

# **MODIFICATIONS IN THE CONTENT OF AVAILABLE ZINC AND COPPER IN SOIL FERTILIZED WITH BIO-WASTE COMPOSTS**

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## Abstract

The aim of this study has been to determine the indirect and direct effects of farmyard manure and sewage sludge composts, produced in the north-eastern part of Poland, on the content of 1 mol HCl·dm<sup>-3</sup> soluble forms of zinc and copper in soil.

In 2004-2007, a field experiment was carried out at the Experimental Station in Bałcyny near Ostróda. The experiment was established on proper grey-brown podzolic soil originating from light boulder clay, which was rich in P, moderately abundant in K and low in Mg. It comprised a four-field crop rotation system (potato, spring barley, winter oilseed rape and winter wheat. The design of the experiment, set up according to the random block method, involved 8 objects (2 x 4): 1) farmyard manure, 2) compost (sewage sludge + straw), 3) dried and granulated sewage sludge, 4) composted sewage sludge. The composts and FYM were introduced to soil once (in 2004) at a rate of 10 t d.m.·ha<sup>-1</sup> or 2 x 5 d.m.·ha<sup>-1</sup> (under potato and winter oilseed rape). In 2004, nitrogen in the soil enriched with natural fertilizers was balanced to 150 kg·ha<sup>-1</sup> according to the N-total content. In 2005, soil cropped with spring barley received only mineral fertilization, whereas winter oilseed rape received the second rate of organic fertilizers (in the series consisting of 2 x 5 d.m.·ha<sup>-1</sup>) and nitrogen was balanced to 120 kg·ha<sup>-1</sup>. In 2006, soil under winter wheat received only mineral fertilization.

Prior to the establishment of the experiment, soil, manure and compost samples were taken. Having been averaged, the samples were subjected to determination of their content of Cu and Zn in 1 mol HCl dm<sup>-3</sup>. The soil, whose reaction was 5.04 in 1 mol HCl dm<sup>-3</sup>, was moderately abundant in available zinc and low in copper. After four years of the trials, the levels of available forms of copper and zinc in the soil fertilized with sewage sludge

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composts, compared to the soil enriched with FYM, were higher. In the first and fourth year of the experiment, the content of both elements was found to increase significantly in the objects fertilized with dry, granulated and composted sludge. Sludge composted with straw significantly raised the content of Zn and Cu in the second and third year of the experiment. However, fertilization of grey-brown podzolic soil with sewage sludge did not change its classification according to the abundance of available forms of copper and zinc.

Key words: sewage sludge, zinc, copper, soil.

## ZMIANY ZAWARTOŚCI PRZYSWAJANYCH FORM CYNKU I MIEDZI W GLEBIE UŻYŹNIANEJ KOMPOSTAMI Z BIOODPADÓW

### Abstrakt

Celem badań było określenie bezpośredniego i następczego wpływu obornika i kompostów z osadów ściekowych, pochodzących z Polski północno-wschodniej, na zawartość w glebie form cynku i miedzi rozpuszczalnych w 1 mol HCl·dm<sup>-3</sup>.

W latach 2004-2007, w Zakładzie Produkcyjno-Doświadczalnym Bałczyny k. Ostródy, na glebie płowej typowej wytworzonej z gliny lekkiej zwałowej, o wysokiej zawartości P, średniej K i niskiej Mg, przeprowadzono doświadczenie z 4-półowym płodozmiianem (ziemniak, jęczmień jary, rzepak ozimy, pszenica ozima). Schemat doświadczenia, założonego metodą losowanych bloków, obejmował 8 obiektów (2x4): 1) obornik, 2) kompost (osad ściekowy+słoma), 3) osad ściekowy suszony i granulowany, 4) osad ściekowy kompostowany. Komposty i obornik zastosowano jednorazowo (2004 r.) w dawce 10 t s.m.·ha<sup>-1</sup> lub 2 x 5 t s.m.·ha<sup>-1</sup> (pod ziemniak i rzepak ozimy). W 2004 r. na obiektach z nawozami organicznymi i obornikiem azot został zbilansowany do 150 kg·ha<sup>-1</sup>, w zależności od zawartości w nich N-ogółem. W 2005 r. pod jęczmień jary zastosowano tylko nawożenie mineralne, a pod rzepak ozimy – drugą dawkę nawozów organicznych (w serii 2 x 5 t s.m.·ha<sup>-1</sup>) i zbilansowano azot do 120 kg·ha<sup>-1</sup>. W 2006 r. pod pszenicę ozimą stosowano tylko nawożenie mineralne.

