
PHYTOTOXICITY AND SPECIATION OF COPPER AND NICKEL IN COMPOSTED SEWAGE SLUDGE*

Monika Jakubus

**Chair of Soil Science and Ground Protection
Poznań University of Life Sciences**

Abstract

In recent years, sewage sludge production in Poland has increased sharply. Composting is one of the most preferable methods for sewage sludge utilization. Compost can improve the physical and chemical properties of soil. However, the quality of sewage sludge composts should be assessed before soil application by using biological and chemical methods. A germination test is used as a biological index to determine the possible phytotoxic effect of composts. Chemical methods are helpful in assessment of availability of metals to plants.

This study has been conducted to validate the effect of composting process on phytotoxicity, speciation and availability of copper and nickel in sewage sludge composted with sawdust and wheat straw. The composting process of organic wastes was carried out in chambers of a bioreactor for 28 days; afterwards each chamber was emptied and the content was stored in a closed room for 3 months to allow the maturation process to complete. Samples for analysis were collected at three characteristic phases of the composting process: mesophilic, thermophilic and mature compost. Determinations of the changes in metal speciation as well as metal bioavailability were achieved, respectively, with the technique of BCR sequential analysis and single extraction method using DTPA. Phytotoxicity of the analyzed composts was evaluated with the germination index using cress seeds.

It was found that an increasing proportion of sewage sludge in composted mixtures increased copper and nickel content in compost fractions as well as bioavailable quantities of these metals. The germination index increased only during the composting process of a mixture containing 30% of sewage sludge. The compost with 75% share of sewage sludge strongly inhibited germination of cress seeds. The process of compost maturation resulted in an increase of copper in fractions I and III. However, the smallest amounts of copper were determined in exchangeable bonds and the highest ones were determined in bonds with organic matter and sulphides. Composting sewage sludge with sawdust and wheat

dr hab. Monika Jakubus, Chair of Soil Science and Ground Protection, Poznań University of Life Sciences, ul. Szydłowska 50, 60-656 Poznań

*The work was financed from the funds for science development in 2005-2008 as Science Project No 2 P06R 00529.

straw reduced the availability of nickel, which resulted in a decline in the content of this metal in exchangeable bonds (fraction I) but an increase in poorly- and non-extractable ones (fractions III and IV).

Key words: sewage sludge, compost, germination index, copper and nickel speciation, bioavailability.

FITOTOKSYCZNOŚĆ I SPECJACJA MIEDZI I NIKLU W KOMPOSTOWANYM OSADZIE ŚCIEKOWYM

Abstrakt

W ostatnich latach w Polsce notuje się znaczne zwiększenie masy osadów ściekowych. Kompostowanie jest uważane za jedną z najbardziej korzystnych metod wykorzystania osadów ściekowych. Kompost może przyczynić się do poprawy właściwości fizycznych i chemicznych gleby. Jednak jakość kompostów powstałych z osadów ściekowych przed ich doglebowym zastosowaniem powinna być oceniana za pomocą biologicznych i chemicznych metod. Indeks biologiczny oparty na teście kiełkowania roślin pozwala określić ewentualny fitotoksyczny efekt kompostów. Natomiast metody chemiczne pomocne są w ocenie stopnia przyswajalności metali dla roślin.

W badaniach określono fitotoksyczność, specjację i bioprzyswajalność miedzi i cynku w osadzie ściekowym kompostowanym z trocinami i słomą. Proces kompostowania odpadów organicznych przebiegał w komorach bioreaktora przez 28 dni, po czym kompostowaną biomasę zdeponowano w zamkniętym pomieszczeniu na okres 3 miesięcy celem zakończenia procesu dojrzwania. Próbkę do analiz pobierano w trzech charakterystycznych fazach kompostowania: mezofilnej, termofilnej oraz kompostie dojrzałym. Zmiany specjacji oraz bioprzyswajalności metali oceniono wykorzystując odpowiednio analizę sekwencyjną BCR oraz ekstrakcję pojedynczą z roztworem DTPA. Fitotoksyczność analizowanych kompostów określono z wykorzystaniem testu kiełkowania nasion rzęchuchy.

Stwierdzono, że efektem większego udziału osadu ściekowego w kompostowanej mieszance były większe bioprzyswajalne ilości miedzi i niklu oraz ich zawartości we frakcjach kompostów. Większą wartość indeksu kiełkowania stwierdzono tylko podczas kompostowania mieszanki, gdzie udział osadu ściekowego wynosił 30%. Kompost, w którym osad ściekowy stanowił 75%, silnie hamował kiełkowanie nasion rzęchuchy. Rezultatem procesu dojrzwania kompostów była większa zawartość miedzi we frakcji I i III. Niezależnie od tego, najmniej zawartość tego metalu oznaczono w próbkach wymiennych, a największą w próbkach z materią organiczną i siarczkami. Proces kompostowania osadu ściekowego ze słomą i trocinami zredukował przyswajalność niklu, czego wyrazem było zmniejszenie jego zawartości we frakcji I, a zwiększenie w próbkach trudno- i nieekstrahowanych (fr. III i IV).

