Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21629

97 (2017) 234–243
November

Changes of PAHs and C humic fractions in composts with sewage sludge and biochar amendment

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Received 6 May 2017; Accepted 11 November 2017

ABSTRACT

Changes in the content of (polycyclic aromatic hydrocarbons) PAHs and transformation of humic substances during composting of maize straw with sewage sludge and biochar amendment were investigated. Biochar was applied as an agent for improving physical and chemical properties of the composting mix. The composting process has lasted 140 d and was carried out in laboratory conditions. The total content of organic carbon, its soluble forms in hot and cold water, as well as fractional composition of humic substances, and the group of 16 PAHs were investigated during the study. The major changes in the content of individual PAHs were noticed in the first 20 d when the temperature of composting mixtures reached 60°C. Biochar is the source of PAHs, but in the biochar-enriched combination the greatest reduction of the content of those compounds was noticed. The lowest decrease of PAHs concentration was detected in the case of maize straw compost characterized by the smallest volume of mesopores. The content of organic carbon soluble in hot water in the composted materials ranged from 15.1% to 20.2%, whereas in cold water extracts varied from 3.6% to 4.8%, as compared with the total Corg concentration. The humic acid:fulvic acid ratio (Cha:Cfa) indicating the organic matter decomposition was highest in the combination where the greatest reduction of PAHs was observed. The biochar-enriched compost was characterized by the largest population of fungi and presumably this group of microorganisms was responsible for effective PAH degradation.

Keywords: Compost; Biochar; PAHs; Humic acids; Fulvic acids; Water soluble organic carbon

1. Introduction

Composting is a method commonly used for organic recycling and disposing of solid biodegradable wastes. High quality composts may be used for agriculture, horticulture, greenery and/or restoration of degraded land. The value of compost is mainly determined by its quality, which depends on the conditions of composting process and composition of raw materials used as substrates. In order to close the loop of product lifecycles in circular economy, recycling of different organic materials, mainly agricultural waste is processed. To obtain the best composting conditions, the carbon to nitrogen ratio should be 22–35:1 [1] capable to favour the growth and activity of microbial populations. The optimal C/N values are achieved through the proper mixture formulations and properties of raw materials rich in carbon and nitrogen, including chicken manure, stable manure, slurry, straw, bark, peat or sewage sludge. The main purpose of

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composting the wastes is to change their properties throughout the mineralization of a part of organic matter and humification of recalcitrant organic compounds to guarantee the safe use of the final product in the environment [2].

Sewage sludges are wastes problematic to dispose. Co-composting of municipal sewage sludges as well as wastes from agricultural and food industry allows to obtain final market product, which is stable and safe in terms of sanitary requirements, and has permissible contents of various groups of organic pollutants. Another group of products applied for co-composting with raw materials is that which enhance the conditions of maturation. Biochar is widely considered as beneficial substrate for the composting process [3], because it helps to increase the sorption capacity and promotes buffering the process by, for example, reduction of the nitrogen loss and increase of microbial activity. Moreover, it can provide the structural support and create interparticle voids to improve gas exchange and prevent excessive compaction of the composting substrate. Vandecasteele et al. [4] have noticed that the improvement of composting method achieved by mixing of biochar with other compost substrates increased the rate of organic matter decomposition; moreover, it significantly reduced the loss of N and greenhouse gas emissions while increasing the availability of phosphorus.

Composting is a multi-function process, dominated by microbiological transformations as mineralization and humification of organic matter originated from wastes [1,5]. Compost is thus a valuable source of humic substances which constitute the most important soil components and greatly affect its properties [6,7]. Therefore fractional composition and content of fulvic and humic acids remaining after composting process, enables the evaluation of the amount of exogenous humic substances, which will directly enter soils amended with composts.

The origin of compost substrates and the rate of biotic and abiotic processes occurring during maturation determine the quality of composts [1]. Despite fertilizing value, they may contain numerous toxic substances [8]. Except heavy metals, they are significant source of polycyclic aromatic hydrocarbons (PAHs) [1,2,9,10].

PAHs are a group of persistent organic pollutants, which have been of scientific interest for several decades [2,11]. The occurrence of PAHs in composts is of particular importance for their disposal in the environment. In this context, the mechanisms of PAH transformation and their availability should be better recognized, because PAHs may undergo mineralization or degradation by various microbial communities to even more toxic metabolites as compared with parent compounds [8,12]. PAHs are treated as undesirable compounds because of their teratogenic, mutagenic and carcinogenic properties. They can form in natural conditions, for example, during forest fires, volcanic eruptions or transformation of organic matter. Because of diverse chemical structure, PAHs differ in their properties and susceptibility to various biotic and abiotic processes, which complicates the fate of these compounds in the environment [10,13].