Przed założeniem doświadczenia pobrano próbki gleby, obornika i kompostów. W próbkach, po uśrednieniu, oznaczono zawartość Cu, Zn w 1 mol HCl·dm<sup>-3</sup>. Gleba o pH=5,04 w 1 mol HCl·dm<sup>-3</sup> charakteryzowała się średnią zasobnością w przyswajalny cynk i niską w miedź. Po czterech latach badań wzrosła zawartość przyswajalnych form miedzi i cynku w glebie użyźnianej kompostami z osadów ściekowych, w porównaniu z glebą nawożoną obornikiem. W pierwszym i czwartym roku istotny wzrost zawartości tych pierwiastków stwierdzono na obiektach z osadem suszonym i granulowanym oraz kompostowanym. Osad kompostowany z dodatkiem słomy istotnie zwiększał zawartość Zn i Cu w drugim oraz trzecim roku badań. Użyźnianie gleby płowej osadami ściekowymi nie zmieniło jednak klasy zasobności w przyswajalne formy miedzi i cynku.

Słowa kluczowe: osad ściekowy, cynk, miedź, gleba.

## INTRODUCTION

Under the current conditions in agriculture, the importance of micronutrients is constantly growing. The negative balance of these elements in soil used for farming is largely conditioned by a dramatic decrease in FYM fertilization levels. A possible replacement for FYM can be seen in application of sewage sludge, especially from wastewater treatment plants in small

towns. Such sludge is typically better as a fertilizer and safer to use in natural environment than sludge obtained in cities, particularly in industrialized areas. Good quality compost produced from sewage sludge as one of its components improves the balance of humus compounds in soil as well as the content of macro- and micronutrients (KLASA et al. 2007, HANEKLAUS et al. 1998, SIUTA 1996, PIGNALOSA et al. 1994, KRZYWY et al. 2002).

The objective of this study has been to determine the direct and indirect effects of FYM and sewage sludge composts, produced in the north-eastern part of Poland, on the content of 1 mol HCl dm<sup>-3</sup> soluble forms of copper and zinc.

## MATERIAL AND METHODS

A field trials was conducted at the experimental Station in Balcyny near Ostróda from 2004 to 2007. The experiment was established on proper grey-brown podzolic soil originating from light boulder clay, which was rich in available P, moderately abundant in K and low in Mg. the soil reaction was 5.04 in 1 mol KCl dm<sup>-3</sup>. The experiment comprised a four-field crop rotation system (potato, spring barley, winter oilseed rape and winter wheat). The design of the experiment, which was set up according to the random block method, involved 8 objects (2 x 4): 1) mixed manure, 2) composted sewage sludge, 3) compost (sewage sludge and cereal straw at a ratio of 1 : 0.5), 4) dried and granulated sewage sludge. The sewage sludge used to make the composts came from wastewater treatment plants in Ostróda (object 2) and Iława (objects 3 and 4). The concentration of macronutrients in the manure and composts has been specified in Table 1.

The composts and manure were introduced to soil once during the whole crop rotation cycle (under potato), adding 10 t d.m. of fertilizer per ha, or twice (under potato and winter oilseed rape) as two rates of 5 t d.m. per 1 ha. In the objects enriched with the organic fertilizers and FYM, nitrogen was balanced to 150 kg·ha<sup>-1</sup> (2004) and to 120 kg·ha<sup>-1</sup> (2005), depending on the N-total content in the soil. Spring barley and winter wheat were nourished only with mineral fertilizers.