Słowa kluczowe: osady ściekowe, kompost, indeks kiełkowania, specjacja miedzi i niklu, bioprzyswajalność.

INTRODUCTION

With continually increasing amounts of sewage sludge deposited at municipal sewage treatment plants (Central Statistical Office 2010) and the binding legal acts (Journal of Law 2010, No 28, item 145) which enforce

their effective and environmentally friendly utilization, sewage sludge composts seem a possible solution. This was indicated in the Act of 27 April 2001 (Journal of Law, No 62, item 628), which stipulated that sewage sludge may be recycled by composting. The composting process based on simultaneous biochemical-microbiological transformations generates compost. It is assumed that this end-product of composting is a stable and mature substance which, when applied into soil, will evoke positive changes in physical, physicochemical and chemical soil properties, and it will stimulate soil microbiological activity (DEBOSZ et al. 2002, JORDÃO et al. 2006, SYDEJ, NAMOTKO 2007, HARGREAVES et. al. 2008). According to these researchers, soil fertilization with compost improves its fertility, as expressed by higher quantities of organic carbon, macro- and micronutrients as well as by better sorption and buffer capacity.

However, broad assessment of the compost fertilizing value should be performed, also including potential hazard to the environment. The risk arises mainly due to the presence of organic and inorganic compounds toxic to living organisms in composted sewage sludge (BARKER, BRYSON 2002, JAKUBUS 2005). It should be borne in mind that inorganic contaminations associated with heavy metals do not undergo biodegradation in the course of sewage sludge composting (NAIR et al. 2008), hence it is recommended to evaluate the risk factor connected with soil application of composts from sewage sludge. From this point of view, potential phytotoxicity of composts expressed by the inhibition of seed germination (WALTER et al. 2006, KO et al. 2008) or the increase in labile metal forms available to plants (HUANG et al. 2005, JORDÃO et al. 2006) is emphasized. According to MIAOMIAO et al. (2009), phytotoxicity is connected with some forms of metals, therefore metal speciation and bioavailability as well as phytotoxic effects should be studied.

In this study, changes in phytotoxicity as well as copper and nickel speciation and bioavailability during the composting process of sewage sludge with straw and sawdust were determined.

MATERIAL AND METHODS

The objective of the investigations was achieved using compost samples from an experiment carried out in controlled conditions by using a double-chamber bioreactor of the capacity of 125 dm³ per chamber. A diagram of the bioreactor together with its description can be found in OLSZEWSKI et al. (2005). Each composting mixture was prepared in two replications, i.e. each replication of a tested composting mixture was in a separate chamber of the bioreactor. The experimental composts were prepared using sewage sludge from a mechanical-chemical sewage treatment plant, wheat straw and sawdust. All organic waste was well mixed prior to transferring to bioreactor

chambers. The moisture of the mixtures was 60% and the amount of air flowing through the mixtures corresponded to the volume of $4 \text{ dm}^3 \text{ min}^{-1}$. Some properties of the components and proportions in the composted mixtures can be found in Tables 1 and 2. Each mixture remained in the bioreactor's chambers for 28 days. Afterwards, each chamber was emptied and the content was placed in a closed room for 3 months to allow complete maturation. Analyses were performed on compost samples collected during three characteristic phases of the composting process: mesophilic, thermophilic and mature compost. Four subsamples of compost were collected in the course of each phase. The gathered samples were mixed together. The material thus prepared served as a mean sample for each compost replication and phase.

Table 1

Some properties of composted waste

Waste	Dry matter	Corg	Nog	Ni	Cu
	(g kg^{-1})	(g kg^{-1} d.m.)		(mg kg^{-1} d.m.)	
Sewage sludge	167.0	330.0	53.0	15.65	262.24
Sawdust	820.0	500.0	1.0	2.33	2.65
Wheat straw	860.0	440.0	3.0	1.29	4.35

Table 2

Composition of investigated composts

Compost	Share in compost (%)			C:N
	sewage sludge	sawdust	wheat straw	
C1	75	20	5	9.2:1
C2	60	35	5	12.1:1
C3	45	50	5	17.0 : 1
C4	30	65	5	26.4:1

Samples were dried out at 105°C for 12 hours. The dried samples was ground into fine powder and stored in plastic bags at 4°C . Copper and nickel speciation was achieved with the BCR sequential analysis. The details of the experimental protocol are given in Table 3. The bioavailable content of metals was determined with the single extraction method using DTPA complexing solution ($0.005 \text{ mol dm}^{-3}$ DTPA + 0.1 mol dm^{-3} TEA + 0.01 mol dm^{-3} CaCl_2 , of pH 7.3) (QUEVAUVILLER et al. 1998). The compost : solution ratio was 1:2. Concentrations of copper and nickel in extracts were determined by flame atomic absorption spectrometry (FAAS) using a Varian Spectra AA 220 FS.

