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Immobilization of Zn and Cu in Conditions of Reduced C/N Ratio during Sewage Sludge Composting Process

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Abstract: In this paper we present results of research on the transformation of chemical forms of two elements (Cu, Zn) that occurred at the highest concentration in sewage sludge being processed in a composting process. The factor that had impact on the direction of the observed transformation was the amount of straw added to the mix with sewage sludge at the batch preparation stage including elimination of an additional source of organic carbon (straw). The analysis of contents of Cu and Zn chemical forms was performed applying Tessiere's methodology. It was ascertained that reduction of supplementation has positive impact on the allocation of tested elements in organic (IV) and residual (V) fractions with a simultaneous decrease of heavy metals mobile forms share in bioavailable fractions, mostly ion exchangeable (I) and carbonate (II). Using an artificial neural network (ANN), a tool was developed to classify composts based on Austrian standards taking into account only I ÷ IV fractions treated as a labile, potentially bioavailable, part of heavy metals bound in various chemical forms in compost. The independent variables that were predictors in the ANN model were the composting time, C/N, and total content of the given element (total Cu, Zn). The sensitivity coefficients for three applied predictors varied around 1, which proves their significant impact on the final result. Correctness of the predictions of the generated network featuring an MLP 3-5-3 structure for the test set was 100%.

Keywords: composting; heavy metals; immobilization; speciation

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1. Introduction

Composting is a method of biological waste treatment, which guarantees, in the case of municipal waste, production of a biologically stable product, which is important in the context of its further management, e.g., by disposal [1]. Annually, 12.8 million tons of household and commercial waste are produced in Poland, whereof over 1.2 million tons, approximately 9.5%, are being processed through composting [2]. The composting process is also used to process sewage sludge originating from municipal wastewater treatment plants; its volume systematically increases. Comparing the data for 2000 and 2018, the volume of sewage sludge amassed in Poland increased by 62%, reaching 583 thousand tons of dry mass [3]. Being a method of biological transformation of biodegradable waste, composting features high dynamics of organic matter transformation due to mineralization and humification, which guarantees production of a product of high fertilizing values [4,5]. Compost manufactured based on municipal sewage sludge is qualified as a soil improver or an alternative substrate (growing media) used in industrial plant production [6,7]. High contents of macroelements cause fertilization with compost to increase the content of organic substances, thus improving soil properties. Unfortunately, due to increased concentrations of heavy metals in sewage sludge, there is a high risk of exceeding their admissible values in compost, thus limiting the possibility of its use [8].

A consequence of systematic use of compost with increased heavy metal concentrations to fertilize soil is the accumulation of microelements in the food chain, thus posing a considerable hazard for human health [9,10]. It should be underlined that in regulations applicable in various countries, maximum admissible values are indicated, defined by the total contents of heavy metals made up of the sum of all chemical forms of a given element (Table 1).

Table 1. Heavy metals limits in selected EU countries. Source: self-elaboration based on [1] Regulation (EU) 2019/1009 [11]; [2] Biala and Wilkinson [12].

Country	Concentration, $mg \cdot kg^{-1}$d.m.							
	As	Cr	Cu	Hg	Ni	Pb	Zn	Cd
Poland [2]	-	100	-	2	60	140	-	5
The Netherlands [2]	15	50	90	0.3	20	100	290	1
Sweden [2]	-	100	100	1	50	100	300	-
France [2]	25	120	300	2	60	180	600	3
Greece [2]	15	510	500	5	200	500	2000	10
Germany [2]	1	100	100	1	50	150	400	1.5
Denmark	25	-	1000	0.8	30	120	4000	25
EU [1]	40	2	-	1	50	50	-	2

Using a sequential chemical extraction method such as the BCR (Community Bureau of Reference)-four-step extraction, or the five-step extraction method developed by Tessiere, comprehensive information on the distribution of heavy metals fractions can be obtained; this is useful for prediction of metals' mobility, bioavailability and leaching rates [13,14]. Speciation testing consisting of sequential extraction of heavy metals from compost samples by dissolution of various elements' chemical forms [15] clearly indicated that part of micro-pollutants can be considered as permanently bound within the medium mineral matrix [16–19].

According to available knowledge the correct course of composting in industrial conditions requires specific technological parameters, including the proportion between total organic carbon (TOC) and total nitrogen (TN). The optimum C/N ratio value was not fixed unequivocally and depending on the raw material type as well as the remaining parameters, i.e., humidity, intensity of aeration, and temperature, generally falls within the 25–35 interval [20]. When the composting process is performed, due to a high concentration of nitrogen in sewage sludge being 2–7% d.m. [21–23], supplementation consisting in addition of material increasing the organic carbon share in the composting mass is used [24–26].

Usage of various types of supplements that act as additional components modifying the composting mass composition as a factor regulating the required C/N parameter value was, and still is, a topic of many research works [27–30]. Considering the risk of origination of gaseous ammonia (NH_3) that has a toxic impact on microorganisms, in the case of increased organic nitrogen concentration [27,31], research on the composting process in which C/N values are lower than those recommended is relatively rare. A good example can be the research work performed by Kulikowska and Sindrewicz [32], who used a reactor of 1.3 m^3 volume and a relevant proportion between dehydrated sewage sludge and barley straw modifying the C/N parameter to attain a 15 value. During the said research work no negative impact of a decreased supplement in the composted mix on the process course was found. Similar conclusions were drawn from tests that were performed at an industrial scale, where the initial C/N ratio value in the batch amounted to 12 [33].

Although composting research pertaining to heavy metals speciation indicates that with the passage of time their concentrations in bioavailable fractions decreases and increases in inert fractions [34], the impact of limited supplementation decreasing C/N values on the direction of heavy metals' chemical forms' transformation has not been made clear. Meanwhile, the most frequently used supplement, i.e., straw, is a scarce material, the increasing market prices of which raise compost production costs; therefore, research works were commenced to verify the following thesis: (i) in the case of sewage sludge composting, any decrease in supplementation, including its elimination, has no negative impact on heavy metals' chemical forms' transformation towards inert forms, and (ii) increased nitrogen concentration decreasing the C/N value does not limit the composting process intensity.

During the commenced research, a change of the selected heavy metals' contents in those fractions that were separated via sequential extraction in compost samples produced from sewage sludge in decreased supplementation conditions was analyzed. The objective of the research work was evaluation of (i) the direction of transformation of zinc and copper chemical forms during composting depending on the batch quality made up of a mix of sewage sludge and straw fixing the C/N value, and (ii) a possibility to use an artificial neural network (NN) as a tool for compost classification taking into account those heavy metals' chemical forms that might pose a real hazard. The results of heavy metals' content analysis for sewage sludge used in the research work show that except for Zn and Cu, concentrations of the remaining elements (Cr, Cd, Ni, Pb, and Hg) did not exceed their admissible values [35], thus justifying limiting the speciation testing range to those two elements.

2. Material and Methods

2.1. Composting Experiment (Device)

Tests were performed on an industrial scale at the Goleniów (Poland) wastewater treatment plant within a project financed under the EU South Baltic [35] project. During the tests the course of mechanically dehydrated sewage sludge with structural materials added in various proportions was monitored. At stage I, a mix of sewage sludge with added barley straw, wood chips, and mature compost (inoculum) in mass proportions of 4:1:0.5:0.5 w/w (E1) was used. At stage II, the mix composition using the same components was 8:1:1:1 w/w (E2). At stage III, straw was abandoned and sewage sludge was mixed only with wood chips in 1:1 w/w proportion (E3) (Table 2).

Table 2. The composition of the mixture to be composted.

Mixture Components	E1	E2	E3
	Mass Proportion		
Sewage sludge	4	8	1
Barley straw	1	1	-
Wood chips	0.5	1	1
Mature compost (inoculum)	0.5	1	-

The composting process carried out in stages I and II was performed under roofed windrows featuring a trapezoid cross-section of approximately 70 m in length. These windrows were mechanically turned over twice per week during the first three weeks of composting, whereas in subsequent weeks, once per week on average. The composting process performed in stage III was done in similar windrows as in stages I and II but under GORECover® semi-permeable membranes in intense aeration conditions by pumping air through ducts located in the reactor concrete floor. The mass of each windrow was approximately 200 tons. Each of those three stages was repeated twice. Physical and chemical characteristics of the raw materials and composting initial mixtures are shown in Table 3.

Table 3. Physical and chemical characteristics of the composting initial mixtures used.

