



Dissipation and sorption processes of polycyclic aromatic hydrocarbons (PAHs) to organic matter in soils amended by exogenous rich-carbon material

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Abstract

Purpose The aim of the research was to assess the effect of biochar addition on aging, degradation, and sorption processes of polycyclic aromatic hydrocarbons (PAHs) to soil organic matter. The study was carried out as a sorption experiment in strictly controlled water and air conditions, which allowed for the accurate observation and prediction of PAH behavior in soils.

Materials and methods Four soils were fortified with a PAH mixture (Fluorene-Flu, Anthracene-Ant, Phenanthrene-Phe, Pyrene-Pyr, Chrysene-Chry) at 20 mg kg⁻¹ of single-compound concentration level. The experiment was carried out in two trials: soils + 5PAHs amended with biochar and soil + 5PAHs without biochar addition with incubation times of 0, 1, 3, 6, and 9 months. After each interval time, the extractable (E-SOM) and stable organic matter (S-SOM) were measured as well as PAHs determined in two forms: total concentration (PAH-tot) and residual concentration (PAH-rest) after E-SOM extraction. The PAH loss and half-life times were estimated according to pseudo first-order kinetics equation.

Results and discussion The amounts of PAH-tot in the soils without biochar decreased by an average of 92%, while in soil with biochar, this was 41% after 9 months of aging. The amount of PAHs-rest bounded with S-SOM after 9 months of incubation varied from 0.9 to 3.5% and 0.2 to 1.3% of the initial PAH concentration, respectively, for soils non-induced and induced by biochar. In soils without biochar, Flu, Ant, Phe, and Pyr exhibited similar $T_{1/2}$ (43–59 days), but Chry was characterized by a much higher and broader $T_{1/2}$ than other hydrocarbons (67–280 days). Biochar addition to the soils significantly influenced the half-life changes for all PAHs. The highest changes were noted for Phe (14-fold increase), and the lowest was for Flu (7-fold increase).

Conclusions The addition of exogenous-rich carbon material such as biochar to the soil significantly changes the behavior and sorption potential of PAHs in the soil. Soils enriched with biochar are characterized by a higher persistence of PAHs, longer aging time, and lower affinity for sorption by native organic matter structures. Soils freshly polluted by PAH are mainly sorbed by E-SOM, which significantly increases their accessibility and reduces formation of bound-residues in the soil.

Keywords Biochar · Exogenous rich-carbon material · Organic contaminants · Soil organic matter · Soil sorbents · Sorption

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are specific environmental pollutants which are resistant to degradation, remain in the environment for long periods of time, and have the potential to cause adverse environmental effect (Agarwal et al. 2009; Bielińska et al. 2018). PAHs are released to the environment mainly through anthropogenic activities (e.g., industry, emission from individual house-heating systems, road transport) (Agarwal et al. 2009). The worldwide distribution of PAHs in soils, which increased during last century by over five orders of magnitude, was related to sorption

ability of those pollutants to soil organic matter (SOM) (Agarwal et al. 2009; Klimkowicz-Pawlas et al. 2017; Ukalska-Jaruga et al. 2019b). PAHs deposited in soils are subject to an “aging process” which often entails an initially rapid and reversible sorption process to SOM, followed by a period of slow diffusion occurring over weeks, months, or even years once they are released into the soil environment (Luo et al. 2012). Extensive literature data have confirmed that the extractability and bioavailability of PAHs decreased significantly with time during aging processes (Oleszczuk et al. 2012; Yang et al. 2012; Koltowski et al. 2016).

It is assumed that soils amended with exogenous organic matter increase pollutant sorption and reduce their availability. Many different amendments have been dedicated for this purpose (Koltowski et al. 2016; Kuśmierz et al. 2016; Dutta et al. 2017; Ćwieląg-Piasecka et al. 2018; Bejger et al. 2018). Recently, a lot of attention has been focused on rich carbon material (ERCM) such as biochar. Biochar is a co-product of biomass pyrolysis that is targeted as a material with applications in environmental protection (e.g., soil remediation) and agricultural management as a source for carbon sequestration (Beesley et al. 2011; Wang et al. 2017). It also improves soil physicochemical and biological properties, including nutrient status, soil structure, and water holding capacity (Lehmann et al. 2011; Herath et al. 2013), as well as modifies microbial community abundance and soil enzyme activity (Gomez et al. 2013).