Table 3

BCR sequential extraction procedure (MOSSOP, DAVIDSON 2003)

Fraction	Extracting agent	Extraction conditions	
		t (h)	temperature (°C)
Fr. I – exchangeable	0.11 mol dm ⁻³ CH ₃ COOH (pH= 7.0)	16	20 - 25
Fr. II – reducible (metals bound to Fe and Mn oxides)	0.5 mol dm ⁻³ NH ₂ OH-HCl (pH=1.5)	16	20-25
Fr. III – oxidisable (metals bound to organic matter and sulphides)	30% H ₂ O ₂ (pH=2.0). and then 1.0 mol dm ⁻³ CH ₃ COONH ₄ (pH=2.0)	1. 2. 16	20-25. 85. 20-25
Fr. IV – residual	<i>aqua regia</i>	2.5	60-70

The analytical accuracy of the laboratory procedures was evaluated with a BCR analysis of reference material CRM 145R (trace elements in sewage sludge), and the data of three replicate analyses obtained for the total content of Cu and Ni are shown in Table 4.

Table 4

Content (mean ± SD) of copper and nickel determined for reference material BCR 145R

Metal	Found value (mg kg ⁻¹ d.m.)	Certified value (mg kg ⁻¹ d.m.)	Precision	Accuracy
Ni	294.4 ± 5.66	251.0 ± 7.71	1.94	17.3
Cu	720.7 ± 8.96	707.0 ± 8.83	1.24	1.94

The germination index (GI) has been used to determine phytotoxicity of the composts. Cress seeds (*Lepidium sativum* L.) were germinated in GI assays. Extracts of compost were obtained by shaking 10 g of fresh matter of compost with 100 cm³ of distilled water for 2 h at room temperature. Ten cress seeds were placed in Petri dishes (10 cm in diameter and 1.5 cm deep) filled with filter paper soaked in 5 cm³ of the compost extract and incubated in the dark at 25°C for 48 h. The control consisted of 5 cm³ distilled water. The percentages of relative seed germination (RSG), relative root growth (RRG) and germination index (GI) were calculated according to the following formulas (MIAOMAIO et al. 2009):

$$RSG (\%) = \frac{\text{mean number of seeds germinated in compost extract}}{\text{mean number of seeds germinated in control}} \cdot 100,$$

$$RRG (\%) = \frac{\text{mean root length in compost extract}}{\text{mean root length in control}} \cdot 100,$$

$$GI (\%) = \frac{RSG \cdot RRG}{100}.$$

Analyses of mean samples were carried out in three replicates. The results were submitted to analysis of variance for two-factor experiments, using F test at the level of significance $p \leq 0.05$. Two basic experimental factors were taken into consideration: compost mixtures (A) and time of composting (B). The least significant differences were calculated using Tukey's test at the level of significance of $\alpha \leq 0.05$ and then homogenous uniform within the factor level were established.

RESULTS

As evident from the data collated in Tables 5 and 6, the experimental factors exerted significant influence on the quantitative changes of the analyzed metals in compost fractions. This impact varied depending on the metal and the type of bond it developed with the solid phase of the composts. Irrespective of the compost chemical composition and composting phase, copper quantities in fractions increased in the following order: fr. I < fr. IV < fr. II < fr. III.

The analogous sequences for nickel changed depending on the phase of the process. In samples collected during the mesophilic phase, most Ni formed bonds with Fe and Mn oxides (4.3 mg kg⁻¹ d.m. for C1 and 4.1 mg kg⁻¹ d.m. for C2) or exchangeable bonds (3.4 mg kg⁻¹ d.m. for C3 and 2.6 mg kg⁻¹ d.m. for C4). Conversely, irrespective of their chemical composition, mature composts were characterized by the following sequence of increasing quantities of this metal: fr. I < fr. II < fr. III < fr. IV.

