had a high content of phosphorus and magnesium, a low level of potassium and alkaline reaction. The design of the experiment comprised 5 doses of municipal sewage sludge from the Łyna Municipal Wastewater Treatment Plant in Olsztyn: 0, 70, 140, 210 and 280 Mg ha⁻¹ of fresh matter. Municipal sewage sludge was applied once. The chemical properties of the sludge are presented in Table 1.

Sewage sludge was mixed with soil to the depth of about 10 cm. Once fertilized with municipal sewage sludge, the soil was sown with mixes of lawn grasses. The available forms of Cu, Zn and Mn after extraction with 1 mol HCl dm⁻³ were determined with the atomic absorption spectrophotometric method. The results were submitted to statistical analysis using the software programme Statistica (version 9.0) by SatSoft, Inc. 2009.

Table 1

Chemical properties of sewage sludge

Determination		Unit	Value
pH in H ₂ O		-	8.43
Corg.			186.53
Total elements	Nog.	g kg ⁻¹ d.m.	33.30
	P		14.40
	K		1.20
	Mg		5.00
Micronutrients	Ca	mg kg ⁻¹ d.m.	27.90
	Cu		251.00
	Zn		1340.00
	Mn		320.00

RESULTS

The content of available copper in soil ranged from 4.65 to 5.89 mg kg⁻¹, which should be regarded as rather small variation. The tested doses of sewage sludge were evidenced to have had a significant effect on the content of copper in soil (Table 2). This effect was also demonstrated by the

Table 2

Content of available copper in soil (mg kg^{-1})

Year	Dose of sewage sludge (Mg ha^{-1})					Mean
	0	70	140	210	280	
2005	4.65	5.41	5.58	5.71	5.89	5.45
2006	4.70	5.60	5.60	5.82	5.78	5.50
2007	4.67	5.55	5.64	5.78	5.82	5.49
2008	4.73	5.46	5.63	5.68	5.77	5.45
Mean	4.69	5.51	5.61	5.75	5.82	

LSD_{0.05} year – n.s., dose – 0.09, year \times dose – n.s.

analysis of correlation and regression (Figure 1). It is worth noticing that the soil pH in $1 \text{ mol HCl dm}^{-3}$ varied within a narrow range (6.50-7.14). Under such condition (no acidification), the solubility of Cu was low. Analogously to our study, DELIBACAK et al. (2009) found out an increase in the content of soluble copper in soil caused by increasing doses of sewage sludge introduced to soil. In contrast, PASCUAL et al. (2004) showed depressed concentrations of available forms of Cu in soil under the influence of a higher dose of sewage sludge (140 Mg ha^{-1}). Such discrepancies, reported by different authors, in the effect of sewage sludge on the content of Cu in soil may be substantiated, for example, by different concentrations of this metal in sewage sludge. On the other hand, sorptive properties of soil, and especially the content of organic matter, can affect the availability of copper in soil.

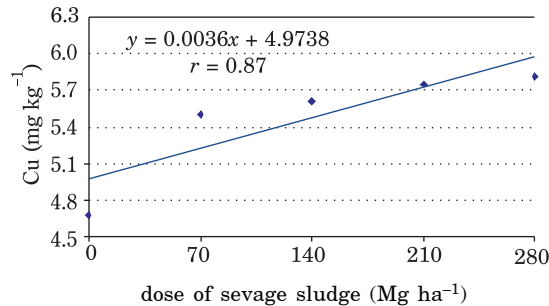


Fig. 1. Changes in the content of available copper in soil depending on the dose of sewage sludge

It is highly probable that the accessibility of available copper in soil can increase in the second and third year after the application of sewage sludge. This tendency can be explained by a larger influx of copper originating from mineralization of organic matter added to soil together with sewage sludge (Figure 2).

