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Impact of humic substances on the bioavailability of copper and zinc during composting of sewage sludge in reduced structural material content conditions

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ABSTRACT

In this paper the results of research work on the transformation of Cu and Zn chemical forms bound with humic acids that occur during sewage sludge composting process are presented. A factor influencing the direction of the observed transformations was the volume of added structural material (including its elimination) to the mix with sewage sludge during the compost batch preparation stage. Composting was carried out in industrial conditions, in periodically turned over windrows differing in the proportion of dehydrated sludge, straw and wood chips 4:1:(0.5 + 0.5) – P1, 8:1:(1 + 1) – P2, respectively and in a windrow without straw added (P3). Test results confirmed impact of the organic matter humification process on the reduction of Cu bioavailability in compost. Cu percentage in humic acids (HA) fraction was increasing during the composting process and varied from 21% to 28% whereas the organic matter humification process did not play a fundamental role in Zn immobilization. The percentage of Zn bound with humic acids (HA), in the final day of composting in particular windrows, was 9.43% – P1, 1.85% – P2 and 3.40% – P3, respectively. Cluster analysis has demonstrated that samples (P3) of the composted sewage sludge without straw added differed fundamentally from the samples taken from P1 and P2 windrows. The samples taken from P3 windrows that presented the lowest contents total of Cu and Zn, carbon contents in humus substances and humic acids. Affiliation of the tested samples to given group (clusters) was influenced, first and foremost, by total Zn and Cu content as well as the content of carbon bound with humus substance and carbon bound with humic acids.

Keywords: Sewage sludge; Composting process; Humic substances; Bioavailability; Heavy metals

1. Introduction

Sewage sludge is a material rich in nutrients for plants, such as organic carbon, nitrogen or phosphorus, which can potentially be used as soil improver and fertilizer. However, direct application of sewage sludge in soil may cause a pollution hazard originating from occurrence of pathogenic microorganisms, heavy metals or phytotoxic organic compounds [1,2]. Composting of sewage sludge and use of compost in agriculture is one of the most economic methods of such waste usage as it combines recycling of materials and utilization of biomass [3,4]. This enables transformation of biodegradable organic waste such as green waste, sewage sludge or catering waste, into stabilized final products such as compost. High impact in the course of composting process has carbon-to-nitrogen (C/N) ratio value, humidity, temperature, pH and aeration [3,5–7]. C/N ratio value is one of key factors having impact both on the composting process as well as compost quality. The initial C/N ratio value has impact on propagation of those microorganisms that control the organic matter decomposition and humification process. C/N value within the 20–30 range is considered as the best

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for composting process [8,9]. Research literature provides many examples of composting of sewage sludge mixes within broad C/N = 15–30 values range [10–15].

Due to high humidity, low C/N value, structural material is being added, such as barley straw, in composting of sewage sludge process, to achieve the best possible composting conditions. The initial C/N ratio value, as well as the quantity and type of structural material added, may have a significant impact on physicochemical properties of compost such as porosity, pH and cation exchange capacity [14,16–19].

Earlier research works have shown that low initial C/N ratio value (<20) has impact on higher nitrogen loss, shorter thermophilic phase and longer compost maturing period [6,9,11,15,20] whereas diminished structural material additive may reduce the composting process cost [21,22].

The biggest problem limiting use of sewage sludge in agriculture is the excessive concentration of heavy metals, which may pose a significant hazard for the natural environment. Many earlier research works have shown that composting process has impact on the limitation of bioavailability of heavy metals [1,18,23–25]. It's been confirmed that increased pH value reduces mobility of heavy metals by their precipitation from the acid-soluble fraction. Also biochemical reactions that lead to decomposition of organic substance play a key role in heavy metals immobilization [16,26–28]. Many research works pertaining to fractionation confirmed that copper is bound mainly with organic matter whereas zinc is bound with Fe/Mn oxides [2,14,25,29,30]. Organic matter may have impact on immobilization of heavy metals through formation of stable complexes originating from interaction between negatively charged interfacial surfaces and metal cations. Humus substances, which are rich in carboxylic and hydroxyl groups, easily form complexes with metals as those substances are amphiphilic, both hydrophobic and hydrophilic [3,14,31]. Due to higher molecular mass and low acidic functional groups content, complexes of metals with humic acids (HA) are less soluble, mobile and bioavailable that those with fulvic acids (FA) [23,27,32].

Earlier research performed on the mechanism of heavy metals immobilization through formation of complex compounds with humic acids, during composting process, rarely took into account the impact of the initial C/N ratio value, the type and quantity of added structural material.

Generation of Cu and Zn complex compounds with humus acids (HA and FA) may play a key role in limitation of bioavailability of said metals, therefore, in suppression of the hazard of ground water pollution with heavy metals that may be caused by application of composted sewage sludge to soil. The objectives of the tests performed were as follows: (i) definition of the direction of changes in Cu and Zn contents bound with humus substance (HS) and humic acids (HA) during composting, (ii) assessment of Cu and Zn bioavailability and (iii) assessment of the impact of limited quantity of the structural material additive on the generation of Cu and Zn compounds with humic acids. The main objective of the research was to determine impact of low initial C/N ratio value originating from reduced straw addition to sewage sludge, on the on the bioavailability of copper and zinc during the composting process.