The persistence and dissipation of PAHs in the environment are significantly influenced by microbial activity. This was also reported by Siebielska [14] who investigated the influence of aerobic and anaerobic conditions on the organic matter transformation during composting. The results indicated that degradation of naphthalene (Napht), phenanthrene (Phe), pyrene (Pyr), benzo(a)pyrene (BaP) and benzo(ghi)perylene (BGP) was more efficient in aerobic conditions as compared with anaerobic ones in tested mixtures prepared from sewage sludges and organic fraction of municipal wastes. Włodarczyk-Makuła [12] found that apart from biological degradation, the important part of PAH dissipation was caused by abiotic processes. She also suggested that abiotic losses of PAHs were due to oxidation or reaction of hydrocarbons with other sludge components and strong binding within the organic matrix [12]. Poor solubility in water, low vapour pressure and hydrophobic properties cause PAH high sorption affinity to organic matter. It was documented [10,13] that four and more-ringed PAHs present in soils after their amendment with compost are mainly adsorbed by organic fraction and/or organic and mineral complexes.

The permissible limits of PAH contents in biodegradable wastes subjected to biological treatment are not implemented in the EU [8], but in some countries, the quality standards for composts used for agricultural purposes were accepted. Such recommendations usually consider the maximum permissible levels of the sum of 16 PAH compounds from US EPA list including: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(g, h, i)perylene. It is worth to consider that the greatest risk caused by the presence of elevated PAH concentrations originates mainly from the products of mechanical–biological processing; whereas, it is relatively smaller derived from composts. However, this depends on the quality of substrates and technology applied for composting.

Compost substrates such as plant biomass, sewage sludge or biochar may contain elevated concentrations of PAHs. High content of aromatic hydrocarbons in plants results from the deposition of hydrocarbon-containing dust particles on the above ground parts of plants, preferably on large-surface wax-coated leaves [15,16]. In sewage sludges, PAHs predominantly originate from domestic by-products, which contain these compounds [16,17]. Biochar can be a source of PAH mixtures of different quantity and composition which are formed during the pyrolysis [10,18]. Composts produced under managed conditions with biodegradable materials potentially containing PAHs need the multidirectional analysis of organic matter transformation, including content and composition of humic substances and dissolved organic carbon as well as the level and of organic pollutants to consider rational and safe use of composts in soil. The aim of the study was to assess changes in the content of PAHs and transformations of humic substances during the co-composting of maize straw with sewage sludge and biochar added to improve physical and chemical properties of the composted mixture.

2. Materials and methods

2.1. Experiment conditions and design

Composting of biomass was carried out over 140 d, from mid-May 2015 to the end of September 2015. The process was conducted in bioreactors of 1.2 × 1.0 × 0.8 m dimensions with a perforated bottom to aerate the active biomass. Laboratory bioreactors were sheltered from rain, but subjected to the influence of the outside temperatures and solar radiation. This resulted in heat exchange between the composted material and surrounding. The experimental design involved three combinations: (1) control – maize straw (M), (2) maize straw + municipal sewage sludge (M + SS), (3) maize straw + municipal sewage sludge + willow biochar (M + SS + BC). The amount of co-composted materials added to raw maize biomass depended on their physical characteristics and water content. The proportions of the compost substrates as regard to their dry weight were as follows: M:SS – 1:0.15 (and M:SS:BC – 1:0.15:0.1) which corresponded to 29.3 kg dry matter of chopped maize straw, 4.4 kg dry mass of municipal sewage sludge (SS) and 3 kg dry mass of willow biochar (BC). Amount of SS was established according to the findings by Gałwa-Widera [19] and did not exceed 45% of compost fresh matter.

Sewage sludge used in the study was acquired from municipal wastewater treatment plant (mechanical–biological system) located in the province of Małopolska (southern Poland). Before disposal, the sludge was oxygen-stabilized in separate open chambers with a continuous aeration in ambient temperature for 5 d. After this period, the sludge was dehydrated by centrifugation. Biochar was obtained during pyrolysis at 300°C of willow biomass (FLUID S.A., Poland). After mixing of substrates, the moisture of the composted mixture was kept at the level of 60% by adding water. Aeration of the composted mixtures was performed six times a day with air flow of 15 L min^{-1} for 60 min through the bioreactor, while homogenization was done manually once every 10 d. The outside temperature as well as the temperature in each bioreactor (at half height of the composted mass) was monitored continuously during the process using DT-171 recorders at 30-min intervals [20]. Representative samples (0.5 kg) were collected every 20 d, immediately after compost homogenization and dried at 25°C before chemical analysis. Samples were collected at the beginning of the composting process and after 20, 60, 100 and 140 d.

2.2. Elemental composition of substrates and composts

The total content of C, H, N, S in substrates and composts was determined using the CHNS analyzer (Vario EL Cube, Elementar, Germany) [21]. The total value of O was calculated according to DIN 51733 [22] as difference:

$$\begin{aligned} \mathrm{O}\,(\%\mathrm{w/w}) = 100 - \mathrm{ash}\,(\%\mathrm{w/w}) - \mathrm{C}\,(\%\mathrm{w/w}) \\ - \mathrm{N}\,(\%\mathrm{w/w}) - \mathrm{H}\,(\%\mathrm{w/w}) - \mathrm{S}\,(\%\mathrm{w/w}) \end{aligned} \quad (1)$$

2.3. Dissolved organic carbon

The DOC content in composts was determined by cold water extraction (CWE) and hot water extraction (HWE) according to the methods described by Ghani et al. [23], and Jones and Willett [24], respectively. Organic carbon soluble in cold water (C-CWE) was determined by shaking 5 g of the soil sample with 50 mL of MiliQ deionized water at 20°C for 24 h. The obtained suspension was centrifuged (20 min, 3,500 rpm), and the solution was decanted and filtered through a Buchner funnel equipped with a sterile membrane filter of 0.45 µm pore size. Organic carbon soluble in hot water (C-HWE) was determined at 80°C for 16 h with soil:MiliQ deionized water in the ratio 1:10 (w/v). All extracts were kept at the refrigerator before analysis. DOC content was determined with CN Multi N/C 2100/2100S analyzer (Analytik Jena, Germany).

