High temperature composting suppresses humification: process rate and humic substances content

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Abstract

Soil fertilization with compost promotes carbon sequestration, mainly in the form of stable organics, that is, humic substances (HS), including humic acids (HA). Therefore, the technological conditions during composting should enable maximal amounts of HS and HA to be obtained in mature compost. Composting needs to be managed to obtain high temperatures to ensure hygienization. However, particularly at a technical scale, the process tends to be overheated. This study examined the effect of overheating during sewage sludge composting on the rate of HS and HA formation, and the HS and HA concentrations in the final product. Two series were performed: in series 1, the maximal temperature was 72.2°C and the thermophilic phase lasted 12 d, whereas, in series 2, these values were 83.1°C and 20 d, respectively. It was found that overheating affected humification kinetics and reduced HS and HA content. In series 2, the rates of HS formation ($r_{\text{HS}} = 1.70 \text{ mg C/g OM d}$) and HA formation ($r_{\text{HA}} = 1.44 \text{ mg C/g OM d}$) were 2-fold lower than in series 1 ($r_{\text{HS}} = 3.51 \text{ mg C/g OM d}$; $r_{\text{HA}} = 2.92 \text{ mg C/g OM d}$). Similarly, the maximal increases in HS and HA concentrations in series 2 (59.65 and 38.89 mg C/g OM, respectively) were 1.4-fold lower than those values in series 1. However, overheating did not affect the humic acids’ elemental composition.

Keywords: Sewage sludge; Composting; Overheating; Humic substances; Humic acids

1. Introduction

Composting is a desirable method for recycling organic wastes, due to the fact that compost is a valuable fertilizer that serves principally as a source of macronutrients (NPK). However, taking into account that one of the key goals in the priorities of the European Union’s Thematic Strategy for Soil Protection [1] is to maintain and increase the level of soil organic carbon, it is desirable to sequester carbon in the form of stable organic matter (i.e., humic substances, HS) that is introduced to the soil. In this light, the composting process should not only be managed so as to ensure the hygienization of waste, but also to “produce” the maximal amount of HS that can be introduced to the soil when the compost is used as a fertilizer or plant cultivation agent.
organics, and their presence in soil influences its cation exchange capacity, pH buffer capacity and retention of heavy metals [4,5].

The factors which significantly affect the efficiency of the composting process are feedstock composition (therein C/N ratio and the share of biodegradable organics), pH, moisture and porosity. All of them, as well as, aeration intensity, influenced mineralization rate, which leads to an increase in temperature.

Previous studies have focused on feedstock preparation to ensure thermophilic conditions and enable the sanitation of composted waste and the retention of nutrients in the compost. Some authors have also analyzed the relationship between feedstock composition and humification progress [6,7]. In contrast, relatively little attention has been devoted to studying the relationship between temperature and humification progress, that is, the humification rate and the concentrations of humic substances (HS) and their fractions, that is, fulvic acids (FA) and humic acids (HA).

It was assumed that compost overheating affects: (i) kinetic constants of the humification process, (ii) the amount of humic substances, humic acids and the fulvic fraction in mature compost, and (iii) properties (characteristics) of humic acids. To make it possible to obtain different temperature profiles while using the same feedstock composition, the aeration intensity was adjusted.

2. Materials and methods

2.1. Feedstock and process configuration

Dewatered sewage sludge was collected from a municipal wastewater treatment plant operated with activated sludge technology. Due to its high moisture content (87.4%) and low C/N ratio (5.9), the sludge was mixed with materials with lower humidity and higher C/N ratios (wood chips as bulking agent and rye straw and grass as amendment). The characteristic of a particular component for feedstock composition is given in Table 1. Taking into account the moisture, organic matter and nitrogen content in lignocellulosic components and the fact that wood chips play a role only as bulking agents and do not compost, proportions of individual components in the feedstock have been established as follows (the same in both series): sewage sludge 67% (w/w), wood chips 15% (w/w), rye straw 13% (w/w) and grass 5% (w/w). The feedstock characteristics were: moisture 72.0% (series 1) and 70.3% (series 2), and content of organic matter (OM), total organic carbon (TOC) and N were 745.1, 365.3 and 23.8 g/kg d.m. in series 1; and 729.1, 354.2 and 22.4 g/kg d.m. in series 2, respectively. Consequently, the OM/N and C/N ratios were 31.3 and 15.3 in series 1, and 32.5 and 15.8 in series 2, respectively.

To create different temperature profiles (with differences in maximal temperature and length of thermophilic phase), different aeration intensities were employed: in series 1, 1.0–1.2 l/min kg; and in series 2, 0.5–0.7 l/min kg.