To assess the above processes the cluster analysis aimed at identification of key factors influencing Cu and Zn contents in HA fraction during sewage sludge composting with variable mass addition of barley straw, being the source of organic carbon, was applied.

2. Material and methods applied

2.1. Composting process

The sewage sludge composting process was performed on industrial scale at the Goleniów wastewater treatment plant premises (in Poland) under the project financed by the EU South Baltic Program [33]. The composting process was performed in three stages P1, P2, P3. Particular stages differed in the quantity of added structural material, that is, barley straw. At P1 stage the mix batch was composed of mechanically dehydrated sewage sludge, barley straw, wood chips and mature compost in 4:1:(0.5 + 0.5) mass proportion, as described later in the text as: 4:1:1. At stage P2 the batch was a mix of the same components in 8:1:(1 + 1) proportion by weight, as described later in the text as: 8:1:2. At stage P3 the composting process was performed for a mix of sewage sludge with wood chips (without straw and inoculum additives) in 1:1 proportion by weight, as described later in the text as 1:1. The composted mix composition is presented in Table 1.

The composting process at P1 and P2 stages was performed under roofed windrows measuring 70 m × 3 m × 1.5 m, which were being aerated by application of natural ventilation and periodical aeration. Composting at P3 stage was performed under intense aeration conditions whereas the windrow was covered by a semi-permeable membrane of GORECover® type.

The pore oxygen concentrations were monitored by an O_2 sensor. During composting the pore oxygen concentrations were 15–21 vol.%.

Composting was carried out in autumn and winter. The composting process took 9 weeks (63 d). Five compost samples of approximately 1 kg in weight were taken from which, after mixing, a sample for laboratory tests as per Polish standard PN-R-04006: 2000, was prepared. Samples from (P1, P2, P3) windrows were taken 6 times: in 0, 10th, 16th, 24th, 29th, 48th and 63rd day of the process. Internal temperature of the windrows was monitored during the composting process.

The mixes intended for composting featured, due to variable barley straw additives, a variable initial C/N ratio values, which were P1 – 19; P2 – 9 and P3 – 9.20, respectively.

Table 1
Composted mix composition

Mix components	P1	P2	P3
	Mass proportion		
Sewage sludge	4	8	1
Barley straw	1	1	0
Wood chips	0.5	1	1
Mature compost (inoculum)	0.5	1	0

2.2. Chemical analysis

In samples of the mix intended for composting and in compost samples the following physicochemical parameters were determined: dry matter content after drying at 105°C, organic matter content (OM) as a residue after ignition at 550°C, total organic carbon (TOC) and total nitrogen (TN). Determination of TOC and TN contents was performed using VarioMax CN macroanalyzer.

Determination of total copper (Cu_T) and zinc (Zn_T) was performed for dried (105°C) and comminated samples of composted sewage sludge by application of the flame atomic absorption spectroscopy (FAAS). The samples were being mineralized with 65% HNO_3, 30% H_2O_2 and 70% $HClO_4$ mix using microwave energy (Milestone 1200 Mega). To determine copper and zinc contents iCE 3500Z Thermo Scientific SOLAAR atomic absorption spectroscope was used.

The extraction of the sum of humic acids (HS) was performed with 0.5 M NaOH based on the modified IHSS method [22]. Carbon in the alkali extracts (C_HS) and (C_HA) was determined using VARIOMAX CN macroanalyzer. Carbon in fulvic acids (C_FA) was determined as the difference between carbon contents in C_HS and C_HA.

In obtained extracts HS (humus substance) and HA (humic acids) contents of copper and zinc contents bound with humus substance (Cu_HS) and with humic acids (Cu_HA) as well as zinc (Zn_HS, Zn_HA) were determined.

Test results were developed using STATISTICA 13.3 of StatSoft software. Analyzed physicochemical parameters are presented as arithmetic mean values for three samples.

3. Test results and discussion

3.1. Temperature variations and organic matter degradation

The results of main physicochemical parameters of the raw materials used in the composting process are presented in Table 2.

Compost batch in P1 featured the highest TOC value, that is, 428.5 g/kg·d.m., organic matter (OM) content – 85.2% d.m. and the highest C/N ratio value 19.00; total nitrogen content (TN) had the lowest value – 23.0 g/kg·d.m. In P2 windrow values of the primary physicochemical parameters of the compost batch were: TOC – 394.0 g/kg·d.m.; OM – 80.7% d.m.; C/N – 9.00 and TN – 42.70 g/kg·d.m., respectively. The compost batch in P3 windrow featured the lowest organic matter (74.5% d.m.) and organic carbon (369.0 g/kg·d.m.) contents. TN content was 40.1 g/kg·d.m. whereas C/N ratio value –9.20.