2.4. Total Corg and fractional composition of humic substances

The organic carbon (Corg) content was determined using a mixture of concentrated sulfuric acid and orthophosphoric acid (1:5 v/v) [25]. Humic substances were determined according to ISO 12782-4: 2012 [26]. Briefly, the multi-stage analysis consisted of the isolation of the fulvic acids (∑Cfa) fractions by dissolving in 1 mol HCl L^{-1}, than in 1 mol NaOH L^{-1}, as well as humic acids (Cha) fraction dissolved in 1 mol NaOH L^{-1}, and then precipitated with 6 mol dm^{3} HCl at pH = 2. The precipitated Cha were dissolved in a small amount of 0.1 mol L^{-1} KOH. The obtained humic acids and fulvic acids extracts were analyzed for the organic carbon content with the C-N Multi N/C 2100/2100S analyzer, Analytik Jena. The content of a non-hydrolyzing carbon (Cnh) was calculated indirectly by the formula:

$$\mathrm{Cnh} = \mathrm{Corg} - (\sum \mathrm{Cfa} + \mathrm{Cha}) \quad (2)$$

where ∑Cfa was the sum of fulvic acid fractions whereas Cha was fraction of humic acids.

2.5. Analysis of the PAHs content

PAHs in substrates and composts were quantified according to a protocol previously described by Gondek et al. [27]. Briefly, 2 g of dry samples of substrate and 5 g of composts were spiked with mixture of five deuterated PAH standards (naphthalene-d8, fluorene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and extracted with dichloromethane (two extraction cycles, temperature 100°C and pressure of 1,500 psi) in accelerated solvent extraction system (ASE 200, Dionex). Extracts concentrated in *n*-hexane were cleaned-up on glass mini-columns filled with 1 g of silica gel, eluted with 5 mL mixture of *n*-hexane/dichloromethane (3/2 v/v), and concentrated to obtain 1 mL of *n*-hexane. PAHs were identified by GC-MS (Agilent 6890N gas chromatograph equipped with Agilent 5973 Network mass spectrometer /70 eV/ and 7683 B series autosampler). DB-5 MS + DG fused-silica capillary column (30 m × 0.25 mm I.D. with a film thickness of 0.25 µm), constant helium flow of 30 cm s^{-1}, and a splitless injection system at 250°C were applied. The GC oven temperature was programmed as follows: 60°C hold for 2 min, raised at 30°C/min ramp to 120°C, and then 5°C/min to the final temperature of 290°C hold for 10 min. Selected ion monitoring mode was applied for PAH molecular ion detection. The instrument was calibrated daily with calibration standards. The identification of individual compounds was based on comparison of retention time data between samples and the standard solution (CRM 131) containing mixture of 16 parent and 5 deuterated PAHs. Method banks and sample duplicates spiked with deuterated standards were routinely analyzed with substrate and compost samples. The recovery for individual compounds from CRM 131 was within 62%–84%, and precision expressed as a relative standard deviation was in the range of 5%–12%. The average recovery of deuterated PAHs for substrates reached 71%, while for composts 89% [28,29].

2.6. Specific surface area S_{BET} and the size and pore volume

The specific surface area (S_{BET}) of substrates and composts as well as the size and pore volume was determined with ASAP 2010, Micromeritics, U.K. Ltd. The specific surface area (S_{BET}) was investigated by physical adsorption of nitrogen at 77°K from the Brunauer–Emmett–Teller equation. Before S_{BET} measurement, the tested samples were subjected to desorption at 105°C under vacuum and purged with pure helium. Degassing time of each sample equalled 16 h. The surface degassing state was monitored automatically [30].

2.7. Theoretical density of the element or compound in composts

Assuming the isolation of the system and the element content and mass balance before and after composting, the equation was introduced to calculate the theoretical density of the element or compound in the compost (Z_k):

$$Z_w \cdot M_w = Z_k \cdot M_k \tag{3}$$

$$Z_k = \frac{Z_w \cdot M_w}{M_k} \tag{4}$$

where Z_k – content (potential content) of an element in the compost after 140 d, Z_w – content of an element in the compost mixture at time 0, M_w – weight of the compost mixture at time 0, M_k – weight of the compost after 140 d.

2.8. Statistical analysis

All samples were determined in duplicate. The paper presents the mean results of the chemical determinations, for which SD was lower than 5%. Statistical analyses were carried out using STATISTICA 12 application (StatSoft 2006). Variations within objects were determined by calculating the standard deviation of replicates (±SD). The coefficient of variation was calculated according to the formula:

$$V = \frac{\mathrm{SD}}{x} \cdot 100\% \tag{5}$$

where x – the arithmetic mean, SD – standard deviation of replicates.