In both series, the composting process was conducted in a two-stage system: the first stage was an aerated bioreactor (1 m³; the air was introduced with a ventilator); and the second was a periodically turned windrow (the air was delivered during turning and by natural convection). A detailed description and schematic diagram of the bioreactor were presented in Kulikowska and Klimiuk [6]. The composting process was conducted for 194 d.

2.2. Analytical methods

Samples were collected in accordance with the guidelines contained in Polish Standard PN-Z-15011-1 and described in detail by the study of Kulikowska and Sindrewicz [7]. The samples were mixed, dried at 105°C and ground to a diameter of 0.5 mm using a RETSCH SM 100 mill. All analyses were done according to Polish Standards (PN-Z; PN-C). Total OM was measured by ignition of the samples at 550°C (PN-Z-15011-3:2001) and TOC by using a TOC analyzer. Total nitrogen was determined by the Kjeldahl Method (PN-Z-15011-3:2001).

The procedure for the extraction of humic substances (HS) and their fractions (fulvic fraction, FF, labile humic acids, L-HA and stable humic acids, S-HA) have been described in a previous publication [6–8]. Shortly, HS, HA and FF were extracted according to the procedure described by Boratyński and Wilk [9]. However, before HS extracting, the samples were washed with distilled water to remove soluble non-humic substances, then samples were defatted with a mixture of chloroform and methanol until a colorless supernatant was obtained (the extractions were carried out in a MARSXpress Microwave oven). After samples defatting, HS was extracted. Firstly, L-HA were...
extracted with 0.1 M Na₃P₂O₇; next, extracts were acidified to pH 1, after which the precipitated L-HA were left to coagulate at 4°C for 24 h. Then, L-HA was separated from the FF by centrifugation. After L-HA separation, S-HA were extracted from the samples using the above procedure but with 0.1 M NaOH. The concentration of L-HA and S-HA was determined as total organic carbon (TOC; Shimadzu Liquid TOC-VCSH Analyzer, Kyoto, Japan). The FF content was calculated by subtracting the content of HA from that of HS. The elemental composition of humic acids was determined in accordance with the procedure in detail described in Kulikowska et al. [10]. Briefly, the HA elemental composition was determined according to the procedure given by Alburquerque et al. [11]. Firstly, the HA (both L-HA and S-HA) samples were washed two times with 0.1 M HCl, then once with distilled water and were centrifugated. The supernatants were discarded and HA samples were freeze-dried. The elemental composition (C, H, N, S) of both L-HA and S-HA was analyzed using a Flash 2000 Organic Elemental Analyzer (Thermo Scientific). The oxygen content was calculated as the difference between the ash-free dry weight (100%) and the sum of the percentage contents of C, H, N and S. The elemental composition was the basis of atomic ratios (H/C, O/C, N/C, O/H) in L-HA and S-HA calculating.

3. Results and discussion

3.1. Temperature profiles and organics removal

3.1.1. Temperature profiles

In general, as assumed, a lower temperature and a shorter thermophilic phase were obtained in series 1, which had a higher aeration rate. In series 1, the temperature exceeded 45°C after 1 d of composting, while in series 2, it reached 56.6°C within 12 h (Fig. 1). As the temperature profiles show, in series 1, the maximal temperature was 72.2°C, and the thermophilic phase lasted 12 d. In series 2, the composting feedstock was overheated, with a maximal temperature of 83.1°C. In this series, the thermophilic phase was longer than in series 1, lasting for 20 d. It should be emphasized that, even in the series with a lower aeration intensity, the amount of air was sufficient for the oxidation of organic matter because, at the beginning of the process, there was an intense increase in temperature, which is related to the oxidation of easily biodegradable organic compounds.

Depletion of readily available substrates and low availability of organic compounds remaining in the composted feedstock cause a decrease in the biological activity of microorganisms and lead to a gradual decrease in temperature. In this study, although relatively high organics removal in both series was noted (Fig. 2), in series 2, a slower decrease in temperature was observed. This phenomenon was connected with lower excess heat being blown off/removed, which usually takes place at low aeration rates.

3.1.2. Organics removal

Because they had the same feedstock, the OM content was similar in both series, 745 g/kg d.m. (series 1) and 729 g/kg d.m. (series 2). At the end of the processes in a bioreactor, OM contents were ca. 570 and 580 g/kg d.m., respectively (Fig. 2a and b). During composting in the windrow, a further decrease of OM was observed, but it was several times lower than in the bioreactor (Fig. 2c and d), which is typical during composting in a two-stage system.