Temperature is strongly correlated with biochemical reactions speed, therefore, it is often used to reflect the activity of microorganisms and determine the stability of composting process [4,14]. In compost windrows with variable straw content (P1 and P2) temperature increased vigorously in the third day of the process. The highest temperature value was noted at stage P3, that is, 70°C. at stage P2 – 66°C and at stage P1 – 63°C. The thermophilic phase (>50°C) lasted longest at P1 stage (55 d). Temperature increase rate in the windrow having the highest straw content (P1) was lower than in two other windrows (P2 and P3). The highest temperature values were noted at stage P3, which could result from compost windrow coverage. The lowest average temperature values in the thermophilic phase were measured in P1 windrow. At this stage the thermophilic phase was the shortest. Temperature distribution was different than in the research works presented by Wu et al. [4] and Guo et al. [16] pertaining to composting of pig manure, where temperature increase rate was higher in those windrows that had ampler structural material input.

The initial moisture content of the samples taken in stages P1, P2 and P3 was 64.80%, 69.10% and 62.70%, respectively. The final value was: 59.20% (P1), 68.60% (P2), 53.50% (P3).

OM content changes at all composting stages demonstrated the same direction. During the first days of the process, considerable reduction of the organic matter content occurred during 30 d and then this value became stable. Deficit of organic matter in all three mixes, compared to the initial value, remained within the range from 12.7% to 14.4% (the highest value was for P3 – 14.4%. and the lowest for P2 – 12.7%). The trend of change of organic carbon contents in tested samples had similar form. High value of OM and TOC peaks in windrow P3, during the 29th day, could be caused by non-homogeneity of the tested sample. In this particular case the structural material was composed of wood chips, which could bring-in a high load of carbon. In compost windrows featuring variable initial C/N, deficit of OM and TOC during the composting process was comparable. Change of TOC contents in all tested windrows is presented in Fig. 1a.

At the initial process stage the samples taken from P1 windrow featured the highest C/N ratio values. After the 29th day of composting C/N ratio values in all windrows became stable. Changes of C/N ratio values are presented in Fig. 1b.

3.2. Change of humus substance contents during the composting process

Fig. 2a shows change of carbon contents in HS (C_HS) fraction that occurred during the composting process. The lowest carbon contents in HS and HA fractions were noted in the samples taken from the windrow in which sewage sludge was composted without straw added (P3). Change of humus substance HS and humic acids HA contents reflected the humification process occurring during sewage sludge composting operation.

Carbon content in HS fraction originating mainly from lignin, polysaccharides and nitrogen components [20,23,27,34] decreased in windrows P2 and P3 by 15.8%, 32.7%, respectively compared to the initial values. This can result from decomposition of easily biodegradable compounds [14,24,26,35]. In the case of compost taken from P1 windrow 10% increase of carbon content in fraction HS increase was noted.

Carbon content in HA fraction in the samples taken from P1 and P2 windrows was maintained within 128.69 to 149.19 g/kg·d.m. range (Fig. 2b). The highest C_HA at the last day of the process was noted in the samples taken from P1 windrow (138.38 g/kg·d.m.) and the lowest content was noted in the samples from P3 windrow (30.50 g/kg·d.m.). During the process course C_HA content increase at stages P1 and P2 occurred. C_HA contents after 9 weeks of composting increased by 3.7% (P1) and 4.7% (P2), respectively

Table 2
Physicochemical parameters of the raw materials used in the composting process

Parameter	Sewage sludge			Straw	Wood chips
	P1	P2	P3		
Dry matter, %	15.6	15.6	14.00	62.0	34.0
Organic matter, % d.m.	78.2	78.2	81.00	94.0	87.0
Total organic carbon, g/kg·d.m.	404.00	404.00	332.0	455.0	444.0
Total nitrogen, g/kg·d.m.	70.54	70.54	68.1	7.10	11.80
Carbon-to-nitrogen	5	5	4.87	64	38
C_HS, g/kg·d.m.	170.99	170.99	171.10	–	–
C_HA, g/kg·d.m.	148.82	148.82	37.40	–	–
C_FA, g/kg·d.m.	60.94	60.94	133.70	–	–
Cu_T, mg/kg·d.m.	252.25	174.75	216.75	3.60	–
Zn_T, mg/kg·d.m.	497.25	370.50	175.75	11.82	–
Cu_HS, mg/kg·d.m.	91.50	70.5	72.50	–	–
Cu_HA, mg/kg·d.m.	22.50	28.50	7.17	–	–
Cu_FA, mg/kg·d.m.	69.00	42.00	65.33	–	–
Zn_HS, mg/kg·d.m.	97.50	52.50	46.67	–	–
Zn_HA, mg/kg·d.m.	39.73	10.50	6.67	–	–
Zn_FA, mg/kg·d.m.	57.77	42.00	40.00	–	–

Dry matter – d.m.