3. Results and discussion

3.1. Chemical and physical parameters of the compost

Maize straw was characterized by the highest content of oxygen and hydrogen (Table 1), which probably influenced the susceptibility of that substrate to biological and chemical degradation. The amount of material remaining after the composting process was presented in our previous publication by Kopeć et al. [20] and carried out: 36%, 39.7% and 43.7%, respectively, for objects M, M + SS and SS + BC what positively correspond to the contents of hydrogen and oxygen in substrate mixtures before composting (Table 1). The higher content of these elements, the higher losses in the composting process. Furthermore, at the same time a significant increase in nitrogen and sulphur concentration was noted. Comparison of the values in Table 1 after the composting process and the theoretical density index indicated a negligible loss of nitrogen in gaseous form what was in line with findings of Vandecasteele et al. [4]. Composting influenced sulphur losses. At final stage, S concentration was lower by 12%, 15% and 22% in objects M, M + SS, M + SS + BC, respectively, as compared with its content in initiate mixtures.

Table 1
The total contents of selected elements in substrates, their mixtures and composts

Material	N (g kg^{-1})	C (g kg^{-1})	H (g kg^{-1})	O (g kg^{-1})	S (g kg^{-1})
Substrates					
M	10.6	393.4	6.15	41.7	1.34
SS	33.1	240.5	4.20	21.5	14.06
BC	9.67	639.1	2.37	19.1	2.60
Mixtures before composting					
M	10.6	393.4	6.15	41.7	1.34
M + SS	13.5	373.4	5.90	39.1	3.00
M + SS + BC	13.2	393.7	5.63	37.5	2.97
Composts after 140 d					
M	31.6	365.6	5.21	35.8	3.32
M + SS	34.6	332.4	4.90	30.5	6.58
M + SS + BC	29.0	361.1	4.38	29.7	5.57
Potential contents (Z_k)*					
M	29.4	1,092	17.08	115.7	3.72
M + SS	34.0	941	14.86	98.3	7.56
M + SS + BC	30.3	903	12.91	86.0	6.81

M, maize straw; SS, municipal sewage sludge; BC, biochar.
*Potential contents of elements resulting from concentration factor (Z_k).

Due to structure and composition (C:N ratio = 7.3) of municipal sludges, their composting without co-substrates is very difficult. The addition of cut maize straw improved the physical properties of M + SS mixture as well created conditions for gas exchange, which affected the growth of microbial populations and increased biological activity [31]. The C:N ratio in initial M + SS mixture was 27.6, while after the process the ratio was 9.60. However, C:N ratio is not a valuable indicator describing compost maturity, but it reveals the potential and efficiency for biochemical transformation. In this case, it may indicate changes that have occurred in the composted biomass. Addition of biochar to the mixture of raw maize straw and sewage sludge has increased C:N ratio, both at the beginning and at the end of the composting process. Although the stable carbon forms present in biochar have reduced dry matter losses during composting by 7.7%. It has not slowed down the composting process evidenced by the temperature curve [20].

Matured composts have differed in physical properties (Table 2). After 140 d, the surface area of maize straw compost (M) was two times smaller as compared with object amended with sewage sludge and biochar (M + SS + BS). Maize straw co-composted with sewage sludge (M + SS) and biochar (M + SS + BC) indicated 38% and 71% higher volume of mesopores, respectively, as compared with compost M, while the average diameter of mesopores in M + SS + BC object was >2 nm smaller compared with other composts. The data indicate that the application of sewage sludge and biochar to the plant biomass significantly increased the potential for contact between substances and the compost structural material [32]. Mesopores facilitate sorption of organic compounds (e.g., xenobiotics) and promote effective aeration of compost mixtures what enhance oxidation processes of xenobiotics [4,33]. The type of xenobiotic and its sorption affinity towards compost organic fraction may reduce their rate and extent of biotic and abiotic transformations during the composting process. Moreover, the addition of biochar improves physical properties of composts but efficient use of such substrate needs its standardization because the sorption surface area of biochar depends on both, type of biomass and temperature of pyrolysis [10].

3.2. Total and dissolved organic carbon

The carbon content in substrates and composts is presented in Table 1. The substrates applied differed with total carbon content which depended on the type of substrate. The biochar indicated a significantly higher total carbon content – C_{total} (639.1 g kg^{-1}) as compared with the maize straw (393.4 g kg^{-1}) and sludge (240.5 g kg^{-1}) but the smallest fraction of organic carbon (extracted by Turin's method) which amounted only 40% of C_{total}, while in sludge and maize it was over twice as much 94% and 93%, respectively.