Material	Stage	Dry Mass	Organic Matter	Total Organic Carbon	Total Nitrogen	C/N	Cu	Zn
			[%]				[mg·kg^{-1}d.m.]	
Sewage sludge	E1	21.4	81.4	33.92	7.48	5.0	225.25	551.75
	E2	15.6	78.2	40.4	7.54	5.0	252.50	497.25
	E3	14.0	81.0	33.20	6.81	4.9	216.75	531.50
Barley straw	E1	62.4	94.2	45.7	0.7	66	3.50	12.75
	E2	62	94.0	45.5	0.71	64	3.60	11.82
Wood chips	E1	34.7	87.0	44.4	1.14	39	-	-
	E2	34.0	87.0	44.4	1.18	38	-	-
	E3	34.2	87.1	44.4	1.12	39	-	-
Compost (at 1 day)	E1	21.7	83.65	41.35	3.05	14.56	144.25	358.75
	E2	20.5	80.30	39.08	4.07	9.61	184.25	418.50
	E3	37.30	74.50	36.90	4.01	9.20	58.50	175.75

2.2. Physical and Chemical Parameters Analyses

During the field tests, temperature change in all composted windrows was monitored. From each windrow, five compost samples of approximately 1 kg in weight were taken, and after their mixing a sample for lab tests, according to the Polish standard PN-R-04006: 2000, was taken [36].

Particular parameters of compost samples were determined using mainly standard research methods in accordance with Polish standards (PN). The lab tests comprised determination of dry matter content (d.m.) after sample drying at 105 °C (PN-R-04006), the organic matter content was determined by the loss on ignition of the dry mass at 550 °C (PN-Z-15011-3), and total organic carbon concentration (TOC)—PN-Z-15011-1,3 and total nitrogen (TN)—PN-R-04006 were determined using a Vario MAX CN analyzer [33]. Samples for the analysis were prepared in accordance with the methodology described in Polish standard PN-Z-15011-3: 2001 [37].

Cu and Zn fractionation was performed using Tessier's modified sequential extraction (Table 4). Tested metals' contents in particular fractions were determined using flame atomic absorption spectrometry (FAAS)-iCE 3500Z THERMO SCIENTIFIC. Total Cu and Zn contents were determined in the same way as fraction V.

Table 4. Analytical procedure (adapted with permission from [34]).

Fraction	Extractant	Extraction Conditions	
		Temperature	Time
FR I Exchangeable	10 cm^3 1 M CH_3COONH_4 pH = 7	20 °C	1 h
FR II Carbonate	20 cm^3 1 M CH_3COONa, pH = 5	20 °C	5 h
FR III Bound with Mn and Fe oxides	20 cm^3 0.04 M $NH_2OH \cdot HCl$ w 25% (v/v) CH_3COOH	95 °C	5 h
FR IV Organics and sulphides	(a) 5 cm^3 0.02 M HNO_3 + 5 cm^{3}30% H_2O_2, pH = 2 (b) 5 cm^3 30% H_2O_2, pH = 2 (c) 10 cm^3 3.2M CH_3COONH_4 w 20% (v/v) HNO_3	(a) 85 °C (b) 85 °C (c) 20 °C	2 h 3 h 0.5 h
FR V Residue	5 cm^3 65% HNO_3 + 1 cm^3 30% H_2O_2 + 1 cm^3 75% $HClO_4$	Microwave mineralization	

2.3. Statistical Analysis

Mobility of elements is defined as an ability to transfer from a sample solid phase with which a given element form is weakly bound, and which can be liberated in natural conditions (e.g., ionic form of carbonates). To define mobility and bioavailability factors of bioavailability (MF) [38] are used. MFs of Cu and Zn were defined as the ratio of the metal content in FI and FII to the total content.

The inactivation rate (*IR*) of heavy metals was calculated as follows [10,13]:

$$IR(\%) = \frac{(R_b - R_a)}{R_b} \times 100, \quad (1)$$

where *IR* is the passivation of the heavy metal (%), R_b is the distribution ratio for the exchangeable fraction (FI + FII) of the heavy metal before composting (%), and R_a is the distribution ratio for the exchangeable fraction (FI + FII) of the heavy metal after composting (%).

The distribution ratio (*R*) for the exchangeable fraction was calculated using:

$$IR(\%) = \frac{C_e}{C_f} \times 100, \quad (2)$$

where C_e is the exchangeable content of the heavy metal (mg·kg^{-1}), i.e., the sum of metals' content present in the FI and FII fractions, and C_f is the total content of the heavy metal (mg·kg^{-1}).

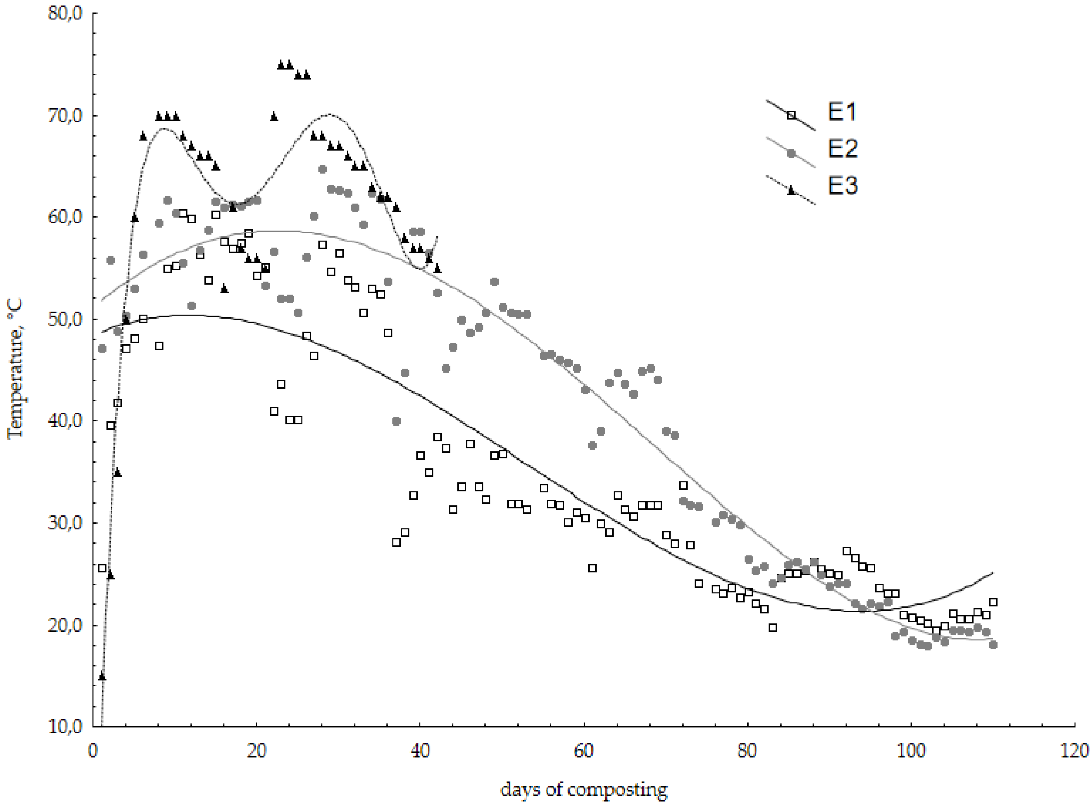
For statistical analysis of test results, Microsoft EXCEL software, 2007 version, and STATISTICA of StatSoft version 13.1 (Campus-Wide License) were used. The scope of applied statistical tools comprised the nonlinear regression issues and selected statistics available in the basic statistics and tables module of STATISTICA. The numerical analysis was performed using the Neural Networks 8 PL module of STATISTICA applet-StatSoft.

3. Results and Discussion

3.1. Statistical Analysis

3.1.1. Change of Temperature, Organic Matter Degradation, Total Organic Carbon, and Total Nitrogen

Temperature is strongly correlated with a reaction's biological velocity; therefore, it is frequently used to reflect the activity of microorganisms and to define composting stability [14]. In compost windrows featuring different initial C/N ratios, a sharp increase of temperature occurred on the third and fourth days of composting followed by a thermophilic phase, which lasted until approximately the 35th day (Figure 1a). Windrows featuring lower C/N ratios (9.20 and 9.61) manifested higher maximum temperature values. At the beginning of the composting process with an initial C/N ratio of 14.56, the temperature increase rate was slower than that observed in the composting process for C/N ratios of 9.20 and 9.61. The highest temperature values were noted in E3 (C/N 9.20), which could be a result of application of the windrow prism cover. The lowest average temperature values were recorded in the windrows at stage 1. In this stage the thermophilic phase was the shortest. Temperature values' distribution had a different course than in the research work of Wu et al. [14] pertaining to a pig manure composting process. The temperature increase rate was lower in those composts that had the lowest C/N (12.5 and 15) ratio values.



