



# Article Evaluation of Agricultural Value of Composts Prepared from Municipal Biowastes in Different Conditions of Composting Process

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**Abstract:** The increasing mass of organic waste as well as the assumptions of a circular economy enforce the rational management of this type of waste. One method of recycling is composting, which makes it possible to use waste efficiently as an organic fertilizer. This paper presents the results of a comparative study of six different composts in terms of their agricultural quality. The aim of this study was to evaluate the bioavailable amounts of metals using single extractions with DTPA solution and to characterize various humic compounds. Particular attention was paid to the amounts of labile carbon (LC), hot water-extractable carbon (HWC), and the quantity and quality of humus substances (HS). Regardless of compost types, they were characterized by a small share of easily decomposable compounds such as fulvic acids (FAs), LC, and HWC, which may indicate the low susceptibility of compost humic substances to microbiological degradation in soil. In general, the bioavailable metal amounts found in the analyzed composts were low; therefore, the tested composts applied to the soil can be considered safe for the environment.

Keywords: organic waste recycling; compost quality; humic substances; bioavailable metals

## 1. Introduction

In view of the environmental concerns, the segregation of wastes, especially municipal wastes, must be a necessary procedure implemented in each country. This is particularly important since the level of consumption is very high, especially in wealthy countries. Despite the fact that Poland has one of the smallest amounts of waste generated per capita per year among the EU countries [1], a precise system of municipal waste selection needs to be introduced. In addition to typical fractions of secondary raw materials, such as paper, plastic, glass, and metals, the biowaste fraction generated in households and public utility institutions is also selectively collected. As indicated by data from the Central Statistical Office [2], the mass of this fraction has been gradually increasing year by year and constitutes a significant percentage share (approximately 30%) of the total mass of municipal waste. Taking into account the growing mass of organic wastes, their presence in the environment cannot be underestimated and absolutely must be properly managed, especially since their landfilling is legally prohibited [3,4]. Organic wastes are not a homogeneous group and can be divided into biodegradable wastes (wood, paper, cardboard, forestry and agricultural residue, municipal sewage sludge) and biowastes (garden and park wastes, food and kitchen wastes from households and restaurants). Due to the highly diversified morphological and chemical composition, this waste should be treated as a unique and very valuable source of nutrients and organic matter. As stated by Scarlat et al. [5], organic wastes can be processed both through organic recycling (composting) and incineration. Referring to the principles of the circular economy and the assumptions of the zero-waste program [6], a rational method of biowaste utilization is its composting, thanks to which we can ensure the return of nutrients and energy to the



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). environment. According to Scarlat et al. [5] and Jakubus and Michalak-Oparowska [7], such a method is common and socially acceptable. The composting process has been presented as an environmentally friendly alternative applied to manage and recycle organic waste to obtain products used as amendments in agriculture [8,9]. As a result of the composting process, the emission of greenhouse gases (CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>) may occur; however, in the case of composting biowaste, it is low and a negligible phenomenon [10].