The kinetics of OM degradation (OMrem) were calculated with the first-order kinetic model:

\[
\text{OM}_{\text{rem}} = A \cdot e^{-k_{\text{OM}} \cdot t} \tag{1}
\]

where \(A\) is the maximum amount of OM that is degraded (g/kg d.m.); \(k_{\text{OM}}\) is the rate constant of OM degradation (d⁻¹); \(t\) is the composting time (d).

The initial rates of OM degradation (\(r_{\text{OM ini}}\)) are described by \(k_{\text{OM}}/A\).

In the reactor in series 1, in which the biomass was subjected to lower temperature, the rate constant of OM removal \((k_{\text{OM,1}})\), the maximum amount of OM removal \((A_{\text{OM,1}})\) and OM removal rate \((r_{\text{OM,1}})\) were 0.32 d⁻¹, 176 g/kg d.m. and 56.3 g/kg d.m. d⁻¹, respectively. In series 2, both \(k_{\text{OM,2}}\) and \(A_{\text{OM,2}}\) were lower (0.28 d⁻¹ and 141 g/kg d.m., respectively), which resulted in the 1.4-fold lower OM removal rate (39.5 g/kg d.m. d⁻¹). In the windrow in both series, as expected, the rate constants of OM removal were an order of magnitude lower than in the bioreactor and maximum amounts of OM removal were 3–4-fold lower (Fig. 2c and d).

Higher temperature and longer duration of the thermophilic phase in series 2 could have reduced the efficiency of lignocellulose degradation, causing a lower loss of organic matter (141 g/kg d.m. in series 2 vs. 176 g/kg d.m. in series 1). It is known that the intense decomposition of cellulose and lignins, in which actinomycetes and fungi are involved, begins when the temperature goes down (i.e., in the cooling phase). As shown by Tuomela et al. [12], the most important lignin degraders are thermophilic fungi, with optimum temperatures of 40°C–50°C, which is also the optimum temperature for lignin degradation in compost. The high temperature of 58°C in the controlled composting test inhibited the mineralization of radiolabelled synthetic lignin (4C-DHP), which was only 8%. This means that temperature was an important factor in the degradation of lignin and lignin-containing materials, and the
temperature of 58°C in the controlled composting test was too high for lignin degradation [13]. The influence of temperature on the decomposition of lignocellulose has also been shown by Fersi et al. [14]. Those authors analyzed the impact of *Trametes trogii* inoculation on lignin and cellulose degradation during composting of green wastes with olive mill wastewater sludge and coffee grounds. They showed that the addition of *T. trogii* at the beginning of the process did not improve lignin degradation due to the high temperature during the process, and low activity of *T. trogii*. In contrast, *T. trogii* inoculation during cooling, when the temperature was ca. 45°C, increased lignin degradation efficiency.

### 3.2. Humification progress

#### 3.2.1. Humification kinetics and humic substances concentration

During composting, in general, humification of organic matter occurs and consequently, in mature compost, high concentrations of HS are observed. However, during sewage sludge composting, high concentrations of HS are already observed in the feedstock. This is connected with the high concentration of HS in sewage sludge [15–17]. A previous study by the author of this study also showed relatively high concentrations of HS and HA in sewage sludge [10]. This means that HS content in sewage sludge depends on the kind of sludge and the stabilization method.

In this study, due to the use of the same feedstock, the concentrations of HS and HA in both series were similar, equaling 121.3 mg C/g OM (HS) and 53.2 mg C/g OM (HA) (series 1) and 115.6 mg C/g OM (HS) and 51.2 mg C/g OM (HA) (series 2). Analysis of the concentration of HS and HA shows that, despite comparable concentrations in composting feedstock, the quantity of HS and HA produced during composting as well as a kinetic constant of humification depends on the temperature.

In both series, the kinetics of HS and HA formation proceeded according to this first-order kinetic equation:

\[
C = C_{\text{max}} \left(1 - e^{-kt}\right) + C_i
\]  

where \(C_{\text{max}}\) is the maximum increase in the concentration of HS or HA (mg C/g OM); \(k\) is the rate constant of humification (HS or HA) (d\(^{-1}\)); \(t\) is composting time (d); \(C_i\) is the initial concentration of HS or HA (mg C/g OM).

A higher value of \(C_{\text{max,HS}}\) (83.6 mg C/g OM) was noted in series 1, which had a lower maximal temperature; it was almost
1.6-fold higher than in series 2 ($C_{\text{max},\text{HS}_2}$, 53.3 mg C/OM), in which the compost was overheating (max. temperature over 80°C) (Fig. 3, Table 2). Such a relationship was noted also for the $r_{\text{HA}_2}$ (Table 2). Similarly, in the series with lower temperature, higher $C_{\text{max},\text{HA}_1}$ (59.7 mg C/g OM) and rate of HA formation $r_{\text{HA}_1}$ (0.049 mg C/g OM d$^{-1}$) were noted. In the series with overheating, $C_{\text{max},\text{HA}_2}$ and $r_{\text{HA}_2}$ were 1.5-fold and 2.0-fold lower, respectively.