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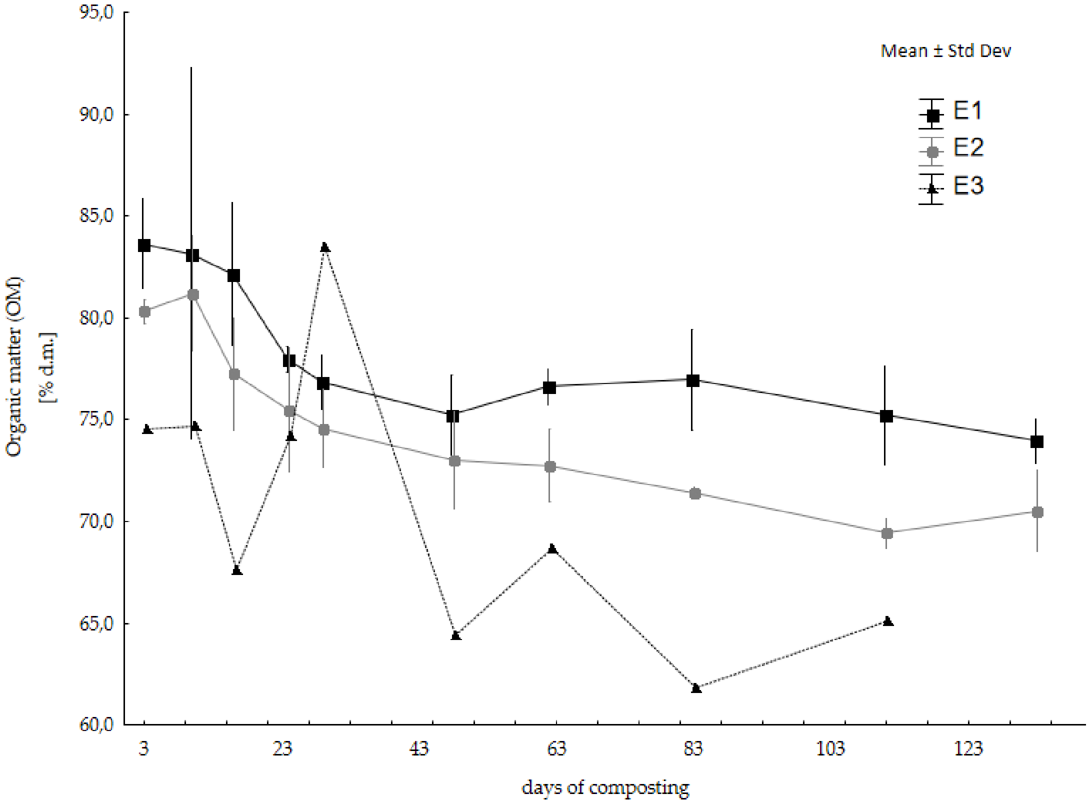

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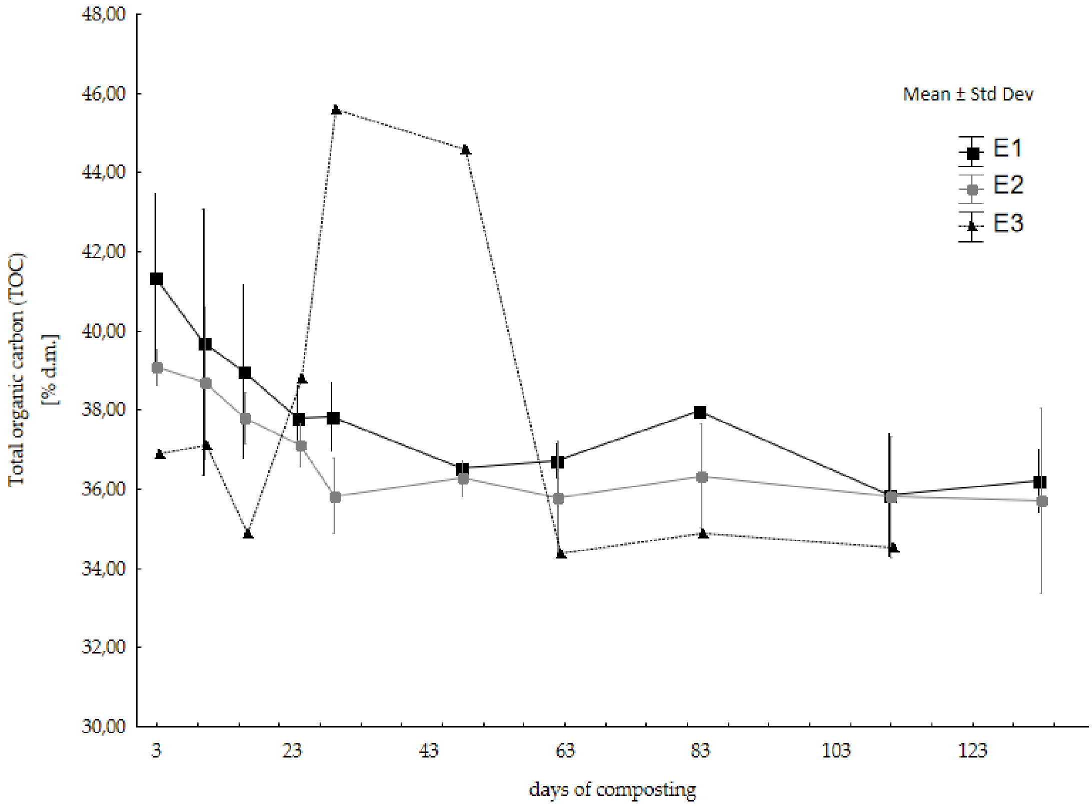

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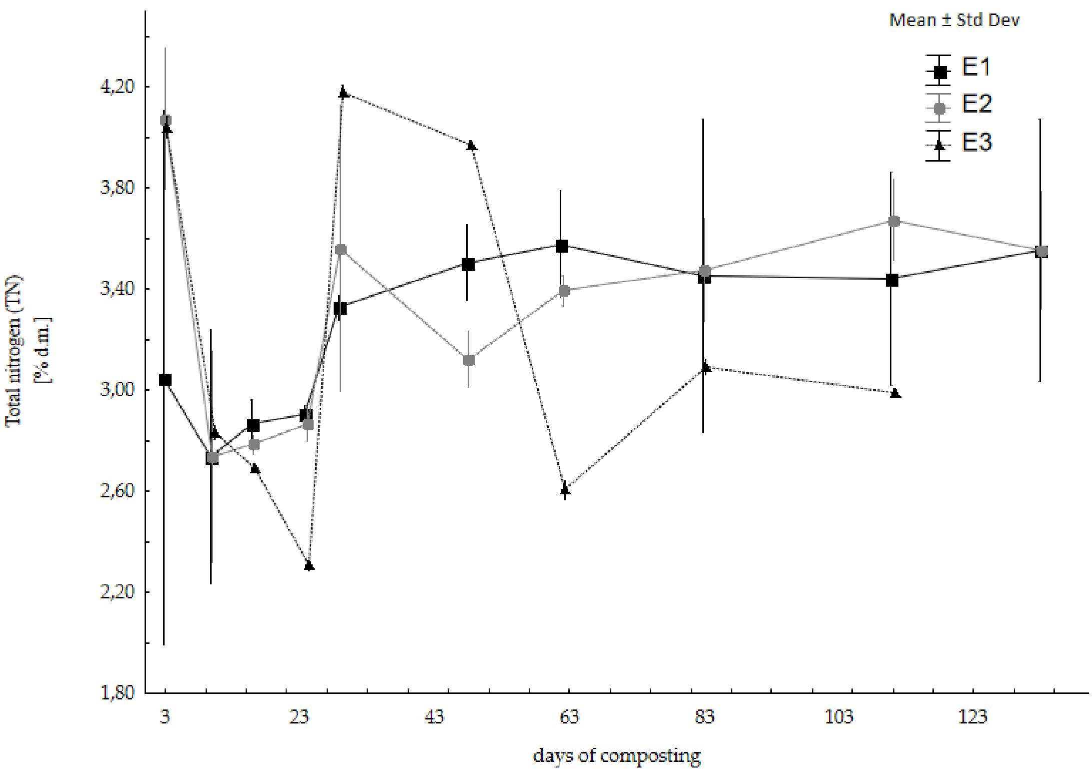


(**d**)

Figure 1. Changes in temperature (**a**), OM (**b**), TOC (**c**), and TN (**d**) during composting.