A majority of studies [11–13] regarding the agricultural utilization of composts focus on their influence on soil fertility as well as describing their chemical composition in the aspect of nutrient mobility and uptake efficiency by plants. At the same time, the statement concerning organic matter abundance in composts is very general, without detailed and precise research conducted to date. Apart from this general information, scarce and limited data are available considering more in-depth studies on various humic parameters. To date, changes of hot water-extracted carbon (HWC) or labile carbon (LC) in composts have not been fully studied. The comprehensive analysis of composts' organic matter composition focusing on the readily soluble and labile fraction is essential, especially in predicting the potential transformation of organic matter introduced with compost doses. In this respect, an important role is played by the degree of humification of the compost organic matter, which can be assessed by analyzing the quality of humic substances or easily soluble carbon. The assessment of compost in such terms is important not only from the point of view of enhancing soil organic matter, but also the release rate of nutrients from organic bonds in the compost. Humic substances (HSs) are the most abundant and reactive components of organic matter and they consist of humic acid (HA) and fulvic acid (FA) compounds containing acidic functional groups responsible for adsorbing nutrients, especially metals. It should be noted that in the case of composts prepared on the basis of municipal biowastes, there may be a risk of their unfavorable enrichment with elements from the group of heavy metals accompanied by the introduction of larger amounts of undesirable metals such as Cd, Cr, and Pb, which are also present in compost composition [8]. It should be noted that this group includes both micronutrients necessary for plants (Cu, Zn, Mn, Ni) and toxic metals (Cr, Pb, Cd). For this reason, composts must meet the requirements given in the Regulation of the Minister of Agriculture and Rural Development [14] describing the limits of heavy metals in organic fertilizers. The limits of heavy metals in composted or fermented household wastes are also given by the EC 889/2008 Commission Regulation [15], which underlines the importance of assessing the quality of this type of fertilizer in terms of heavy metal content. However, it should be emphasized that the values given there refer to the total amounts of metals that are of low suitability in the assessment of the degree of environmental impact [16]. Therefore, it is reasonable to assess the amount of bioavailable metals in composts using single extraction techniques. Single extraction allows the separation of the tested matrix into a fraction that is bioavailable and hardly available for plants in a given extraction solution. The group of single extractants is large and includes chemical solutions of different ionic strength and, hence, properties and extraction capacity. Among the multitude of various solutions, the DTPA chelate takes special place because of its greater usefulness attributed to the possible determination of the current bioavailability of micronutrients. Moreover, it is also recommended by the International Organization for Standardization (ISO) [11]. Considering the application of compost into soil and its impact on this environment, compost evaluation should be based on an assessment of abundance both for metals and humic compounds. Therefore, this study was focused on the valorization of the composts prepared from various biowastes selectively collected by inhabitants in cities of different sizes. Additionally, factors related to the composting processes carried out concerning different conditions of process (aerobic and aerobic-anaerobic) and different lengths of the maturation period were taken into account. Next to the typically determined amounts of organic matter, total organic carbon, and humification parameters, more sophisticated analyses dedicated to humic substances, labile carbon and hot water-extracted carbon, were also performed. Additionally, the

assessment of bioavailable metal amounts was conducted. The obtained data gave an opportunity to estimate the potential agricultural usability of the tested composts.

#### 2. Materials and Methods

#### 2.1. Composting Procedure and Raw Materials

The various biowastes (garden and park wastes, food and kitchen wastes from households and restaurants) collected separately by inhabitants of agglomerations/towns of different sizes were used in the composting process. As a result, six different composts (C1–C6) were analyzed in this study. Table 1 presents selected properties of the raw materials used in the composting process, and detailed information concerning used biowastes and process conditions is given in Table 2. In order to determine the basic parameters of the raw materials, the same analytical procedures were used as in the analysis of the tested composts, which is presented in detail in Section 2.2. Before the composting process, the raw materials were mechanically chopped into smaller-sized particles to ensure the preferred particle size in the range of 15–40 mm. The biowastes used in the process were mixed together in such proportions as to create the optimal conditions for composting, ensuring first of all the C:N value in the range of 25–30:1. In the case of the aerobic composting process (AC), the mixtures were placed in long narrow piles prepared as static, triangularshaped profiles with approximate dimensions of 8 m in length  $\times$  1.2 m in height  $\times$  3 m in width. During the first month, to ensure adequate aeration conditions, a specialized mixing machine mixed the piles weekly, while subsequently the process was performed at monthly intervals.

Table 1. Chosen parameters of raw materials used for composting process.

Parameter	Unit	Minimum Value	Maximum Value	
pH		6.6	7.2	
Ntot	- g·kg <sup>-1</sup>	5.2	26.8	
TOC	- 6*6	210.3	348.4	
C:N		14:1	39:1	
Fe	$g \cdot kg^{-1}$	1.4	8.8	
Mn		72.4	175.6	
Zn	-	22.8	138.7	
Cu	- mg∙kg <sup>−1</sup>	1.85	17.5	
Pb	- mg.kg	5.1	11.7	
Cr		3.2	15.3	
Ni	-	1.4	5.9	

All of the composts prepared in the aerobic composting process were produced in composting facilities for commercial purposes. The used raw materials, composting technology, and the length of the maturation period followed standards of the individual composting process carried out and were not subject to the researcher's interference. In the case of the aerobic–anaerobic composting process (AANC), compost was prepared as a fertilizer for their home gardens by private home owners and the process was carried out in a home composter made of thermoplastic. The raw materials were successively collected in the container without any mixing of the bulk volume, and as result, a crust on the upper layer was established, leading to the development of anaerobic conditions in the center of the container, whereas the top layer was exposed to ambient air and thereby to aerobic conditions. Under such conditions, the organic waste mixture was kept for a year. After this time, the whole mass was mixed to homogenize it and then transferred to dark plastic bags to complete the maturation stage.