Variation coefficient (V) for total carbon and organic carbon content in compost samples carried out 28.5% and 14.6%, respectively. Maize straw compost (M) indicated (Fig. 1) the highest content of C_{total} (365.63 g kg^{-1}) with a high participation of Corg (88%). Co-composting of the maize straw with sewage sludge (M + SS) as well as sludge and biochar (M + SS + BC) had a negligible impact on the total carbon but influenced Corg content. Significant decrease of Corg amount by 16% and 22% was noticed in objects M + SS and M + SS + BC, respectively, as compared with the control compost M – Fig. 1. The reduction of organic carbon quantity is usually noticed during composting process. It was also indicated in M + SS + BC compost, although biochar contains aromatic C structures, more resistant to microbial degradation. A decrease of Corg in matured composts results from the intensive mineralization of organic matter [1,14]. A part of C-rich organic substances is utilized by microorganisms as a source of carbon and energy. Final products of microbial transformations may be: water, carbon dioxide, methane, hydrogen sulphide and ammonia.

The content of dissolved organic carbon (Fig. 2) and fractional composition of humic substances (Fig. 3) were studied to assess the quality and the rate of organic matter

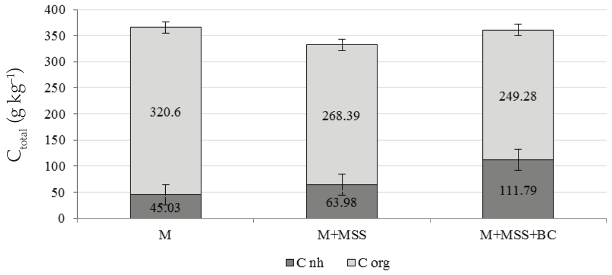

Fig. 1. The share of organic carbon and non-hydrolyzing carbon in the C_{total} content in the studied composts; ±standard deviation, n = 2.

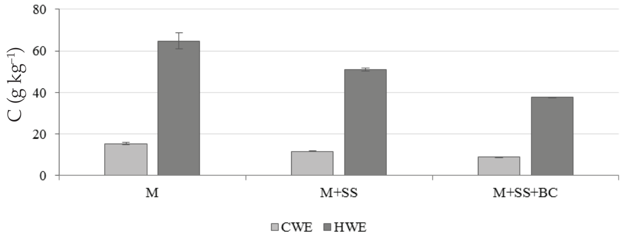

Fig. 2. Organic carbon content in cold water extracts (CWE) and hot water extracts (HWE) in matured composts; ±standard deviation, n = 2.

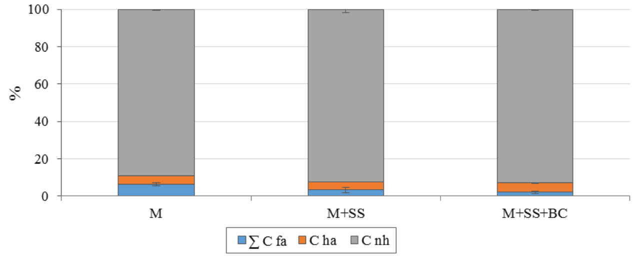

Fig. 3. The share of fractions of humic substances in matured composts; ±standard deviation, n = 2.

Table 2
Structural parameters of compost calculated on the basis of low-temperature nitrogen adsorption isotherms

Object	S_{BET} (m^2 g^{-1})	$V_{mesopores}$ (cm^3 g^{-1})	Average diameter of mesopores (nm)	Maximum diameter of mesopores (nm)
M	0.54	0.0021	17	79
M + SS	0.72	0.0029	18	79
M + SS + BC	1.07	0.0036	15	70

M, maize straw; SS, municipal sewage sludge; BC, biochar.

transformation in composts. The wide share of organic carbon water-soluble forms in the overall carbon pool was noticed. Their content depended on the temperature of water used for the extraction (cold or hot water). The organic carbon content in hot water extracts (C-HWE) was significantly higher as compared with Corg extracted with cold water (C-CWE) (Fig. 2). C-HWE constituted from 15.1% to 20.2% and C-CWE carried out only 3.6%–4.8% of Corg and showed significantly lower quantity variation. The study indicated that the addition of sewage sludge and biochar reduced the content of Corg soluble forms. The amendment of maize straw with sewage sludge (M + SS) caused the reduction of C-CWE by 24.5%, while C-HWE by 21.3% comparing with compost M. Co-composting of maize straw with sewage sludge and biochar (M + SS + BC) much improved stabilization of the organic matter and reduced content of the C-CWE fraction by 42.2%, and C-HWE fraction by 41.8% as compared with the control compost (M). Dissolved organic carbon may play different functions in the environment, but, predominantly, constitutes the main source of available carbon for soil fauna and flora [34,35]. C-HWE is an aliphatic–aromatic carbon fraction and binds less available and more stable organic compounds, for example, xenobiotic [34] but composting may significantly modify its characteristics [36]. C-CWE is a readily available, low-molecular and predominantly aliphatic fraction suspended in the solution which undergoes faster biodegradation during compost maturation [36].