The mutual impact of the experimental factors was least noticeable with regard to the copper content in the compost residual fraction. Following sewage sludge composting with straw and sawdust, the copper content declined but the recorded differences were non-significant (Table 5). In each consecutive phase, the content of this metal also decreased in fraction II and, consequently, in mature composts it was 40 to 60% lower than in samples from the mesophilic phase. The process of composting sewage sludge with straw and sawdust led to an increased copper content in exchangeable and organic bonds. As evidenced by the data collated in Table 5, the copper content in fraction I of samples collected during the mesophilic phase was the lowest, ranging from 1.54 mg kg⁻¹ d.m. to 1.74 mg kg⁻¹ d.m. (C1-C3) and 3.07 mg kg⁻¹ d.m. (C4). On the other hand, mature composts were characterized by 4- to 4.5-fold (C1-C3) and two-fold (C4) higher content of the metal. It is noteworthy that during the thermophilic phase, the copper content in the discussed bonds in the composts with the highest sewage sludge proportion (C1 and C2) was the highest, ranging from 9-10 mg kg⁻¹ d.m., which was 6 times more than during the mesophilic phase (Table 5). Such big differences in copper quantities in organic bonds were not record-

Table 5

Content of copper in separate fractions depending on the type of compost and composting phase (mg kg⁻¹ d.m.)

Composting phase	Fractions			
	I	II	III	IV
C1				
Mesophilic	1.54c*	31.28a	140.55c	13.64b
Thermophilic	9.04a	30.05a	180.00b	23.45a
Mature compost	6.49b	17.53b	212.87a	13.14b
C2				
Mesophilic	1.74c	36.31a	118.04a	14.58a
Thermophilic	10.72a	26.36b	141.30b	13.59ab
Mature compost	7.91b	13.28c	175.77c	10.23b
C3				
Mesophilic	1.61b	41.19a	72.98b	7.03a
Thermophilic	5.44a	31.01b	88.25b	7.89a
Mature compost	6.80a	23.41c	112.79a	6.53a
C4				
Mesophilic	3.07b	24.42a	47.92a	9.87a
Thermophilic	5.83a	25.48a	74.60b	6.81a
Mature compost	5.62a	14.5b	91.95c	5.71a

* values in columns followed by the same letter do not differ significantly

ed. The content of copper in fraction III of all the examined composts increased gradually from the mesophilic phase, through the thermophilic one, reaching maximum values in mature composts, in which it was 1.5- (C1-C3) and 2-fold (C4) higher than in samples collected at the beginning of the experiment (Table 5).

The experimental factors exerted the weakest impact on nickel in fraction I of the examined composts (Table 6). This effect was statistically non-significant for the compost with the highest proportion of sewage sludge in its composition. In contrast, in composts C3 and C4, the content of nickel in the analyzed bonds was found to decrease. Mature composts C3 and C4 were characterized respectively by 55 and 53% lower quantity of this metal in comparison with its level determined in samples from the mesophilic phase. The analysis of the data contained in Table 6 suggests that the lack of a mutual impact of the experimental factors also became apparent in respect to the Ni content in fraction II of compost C4. Nonetheless, in all the examined composts, an increase in Ni in bonds with Fe and Mn oxides was

Table 6

Content of nickel in separate fractions of composts depending on the type of compost and composting phase (mg kg⁻¹ d.m.)

Composting phase	Fractions			
	I	II	III	IV
C1				
Mesophilic	3.32a*	4.34b	3.70c	3.52b
Thermophilic	3.68a	5.03b	5.06b	4.63b
Mature compost	3.21a	5.98a	6.29a	6.98a
C2				
Mesophilic	3.50a	4.06b	3.67c	2.82c
Thermophilic	3.15a	4.16b	4.72b	4.18b
Mature compost	3.68a	5.14a	6.27a	6.51a
C3				
Mesophilic	3.42a	2.78a	2.38c	2.42b
Thermophilic	2.09b	3.20a	3.29b	3.46b
Mature compost	1.55b	3.71a	4.22a	5.26a
C4				
Mesophilic	2.56a	2.10a	1.18b	1.58b
Thermophilic	1.75b	2.34a	1.40b	2.57ab
Mature compost	1.19b	2.79a	2.50a	3.63a

* cf. Table 5

observed (in the order of 26-38%) while the process of composting sewage sludge progressed (Table 6). Changes in the nickel content in fractions III and IV of the examined composts which occurred during the composting process were identical. The lowest, i.e. 30%, sewage sludge proportion in composted matter, led to 2 times greater amount of nickel in the mature compost C4 determined in samples representing the mesophilic phase. In conditions of the remaining composts, the appropriate difference ranged from 71 to 77% (Table 6). The composition of a composted mixture did not have such a strong impact on quantitative changes of nickel in the residual fraction as in organic bonds. The data in Table 6 indicate that the content of this metal in fraction IV increased gradually from the beginning of the composting process of sewage sludge mixed with straw and sawdust and was eventually twice as high in mature composts.