Compost Number/Raw Materials * Used	Size of Agglomeration	Method of Composting	Maturation Period		
C1/garden and park wastes, food and kitchen wastes from households and restaurants	Medium	AC	Approximately 3 months depending on weather conditions		
C2/as above	Medium A		Approximately 6 months depending on weather conditions		
C3/as above	Large	AC	Approximately 3 months depending on weather conditions		
C4/as above	Large	AC	Approximately 6 months depending on weather conditions		
C5/as above	Small	AC	Approximately 6 months depending on weather conditions		
C6/food scraps from kitchen, and yard trimmings as plant residues and mowed grass clippings	Large	AANC	Approximately 6 months depending on weather conditions		

Table 2. Characteristics of composting process conditions.

\* Composition of used raw materials—see Table 1.

The compost samples were collected after the maturation stage from the individual composting facilities and private gardens. Subsamples were gathered from different places of each composting pile (the top, middle, and bottom) and then the three approximately 100 g samples were thoroughly mixed together to create one mean bulk sample of approximately 300 g. In the case of composts prepared using the AANC method, the samples were taken from the bags after their contents had been mixed. The compost samples were dried at 105 °C for a period of 12 h. The dried samples were ground into a fine powder and stored in plastic bags at a temperature of 4 °C.

#### 2.2. Chemical Analysis of Compost

Organic matter (OM) in the composts was determined by the loss-on-ignition test (dry combustion for 6 h at a temperature of 550 °C in the MRT-20 furnace, CZYLOK). The pH of the composts was assessed in H<sub>2</sub>O and the compost: solution ratio was 1:2.5 (w/v) using a MeterLab PHM20 pH meter. To determine the bioavailable amounts of micronutrients (Fe, Zn, Mn, Cu, and Ni) as well as heavy metals (Pb and Cr) in the analyzed composts, one-step (single) extraction with DTPA solution (0.005 mol  $\cdot$ dm<sup>-3</sup> DTPA + 0.1 mol dm<sup>-3</sup> TEA + 0.01 mol dm<sup>-3</sup> CaCl<sub>2</sub>, pH = 7.3; at a 1:2 ratio; 2 h of shaking at room temperature) was used [17]. Concentrations of metals in the obtained extract were assessed using atomic absorption spectrophotometry in a Varian Spectra AA 220 FS apparatus. Total nitrogen (Ntot) content was assayed using a Vario Max CNS elemental analyzer. The total organic carbon (TOC) and labile carbon (LC) were determined by wet combustion [18] and by KMnO<sub>4</sub> oxidation, [19] respectively. Hot water-extractable organic carbon (HWC) was determined according to the method presented by Ghani et al. [20], with the final determination of organic carbon by wet combustion [18]. Humus fractionation was performed according to the method proposed by Kononova and Bielczikova, in which humic substances (HSs) were determined in a mixture of 0.1 mol·dm<sup>-3</sup> Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + 0.1 mol·dm<sup>-3</sup> NaOH solution [21]. The fulvic acid (FA) fraction was separated after precipitation of humic acids at pH 1.5 (HA). Carbon in the obtained fractions ( $C_{HS}$  and  $C_{FA}$ ) was oxidized by  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KMnO}_4$  in the H<sub>2</sub>SO<sub>4</sub> medium. The humic acid carbon (C<sub>HA</sub>) was calculated by subtracting  $C_{FA}$  from  $C_{HS}$ . The optical density ( $Q_{4/6}$ ) of the obtained fractions was determined at 465 nm and 665 nm and measurements were made with the UV-Vis Cary 60 device. When comparing composts produced from similar raw organic materials, the humification indexes are especially important, such as the humification ratio (HR), humifi-

$$HR(\%) = \frac{CHS}{TOC} \times 100$$
(1)

$$HI(\%) = \frac{CHA}{TOC} \times 100$$
 (2)

$$DP = \frac{CHA}{CFA}$$
(3)