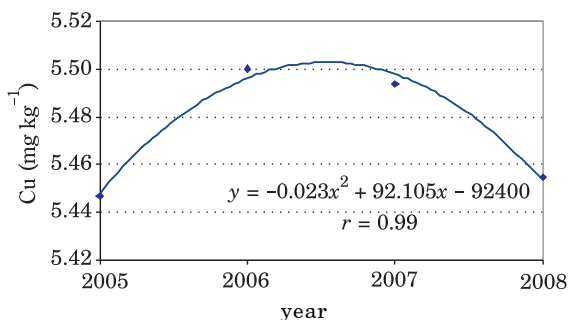


Fig. 2. Changes in the content of available copper in soil in the following years of the experiment

The content of available zinc in soil changed significantly in the subsequent years of the research (Table 3). A non-significant increase occurred in the second year compared to the first one. In the subsequent years, the accumulation of available Zn in soil tended to decrease but its significant limitation did not occur until 2008 (Figure 3). Contrary results were obtained by IŻEWSKA et al. (2006), who found a significant rise in the content of soluble zinc in soil three years after the soil amendment with sewage sludge. In turn, PATORCZYK-PYTLIK (2004) reported that even six years after application of sewage sludge to soil labile forms of zinc constituted 29% of the total content of zinc in soil.

Table 3

Content of available zinc in soil (mg kg⁻¹)

Year	Dose of sewage sludge (Mg ha ⁻¹)					Mean
	0	70	140	210	280	
2005	67.31	76.33	83.45	86.37	95.01	81.69
2006	66.65	77.55	86.05	90.38	91.85	82.50
2007	68.57	74.83	82.94	88.64	92.16	81.43
2008	68.70	72.28	80.29	87.97	92.03	80.25
Mean	67.81	75.25	83.18	88.34	94.90	67.81

LSD_{0.05} year – n.s., dose – 1.44, year x dose – 2.88

The zinc introduced to soil with sewage sludge was relatively quickly converted into more easily assimilable forms but then, due to the processes occurring in soil, it underwent retardation. The conditions present in our experiment, i.e. a high content of organic matter, high soil abundance in available phosphorus and alkaline soil reaction, did not favour the appearance of excessive amounts of Zn available forms in soil. Similar results were achieved by PATORCZYK-PYTLIK (2004), who noticed a considerable loss of the available forms of zinc in each year of a three-year pot experiment.

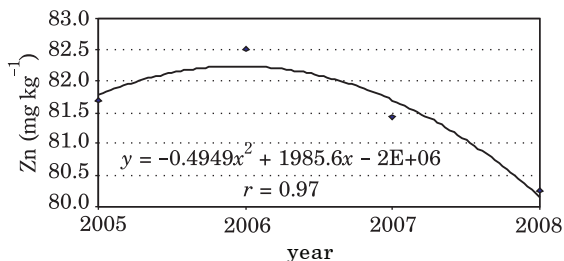


Fig. 3. Changes in the content of available zinc in soil in the following years of the experiment

As the dose of sewage sludge added to soil increased, so did the content of soluble zinc in soil (Table 3, Figure 4). The highest dose of sewage sludge (280 Mg ha⁻¹) caused an over 36% increase in the concentration of this element in soil compared to the control soil.

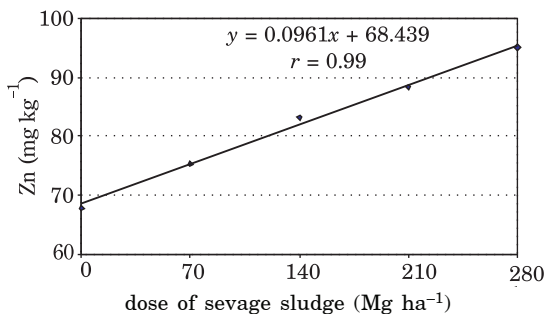


Fig. 4. Changes in the content of available zinc in soil depending on the dose of sewage sludge

The results congruent with ours were reported by DELIBACAKA et al. (2009), who also demonstrated higher concentrations of zinc in soil induced by higher doses of sewage sludge in the initial period of the experiment. However, the results obtained by PASCUAL et al. (2004) are contrary as the quantities of available zinc in soil decreased under the effect of incremental doses of sewage sludge.