3.3. Humic compounds

The fractional composition of humic substances has indicated a significant variation, mainly dependent on the compost type (Fig. 3). The largest amount was assigned to the non-hydrolyzing carbon (Cnh) which accounted for over 89% of Corg. Content of humic acids (Cha + ΣCfa) carried out 7%–11% of total Corg pool. Their highest content (34.6 g kg^{-1}) was found in the maize straw compost. Addition of sewage sludge and biochar affected the reduction of humic acids to 20.2 and 17.5 g kg^{-1} in M + SS and M + SS + BC composts, respectively. The increase of stable carbon forms in matured composts confirms a possible intensive polymerization of humic acids and creation of higher molecular weight structures with more aromatic nature [6,7,14]. The decrease of C-humic acids indicated the decreased of Cfa (30% for M + SS and 35% for M + SS + BC) but did not influence the Cha quantity. The Cha content in all composts was similar and ranged from 11.5 to 13.9 g kg^{-1}. The reduction of Cfa amount in all objects probably resulted from the on-going mineralization process of easily available (biodegradable) forms of organic matter [6,37]. The largest Cha:Cfa ratio of 2.5 was noticed in the compost enriched with sewage sludge and biochar (M + SS + BC). In the case of compost produced from maize straw (M) and maize straw with sewage sludge amendment (M + SS), the ratio was 1.3 and 0.7, respectively. A high degree of humification in composts M + SS and M + SS + BC confirms the considerable participation of high molecular weight humic acids and thus high compost maturation. Similar results were obtained by Fourti et al. [6] and Siebielska [14].

3.4. Polycyclic aromatic hydrocarbons

The substrates subjected to composting varied from their origin, the content individual PAHs and characteristics described by sums of hydrocarbons differed with ring numbers in a molecule (Table 3). The highest total content of Σ13 and

Table 3
The PAHs content (mg kg^{-1} dm) in substrates of composted materials

No.	PAH	*n*	Substrates		
			M	SS	BC
1	Naphthalene (N)	2	0.364	0.519	0.194
2	Acenaphthylene (Acy)	3	0.224	0.052	0.014
3	Acenaphthene (Ace)	3	0.217	0.056	0.058
4	Fluorene (F)	3	0.235	0.130	0.175
5	Phenanthrene (P)	3	0.502	0.966	1.094
6	Anthracene (Ant)	3	0.275	0.085	0.126
7	Fluoranthene (Fl)	4	0.374	0.315	1.163
8	Pyrene (Pyr)	4	0.367	0.280	0.926
9	Benzo(a)anthracene (BaAnt)	4	0.150	0.171	0.594
10	Chrysene (Chr)	4	0.352	0.176	0.578
11	Benzo(b)fluoranthene (BbF)	5	0.437	0.151	1.405
12	Benzo(k)fluoranthene (BkF)	5	0.290	0.059	0.314
13	Benzo(a)pyrene (BaPyr)	5	0.121	0.043	0.481
14	Dibenzo(a,h) anthracene (DBahAnt)	5	0.092	0.000	0.063
15	Indeno(1,2,3-cd) pyrene (IPyr)	6	0.177	0.021	0.459
16	Benzo(g,h,i)perylene (BghiPer)	6	0.162	0.040	0.389
	∑16 PAHs[a]	2–6	4.340	3.065	8.035
	∑13 PAHs[b]	3–6	3.535	2.438	7.769
	∑2 + 3-ringed PAHs[c]	2 + 3	1.817	1.809	1.661
	∑4-ringed PAHs[d]	4	1.244	0.942	3.261
	∑5 + 6-ringed PAHs[e]	5 + 6	1.280	0.315	3.112
	∑2 + 3-ringed PAHs/∑16 PAHs (%)		42	59	21
	∑4-ringed PAHs/ ∑16 PAHs (%)		29	31	41
	∑ 5+6-ringed PAHs/∑16PAHs [%]		29	10	39

M, maize straw; SS, municipal sewage sludge; BC, biochar; *n*, number of rings.
[a] Sum of compounds no. 1–16.
[b] Sum of compounds no. 4–16.
[c] Sum of compounds no. 1–6.
[d] Sum of compounds no. 7–10.
[e] Sum of compounds no. 11–16.

Σ16 PAH compounds was found in biochar. This material had a particularly high content of 4- and 6-ring compounds particularly phenanthrene, fluoranthene and benzo(k)fluoranthene.

In maize straw and sewage sludge, the sum of 16 PAHs was less than 6 mg kg^{-1}. That value was mentioned as the end-of-waste criterion for compost and digestates, as proposed in the Third Working Paper [8] concerning the criteria for biodegradable biologically treated waste [8]. In contrast to biochar, in both those materials dominated PAHs accounted for compounds with fewer rings. It is also noteworthy that the content of 4-, 5- and 6-ring compounds was smaller in sewage sludge than in maize straw.

The results presented in Table 3 indicated minor changes of PAH content as regard to the sums of different individual compounds in compost M as compared with the raw maize straw. A significant decrease concerned predominantly a group of 2- and 3-ring compounds, although a reduction in the dry matter was observed during the process, which was discussed in the previous section. Therefore, the results after 140 d of composting and theoretically calculated “potential content” pointed out to the degradation of PAHs as regard to raw compost mixtures. If the degradation process had not taken place, the increase of the quantity of PAHs should be several times greater in all the objects. In the research by Włodarczyk-Makuła [38], the balance of PAHs loads of the methane fermentation process was calculated. An approximate twofold decrease in dry matter of sludge was observed. During sewage sludge digestion process, 3- and 4-ring compounds were released from a solid phase to supernatants.