Before the experiment was established, samples of soil, manure and composts had been collected. In averaged samples, the content of Cu and Zn in 1 mol HCl dm<sup>-3</sup> was determined by atomic absorption spectrophotometry, using an AA-6800 Shimadzu apparatus.

Before the trials were started, the soil was characterised by moderate zinc and low copper abundance (Table 2). The results of the experiment (from each plot) underwent analysis of variance, which tested significance of differences caused by particular experimental factors, at the significance level of  $p=0.05$ .

Table 1

Content of macronutrients in FYM and sewage sludge composts ( $\text{g} \cdot \text{ha}^{-1}$  d.m.)

Element	FYM	Sewage sludge		
		composted	with straw	dried and granulated
N	5.80	46.60	10.70	18.00
P	1.02	29.90	7.60	12.30
K	5.11	-	1.20	1.40
Mg	1.30	7.80	1.80	3.70
Ca	1.10	33.90	10.80	15.10

Results of determinations on certified material

Value ( $\text{mg} \cdot \text{kg}^{-1}$ d.m.)	Virginia Tobacco Leaves CTA-VTL-2	
	Cu	Zn
Certified	18.2±0.9	43.3±2.1
Determined	18.8±0.6	42.3±1.1

Table 2

Content of soluble forms of zinc and copper in soil, sewage sludge and manure before assuming experience ( $\text{mg} \cdot \text{kg}^{-1}$ )

Metal	Soil	Manure	Sewage sludge		
			composted	with straw	dried and granulated
Cu	1.47	5.41	340.01	4.48	18.16
Zn	9.11	35.12	1310.0	109.51	270.40

## RESULTS AND DISCUSSION

Sewage sludge is most often very rich in organic substance and alkaline cations. They can therefore serve to neutralise acid soils (ŻUKOWSKA et al. 1999, CZEKAŁA 1999). The effect of the different forms of sewage sludge composts tested in this experiment on soil pH depended primarily on how they were applied (Table 3). In the first year, compared to the initial value ( $\text{pH} = 5.04$ ), the sewage sludge composts had a positive effect on the soil reaction on all the plots. However, the subsequent effect of the composts, especially when added to soil as a single rate of 10 t d.m. per ha, was much weaker. In the series consisting of  $2 \times 5$  t d.m. per ha, the second rate of manure or the composts changed the soil reaction even more profoundly than in the first year of the experiment.

Table 3

Year	Way of applying	Manure	Sewage sludge		
			composted	with straw	dried and granulated
2004	<i>a</i>	5.27	5.45	5.36	5.39
	<i>b</i>	5.06	5.37	5.11	5.37
2005	<i>a</i>	4.95	5.10	5.02	5.09
	<i>b</i>	4.90	5.06	4.95	5.03
2006	<i>a</i>	5.02	5.21	5.18	5.27
	<i>b</i>	5.03	5.21	5.09	5.21
2007	<i>a</i>	5.27	5.18	5.22	5.20
	<i>b</i>	5.11	5.46	5.25	5.46