The content of available Mn in soil was strongly affected by the doses of sewage sludge introduced to soil (Table 4). Each increase in the dose of this waste by 70 Mg ha⁻¹ caused a significant increase in the concentration of easily soluble forms of manganese in soil. Such strong influence of the doses of sewage sludge on the content of available Mn in soil was confirmed by the regression and correlation analysis (Figure 5). Higher accumulation of available manganese in soil under the influence of sewage sludge has also been demonstrated by IŻEWSKA et al. (2006). In contrast, PASCUAL et al. (2004) inform that the content of this metal decreased under the effect of higher

Table 4

Year	Dose of sewage sludge (Mg ha ⁻¹)					Mean
	0	70	140	210	280	
2005	120.68	129.05	137.39	142.63	148.48	135.65
2006	122.05	125.18	137.80	144.32	148.07	135.49
2007	121.96	134.05	137.31	142.73	153.20	137.85
2008	121.16	131.63	138.24	142.51	151.43	136.99
Mean	121.46	129.98	137.68	143.05	150.29	

LSD_{0.05} year – n.s., dose – 1.65, year x dose – n.s.

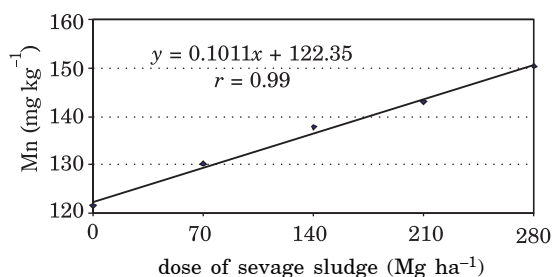


Fig. 5. Changes in the content of available manganese in soil depending on the dose of sewage sludge

doses of sewage sludge. Based on the calculations performed in this study, somewhat weaker increase in the concentration of available Mn in soil was also shown in the following years (Figure 6). The course of the regression curve reveals that the effect of sewage sludge was more evident in the first three years. In the last year of the experiment, the amount of soluble manganese in soil did not undergo any considerable changes.

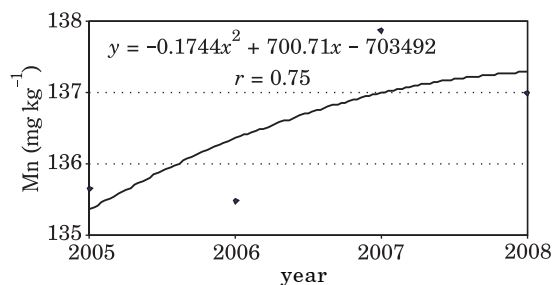


Fig. 6. Changes in the content of available manganese in soil in the following years

Manganese is a very reactive element in the environment; it easily changes its oxidation degree. In the present experiment, however, the soil pH did not change much and the soil was not waterlogged, which otherwise may have induced reactive conditions.

CONCLUSIONS

An increase in available Cu in soil in response to the introduced sewage sludge was most evident in the second and third year after the application of sewage sludge.

The content of soluble Zn in soil began to decrease in the second year after the application of sewage sludge, but its significant limitation occurred in the fourth year.

Sewage sludge significantly increased the content of soluble manganese in soil in the first three years.

Based on the present experiment, we can recommend the tested sewage sludge for non-agricultural use (lawns, slopes, rehabilitation of degraded areas).