Obtained results indicate that the maximal temperature in the composted feedstock and the duration of the high-temperature phase in the bioreactor affected both the kinetics of HS and HA formation and the amount of HS and HA in the final product. However, it is worth emphasizing that, in both experiments, the formation of HS and HA occurred mainly during the first 60–70 d of the process, after which the concentration of humic substances changed relatively little.

The HS and HA concentrations in the composting biomass were lower in the series with the higher temperature (83.1°C). Such a high temperature could have a disadvantageous effect on the activity of laccase, for which the optimum temperature is below 60°C. Laccase oxidizes phenol to form reactive radicals, which form humus by polymerization with nitrogen-containing compounds. According to Cheftez et al. [18], laccases are most active at 50°C–60°C. At temperatures above 80°C, their activity is only 4.0%–8.5% of its maximum value. Šnajdr and Baldrian [19] also showed that, although fungi (Pleurotus ostreatus and Trametes versicolor) were able to grow and produce laccase and Mn-peroxidase (MnP) at 5°C–35°C, production was highest at 25°C–30°C in P. ostreatus and at 35°C in T. versicolor. However, the optimal temperatures for enzyme activity were 50°C and 55°C for P. ostreatus and T. versicolor laccases, respectively, and 60°C for MnP.

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Humic substances (HS)</th>
<th>Humic acids (HA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{\text{max,HS}}^{a}$</td>
<td>$k_{\text{HS}}$ (d$^{-1}$)</td>
</tr>
<tr>
<td>Series 1</td>
<td>83.58</td>
<td>0.042</td>
</tr>
<tr>
<td>Series 2</td>
<td>53.23</td>
<td>0.032</td>
</tr>
</tbody>
</table>

$^{a}$mg C/g OM

$^{b}$mg C/g OM d

Fig. 3. Humification progress during sewage sludge composting (a, b) series 1 and (c, d) series 2.
In humic acids, two kinds are distinguished: labile humic acids (L-HA) and stable humic acids (S-HA). L-HA are macromolecules characterized by small or medium size; they have an aromatic character and are weakly bound to mineral surfaces via cation bridges. In contrast, S-HA is larger macromolecule of aliphatic character [20,21]. In both series in the present study, S-HA predominated. However, at the lower temperature in the bioreactor, L-HA content did not exceed 12% of L-HA content, whereas, at the higher temperature, it reached 27%.

The present study indicates that very high temperature inhibited humification (both concentration of HS and humification rate), but in the literature, it has been reported that hyperthermophilic composting (HTC), with a maximal temperature of 96.6°C, favored humification [22]. According to the cited authors, HA concentration increased during thermophilic composting (TC, with maximal temperature 55.9°C) from 20.1 to 23.2 g/kg, but in HTC, from 18.83 to 32.75 g/kg. That is a rather unusual phenomenon. Although elevated temperatures in the thermophilic phase of composting are essential for degradation of lignocellulose and humification, the optimal activity of laccase and Mn-peroxidase have been noted at 50°C–60°C [19]. An et al. [23] found a thermostable laccase in brown rot fungi, which can oxidize 2,2′-azino-di-(3-ethylbenzothiazoline)-6-sulfonic acid (ABTS) and 2,6-dimethoxyphenol (DMP), the optimal temperature for oxidation of ABTS and DMP was only 60°C.

3.2.2. Humic acids characterization

HA can be characterized in terms of their elemental composition (C, H, N, O).

From the data in Table 3, it can be seen that C predominated in HA from composts of different origins, accounting for just above 50% (by weight), and even as high as 58.5% in compost from olive oil extraction residues, as reported by Droussi et al. [27]. In most cases, including the present study, the content of C in compost is comparable to its content in soil HA. An extremely low C content was noted by Amir et al. [26] in tannery sludge compost.

The content of N and S in HA varies widely depending on the type of compost. The highest reported content of nitrogen was found in HA extracted from municipal solid waste [24]. However, in other samples, including the HA from sewage sludge compost in this study, the content of nitrogen is only slightly higher than that in HA from the soil, as reported Steelink [32], but lower than in soil reported by Garcia-Gil et al. [31]. Moreover, in the present study, relatively high content of S was observed. However, the highest concentration of S in HA was reported by Droussi et al. [27].