*a* – once in the crop rotation 10 d.m. t · ha<sup>-1</sup>

*b* – twice in the crop rotation for 5 t d.m. · ha<sup>-1</sup>

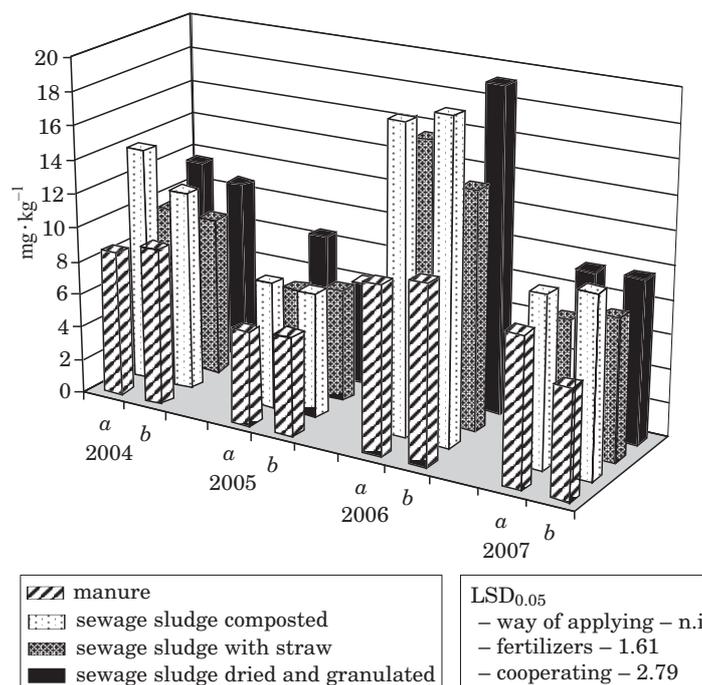


Fig. 1. Content of Zn in soil after the harvest of plants (*a* – fertilizing once in the crop rotation 10 t · ha<sup>-1</sup>; *b* – fertilizing 2 × 5 t · ha<sup>-1</sup> in the crop rotation)

BARAN et al. (1996) as well as ŻUKOWSKA et al. (1999) also found out that sewage sludge had alkalizing influence on soil, especially in the first year after its application. In turn, a study completed by JAKUBUS (2006) suggested that sewage sludge had statistically non-significant influence on soil reaction.

After four years of our trials, the concentration of available form of zinc in FYM fertilized soil was on average  $8.2 \text{ mg}\cdot\text{kg}^{-1}$ , whereas in the soil enriched with different forms of bio-waste composts, it ranged on average from  $9.8 \text{ mg}\cdot\text{kg}^{-1}$  (sewage sludge composted with straw) to  $12.3 \text{ mg}\cdot\text{kg}^{-1}$  (sewage sludge composted alone). In the consecutive years of the experiment, the amount of this form of zinc increased significantly in soil fertilized with composted sludge or dried and granulated sludge relative to that found in FYM fertilized soil (Figure 1). However, in none of the years of the trials, the way these fertilizers were applied (once or twice during the whole crop rotation cycle) had any significant effect on the abundance of soil in zinc.

The tendencies observed while analyzing the effect of the composts on abundance of soil in available copper were similar to those noticed for zinc (Figure 2). After four years of fertilization with manure, the average abundance of soil in this element did not change ( $1.49 \text{ mg}\cdot\text{kg}^{-1}$ ) when compared to its abundance before the experiment ( $1.47 \text{ mg}\cdot\text{kg}^{-1}$ ). In the objects fertilized with bio-waste composts, the concentration of Cu in soil was modified by the type of compost applied and ranged on average from  $1.59 \text{ mg}\cdot\text{kg}^{-1}$

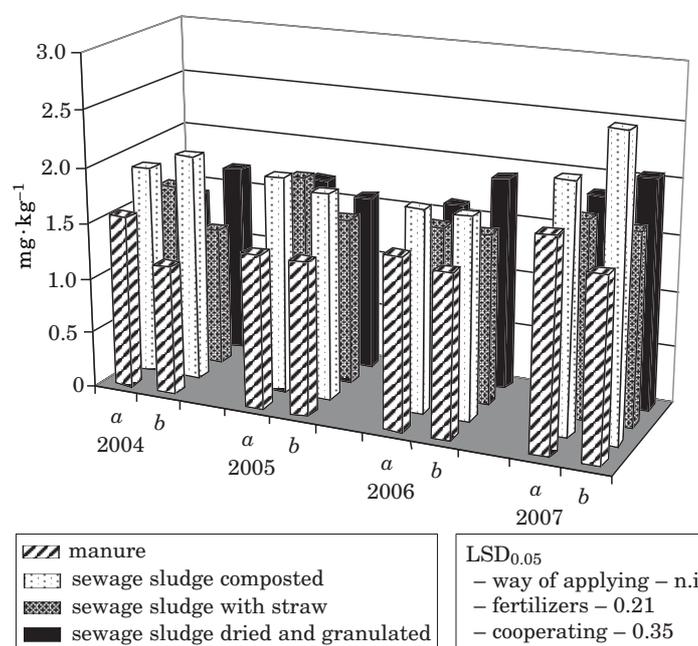


Fig. 2. Content of Cu in soil after the harvest of plants (explanations for Figure 1)

(sewage sludge composted with straw) to  $2.15 \text{ mg} \cdot \text{kg}^{-1}$  (sewage sludge composted alone).