REFERENCES

- CASADO-VELA J., SELLÉS S., NAVARRO J., BUSTAMANTE M. A., MATAIX J., GUERRERO C., GOMEZ I. 2006. *Evaluation of composted sewage sludge as nutritional source for horticultural soils*. Waste Manag., 26: 946-952.
- CZEKAŁA J. 2009. *Sewage sludge – fertilizer or waste?* Wodociągi – Kanalizacja, 1: 30. (in Polish)
- DELIBACAK S., OKUR B., ONGUN A. R. 2009. *Influence of treated sewage sludge applications on temporal variations of plant nutrients and heavy metals in a Typic Xerofluvent soil*. Nutr. Cycl. Agroecosyst., 83: 249-257.
- IŻEWSKA A., KRZYWY E., WOŁOSZYK CZ., BALCER K. 2006. *Content of heavy metals in light soil in the third year after application of sewage sludge and composts made from sewage sludge*. Zesz. Probl. Post. Nauk Rol., 512: 173-181. (in Polish)
- JAKUBUS M. 2006. *Influence of long-term application of sewage sludge on changes in the selected chemical properties of soil*. Zesz. Probl. Post. Nauk Rol., 512.1: 209-219. (in Polish)
- KALEMBASA S. PAKUŁA K., BECHER M. 1999. *Content of macro- and micronutrients in sewage sludge produced at selected WTPs near Siedlce*. Fol. Univ. Agric. Stet. Agric., 77: 125-128. (in Polish)
- KLASA A., GOTKIEWICZ W., CZAPLA J. 2007. *Modifications of physico-chemical soil properties following application of sewage sludge as soil amendment*. J. Elementol., 12(4): 287-302.
- MAZUR Z., SIENKIEWICZ S. 2009. *Effect of urea applied with composts on concentration of Cu, Zn and Mn in corn fresh matter*. J. Elementol., 14(2): 323-330.

- MERCIK S., STĘPIEŃ W., GĘBSKI M. 2003. *Uptake by plants and solubility of Cu,Zn,Pb and Cd in different extraction solutions depending on soil acidity.* Zesz. Probl. Post. Nauk Rol., 493: 913-921.
- PASCUAL I., ANTOLÍN M. C., GARCÍA C., POLO A., SÁNCHEZ-DÍAZ M. 2004. *Plant availability of heavy metals in a soil amended with a high dose of sewage sludge under drought conditions.* Biol. Fertil. Soils, 40: 291-299.
- PATORCZYK-PYTLIK B. 2004. *Chemical forms of zinc in soil two, four and six years after application of sewage sludge and vermicompost.* Zesz. Probl. Post. Nauk Rol., 505 (2): 945-952. (in Polish)
- SADEJ W., BOWSZYS T., WIERZBOWSKA J. 2007. *Modifications of the physicochemical properties of grey soil fertilized with sewage sludge.* Zesz. Probl. Post. Nauk Rol., 520: 363-369. (in Polish)
- SINGH R. P., AGRAWAL M. 2008. *Potential benefits and risks of land application of sewage sludge.* Waste Manage., 28: 347-358.
- SËREN O. P., PETERSEN J., RUBĆK G. H. 2003. *Dynamics and plant uptake of nitrogen and phosphorous in soil amended with sewage sludge.* Appl. Soil Ecol., 24: 187-195.
- SPEIR T. W., VAN SCHAİK A. P., LLOYD-JONES A. R., KETTLES H. A. 2003. *Temporal response of soil biochemical properties in a pastoral soil after cultivation following high application rates of undigested sewage sludge.* Biol. Fertil. Soils, 38: 377-385.
- SPIAK Z., KULCZYCKI G. 2004. *Content of micronutrients in sewage sludge from selected WTPs in the Province of Lower Silesia.* Zesz. Probl. Post. Nauk Rol., 505: 973-978. (in Polish)
- SPYCHAJ-FABISIAK E., KOZERA W., MAJCHERCZAK E., RALCEWICZ M., KŃAPOWSKI T. 2007. *Effect of organic waste and farmyard manure on fertility of light soil.* Acta Sci. Pol., Agric., 6(3): 69-76. (in Polish)
- STĘPIEŃ W., SZULC W., MERCIK S. 2000. *Estimation of the fertilization value of raw and amended sewage sludge.* Fol. Univ. Agric. Stetin., Agric., 84: 465-470. (in Polish)