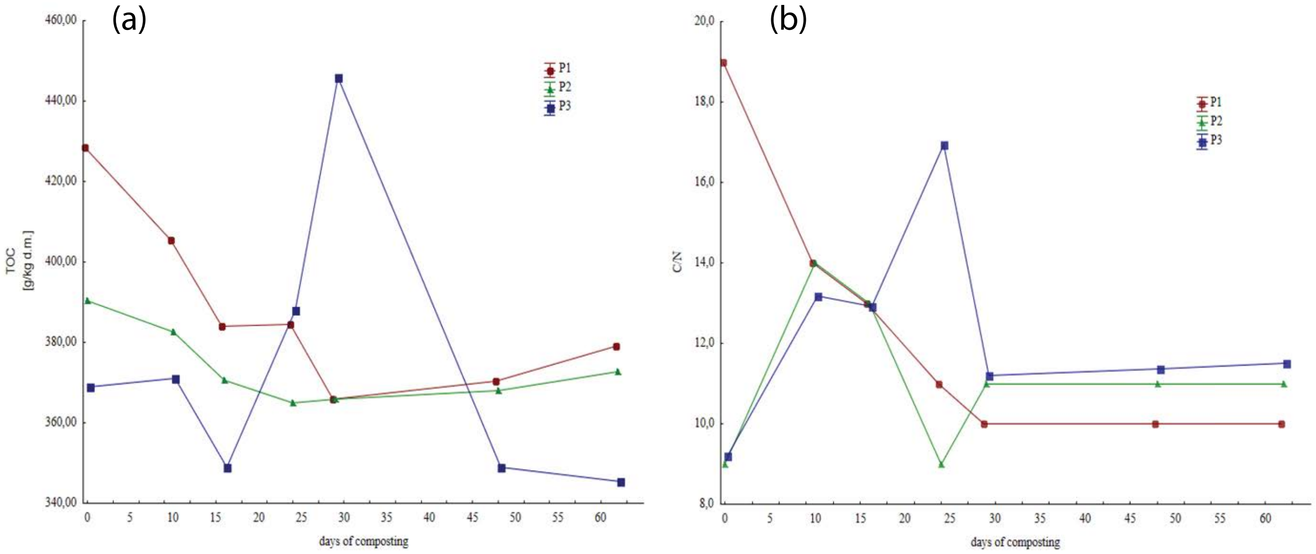

Fig. 1. Change of total organic carbon (a) and carbon-to-nitrogen (b) values at particular stages P1, P2, and P3 during the composting process.

compared with the contents at the process beginning. The results were compatible with those presented by Wang et al. [14] and Guo et al. [16]. However, in the case of sewage sludge being composted without straw additive (P3), reduction of C_HA content by 21.3% was noted; this could be caused by lower rate of HA macromolecular compounds synthesis [35]. Increase of C_HA content indicates the humification process in progress and compost maturity degree [16,22,32,36].

3.3. Cu content in HS and HA fractions

Total copper content (Cu_T) in the compost batch, at particular composting stages P1, P2, P3 was: 106.00, 174.75 and 58.00 mg/kg·d.m., respectively. Cu_T concentration was increasing during the composting process.

During the composting process copper content in HS and HA fractions was increasing at all stages. Samples of

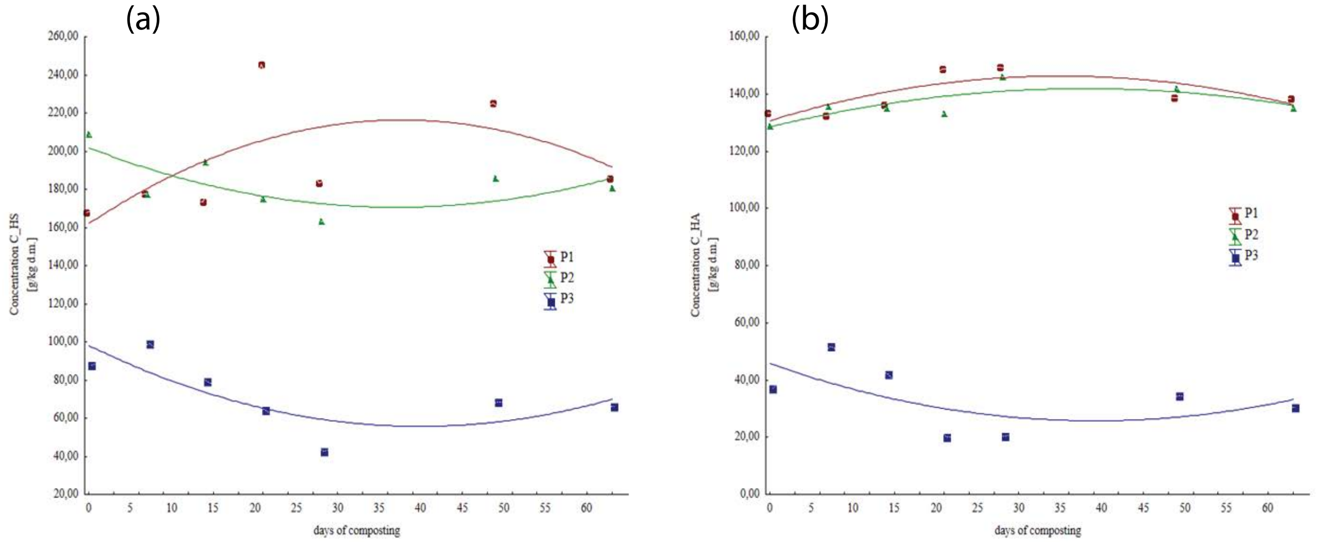

Fig. 2. Change of carbon contents in C_HS (a) and C_HA (b) at particular stages P1, P2, and P3 during the composting process.