Similar results have been obtained by PATORCZYK-PYTLIK and SPAIK (1996), SZULC and RUTKOWSKA (2002) or IŻEWSKA et al. (2006). CZEKEAŁA (2004), on the other hand, found no significant influence produced by sewage sludge fertilizers on the content of micronutrients extracted by  $1 \text{ mol HCl dm}^{-3}$  solution.

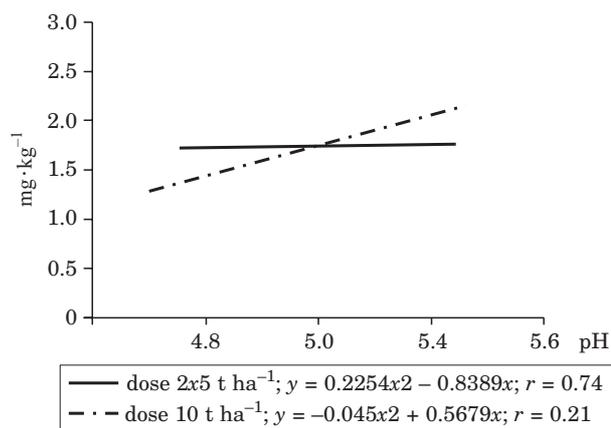


Fig. 3. Relation between the content Cu in the soil and her reaction

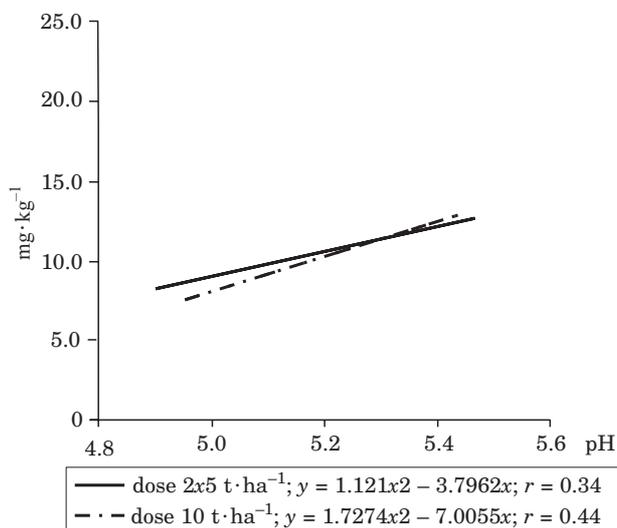


Fig. 4. Relation between the content Zn in the soil and her reaction

The analysis of correlation and regression (Figures 3, 4) showed that the amount of available copper in soil fertilized with manure and organic fertilizers depended on the soil reaction to a greater degree than that of zinc ( $r = 0.71, 0.21$  for copper versus  $r = -0.34, 0.44$  for zinc). LIKEWISE, KUCHARZEWSKI et al. (2004) determined positive correlation between the content of zinc or copper and soil reaction.

## CONCLUSIONS

1. Fertilization of soil with sewage sludge composts had a positive effect on soil reaction. Double application of the fertilizers during the whole crop rotation cycle (each time 5 t d.m. ha<sup>-1</sup>) was more favourable than a single treatment (10 t d.m. ha<sup>-1</sup>).

2. The concentration of available zinc and copper in soil was modified to a greater extent by the type of sewage sludge and sewage sludge composts than the way these fertilizers were introduced to soil.

3. The highest level of available forms of copper and zinc was found when sewage sludge had been used – composted as well as dried and granulated sewage sludge composts.

4. The fertilization of soil with different forms of sludge produced while treating municipal wastewater and sewage increased the soil content of mobile forms of zinc and copper. However, the threshold levels of these elements were never exceeded.

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