The content of bioavailable copper and nickel also changed after the application in the examined sewage sludge composts. As evident from the data presented in Figure 1, the lowest Cu (17.78 mg kg⁻¹ d.m.) and Ni

(1.25 mg kg⁻¹ d.m.) content was determined in compost C4, while the maximum one (83.27 mg Cu kg⁻¹ d.m. and 3.23 mg Ni kg⁻¹ d.m.) – in compost C1. The difference between these extreme values was 6.5- and 2.5-time for copper and nickel, respectively. The mutual impact of both experimental factors was significant only in the case of copper (Figure 1). While composting sewage sludge together with straw and sawdust, the content of bioavailable copper increased gradually from the beginning of the process, reaching the highest level in mature composts. Irrespective of the composition of the composted mixture, 2.5-3.0-fold more bioavailable copper was found in the mature material. No such trends in quantitative changes were determined for nickel. The content of bioavailable nickel, irrespective of the composting phase, remained similar and statistically significant differences were determined only in the case of compost C4 (Figure 1).

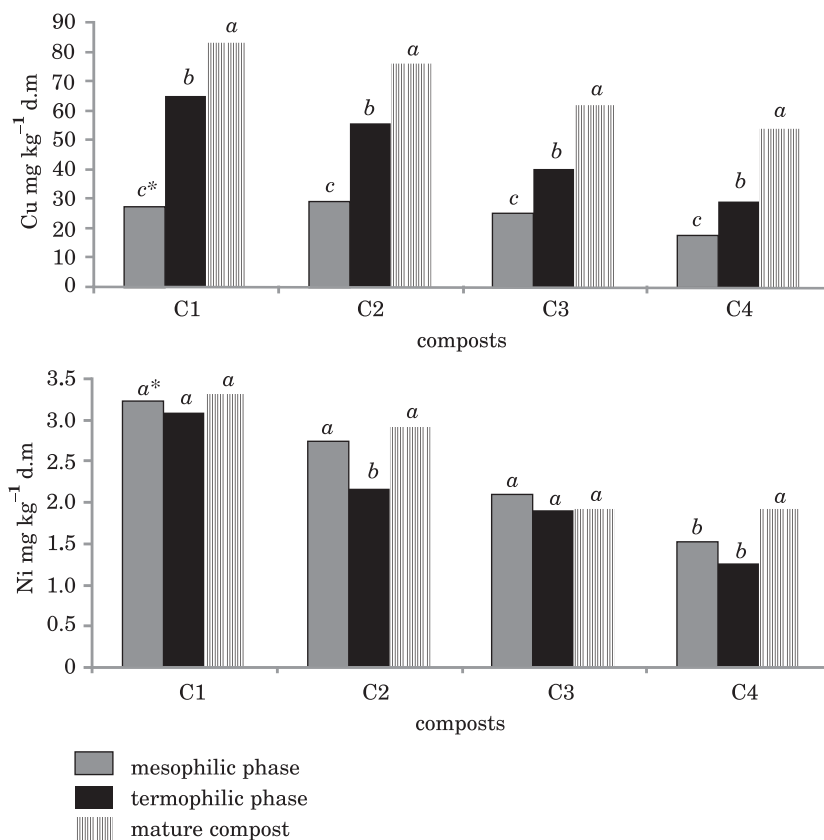


Fig. 1. Bioavailability of copper and nickel in dependence on type of compost and composting phase

*values followed by the same letter do not differ significantly

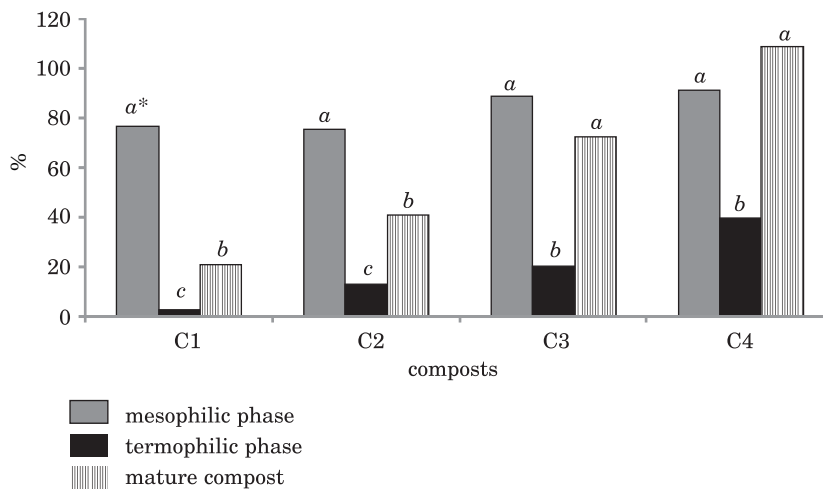


Fig. 2. Influence of composting process on index germination changes in analysed composts