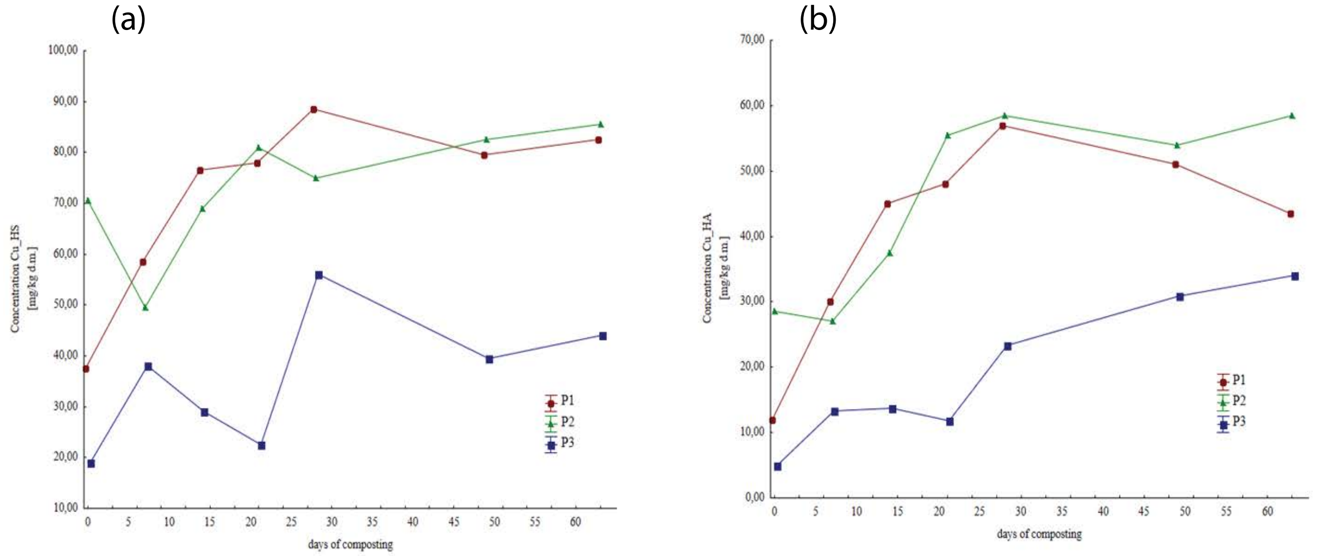

Fig. 3. Change of copper contents in Cu_HS (a) and Cu_HA (b) at particular stages P1, P2, and P3 during the composting process.

composted sewage sludge from P3 windrow, without straw added, featured the lowest Cu contents in HS and HA fractions (Fig. 3a and b). Cu content increase in HS and HA had been observed by Ingelmo et al. [26], Labroda et al. [27] and Kang et al. [32].

The highest Cu content in HS fraction (in the compost batch) was noted in the samples taken from P2 windrow (70.50 mg/kg·d.m.). At the initial composting stage, until the 16th day of the process, Cu_HS and Cu_HA contents were higher in P1 than in P2, whereas, after the 24th day copper content in both fractions was insignificantly higher in the samples taken from windrow P2 than from P1 (Fig. 3a).

The highest increase of copper content in fractions HS and HA was noted in the samples taken from P3 windrow (no straw added). Cu_HA content in the samples taken from said windrow during the last day of the process increased by 85.3% compared with the concentration at the composting process beginning whereas Cu content in HS fraction increased by 56.8%. The lowest increase of Cu_HS and Cu_HA concentration was noted for stage P2, in which the mass proportion of the mix components to be composted was 8:1:2. The concentration values were 20.3% and 51.3%, respectively.

Percentage of copper bound with humus substance (HS), at all stages, varied from 24% to 48% of the total Cu content. At stage P1 (the biggest straw input) and stage P3 (no straw added) 1.1-fold increase of Cu_HS percentage in the samples taken during the last day of composting, compared with the initial value, was noted whereas at stage P2 Cu percentage in HS fraction, at the last day of the process, decreased by 5% compared with the value determined for the compost batch.

Samples of composted sewage sludge at stage (P1) in the initial composting phase (up to the 16th day) featured the highest percentage of copper occurring in HA fraction than for the samples from stages P2 and P3. Cu percentage in HA fraction, stage P1, in the samples taken at the process beginning, made 11.32% of the total Cu content whereas in the samples taken after the 63rd day – 21.80%. Compost samples from stages P2 and P3, taken on the last day of the process, demonstrated comparable percentage of Cu_HA (P2 – 26.23%; P3 – 27.76%).

The highest increase of copper percentage in HA acids fraction was observed in the samples taken from P3 windrow (sewage sludge with no straw added). Cu content in this fraction increased 3.25-fold compared with the initial content. Cu percentage in HA fraction at P1 stage increased twice whereas in P2 stage – 1.6-fold. At the final phase of composting process polymerization and condensation of low-molecular compounds originating from mineralization of organic matter occurs. Macro-molecular aromatic polycondensed humic acids structures are formed [23,24,31,32]. Therefore, a supposition can be made that those heavy metals, which are bound with humic acids as the solid phase, are insoluble and stable. Copper is an element featuring high affinity to –OH, –COOH function groups of humic substance [14,29].