Organic matter content (OM) decreased in all three stages during the composting process (Figure 1b). The highest organic matter content at the initial composting phase featured the samples from the first composting stage (E1)—83.65%, whereas the lowest OM content value was noted for stage 3 compost—74.50%. In the last day of the composting process, OM content values were 73.95% (E1), 70.50% (E2), and 65.10% (E3). In E2 and E3, the highest OM loss was noted after the 16th day of the composting process, whereas in E1, it was after the 24th day. OM losses can be associated with the chemical composition of composted materials, particularly with fiber concentration. In compost windrows featuring different initial C/N ratios, loss of OM during the composting process was comparable [13,14].

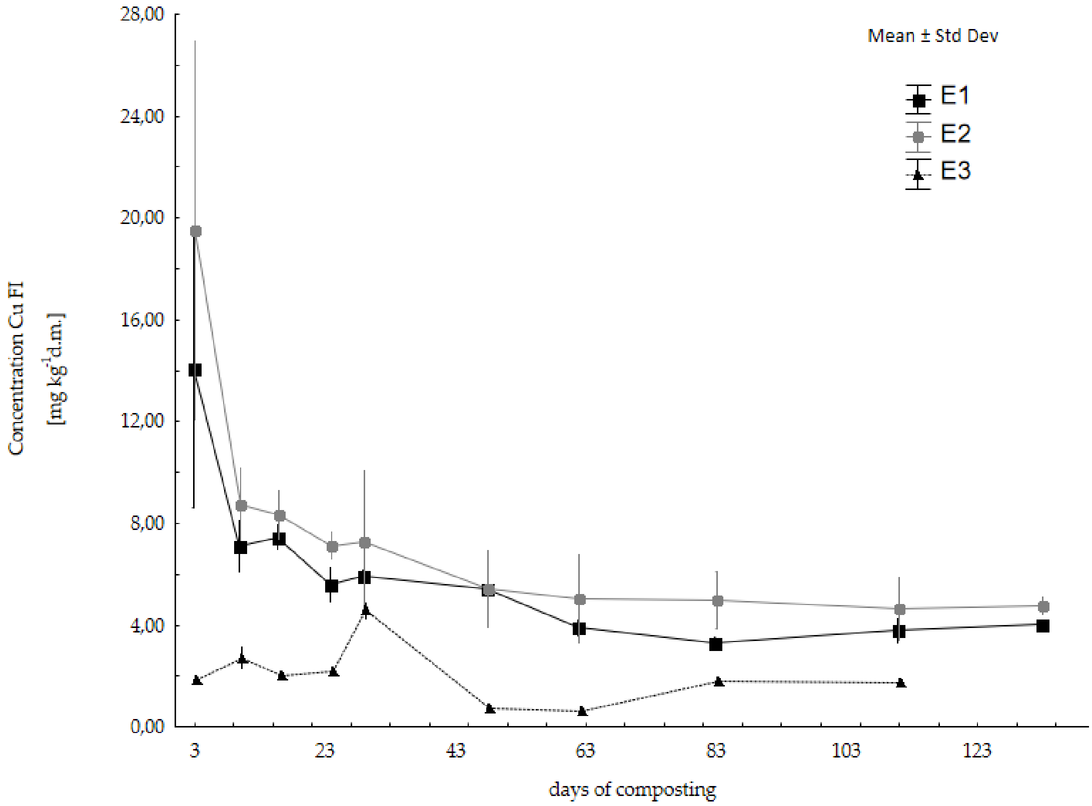
Change of total organic carbon (TOC) contents during the composting process manifested a similar pattern. The highest TOC value at the process beginning was noted in stage 1 windrows, at 41.35%, and the lowest value at stage 3, at 36.90% (Figure 1c). At the initial phase of the composting process the lowest total nitrogen (TN) value was noted for sewage sludge that had the highest initial values of C/N ratio (14.56), at 3.05% (E1). In those sewage sludge mixes with a reduced volume of straw (E2) and/or without (E3), initial TN content was 4.07% and 4.01%, respectively. TN content values noted during the composting thermophilic phase (up to the 24th day) decreased, which could be caused by liberation of NH_4^+ ions and emission of gaseous ammonia (NH_3), which could increase odor onerousness (Figure 1d). At the final composting phase in those windrows that had the highest C/N ratio values, a slight increase of TN contents were noted. A slow increase of nitrogen concentration in compost at its maturity phase should be considered as beneficial due to the fertilizing values of this element [1,14,33].

3.1.2. Zinc and Copper Speciation

The average total copper content in sewage sludge used for composting purposes in E1, E2, and E3 amounted to 225.25 mg kg^{-1}d.m., 252.25 mg kg^{-1}d.m., and 216.75 mg kg^{-1}d.m. respectively. Total Cu content in tested compost samples taken from E1, E2, and E3 windrows increased respectively from 144.25 mg kg^{-1}d.m., 184.25 mg kg^{-1}d.m., and 58.50 mg kg^{-1}d.m. to 209.38 mg kg^{-1}d.m., 239.83 mg kg^{-1}d.m., and 122.50 mg kg^{-1}d.m. Total Cu content in produced composts did not exceed its admissible values (300 mg kg^{-1}d.m.) defined for organic fertilizer and soil improvers, which pertain to putting fertilizers on the market [11]. The highest Cu content increase was noted for E3, where Cu content increased 2.1-fold compared with the initial content, and the lowest increase of total Cu content (1.3-fold) was noted for E2. Similar results were noted in many research works and such an increase has been attributed to the loss of mass caused by organic matter decomposition, CO_2, and water liberation, as well as mineralization processes [13,14,19]. The changes of copper compounds contents in particular fractions taken from windrows at the E1, E2, and E3 stages are presented in Figure 2a–e.

In all windrows featuring different initial C/N ratio values, the highest concentrations were noted for Cu compounds bound with the organic matter (FV). The results were in line with the well-known Cu affinity to organic substances, which contributed to the generation of humic substances and confirmed high Cu affinity to the –OH or –COOH humic substances functional groups [39]. The highest Cu content in particular fractions was noted for samples taken from the windrow of E2 whereas the lowest Cu contents were noted in samples taken from E3, which was influenced by the initial Cu content.

Copper in tested samples was mainly bound with organic matter (FIV). The Cu compounds' percentage share in this fraction, at all stages, was within 59.56–77.60% of the total value interval. During composting performed in windrows of C/N 14.56 and 9.61 (E1, E2), an increase of the Cu percentage in FIV was noted (Table 5). Ion exchangeable Cu compounds liberated through OM degradation are bound by phenol and quinone groups of originating humic acids confirming high Cu affinity to the –OH and –COOH functional groups [19,39]. Origination of humic acids during the composting process has a significant impact on the limitation of Cu bioavailability [18,39].



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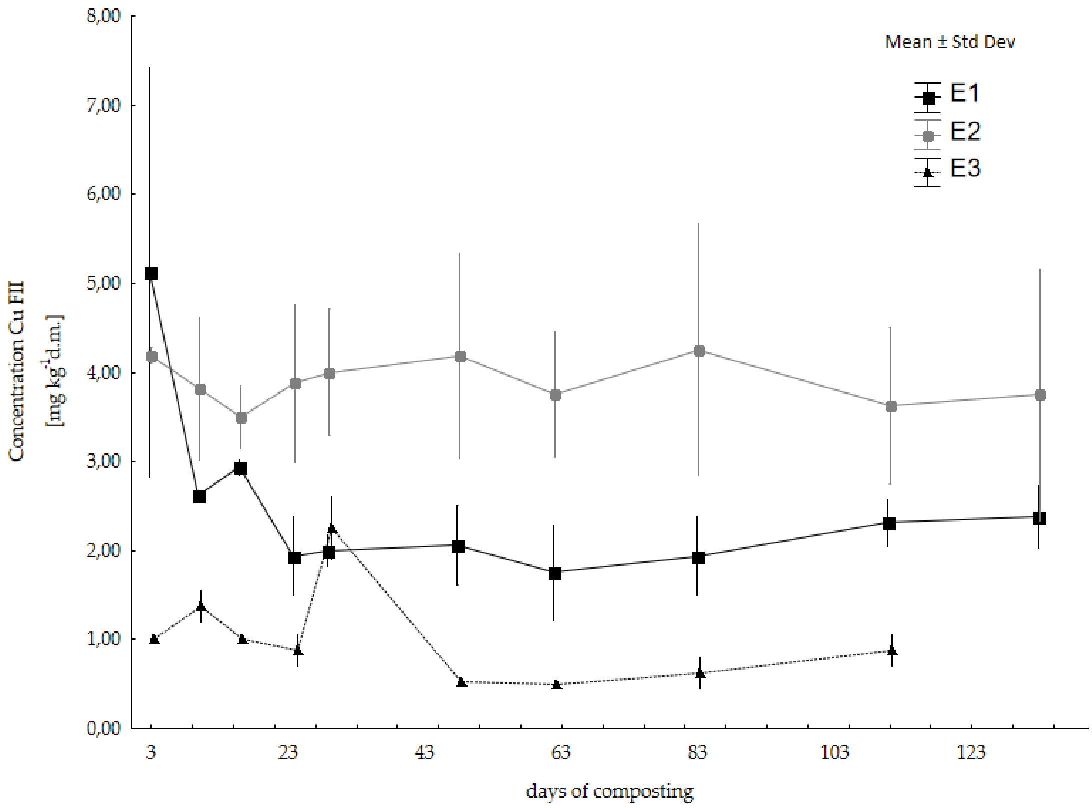