#### 2.3. Statistical Analysis

The assessment of all parameters in the composts was performed in three replications and the presented results are their mean values. The obtained results were subjected to the formal evaluation with the assistance of one-way ANOVA. Each of the 13 parameters was tested independently using the F-test at the significance level  $\alpha = 0.05$  (F<sub>0.05</sub> = 2.77). Degrees of freedom for the compared objects (composts) was df = 5, whereas the value of degrees of freedom for the error was df = 18. The calculated F statistic for the analyzed parameters amounted to: F<sub>TOC</sub> = 47.48; F<sub>CHS</sub> = 295.01; F<sub>CHA</sub> = 279.23; F<sub>CFA</sub> = 18.68; F<sub>HWC</sub> = 199.94 F<sub>CL</sub> = 34.43; F<sub>Fe</sub> = 105.35; F<sub>Ni</sub> = 59.29; F<sub>Zn</sub> = 530.40; F<sub>Mn</sub> = 87.23; F<sub>Pb</sub> = 157.75; F<sub>Cr</sub> = 71.72 and F<sub>Cu</sub> = 386.55.

The null hypothesis, that the average values of the examined parameter are equal for each of the six composts, was tested against the alternative hypothesis stating that not all averages are equal. As a result of the rejection of the null hypothesis, the least significant differences were calculated using the Tukey method at the significance level  $\alpha = 0.05$ . Tukey's analysis was performed to distinguish homogeneous groups among the six composts (a mean comparison for which the *p* value < 0.05 is considered different and these differences were characterized using Tukey's honest significant difference test (HSD)). These composts were included into homogeneous groups, for which the average contents of the tested parameter did not differ significantly. The homogeneous groups of composts are indicated by the same lowercase letters. In addition, Pearson's correlation coefficients were calculated for the analyzed parameters. The data were analyzed using the STATOBL software working in the Windows environment.

The datasets were also analyzed using the canonical variate analysis [23], which enables a graphical presentation of the estimation results for the similarities between the composts in relation to the analyzed parameters.

#### 3. Results and Discussion

#### 3.1. Basic Properties of Composts

When assessing the quality of composts, it is not only important to investigate their chemical composition, but also the degree of stability and maturity, because an unstable and immature organic material may have adverse effects on plant growth and the environment [24,25]. There are numerous methods of determining the maturity and stability of composts concerning physical, chemical, microbiological, and biological parameters [9]. In routine practice, the most popular and easiest approach to evaluate compost maturity is to use the C:N ratio. The application of the C:N ratio as an indicator of compost maturity is widely discussed in literature [26], although there is no unified, standardized limit value of this parameter. Thus, the authors [26–29] propose various threshold values, but according to the most obligatory statement, a C:N ratio within the range of 10–15 shows a stable, mature amendment. Taking under consideration such a criterion, all of the analyzed organic fertilizers met this requirement, because the values of the C:N ratio were very similar and ranged between 11:1 and 14:1 (Table 3).

Compost Number	pH *	OM (g⋅kg <sup>-1</sup> )	C:N	Q <sub>4/6</sub>	HI (%)	HR (%)	DP (C <sub>HA</sub> :C <sub>FA</sub> Ratio)
1	7.1	337.6	11:1	13.7	28.7	21.8	3.1
2	7.1	262.6	13:1	14.4	14.3	11.0	1.7
3	6.5	319.6	13:1	14.3	22.6	13.6	1.5
4	7.2	279.9	14:1	7.2	19.9	11.1	1.4
5	7.0	328.4	11:1	7.1	20.8	15.3	1.8
6	7.3	243.8	13:1	6.6	8.9	6.3	1.3

Table 3. Basic properties of the analyzed composts.

\* For descriptions, see Section 2.