3.4. Zn contents in HS and HA

Total zinc content (Zn_T) in the compost batch at particular composting stages P1, P2, P3 was: 312.00, 370.50 and 175.75 mg/kg·d.m., respectively. Zn_T concentration was increasing during the composting process.

Zn content increase in fraction HS was noted in all composting stages. The highest Zn content increase during the last day of the composting process was noted for the samples taken from P3 and P2 windrows and it was 31% as well as 27%, respectively compared with the initial content. The compost samples from P1 windrow featured the lowest Zn_HS concentration increase during the composting process (20%). Zinc content changes in HS fraction are presented in Fig. 4a. Zn_HS percentage at P1 stage was maintained within the range from 16.18% to 22.40%, at P2 from 13.85% to 17.13%. The samples of composted sewage sludge from stage P3 featured the highest Zn_HS percentage (from 18.62% to 26.55% of total C content). During the composting process Zn_HS percentage in the samples taken from P1 and P3 windrows was decreasing. Only in the samples from P2 windrow 4% increase was noted.

The highest Zn concentrations in HA fraction were noted in the samples taken from P1 windrow, and the lowest ones, in the samples taken from P3 windrow (Fig. 4b). During the composting process Zn content in HA fraction, in the samples taken on the last day, increased by approximately 31% at P1 and P3 stages compared with the initial value whereas Zn_HA content in the samples taken from P2 windrow on the 63rd day was lower by 16.7% compared with the initial value. Changes of zinc contents in HA fraction are presented in Fig. 4b. During the composting process percentage of Zn in HA fraction was increasing in the samples taken from P1 windrow whereas in the samples taken from P2 and P3 windrows it was lower than the initial value. Zn_HA percentage in P3 had the lowest value and was maintained from 0.42% to 3.79%. The highest Zn_HA percentage was noted at P1 stage and it was maintained from 8.67% to 16.15%. At this stage, during the first phase of composting, Zn content was increasing (until the 16th day) and then decreasing. A supposition can be made that Zn, which was bound with organic matter during its mineralization, was transformed into mobile forms. Similar results were obtained by Kang et al. [32]. Low Zn_HA percentage shows poor affinity of this element to humic acids because Zn sorption by organic matter depends on the reaction and almost disappears at low pH values. However, considering amphoteric properties

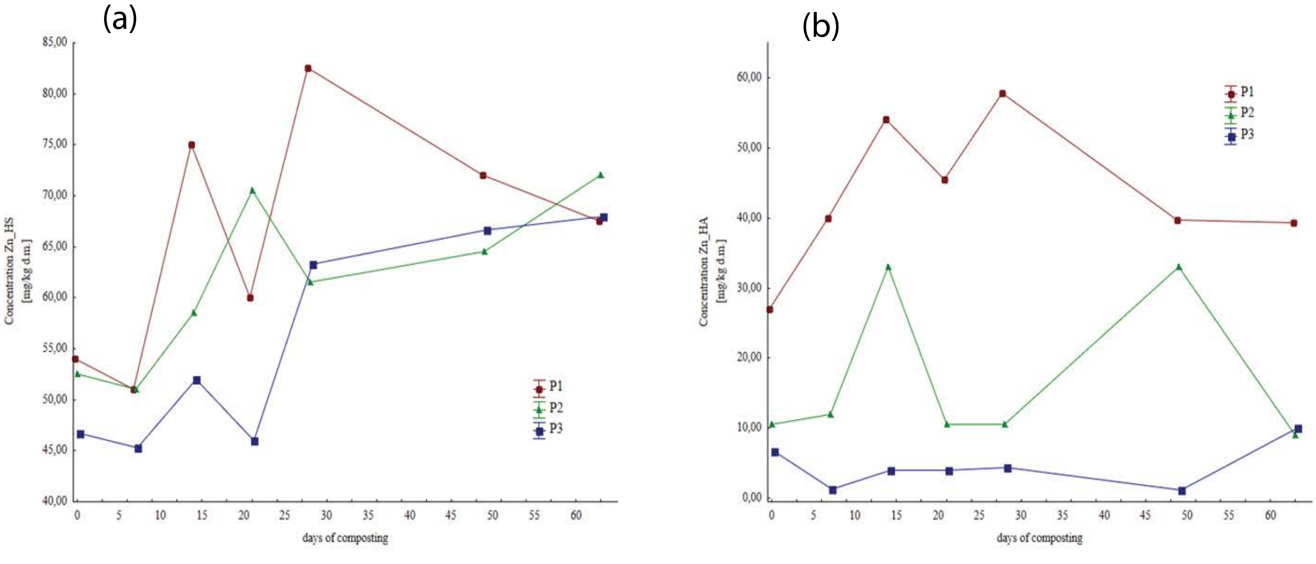

Fig. 4. Change of zinc contents in Zn_HS (a) and Zn_HA (b) at particular stages P1, P2, and P3 during the composting process.

of Zn oxide, its capability to create complex anions as well as organic-mineral compounds and high solubility, it is a mobile and bioavailable element [32,37]. Similar results were obtained by Kang et al. [32] and Ingelmo et al. [26].