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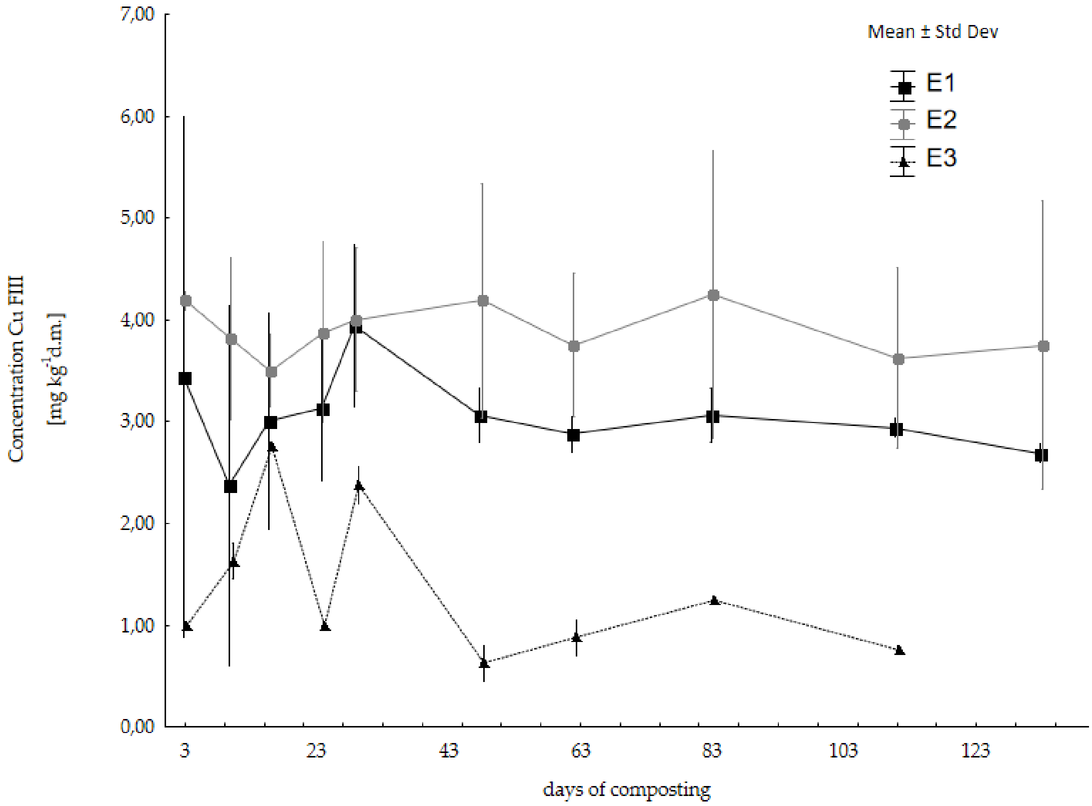

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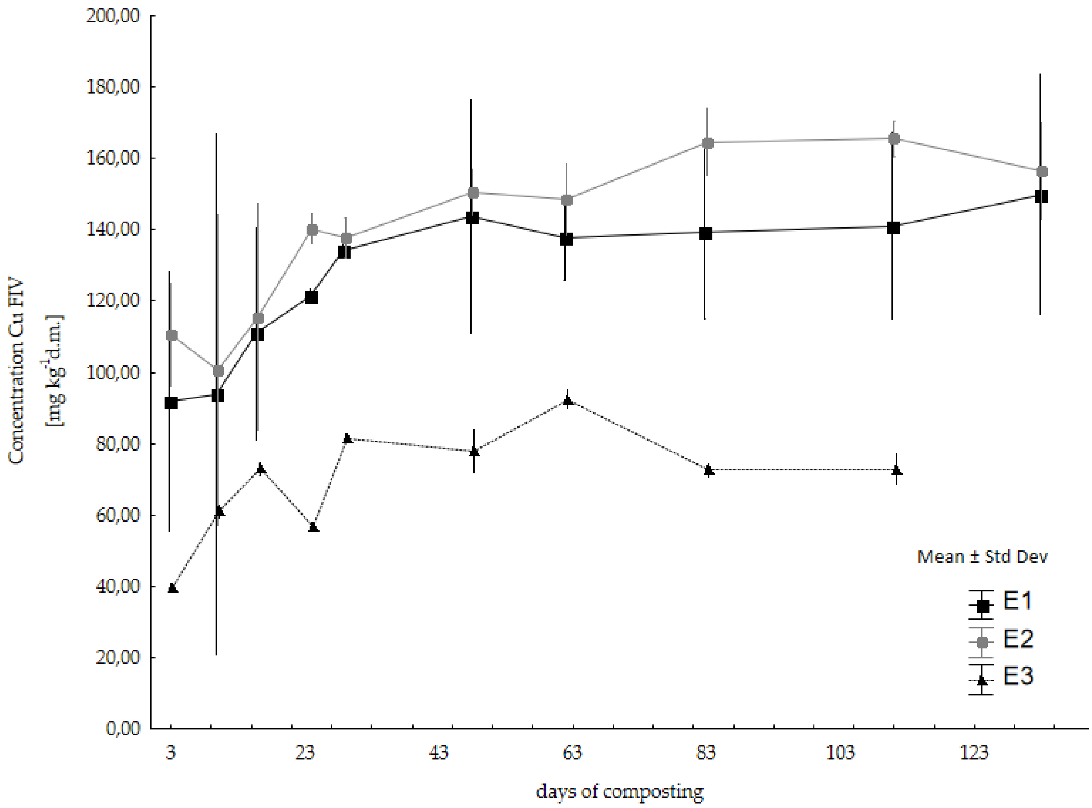

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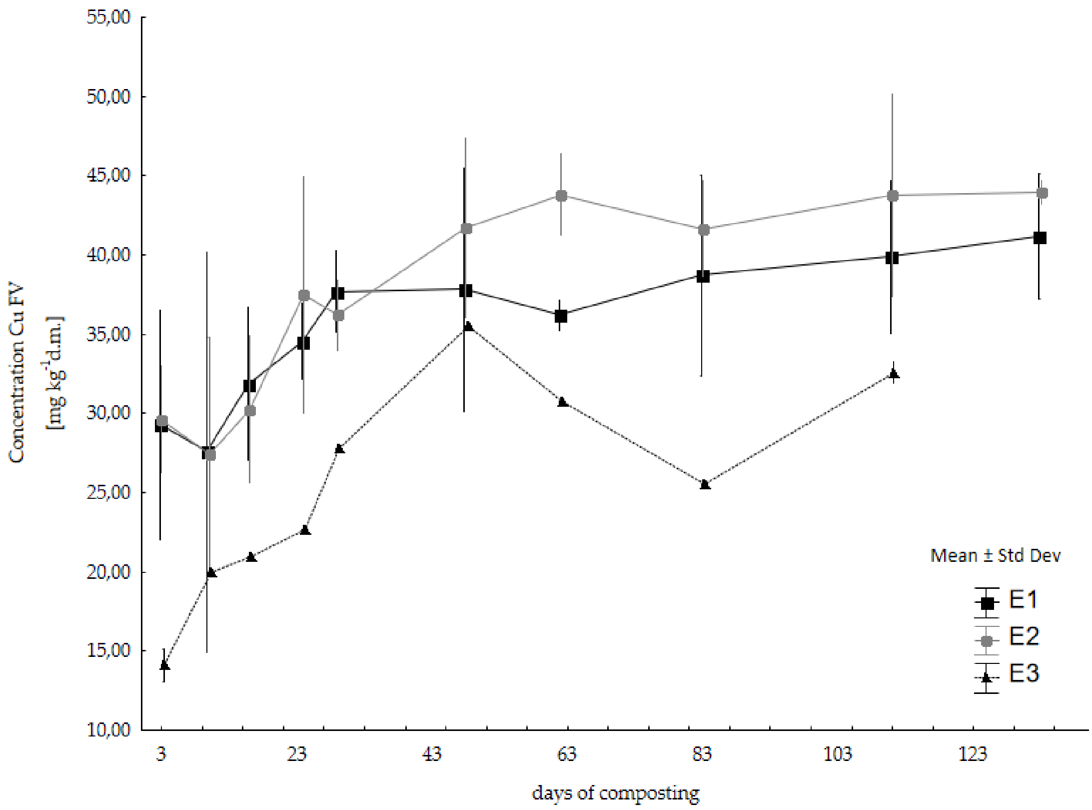


(e)

Figure 2. Concentration of Cu in particular fractions FI (**a**), FII (**b**), FIII (**c**), FIV (**d**), and FV (**e**) in stages E1, E2, E3.