As shown by the obtained data (Table 3), the tested composts were also characterized by comparable values of basic parameters such as pH (6.5–7.3) and organic matter  $(243.8-337.6 \text{ g}\cdot\text{kg}^{-1})$ . However, the composts differed from each other in such humification parameters as  $Q_{4/6}$ , HI, HR, and DP ( $C_{HA}$ : $C_{FA}$  ratio). The evaluation of humification parameters in composts is essential, because the humified fraction of organic compounds is the most important and responsible for the fertility and quality of humic compounds. The values of  $Q_{4/6}$  for C1, C2, and C3 were similar (13.7–14.4) as well as for C4, C5, and C6 (6.6–7.2) (Table 3). It should be underlined that  $Q_{4/6}$  values indicate the optical density of humic substances, with lower values determined at an increase in the degree of humic substance density, which corresponds to a more humified organic material, representing better chemical properties. According to Ozdemir et al. [30], an optical density ranging from 3.23 to 8.8 indicates the successful maturation of composts, and taking into consideration this threshold, only composts 4 to 6 met such a criterion. Another valuable description of humic compounds in composts is based on the  $C_{HA}$ :  $C_{FA}$  ratio, which is widely used to describe the relative speed of HA and FA transformation, as well as the maturity of compost. Unfortunately, similar to the case of the C:N ratio, there is no agreement between authors in relation to the correct threshold of DP. According to Iglesias-Jimez and Pérez-García [31], a value of the polymerization degree needs to be higher than 1.9, whereas Azim et al. [26] stated that the correct threshold value needs to be greater than 1.0 and Alvarenga et al. [32], by contrast, considered the limit value of 2.5. Taking into account the lowest mentioned value of DP, all of the investigated composts met this criterion, but including the highest one, only compost number 1 was well-matured (Table 3). Composts 2, 3, 4, and 5 showed a very comparable range of HI (14.3%–22.6%) and HR (11.0%–15.3%). The highest values of HI and HR were found for C1, at 28.7% and 21.8%, respectively, while compost 6 exhibited the lowest (HI-8.9% and HR-6.3%). Similar values were reported by Jakubus [9], Asquer et al. [28], Bustamante et al. [33], and Jakubus and Michalak-Oparowska [34].

#### 3.2. Characteristic of Various Carbon Combinations in Composts

Although the use of composts as organic amendments is well documented, very few studies have been conducted on the quality and quantity of compost humic substances, so in the presented study, an extended analysis of the composts was performed. Among the analyzed composts, C1 was characterized by the highest amounts of carbon (TOC, C<sub>HS</sub>, C<sub>HA</sub>, HWC, LC), with compost 6 being the lowest (TOC, C<sub>HS</sub>, C<sub>HA</sub>, C<sub>FA</sub>, HWC, LC). At this point, it should be noted that C2 was also characterized by significantly lower amounts of the studied parameters compared to the chemical composition specified for C1, C3, C4, and C5. The amounts of TOC and LC found for C2 and C6 did not differ statistically between each other. Composts 3 and 5 did not differ significantly in the case of C<sub>HS</sub> (34.23 g·kg<sup>-1</sup> for C3 and 33.17 g·kg<sup>-1</sup> for C5), as well as the amounts of C<sub>HA</sub> (20.69 g·kg<sup>-1</sup> for C3 and 21.38 g·kg<sup>-1</sup> for C5). Composts 1 and 5 did not differ in the amount of LC, which was 2.50 g·kg<sup>-1</sup> and 2.30 g·kg<sup>-1</sup>, respectively. Organic fertilizers number 1, 3, and 5 presented very comparable levels of TOC (152.32–163.68 g·kg<sup>-1</sup>) and C<sub>FA</sub> (11.32–13.53 g·kg<sup>-1</sup>). Similar amounts of C<sub>FA</sub> to those mentioned previously were

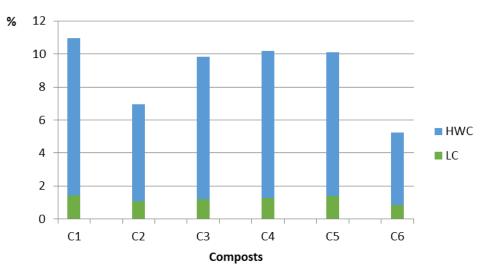
found for C4 (11.48 g·kg<sup>-1</sup>) (Table 4). Very comparable amounts of humic substances in composts were showed by Jakubus [9] and Jakubus and Michalak-Oparowska [34].

**Table 4.** Total, labile, hot water-extractable carbon content, and amounts in humic substances of composts  $(g \cdot kg^{-1})$ .

Compost Number	TOC *	C <sub>HS</sub>	C <sub>HA</sub>	C <sub>FA</sub>	HWC	LC
C1	163.68 a	46.97 a	35.64 a	11.32 a	15.57 a	2.50 a
C2	127.49 c	18.24 d	11.48 d	6.76 b	7.49 d	1.35 cd
C3	152.32 ab	34.23 b	20.69 b	13.53 a	13.04 c	1.84 b
C4	135.38 b	26.98 c	15.50 c	11.48 a	12.11 cd	1.71 bc
C5	159.62 a	33.17 b	21.38 b	11.79 a	13.85 b	2.30 a
C6	118.81 c	10.02 e	5.65 e	4.37 c	4.97 e	0.93 d

Significant differences between the means are marked with different letters. \* For descriptions, see Section 2.