3.5. Statistic analysis

Due to limited quantum of data tau Kendall's correlation was selected; like rank correlation it is a measure of monotonic dependence of random variables and shows any monotonic relationship, also a non-linear one (StatSoft 2006).

Non-parametric tau Kendall's statistics manifested statistically important (at assumed level of confidence $\alpha = 0.05$) correlations. Cu_HA content was positively correlated with C_HA content ($r = 0.539$) and with Cu_T content ($r = 0.778$). However, between Cu_HA and C/N ratio value a negative correlation occurred ($r = -0.374$). Similar relationships were obtained for Cu_HS variable. Cu_HS content was strongly positively correlated with Cu_T ($r = 0.826$) and C_HS ($r = 0.463$) and negatively correlated with C/N ($r = -0.428$). Similar results pertaining to high positive correlation of Cu_HA with C_HA was obtained by Kang et al. [32], Ingelmo et al. [26] as well as Laborda et al. [27].

For qualitative variable Zn_HA statistically significant correlation between C_HS ($r = 0.544$); C_HA ($r = 0.593$); Zn_T ($r = 0.361$) and Zn_HS ($r = 0.344$) variables was obtained.

Also cluster analysis was performed in order to asses impact of particular variable values on the analysed process and to demonstrate similarities between groups in terms of selected qualitative variables [38]. In this case, the qualitative variables comprised Cu_HA and Zn_HA contents. To develop the qualitative model a tree algorithm was applied (STATISCA 13.1) called as the hierarchical cluster analysis, which is used to identify similarities in measurement data.

This analysis led to obtaining three differential groups. Affiliation to particular group was mostly influenced by carbon content in HS and HA (C_HS, C_HA) fractions as well as total copper content whereas the lowest impact has been attributed to TOC content and C/N ratio value (Fig. 5).

The first group was composed mainly of samples taken from windrow P1 during the first weeks of the composting process. Samples demonstrating the highest contents of C_HS, C_HA and Cu_T – were put into the second group; these were mainly compost samples taken after the 24th day of composting at P1 and P2 stages. The third group was composed of samples taken at stage P3, which demonstrated the lowest C_HS, C_HA and total Cu content values. Samples of composted sewage sludge taken from the windrow containing no straw clearly differed from the other ones (Fig. 6).

In the case when the qualitative variable was Zn_HA content, similar arrangement of the objects into groups was obtained as in the case of Cu_HA variable. The analysis resulted in three clusters. Affiliation to given group was predominantly influenced by total zinc content (Zn_T), carbon content in HS and HA fractions, whereas the least significant impact had Zn content in HS fraction, C/N ratio value and TOC content (Fig. 7).

The third group was composed of samples taken from windrow P3, which manifested the lowest total Zn content

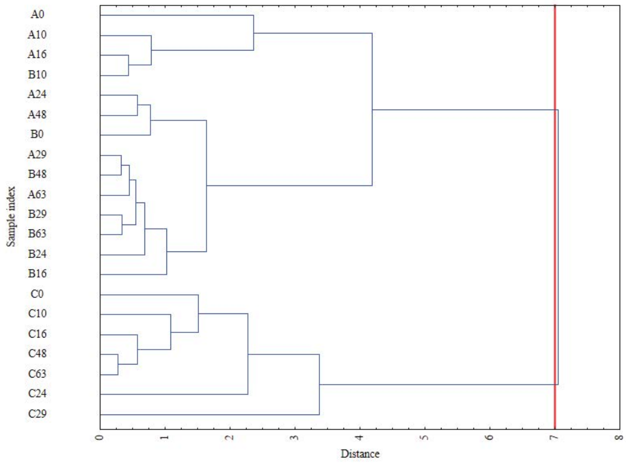

Fig. 6. Dendrogram – hierarchical relation between objects (Cu_HA qualitative variable) (A, B, C stages of composting, that is, P1, P2, P3, respectively; figures indicate subsequent days of composting).

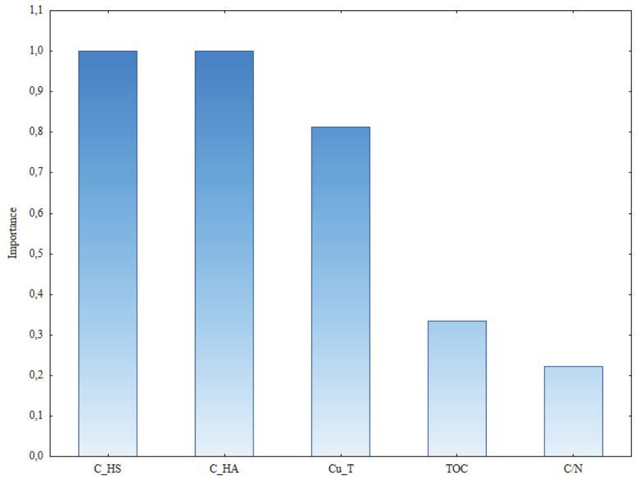

Fig. 5. Significance of predictors for Cu_HA variable.