Elemental composition affects atomic ratios (H/C, C/N, O/C, O/H). Atomic ratios allow assessing the structure of humic acid molecules by evaluation of the degree of condensation of the aromatic rings (on the basis of the H/C ratio) and the degree of HA maturity (on the basis of the C/N, O/C, O/H ratios and internal oxidation ω) [33,34].

The degree of aromatization of humic acids can be estimated on the basis of their H/C ratio because this ratio is inversely proportional to their aromaticity [35]. The values of the H/C atomic ratios of the HA extracted from sewage sludge compost in this study ranged from 1.20 to 1.30 (Table 4). These values demonstrate that the HA contained aromatic rings bonded to an aliphatic chain including up to 10 carbons [35]. The data in Table 3 indicate that, in all analyzed compost and soils, the H/C ratio in HA was in the range 0.7–1.5, which indicates a similar degree of HA aromatization in all these studies.

The progress of OM humification is connected with an increase in oxygen content and a decrease in hydrogen

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Elemental composition of humic acids (HA)</th>
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<tbody>
<tr>
<td>Origin of HA</td>
<td>C (% weight)</td>
</tr>
<tr>
<td>Sewage sludge compost (L-HA) (series 1)</td>
<td>50.3</td>
</tr>
<tr>
<td>Sewage sludge compost (L-HA) (series 2)</td>
<td>50.1</td>
</tr>
<tr>
<td>Sewage sludge compost (S-HA) (series 1)</td>
<td>51.2</td>
</tr>
<tr>
<td>Sewage sludge compost (S-HA) (series 2)</td>
<td>51.5</td>
</tr>
<tr>
<td>Sewage sludge compost</td>
<td>50.1</td>
</tr>
<tr>
<td>Sorghum–tomato compost</td>
<td>52.8</td>
</tr>
<tr>
<td>Urban waste compost</td>
<td>51.7</td>
</tr>
<tr>
<td>Urban waste vermicompost</td>
<td>50.2</td>
</tr>
<tr>
<td>Chicken manure–soybean vermicompost</td>
<td>51.4</td>
</tr>
<tr>
<td>Tannery sludge compost</td>
<td>42.5</td>
</tr>
<tr>
<td>Olive oil extraction residues compost</td>
<td>58.5</td>
</tr>
<tr>
<td>Spent mushroom substrate</td>
<td>53.8</td>
</tr>
<tr>
<td>Municipal waste compost</td>
<td>36.5</td>
</tr>
<tr>
<td>Soil amended with compost</td>
<td>57.3</td>
</tr>
<tr>
<td>Soil</td>
<td>51.2</td>
</tr>
<tr>
<td>Soil</td>
<td>53–58</td>
</tr>
</tbody>
</table>
content. These changes affect the values of the $O/H$ and $O/C$ atomic ratios, which are indicators of the degree of oxidation of HA. The $O/H$ value also reflects the degree of humification of HA molecules: a higher $O/H$ ratio indicates a greater degree of humification. In soil HA, the $O/C$ value is about 0.5, while in fulvic acids (FA), it is about 0.7. The higher $O/C$ ratio in FA is due to its large number of $-\text{COOH}$ groups [33]. In the present study, $O/H$ values were slightly higher in labile humic acids (L-HA) than in stable humic acids (S-HA).

An important parameter describing the advancement of the humification process is the degree of internal oxidation ($\omega$) of HA molecules. This parameter reflects the relative amounts of carbon-hydrogen bonding and carbon bonding with nitrogen and oxygen. $\omega$ was calculated according to the formula $\omega = [2O + 3N]–H]/C$, where: $O, N, H, C$ are the percent contents of these elements.

In the present study, L-HA had a higher degree of internal oxidation (0.177–0.220) than S-HA (0.068–0.080). The lower $\omega$ of S-HA may indicate that their structures contain aliphatic compounds with a low degree of oxidation. A study by Kwiatkowska-Malina [36] showed the $\omega$ values of humic acids extracted from soils fertilized with a lignite preparation were 0.058–0.212. These acids were characterized by a higher degree of aromaticity and greater susceptibility to oxidation than those in the control soil. According to the author, this means that the introduction of lignite (as a source of organic matter) into soil caused structural changes in humic acids.

4. Conclusions

It was found that overheating affected humification kinetics and reduced, by ca. 40%, HS and HA content in mature compost. It means that preventing the compost from overheating, by regulating the intensity of aeration, allow to produce compost with a high concentration of HS and HA. Application of compost rich in humic substances may contribute to the improvement of soil fertility. Overheating did not affect the humic acids’ elemental composition.

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