In general, when characterizing and assessing the quality of composts, the total content of carbon or the amount of organic matter are taken into account, without a thorough analysis of the quality and quantity of humus compounds [9,25,35]. Moreover, in the literature, the subject of the amount of labile or water-soluble carbon in relation to composts is not recognized at all. Considering the soil application of composts, the transformation of carbon compounds in the environment, especially labile and easily decomposable compounds, is of key importance. Hence, the analysis of these kinds of carbon connections is justified. The conducted research shows that, irrespective of the compost, the amounts of LC were the lowest, ranging from 0.83% (C6) to 1.4% (C1) of the TOC share (Figure 1). The amounts of HWC were approximately five to seven times greater than those found for LC, and at the same time, were comparable to those obtained for the  $C_{FA}$  (Table 4).



**Figure 1.** Percentage shares of different fractions of carbon (LC—labile carbon, HWC—hot waterextractable organic carbon) in its total content.

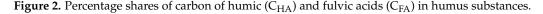
The percentage share of HWC in TOC ranged from 4.4% (C6) to 9.5% (C1) (Figure 1). Despite quantitative differences between the separated C forms (TOC, HS, HA, FA, LC, HWC), highly significant positive correlations were found between them (Table 5), pointing to a close relationship. In general, the amounts of C in the abovementioned bonds increased proportionally. Taking into consideration the fact that hot water-extractable organic carbon represents a mobile and readily soluble fraction of organic matter and is subject to change, it may directly reflect the organic matter transformation process [36,37]. According to Ghani

et al. [20], HWC is a component of the labile organic matter and is a sensitive measure of subtle changes within the ecosystem, particularly the susceptibility of humic compounds to chemical and microbiological processes, which leads to their solubility and mobility. According to these statements, the amounts of HWC or LC found in this study should be considered small and the susceptibility of carbon compounds of the tested composts to rapid transformation is too low. The data of  $C_{HA}$  and  $C_{FA}$  confirm this. Despite a small quantitative difference in the carbon between humic and fulvic acids, the percentage share of C<sub>HA</sub> in C<sub>HS</sub> was much higher, ranging from 56.4% (C6) to 75.9% (C1) (Figure 2). The predominant amount of C<sub>HA</sub> clearly indicates a significant polymerization of compost humic compounds. Humic acids (HAs) and fulvic acids (FAs) represent the majority of the humic substances, but there are differences between them [38-40]. HAs have a more complex structure than FAs, because of their higher molecular weight and a lower number of oxygen-containing groups compared to FAs. Moreover, HAs contain many acidic functional groups and have a considerable cation exchange capacity, thus absorbing various nutrients [41]. This is why they play an important role in the creation of soil fertility due to their influence on soil properties and quality of soil humic substances.

Table 5. Simple correlation coefficient.

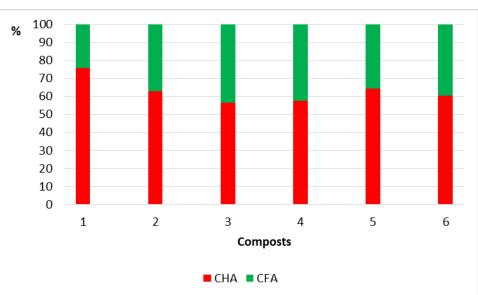
	Cr	Cu	Zn	Pb	LC ***	C <sub>HS</sub>	C <sub>HA</sub>	C <sub>FA</sub>	TOC
HWC	0.613 **	0.727 **	0.655 **	0.496 *	0.620 **	0.652 **	0.625 **	0.530 **	0.671 **
TOC	n.s.	n.s.	n.s.	n.s.	0.860 **	0.939 **	0.860 **	0.877 **	
FA	n.s.	n.s.	n.s.	0.532 **	0.799 **	0.780 **	0.613 **		
HA	n.s.	n.s.	n.s.	n.s.	0.796 **	0.973 **			
HS	n.s.	n.s.	n.s.	n.s.	0.865 **				

\*\*\*—descriptions in Section 2; n.s.—not significant; \*—p = 0.05; \*\*—p = 0.01.