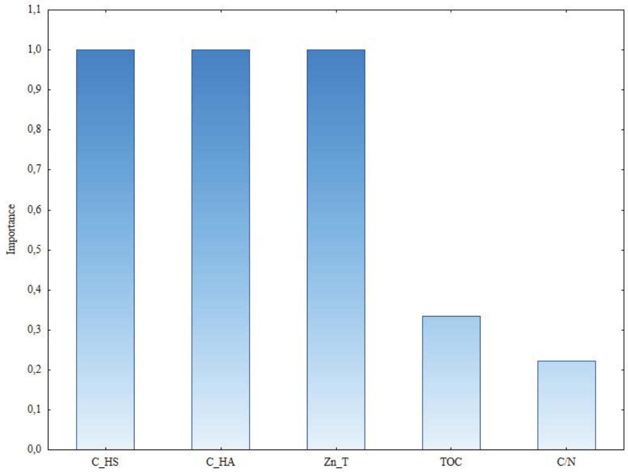

Fig. 7. Significance of predictors for Zn_HA variable.

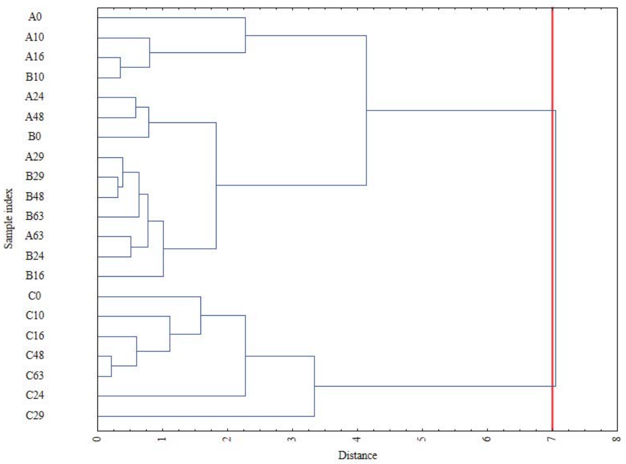

Fig. 8. Dendrogram – hierarchical relation between objects (Zn_HA qualitative variable) (A, B, C stages of composting, that is, P1, P2, P3, respectively; figures indicate subsequent days of composting).

and lowest Zn_HS, C_HS and C_HA contents. The first cluster was composed of those samples that had the highest TOC content as well as C/N ratio values; these were mostly samples taken at the first composting phase from the windrow with the biggest straw input (P1). The second group was composed mainly of samples taken as of the 16th day of the process from P1 and P2 windrows. The relationship of affiliation and similarities between tested windrows is presented in Fig. 8. [Average values distribution is demonstrated by a dendrogram].

Tau Kendall's test (non-parametric statistics) was applied. For analysis purposes, as quantitative variables, those parameters were selected for which statistically significant correlation between variable Zn_HA: C_HS ($r = 0.544$); C_HA ($r = 0.593$); Zn_T ($r = 0.361$) and Zn_HS ($r = 0.344$) was obtained.

The cluster analysis has demonstrated that samples of composted sewage sludge without added straw (P3) differed fundamentally from the samples taken from P1 and P2 windrows. Affiliation of the tested samples to given group (clusters) was influenced, first and foremost, by total Zn and Cu contents as well as the contents of carbon bound with humus substance C_HS and carbon bound with humic acids C_HA.

4. Conclusions

The issue of transformation of heavy metals during composting process, volume of which increases with the increase of sewage sludge share in the compost mass, is extremely important. It is significant in the context of assessment of real hazard for the natural environment in the event of use of sewage sludge based compost in agriculture. Increased content of copper and zinc compounds in sewage sludge used in the composting process may have negative impact on the biochemical transformation processes, and at the same time, pose a hazard for ground water pollution.

The tests performed had demonstrated that limited input of the structural material, that is, barley straw, has no negative impact on the composting process. However, absence of straw as a source of carbon has impact on this element's presence in HS and HA fractions.

It appears from the tests performed that during composting stable Cu complexes with humic acids are formed. Percentage of copper in humic acids fraction, at all composting stages, reached the values from approximately 21% to approximately 28%, which proves immobilization of said element. Therefore, it can be maintained, that organic matter humification process has impact on the limitation of Cu bioavailability in compost. Compared with Cu, Zn demonstrated much lower percentage in HA fraction, which confirms its lower affinity to humic acids. Therefore, it can be noted that the process of origination of humic acids has no fundamental impact on Zn compounds immobilization during composting process. The tests performed have demonstrated significant impact of total Cu and Zn contents as well carbon content in HS and HA fractions on the content of said metals bound with humic acids.

Based on the cluster analysis, differences between clusters were found due to the content of Cu_T, Zn_T, C_HS, and C_HA. 3 major groups were obtained: group 1 clustered samples with high contents of C_HA and C_HS which where the highest addition of straw was present; group 2 clustered samples with the highest content of Zn_T and Cu_T which were reduced amount of straw; group 3 clustered samples that presented the lowest contents of Cu_T, Zn_T, C_HS and C_HA which where sewage sludge were composted without the addition of straw. Cluster analysis can be a useful tool to associate the content of Zn_HA and Cu_HA to the quantity of added structural material.

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