Table 5. Increments of Cu and Zn fractions during composting (end vs. start. %) for composts with different initial C/N and inactivation rate (IR) values.

Element	Stage	FI	FII	FIII	FIV	FV	MF	IR
Cu	E1	−7.86	−2.37	−0.60	4.80	−5.19	−10.03	77.74
	E2	−8.79	−2.02	−0.65	6.57	2.63	−11.51	80.31
	E3	−1.76	−1.43	−1.18	−8.01	10.25	−2.38	61.31
Zn	E1	−1.19	−13.12	0.62	15.93	−0.61	−16.45	41.66
	E2	−2.01	−14.26	3.05	9.39	−5.58	−16.74	50.31
	E3	−6.49	−8.78	−4.00	16.15	0.39	−17.23	51.91

Cu percentage in the V fraction varied from 16.38% to 27.51%. The lowest Cu percentage was noted in fractions III and II, making approximately 2% of the total content. Ion exchangeable water soluble Cu compounds varied from 0.41% do 3.46% of the total content.

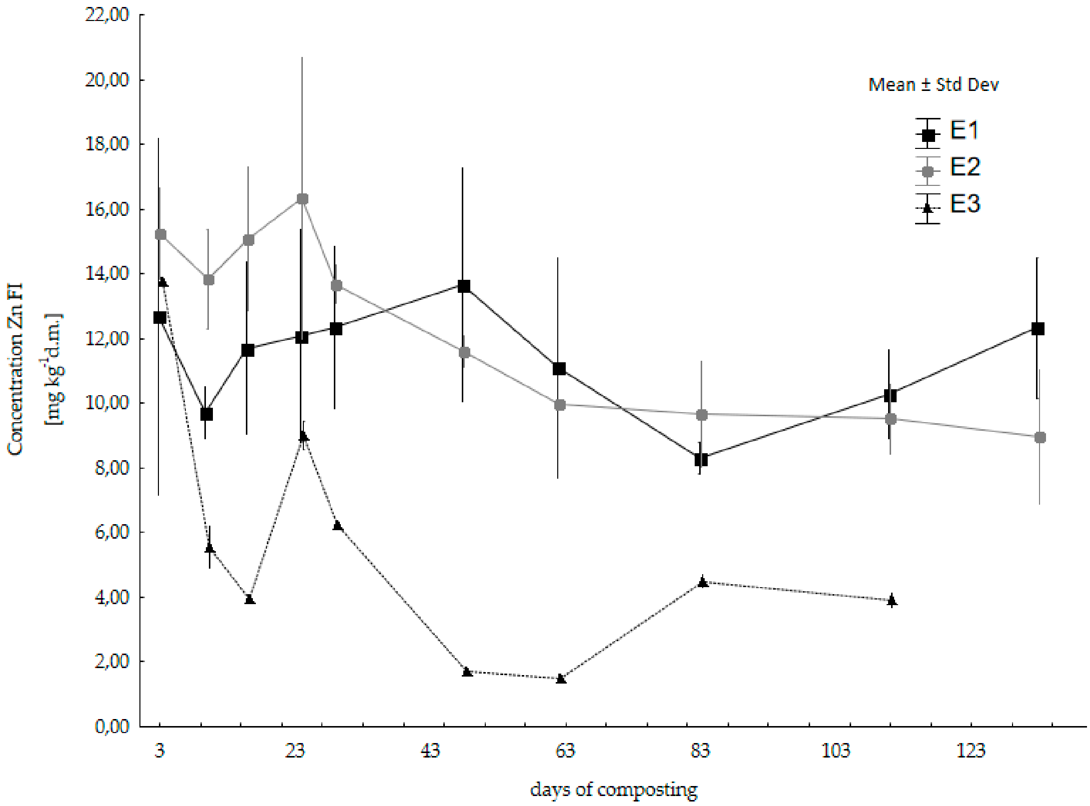
The lowest Cu percentage in fractions I, II, III, and IV was noted for compost samples taken at the E3 stage. This compost featured the highest Cu compounds percentage in fraction V. Compost samples taken at the E2 stage featured the highest Cu percentage in fraction III, whereas sewage sludge composted with the highest straw content (E1) had the highest Cu percentage in fractions I, II, and IV.

Comparing the obtained test results with those presented by Xu et al. [13], the sum of fractions I and II at the initial composting phase was similar (13.16%), whereas Cu distribution in the remaining fractions differed considerably.

Average total zinc content in sewage sludge used for composting at the E1, E2, and E3 stages amounted to 551.75 mg kg^{-1}d.m., 497.25 mg kg^{-1}d.m., and 531.50 mg kg^{-1}d.m., respectively. Similar results were obtained in other studies in which the increase in OM was attributed to weight loss due to microbial degradation [14,19].

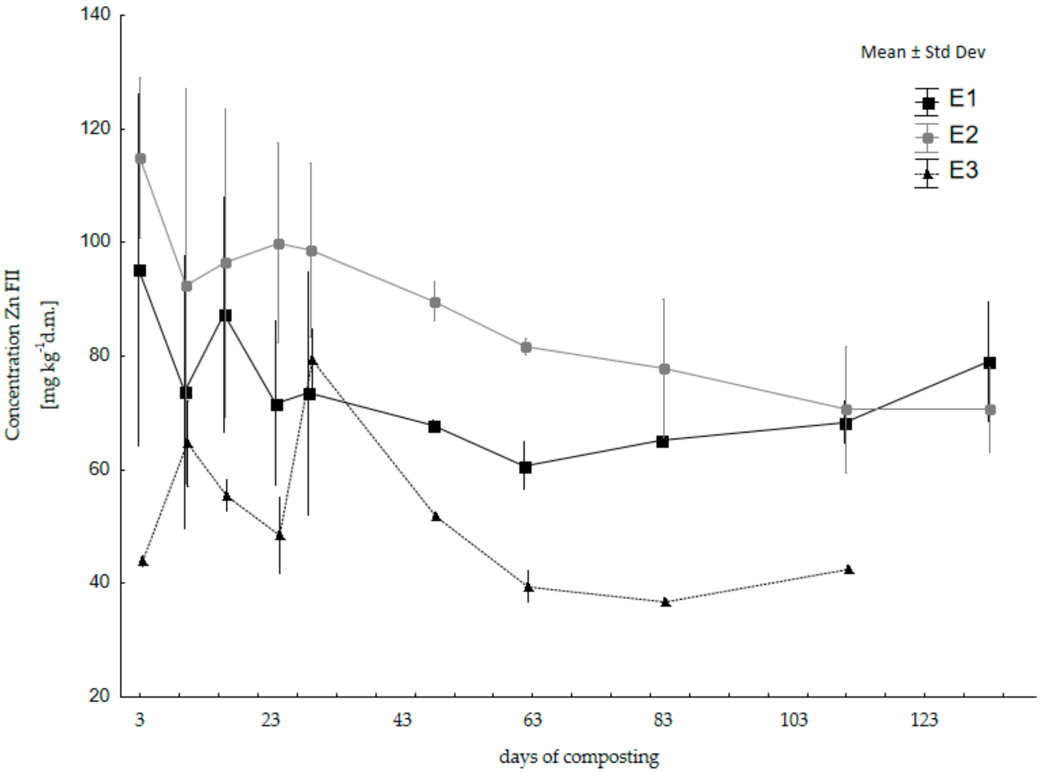
In tested compost samples of the 1, 2 and 3 stages, total Zn content increased from 358.75 mg kg^{-1}d.m. to 465.70 mg kg^{-1}d.m., 418.50 mg kg^{-1}d.m. to 520.08 mg kg^{-1}d.m., and 175.75 mg kg^{-1}d.m. to 294.50 mg kg^{-1}d.m., respectively. Total Zn content in produced composts did not exceed the admissible contents (800 mg kg^{-1}d.m.) fixed for organic fertilizer and soil improvers [11]. The highest Zn content increase was noted in E3, where Zn content increased 1.7-fold compared with the initial content, whereas in E1 and E2 Zn content in compost samples taken at the terminal process phase increased 1.3- and 1.2-fold, respectively. Change of zinc compounds contents in particular fractions taken from windrows at the E1, E2, and E3 stages are presented in Figure 3a–e.