#### 3.3. Amount of Bioavailable Metals in Composts

Irrespective of the compost, the amount of bioavailable metals decreased as follows: Fe > Mn > Zn > Cu > Pb > Ni > Cr. The data contained in Table 6 clearly show that C6 is the fertilizer characterized by the lowest abundance of bioavailable metals (except for Mn, for which the content was the lowest in C4) and simultaneously it is impossible to indicate one compost that contains the highest amounts of all tested metals. Thus, compost 2 had the highest contents of Ni (4.66 mg·kg<sup>-1</sup>) and Cr (4.45 mg·kg<sup>-1</sup>), C5 was characterized



by the highest amounts of Fe (4.58 g·kg<sup>-1</sup>) and Mn (166.12 mg·kg<sup>-1</sup>), C3 represents the highest amount of Zn (117.53 mg·kg<sup>-1</sup>), and C4 the highest amounts of Cu (14.61 mg·kg<sup>-1</sup>) and Pb (10.33 mg·kg<sup>-1</sup>). It is worth noting that the amounts of Fe were comparable for C2 (2.90 g·kg<sup>-1</sup>) and for C3 (2.94 g·kg<sup>-1</sup>). These two composts did not differ in the amount of Zn (112.84 mg·kg<sup>-1</sup> for C2 and 117.53 mg·kg<sup>-1</sup> for C3). The bioavailable amounts of Mn, Pb, and Ni did not differ statistically in the case of C3 and C4. The amounts of bioavailable Mn were comparable for C2 (81.18 mg·kg<sup>-1</sup>) and C6 (84.37 mg·kg<sup>-1</sup>). For compost 2 and 4, the amount of Cu was determined at the same level (13.67 mg·kg<sup>-1</sup>–14.61 mg·kg<sup>-1</sup>), similarly as for C3 and C5 (8.75 mg·kg<sup>-1</sup>–9.32 mg·kg<sup>-1</sup>). A very comparable quantitative level of metals was determined by Jakubus [8].

Compost Number	Fe	Mn	Zn	Cu	РЬ	Ni	Cr
C1	2.02 cd	70.61 bc	65.33 c	10.43 b	4.55 cd	2.54 c	2.70 с
C2	2.90 b	81.18 b	112.84 a	13.67 a	5.97 b	4.66 a	4.45 a
C3	2.94 b	72.92 bc	117.53 a	8.75 c	9.88 a	3.23 b	3.42 b
C4	2.42 c	60.04 c	85.60 b	14.61 a	10.33 a	2.86 bc	2.66 cd
C5	4.58 a	166.12 a	54.40 d	9.32 c	5.11 bc	3.23 b	2.07 d
C6	1.90 d	84.37 b	28.21 e	2.35 d	4.00 d	1.55 d	1.18 c

**Table 6.** Bioavailable amounts of metals in composts ( $mg \cdot kg^{-1}$ , except Fe expressed in  $g \cdot kg^{-1}$ ).

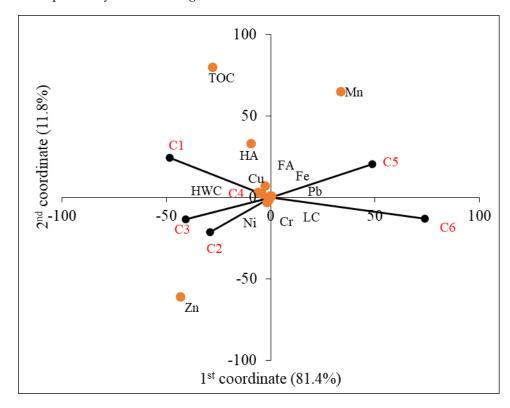
Significant differences between the means are marked with different letters.