*values followed by the same letter do not differ significantly

The germination index values presented in Figure 2 were evidently and statistically significantly modified by the experimental factors, ranging from 2.44% (C1) to 109.15% (C4). Mature composts in which sewage sludge constituted 45 to 75% of the total composition were characterized by 75 (C1), 46 (C2) and 18% (C3) lower GI values in comparison with the ones determined during the mesophilic phase. Mature compost containing 30% of sewage sludge (C4) was an exception, as the GI value determined in it was by 20% higher than in the initial mixture (Fig. 2). It was typical of the examined composts that the lowest GI values were determined during the thermophilic phase. These values were found to be lower when the share of sewage sludge in composted mixture was higher, i.e. 2.44% for C1 but 39.43% for C4 compost. During the mesophilic phase of the composting process, the discussed index attained values which were 32- (C1), 6- (C2), 4- (C3) and 2-fold (C4) higher than found during the thermophilic phases (Figure 2).

DISCUSSION

Unlike most of the organic compounds, metals remain in mature composts, after all the transformations of organic matter, which can be considered disadvantageous to their bioavailability. Numerous researchers (BARKER, BRYSON 2002, JORDÃO et al. 2006, JAKUBUS, CZEKAŁA 2010, JAKUBUS 2010) empha-

size that during the composting process, metal availability and mobility are reduced due to their strong complexing by the forming humus. The fact that nickel mobility was reduced while composting sewage sludge with straw and sawdust was confirmed by the results of our experiments. Nickel is a mobile and water-soluble element. Besides, it tends to bind with soluble organic matter (KABATA-PENDIAS, PENDIAS 1999). Such metal bonds are so easily released that their number tends to rise in the initial phases of composting. However, further transformations which humic compounds in compost undergo make them form complexes with metals which are either poorly extractable or totally unextractable. It is therefore possible that nickel in the exchangeable fraction can undergo such quantitative transformations during the composting process of sewage sludge. Suggestions that quantitative transformations of nickel, from easily activated bonds to poorly extractable ones, occur during the sewage sludge composting process can also be found in papers published by GONDEK (2006), ZHENG et al. (2007), LIU et al. (2007), JAKUBUS and CZEKAŁA (2010). In the experiments described in this article, such transformations were particularly evident in composts C3 and C4 with a small share of sewage sludge (30% and 45%, respectively) but with a high content of sawdust (65% and 50%, respectively). According to JAKUBUS (2010), sawdust in composting mixtures can act as a sorbent of the metals released from the decomposing sewage sludge organic matter. Sawdust, as organic material from timber, undergoes slow degradation and can therefore, at least theoretically, enlarge the pool of poorly available metals.

Despite its considerable affinity with organic matter, nickel develops organic ligands characterised by poorer stability when compared with those formed by copper (NOMEDA et al. 2008). HUANG et al. (2005) came to the conclusion that sulphur compounds as well as functional groups of humic acids play a key role in this phenomenon. Also in the presented studies, this kind of preferential development of copper bonds with organic matter was demonstrated. The highest contents of the discussed metal in the organic fraction were also reported in studies by WALTER et al. (2006) and FARRELL and JONES (2009). The composting process to which sewage sludge mixed with straw and sawdust was subjected increased quantities of Cu both in the exchangeable as well as in the organic fractions. Analogous quantitative changes in copper in the same compost fractions were also presented by MIAOMIAO et al. (2009). JAKUBUS (2010) attributed this phenomenon to copper binding by soluble fulvic acid organic substances in sewage sludge and to possible precipitation of this metal in the form of carbonates. In the design of the sequential analysis applied in this study, carbonate forms and labile organic substances are described by fraction I.

Sequential analysis makes it possible to assess quantitative changes in forms and solubility of metals present in composts, which is particularly useful information when these composts are applied into soil. However, it is a time-consuming technique and therefore not routinely applied in practice.