The highest Zn contents in fractions II, III, IV, and V were noted for samples taken from the windrow at stage 2. The highest concentrations of soluble and ion exchangeable Zn compounds at the thermophilic composting phase were noted for compost samples taken at stage 2 (E2). Composted sewage sludge without straw added (E3) had the lowest Zn contents in all fractions. Zn redistribution in particular fractions differed from Cu redistribution. Zn in the tested samples was bound mainly with Fe/Mn oxides (FIII)—from 29.40% to 47.86%, organic matter (FIV)—from 14.57% to 40.78%, and carbonates (FII)—from 12.93% to 31.64%. The lowest Zn percentage was noted for fractions I and V. Ion exchangeable Zn compounds' contents made up from 0.49% to 7.81% of the total Zn content. Zn percentage in the residual fraction varied from 2.77% to 15.43%. Similar results concerning the distribution of Zn in the next five fractions in composted sewage sludge were obtained by Wang et al. [9]. The percentage of Zn compounds bound to Fe/Mn oxides was higher by 40% to 56.9%, while Zn content in the organic fraction decreased by approx. 7.7% [19].



(a)

Figure 3. *Cont.*



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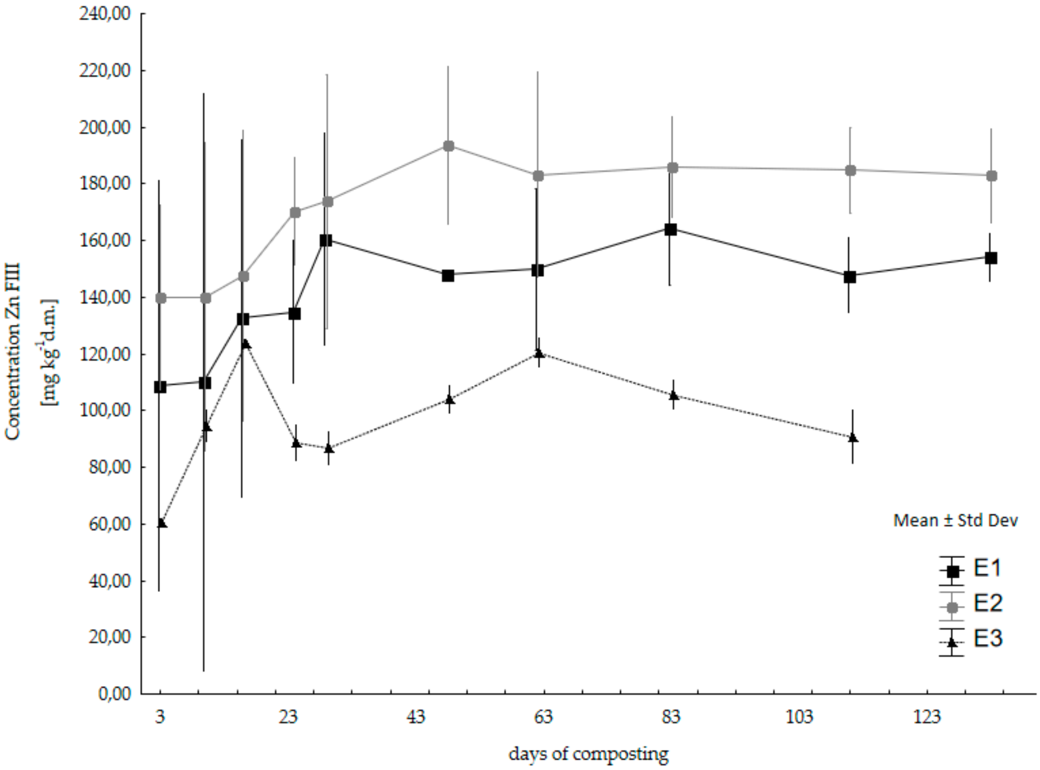

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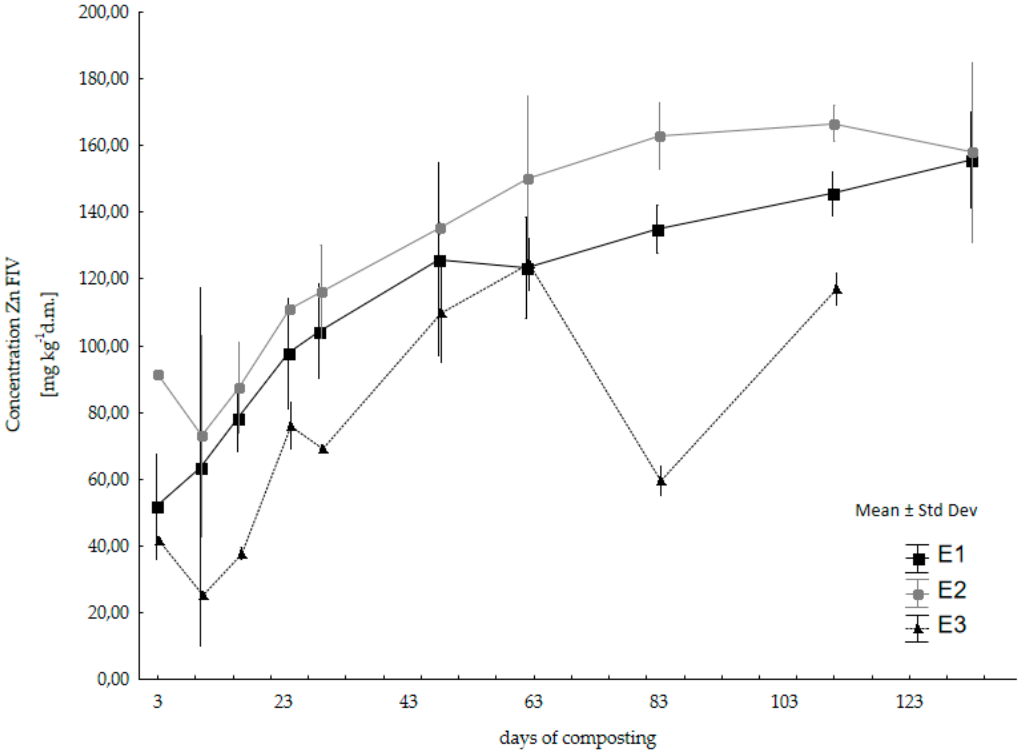

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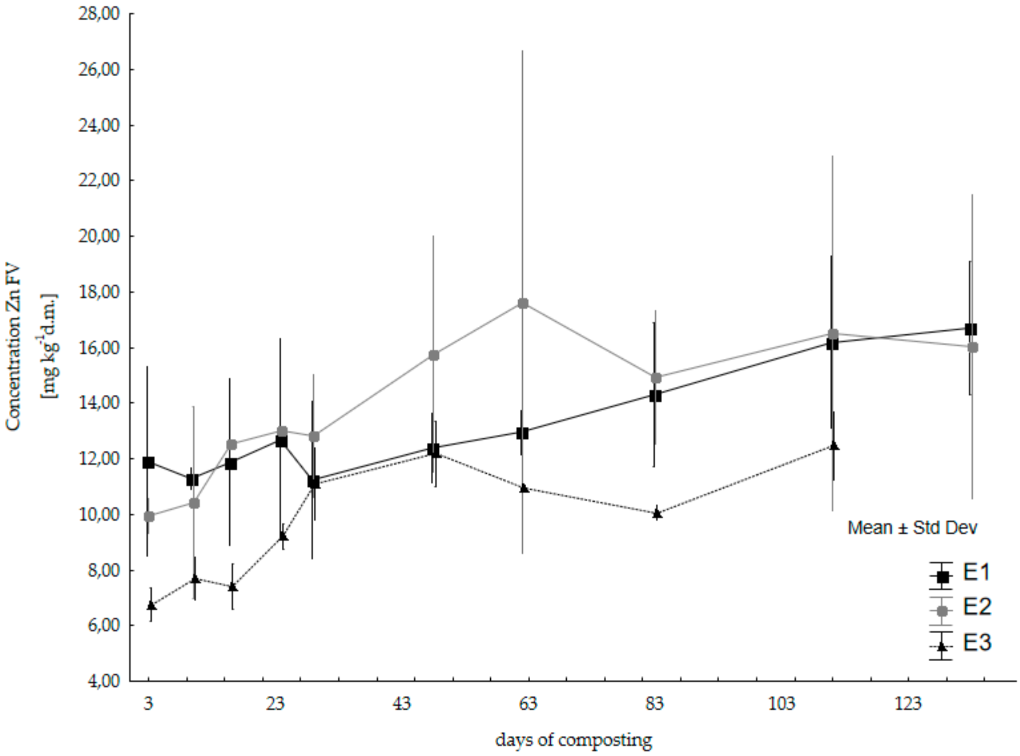

(**e**)

Figure 3. Concentration of Zn in particular fractions FI (**a**), FII (**b**), FIII (**c**), FIV (**d**), and FV (**e**) in stages E1, E2, E3.