PAHs undergo various chemical reactions that can be divided into two groups: substitution reactions and addition reactions, which lead to destruction of unsaturated bonds. Aromatic hydrocarbons are sensitive to light, oxygen, ozone and other oxidants. In the presence of light and oxygen, some of PAHs undergo a photochemical reaction and transformation to diol forms, quinones and aldehydes as the final stage. However during composting, light penetration is limited, but aeration is an important factor in transformation processes of PAHs. Ciesielczuk et al. [9] has found that a lack of air may cause an increase of the content of PAHs during the composting process, and finally create a real risk to the biotic environment. He also concluded that after 6 months of compost storage in anaerobic conditions, previously unidentified compounds were found.

In the case of M + SS compost, the greatest reduction of PAHs content has occurred in the first 20 d what affected all compound groups differentiated by a number of rings. Indicators describing the sums of various PAHs in M + SS + BC material were high before composting and resulted from a significant share of PAHs in biochar. Composting of this mixture during the first 20 d caused a 3 to 4 times decrease of PAHs considering their content in different groups.

Fig. 4 presents the detailed information on the content and dynamics of changes of individual PAHs over time. There are many factors influencing the content and relations between the analyzed hydrocarbons. These factors include physical, chemical and biological interactions. Noteworthy are hydrocarbons such as P, F, BbF. Their high content was maintained in all composts during the first 20 d of the process; whereas, in the case of maize straw compost, there was a significant reduction of their content after that period. Oleszczuk [39] stresses the special degradation kinetics of phenanthrene linking it with its binding ability to active centres within matrix and displacing there other previously absorbed compounds. The process of slow sorption of phenanthrene within organic matter is hardly reversible or irreversible; therefore the persistence and significant content of this compound was noticed in composted mixtures after certain time periods.

Włodarczyk-Makuła [40] has calculated the half-life times describing PAHs dissipation in the experiment with sewage sludge. They ranged widely (126–2,048 d) and were specific for individual PAHs. In our study, the reduction of some PAHs content might have occurred before the date of first sampling designated on 20th day of the experiment. These findings confirm the results of Bikovens et al. [7] and Winquist et al. [41]. Winquist et al. [41] yielded PAHs reduction up to 94% but they investigated artificially contaminated materials cleaned up by laboratory-induced fungi. In that experiment the 2- to 3-ring compounds were reduced most intensively. Those findings were also confirmed by Oleszczuk [39], and Saveyn and Eder [8]. A rapid loss of low molecular weight PAHs (LMW-PAHs) containing <4 rings in composts was also confirmed by Włodarczyk-Makuła [40]. Cited author notice that these changes may result partly from abiotic processes, for example, increased volatilization of LMW-PAHs in the first phase of the composting process when temperature is rising, but also biotic, that is, when a faster biodegradation may occur due to a relatively better bioavailability of those compounds. It was also suggested that the decrease of LMW-PAHs in industrial conditions is due to the creation of higher amount of effluents in heat phase of composting and probably moving to the liquid phase PAHs with a small number of rings indicating higher solubility. Cao et al. [42] mentioned that the importance of biochar in the sorption of PAHs increases in the case of properly chosen substrates. In the cited study, the presence of lignocellulosic biomass co-composted with biochar favoured microbial activity and the removal of benzo(a)pyrene and phenanthrene. The application to the soil of biochar-enriched compost may cause completely different relations among PAHs; however, the decrease of PAH load should be expected over time [43,44] believe there is no risk of PAHs introducing to the soil with green waste compost, but much attention should be paid to the conditions under which such composts are to be used when crops for human food or animal fodder are grown.

According to Włodarczyk-Makuła [12,40], the changes of PAH content in composts may originate from the intake of hydrocarbons by microorganisms and their release after disintegration of cells. Microorganisms can accumulate aromatic compounds and after cell lysis PAHs are released again into the environment. The effectiveness of PAHs biodegradation within metabolic processes is influenced by sufficiently long incubation time, although Bikovens et al. [7] emphasize the importance for PAHs biodegradation mainly the thermophilic phase of composting.

Our another study concerning biological activity and the number of microorganisms in the same composts indicated the increase of fungi number in object with sewage sludge (M + SS) as compared with control maize straw combination (M) [31]. Addition of biochar also created favourable conditions for fungi growth in the final product. The role of these organisms in PAHs degradation was stressed by