Alternatively, application of complexing reagents, e.g. EDTA and DTPA, is recommended for determination of compost fertilizer suitability expressed by the content of bioavailable metals. According to HUANG et al. (2005), bioavailability is identified with the degree of solubility and is the highest for water-soluble, exchangeable and carbonate forms of metals, but the lowest – for residual ones. In our investigations, the nickel content determined with DTPA solution was comparable with the one determined in fraction I of the examined composts. On the other hand, the content of bioavailable copper constituted the sum of the copper content in fractions I, II and partly III. In comparison with the content determined in samples from the mesophilic phase, more copper and the same amount of nickel were extracted from mature composts using DTPA solution. Similar effects of the sewage sludge composting process on changes in the content of bioavailable Ni and Cu were reported by QIAO and HO (1997) as well as FANG and WONG (1999). However, as evident from the results presented by HUANG et al. (2005) or WONG and SELVAN (2006), it is by no means a rule because composting can also lead to a decrease in the content of bioavailable forms of these metals.

The decomposition of phytotoxic organic compounds occurs during the composting organic waste and can be assessed with biological methods. In practice, phytotoxicity of compost is evaluated according to the plant germination index, which is a rapid and sensitive technique for identification of substances strongly inhibiting plant germination and development (WALTER et al. 2006, KO et al. 2008, MIAOMIAO et al. 2009, GAO et al. 2010). These authors, after ZUCCONI et al. (1981), attribute inhibition of plant germination to ammonium, acetic acid, phenol or low-molecular fatty acids, that is the compounds released in the course of organic matter degradation; their presence indicates immaturity of composts.

Small values of the GI obtained in this study for the examined composts in their thermophilic phase suggests the possibility of such toxic influence on cress seeds. The results indicate that the main source of these compounds was sewage sludge, a suggestion which was confirmed by the fact that higher proportions of this component in composted mixtures induced stronger germination inhibition of cress seeds. ZUCCONI et al. (1981, after GAO et al. 2010) maintain that the GI value above 80% is an indicator of mature, non-phytotoxic compost. In our investigations, such values were determined only for compost C4 with 30% content of sewage sludge, and they were found to increase in the course of composting. According to literature data (BUSTAMANTE et al. 2008, KO et al. 2008, GAO et al. 2010), this is a dominant tendency in GI value changes. Nevertheless, similar GI values determined for C4 at the beginning and at the end of composting require caution in data interpretation. It is difficult to accept the fact that the examined experimental mixtures were characterized by the same degree of phytotoxicity at the beginning and at the end of the process, as suggested by the results. KO et al. (2008) reported a similar problem but interpreted it by an extremely small

threshold value of the germination index and suggested raising it 110, the value that can reliably determine compost maturity. WALTER et al. (2006) attribute the ambiguity of the results to the selected test plant. Irrespective of the results, the germination index for compost phytotoxicity assessment appears to be a prompt and important diagnostic method.

CONCLUSIONS

1. A higher proportion of sewage sludge in the composted mixture contributed to a stronger inhibition of cress seed germination and to obtaining higher quantities of bioavailable copper and nickel as well as their concentrations in the fractions.

2. Composting sewage sludge with straw and sawdust caused an increase in copper in fractions I and III and its reduction in fractions II and IV.

3. Sequential analysis of nickel in the examined composts confirmed reduced mobility of this metal during the composting process.

REFERENCES

- BARKER A.V., BRYSON G. M. 2002. *Bioremediation of heavy metals and organic toxicants by composting*. Sci. World J. 2: 407-420.
- BUSTAMANTE M.A., PAREDES C., MARHUENDA-EGEA F.C., PEREZ-ESPINOSA A., BERNAL M.P., MORAL R. 2008. *Co-composting of distillery wastes with animal manures: carbon and nitrogen transformations in the evaluation of compost stability*. Chemosphere, 72: 551-557.
- Central Statistical Office 2010. <http://stat.gov.pl/>
- DEBOSZ K., PETERSEN S.O., KURE L.K., AMBUS P. 2002. *Evaluating effects of sewage sludge and household compost on soil physical, chemical and microbiological properties*. Appl. Soil Ecol., 19: 237-248.
- FANG M., WONG J.W.C. 1999. *Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting*. Environ. Pollut., 106: 83-89.
- FARRELL M., JONES D.L. 2009. *Heavy metal contamination of mixed waste compost: Metal speciation and fate*. Biores. Technol., 100: 4423-4432.
- GAO M., LIANG F., YU A., LI B., YANG L. 2010. *Evaluation of stability and maturity during forced-aeration composting of chicken manure and sawdust at different C/N ratio*. Chemosphere, 78: 614-619.
- GONDEK K. 2006. *Zawartość różnorodnych form metali ciężkich w osadach ściekowych i kompostach [Content of different forms of heavy metals in sewage sludge and composts]*. Acta Agroph. 8 (4): 825-838. (in Polish)
- HARGREAVES J.C., ADL M.S., WARMAN P.R. 2008. *A review of the use of composted municipal solid waste in agriculture*. Agric. Ecosyst. Environ., 123: 1-14.
- HUANG G.F., WONG J.W.C., NAGAR B.B., WU Q.T., LI F.B. 2005. *Bioavailability of heavy metals during humification of organic matter in pig manure compost*. www.eco-web.com/editorial/050915.html.
- JAKUBUS M. 2005. *Sewage sludge characteristic with regard to their agricultural and reclamation usefulness*. Fol. Univ. Agric. Stetin., Agric., 244(99): 73-82.