During composting, at all stages, reduction of Zn compounds' contents in the most mobile fractions, i.e., ion exchangeable (FI) and carbonate (FII), occurred. An increase of organic matter-bound zinc forms' contents was noted. In samples taken from windrows at the E1 and E2 stages, an increase of zinc compounds with Fe/Mn oxides' contents as well as a decrease of their percentage in the residual fraction were noted during composting. In the case of compost samples taken at the E3 stage, the trend was reversed (Table 5). The highest percentage in FV was noted for samples taken at the E2 stage, making up from 15.37% of the total content at the beginning of the process down to 9.79% on the last day. The highest increase of Zn compounds in organic fractions was noted for E3 (16.15) and E1 (15.93). In samples taken from the windrow on the last day of the process, the percentage of ion exchangeable Zn compounds was the lowest at stage 3 and amounted to 1.32% and the highest was at E1, at 2.72%. The lowest percentage in the carbonate fraction during the process course was at E3. Samples taken during the last process day at E2 manifested the highest Zn compounds' percentage in fraction III, at 37.33%, whereas at E3 the share of Zn compounds bound with Fe/Mn oxides was the lowest and amounted to 30.80%. The highest content of Zn compounds (last day) bound with organic substance was noted for E3, at 39.68%, and the lowest for E2, at 31.69%.

During composting the percentage of Zn compounds in the ion exchangeable (FI) and carbonate (FII) fractions decreased. The highest loss of ion exchangeable (FI) Zn compounds was noted in the compost of initial C/N = 9.20 (E3). Compost samples taken at E1 and E2 featured a higher loss of those Zn forms contents, which were bound with carbonates, compared with E3.

3.1.3. Cu and Zn Mobility Factor

The MF mobility factor, calculated as the ratio of the heavy metal sum in fractions F1 and FII to the total content, may be used to asses potential mobility of heavy metals [14]. During the composting process, MF values for tested elements decreased at all composting stages, which proves a reduction of Cu and Zn mobility. Similar results were obtained by Wu et al. and Wang et al. [14,18]. The MF value for Zn was much higher than that for Cu, thus indicating that potential Zn mobility was higher during composting than that of Cu. The lowest MF values for Cu, during the composting process, were noted for E3 compost (C/N = 9.20) and amounted from 4.99 to 1.18. This compost featured the lowest MF value decrease during the composting process. The highest MF value decrease was noted for compost in which C/N amounted to 9.61—E2 (decrease by 11.51), although at this stage Cu content in the FI and FII fractions was highest. The MF values for samples taken at the end of the composting process at the E1, E2, and E3 stages amounted to 2.95, 2.92, and 2.39, respectively.

The Zn MF value for all stages remained within the 38.40 (initial value) to 17.42 (final value) interval. The lowest Zn MF values were noted for those compost samples that featured the lowest initial C/N value (E3, 9.20). At all composting stages, the MF value decreased by approximately 17%. In those composts that had initial C/N values of 14.56 (E1), the MF value by the end of the composting process was highest (Table 5).

Reduced Cu MF may protect plants against Cu in soil with compost added, whereas higher Zn bioavailability promotes alleviation of Zn deficit in the human food chain.

Metals that occur in the organic matter (FIV) and residual (FV) bound fractions show low mobility and minor bioavailability. Inactivation rates (*IR*) for Cu and Zn were calculated in order to assess the change of exchangeable fraction content percentage before and after the composting process. Cu *IR* values for E1, E2, and E3 amounted to 77.7, 80.30, and 61.3, respectively (Table 5). The highest impact on Cu immobilization was noted during the composting process of biomass with initial C/N = 9.61 (E2). Zn *IR* values were highest in compost samples with initial C/N = 9.61 (E2) and 9.20 (E3), which amounted to 50.3 and 51.9, respectively. High *IR* values prove a significant impact of the composting process on copper and zinc passivation. Xu et al. [13] obtained in their research work other results and proved the absence of composting impact on Cu and Zn transformation into forms that are hardly available for living organisms.

3.2. Numerical Analysis

An artificial neural network of classification type was used to perform numerical analysis. Using test results, a database composed of 32 cases, 13 independent variables and one dependent variable, was created. As the proportion between the cases and independent variables (predictors) was about 3:1 and was lower than the recommended 10:1 [40], the number of predictors was reduced to three, i.e., time, C/N, and total content of the given element. The dependent variable was a qualitative variable marked with letters A and B referring to compost quality classes in accordance with the regulations applicable in Austria [12]. The criterion of qualification of each case to a given class was the value of the resultant variables X(Cu) and Y(Zn), making a sum of concentrations of a given element determined in all four fractions except for fraction V. The classification was performed based on the following rule:

If the concentration was $150 < X\ (Cu) \leq 500$ mg·kg^{-1}d.m., then class B;
If the concentration was $70 < X(Cu) \leq 150$ mg·kg^{-1}d.m., then class A;
If the concentration was $500 < Y(Zn) \leq 1800$ mg·kg^{-1}d.m., then class B;
If the concentration was $200 < Y(Zn) \leq 500$ mg·kg^{-1}d.m., then class A;
If the concentration was $Y(Zn) \leq 200$ mg·kg^{-1}d.m., then class A+

Due to the simulations being performed separately for the two analyzed elements, i.e., Cu and Zn, neural networks of the architectures MLP 3-5-3 and MLP 3-6-3 were chosen, respectively. Correctness of the dependent variable prediction results for the cases used at the network teaching stage is shown in Table 6. Correctness of estimates at the network testing stage amounted to 100% in both tested heavy metal cases.

Table 6. Prediction of correctness for the teaching set.

Dependent Variable		Number of Estimates			
		Category			All
		a+	a	b	
Cu	correct	0	5	12	17
	incorrect	2	4	1	7
Zn	correct	0	23	0	23
	incorrect	1	0	0	1

The method of learning that was aimed at minimizing the neural network error values following modification of values of the weight coefficients of neuron input signals was the Quasi-Newton (BFGS) algorithm [41].

The analysis of sensitivity defining the weight of the independent variables (Table 7), as predictors in the adopted NN model, proved significance of all three variables, i.e., time, C/N, and total given element content for the neural network prediction quality.

Table 7. Independent variables sensitivity test results.

NN	Independent Variables			Quality of	
	Total Cu, Zn	C/N	Time	Teaching	Testing
Cu—MLP 3-5-3	1.015	1.413	1.008	70.83	100
Zn—MLP 3-6-3	1.004	1.005	0.999	95.83	100

The developed model of the artificial neural network allows to determine the real risk of compost contamination with heavy metals. Some heavy metals can be permanently bound in the soil matrix-fraction no. V. Desorption of heavy metals bound by, e.g., clay minerals, theoretically occurs at pH = 1 but in real environmental conditions is unlikely [15,17,18]. The analysis of the values of the parameters constituting independent variables in the proposed model, i.e., the total content of a given element and the concentration of organic carbon and total nitrogen at any time during the composting process, allows for compost classification taking into account the presence of only mobile fractions, and is thus potentially hazardous to the environment.

4. Conclusions

Although sewage sludge is a source of fertilizers, unfortunately, it contains heavy metal concentrations that can exceed admissible values. In our research work we analyzed the trend of Cu ad Zn chemical forms' transformations under reduced supplementation during composting conditions, taking into account:

(1) The impact of limited volumes of straw added as a source of organic carbon;
(2) The presence of mobile forms of tested metals based on sequential extraction;
(3) The classification of mature compost based on adopted standards using a neural network of standard classification type.

Our research work proved that composting of a sewage sludge mix with relatively low structural material input and, consequently, low initial C/N values, had no negative impact on biochemical transformations' velocity. The initial C/N value had an impact on the distribution of both tested elements in a manner correlated with the partial decomposition of organic substance. A lower risk of Cu and Zn liberation due to reduction of mobile heavy metals' fractions' shares with a simultaneous increase of their share in stable fractions was ascertained.

The developed neural network is a tool allowing to predict compost classes depending on three parameters, including C/N. The C/N value depends on the share of the supplement making an additional source of organic carbon, added at the batch formation stage. Therefore, using the developed NN model, the simulation of compost quality in accordance with classifications applicable in Austria for various initial conditions and any composting time can be performed.

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