As mentioned earlier, the group of heavy metals also includes toxic ones, such as Pb and Cr. Taking into account the negative impact of heavy metals on the soil environment and their easy incorporation into the food chain, all fertilizers (including composts) that are used for fertilizing purposes must meet the criteria for metal content to prevent environmental pollution. According to the Regulation of the Minister of Agriculture and Rural Development of 18 June 2008 [14], compost cannot exceed, among other things, 100 mg·kg<sup>-1</sup> Cr and 140 mg·kg<sup>-1</sup> Pb. The EU guidelines [15] in this regard are more restrictive, because the amount of Pb cannot be higher than 45 mg·kg<sup>-1</sup>, and Cr greater than 70 mg·kg<sup>-1</sup> d.m. The abovementioned values from both legal acts are given in total amounts, which significantly exceed the bioavailable amounts, while the quantitative differences between the total and bioavailable amounts of Pb are considerable, ranging from 4.4 to 35 times for Pb, whereas for Cr it is from 16 to 86 times. Such small amounts of bioavailable metals significantly confirm the high environmental safety of the analyzed composts, which is especially important in plant production.

The significant differences between the investigated composts for individual metals should be interpreted by the fact that biowastes used for composting were similar in terms of their morphology, but originated from various sources (different size of agglomeration and the degree of potential pollution by metals, various chemical composition). In this respect, C6 draws special attention, because this fertilizer was not prepared commercially, but only for private use, so the source of biowastes was only from a private garden located far from the city center, i.e., located in the suburbs of a big agglomeration and thus these wastes were not exposed to potential pollution. Such a possibility is also indicated by Jakubus and Michalak-Oparowska [34], who found similar small amounts of metals in the compost used as a fertilizer by private home owners as those found in this study.

Noteworthy is the highly significant relationship between the amounts of HWC and the contents of Cr, Cu, Zn, and Pb in the composts tested (Table 5). This proves and emphasizes the important role of hot water-extracted carbon in the sorption of metals, and thus controlling their potential mobility in the soil environment. Taking into account the small amounts of bioavailable metals, as well as hot water-extracted carbon, the tested composts, with their potential application to soil, should not pose a threat to the environment.

Figure 3 provides a visual representation of the common tendencies for composts regarding quantitative changes in the studied parameters, as presented in Tables 4 and 6. The analyses of the average amounts of metals as well as the humus compounds, labile carbon, and water-extractable carbon show that they were comparable in compost groups 1, 2, and 3, similarly as for 5 and 6. Compost 4 was the one that showed intermediate values between the two compost groups. When interpreting the quantitative variability of the examined properties, it should be emphasized that, on average for the composts, the lowest quantitative variability was observed for Pb, Cr, Cu, Ni, LC, and C<sub>FA</sub>. Their values were stable compared to those determined for Zn, Mn, TOC, and C<sub>HA</sub>. Noteworthy is the emphasis on the relationship between TOC and Pb, Cr, Ni, and Zn, the amounts of which decreased with increasing TOC content. However, the increase in the amount of TOC was accompanied by the increasing amounts of Mn, Fe, Cu, LC, and HWC.



**Figure 3.** Canonical variate analysis showing the relationship between the individual composts (C1–C6) and analyzed parameters.

#### 4. Conclusions

It is concluded that regardless of the prevailing conditions during the processes (aerobic or aerobic–anaerobic), they produced good quality composts. On the basis of the obtained results, it can be concluded that neither the length of the maturation period nor the size of the agglomeration from which the biowastes were selectively collected had a decisive influence on the chemical composition of the composts. Additionally, the amount of bioavailable metals in the composts mainly depends on the chemical composition of the used biowastes, i.e., the level of potential heavy metal pollution. Regardless of the above, the bioavailable amounts of metals found in the composts were small and the compost prepared in the aerobic–anaerobic conditions was characterized by the lowest contents of metals. Thus, it may be stated that the analyzed composts should not have any potential negative influence on the soil environment during application.

The findings of this work indicate the considerable significance of hot water-extractable carbon in compost evaluation in terms of their agricultural utilization. This was confirmed by the close relationships between HWC and most of the metals, as well as LC, TOC, and HS (including HA and FA). In addition, the special role of labile carbon should be

underlined, because, as shown by this research, the amount of LC, apart from  $C_{FA}$ , was a stable, unchanging parameter. Such a property may indicate its potential practical use in quick, simple, and routine compost quality assessment. Summing up, composts as organic fertilizers prepared from municipal biowastes were found to be a valuable source of humic substances of satisfactory quality. Small amounts of readily soluble carbon compounds suggest that after their application to soil, composts of this type will transform in a uniform manner, slowly releasing their components, while increasing the resources of the native humus, thus increasing the attractiveness of biowaste management by composting.

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