- JAKUBUS M 2010. *Zmiany specjacji i bioprzyswajalności mikroelementów podczas kompostowania osadów ściekowych z różnymi bioodpadami [Changes in speciation and bioavailability of microelements during the composting of sewage sludge with various types of bio-waste]*. Wyd. Uniw. Przyr. w Poznaniu. Rozpr. Nauk. 405: 156. (in Polish)
- JAKUBUS M., CZEKAŁA J. 2010. *Chromium and nickel speciation during composting process of different biosolids*. Fres. Environ. Bull., 19(2a) :289-299.
- JORDÃO C.P., NASCENTES C.C., CECON P.R., FONTES R.L.F. AND PEREIRA J.L. 2006. *Heavy metal availability in soil amended with composted urban solid wastes*. Environ. Monit. Assess., 112: 309-326.
- Journal of Law 2001, No. 62, pos. 628.
- Journal of Law.2010, No. 28, pos.145.
- KABATA-PENDIAS A., PENDIAS, H. 1999. *Biogeochemia pierwiastków śladowych [Biogeochemistry of trace elements]*. PWN, Warszawa, pp. 398. (in Polish)
- KO H., KIM K., KIM H., KIM CH., UMEDA M. 2008. *Evaluation of compost parameters and heavy metals contents in composts made from animals mature*. Waste Manag., 28: 813-820.
- LIU Y., MA L., LI Y., ZHENG L. 2007. *Evolution of heavy metal speciation during the aerobic composting process of sewage sludge*. Chemosphere, 67: 1025-1032.
- MIAOMIAO H., WENHONG L., XINQIANG L., DONGLEI W., GUANGMING T. 2009. *Effect of composting process on phytotoxicity and speciation of copper, zinc and lead in sewage sludge and swine manure*. Waste Manag., 29: 590-597.
- MOSSOP K.F., DAVIDSON CH.M. 2003. *Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments*. Anal. Chem. Acta, 478(1): 111-118.
- NAIR A., JUWARKAR A.A., DEVOTTA S. 2008. *Study of speciation of metals in an industrial sludge and evaluation of metal chelators for their removal*. J. Hazard. Mat., 152: 545-553.
- NOMEDA S., VALDAS P., CHEN S.-Y., LIN J.-G. 2008. *Variations of metal distribution in sewage sludge composting*. Waste Manag., 28: 1637-1644.
- OLSZEWSKI T., DACH J., JĘDRZEJ A. 2005. *Modelowanie procesu kompostowania nawozów naturalnych w aspekcie generowania ciepła [Modelling the process of composting natural fertilizers in the context of heat generation]*. J. Res. Appl. Agric. Engin., 50(2): 40-43. (in Polish)
- QIAO L., HO G. 1997. *The effects of clay amendment and composting on metal speciation in digested sludge*. Wat. Res., 31(5): 951-964.
- QUEVAUVILLER P., LACHICA M., BARAHONA E., GOMEZ A., RAURET G., URE A., MUNTAU H. 1998. *Certified reference material for the quality control of EDTA- and DTPA- extractable trace metals contents in calcareous soil (CMR 600)*. Fres J. Anal. Chem., 360(5): 505-511.
- SYDEJ W., NAMIOTKO A. 2007. *Zmiany właściwości fizykochemicznych gleby użyłnianej kompostami z odpadów komunalnych o różnym stopniu dojrzałości [Changes in physicochemical properties of soil amended with municipal waste composts of different maturity]*. Zesz. Probl. Post. Nauk Rol., 520: 371-378. (in Polish)
- WALTER I., MARTINEZ F., CALA V. 2006. *Heavy metal speciation and phototoxic effects of three representative sewage sludges for agricultural uses*. Environ. Pollut., 139: 507-514.
- WONG J.W., SELVAM A. 2006. *Speciation of heavy metals during co-composting of sewage sludge with lime*. Chemosphere, 63: 980-986.
- ZHENG G.-D., GAO D., CHEN T.-B., LUO W. 2007. *Stabilization of nickel and chromium in sewage sludge during aerobic composting*. J. Hazard. Mat., 142: 216-221.
- ZUCCONI F., PERA A., FORTE M., DE BERTOLDI M. 1981. *Evaluating toxicity of immature compost*. Biocycle, 22: 54-57.