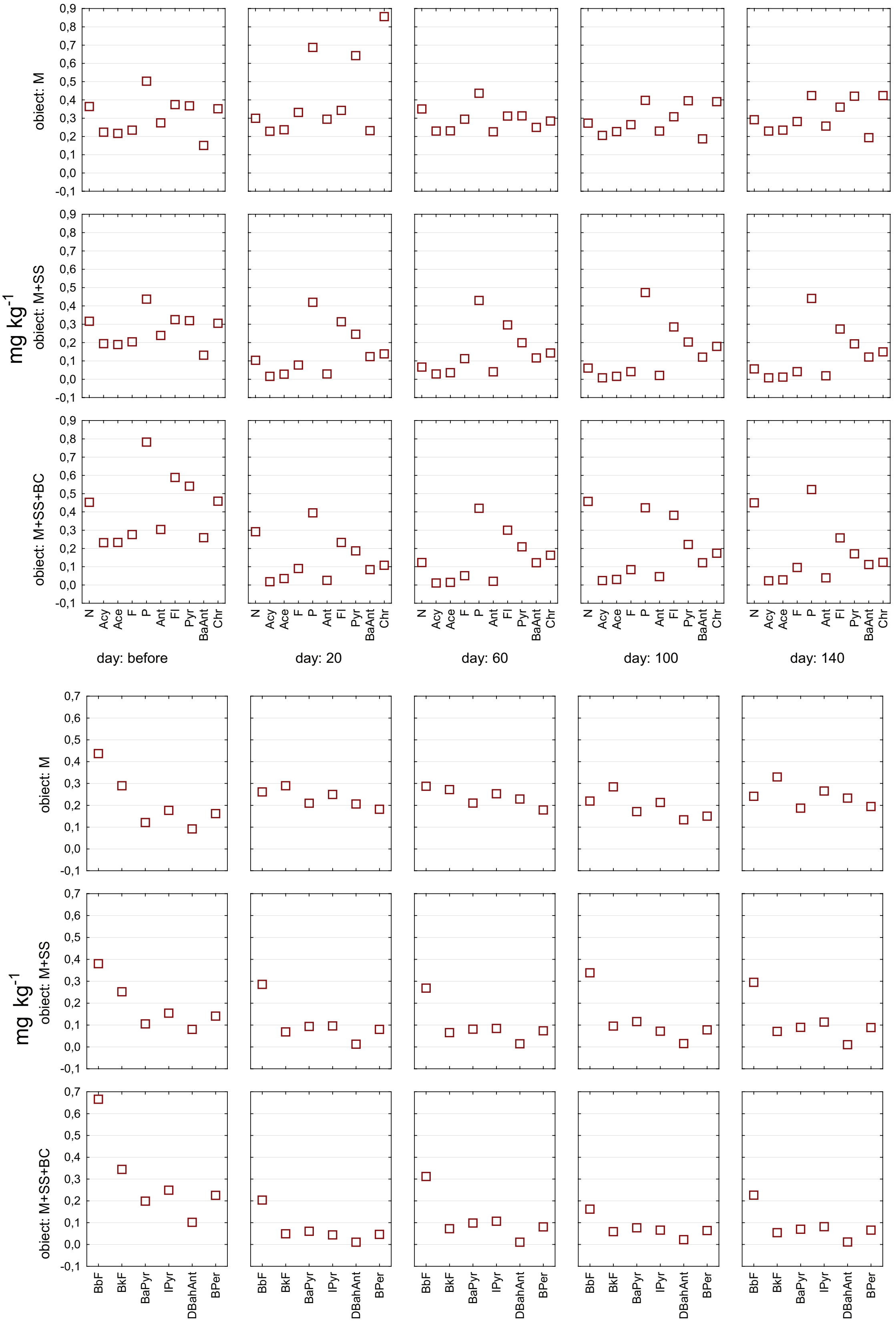

Fig. 4. The changes of individual polycyclic aromatic hydrocarbons (PAHs) content during the composting.

Winquist et al. [41], who have stimulated PAHs biodegradation by application of *Phanerochaete velutina* strain. Jindo et al. [45] have also found a greater share of fungi in compost containing biochar. They considered that biochar is beneficial for a group of organisms which effectively promote humification, although stating at the same time that the mass of microorganisms in biochar-enriched compost was lower.

Włodarczyk-Makuła [12] has considered that sewage sludge represents a complex organic and inorganic matrix and therefore PAHs adsorbed on the solid particles may not always be easy to desorb or extract [15]. Moreover, in such a form, they are inaccessible for microorganisms. This finding corresponds to the data obtained in our study because the range and dynamics of PAHs dissipation in composts have not always been clear. Thus, production of compost at an industrial scale needs to keep the temperature regime, because thermal phase is of the highest importance for effective PAH degradation [8]. This is caused both, by abiotic losses of hydrocarbons and activation or inhibition of microbial groups involved in transformation of these compounds. In this phase, the losses of dry matter of the composted material are also significant. Understanding and modelling of PAHs transformation in the environment and during composting still need the effort from researchers of different areas of expertise [12,13,46].

4. Conclusions

1. The significant changes of PAHs content in the composted mixes took place during the first 20 d when the temperature has reached 60°C.
2. The content of hot water extracted carbon ranged from 15.1% to 20.2% of Corg, while cold water extracted fraction carried out 3.6%–4.8% of Corg.
3. Biochar is the source of PAHs but in biochar-enriched compost, the decrease of PAHs content characterized by various indicators was greatest.
4. The Cha:Cfa ratio was the highest in composts with the greatest reduction of PAHs content.
5. The smallest decrease of PAHs quantity was found in the maize straw compost indicating the lowest volume of mesopores.
6. Compost enriched with biochar had the largest number of fungi and probably this group of microorganisms is responsible for the effective PAHs biodegradation in the final phase of composting.

Acknowledgement

The research was financed by the Ministry of Science and Higher Education of the Republic of Poland.

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