Increasingly, various researchers propose the application of ERCM to immobilize PAHs in soils (Beesley et al. 2011; Ghosh et al. 2011; Koltowski et al. 2016; Kuśmierz et al. 2016; Dutta et al. 2017). These sorbents mainly reduce the freely dissolved fraction of the contaminants that reach the pore water by diffusion, sorption, and partitioning processes (Pignatello 2012; Wang et al. 2017). The organic sorbents affect mainly non-bound or poorly bound PAHs in the soil due to the abundance of organic functional groups (Koltowski et al. 2016; Dutta et al. 2017). The strong sorption of PAH compounds by sorbents reduces the uptake by soil organisms, and consequently, lowers their toxicity. Nevertheless, the sorption properties of biochar depend on production conditions and the feedstock type (Tag et al. 2016). Factors influencing biochar properties include the type of pyrolysis process, biochar feedstock resources, and treatment during and after pyrolysis (Bucheli et al. 2015; Tag et al. 2016; Buss et al. 2016; Wang et al. 2017). Buss et al. (2016) and Wang et al. (2017) noted that biochar prepared at low temperatures (350–650 °C) has a larger sorption surface and a lower content of harmful co-products (e.g., PAHs) that are usually formed during its production. Taha et al. (2014) demonstrated that biochar production at lower temperatures results in a product containing more surface functional groups and higher cation exchange capacity compared to biochar produced at higher temperatures. Thus, low-temperature biochar

is considered to sorb polar and ionic organic compounds more efficiently due to a large share of residual amorphous organic matter present in its carbonaceous matrix (Li et al. 2013; Kearns et al. 2014).

Previous research suggested that the application of biochar could increase total PAH content and at the same time increase the sorption capacity of organic matter, which may form a bound-residue fraction of PAHs in soil. These studies indicate that biochar might represent a source and/or a sink of PAHs. Until now, all of these aspects had to be considered in soil amended with biochar and exposed to pollution. Literature data also indicate that biochar might limit the availability of PAHs, but there is still a lack of information on processes influencing that effect. It is believed that biochar affects the transformation or retention of PAHs, consequently increasing the aging processes of contaminants (Cornelissen et al. 2005; Koltowski et al. 2016; Kuśmierz et al. 2016). In addition, there is little knowledge related to the processes involving biochar to modify PAH sorption on naturally accumulated soil organic matter. This is an important issue for soil quality assessment and environmental protection activities.

The aim of the research was to assess the effect of exogenous rich carbon material application on aging, degradation, and sorption processes of PAHs to soil organic matter.

2 Material and methods

2.1 ERCM-biochar properties

Biochar was obtained from a commercial manufacturer (Fluid S.A. Company) and produced by slow pyrolysis where the plant biomass in the form of chips and chaff derived from various types of conifers was autothermally decomposed at a temperature range of 350–650° (average temperature inside the reactor remains above 630 °C) in an oxygen-poor atmosphere (1–2% O₂). These temperature and conditions of the production processes allow keeping an appropriate level of anaerobic carbonizing.

The obtained biochar was highly carbonized, with a 78% C content, and atomic H/C and O/C ratios of 0.13 and 0.15, respectively (Table S2, Electronic Supplementary Material—ESM), which is consistent with a high degree of aromaticity. The ash content was moderately high and did not exceed 5%. The quality of the tested biochar is higher than in the case of—most available on the consumer market—charcoal, and meets, among others, the requirements of DIN EN 1860-2 on charcoal.

The sum of 5 PAHs in biochar was 328.4 µg kg⁻¹ (Table S2—ESM). Phe predominated in the biochar, accounting for 44% of all PAHs, followed by Pyr (23%). PAHs derived from biochar represent a small or negligible proportion

of these compounds introduced to soil (Hiber et al. 2012; Oleszczuk et al. 2016).

2.2 Description of the experiment

Four soils (S1–S4) selected for the experiment were derived from the surface layer (0–30 cm) of agricultural lands. They were chosen to reflect the variability of the physicochemical properties influencing differences in organic matter content and composition, as well as the low content of Σ 5PAHs (0.21–0.46 $\mu\text{g kg}^{-1}$). The experiment was conducted in two trials: soil spiked with a 5PAH mixture without ERCM amendment (trial I: S1–S4) and soils spiked with a 5PAH mixture amended with ERCM (trial II: S1B–S4B). A detailed description of the ERCM which was chosen as biochar and soil used in the experiment is given in supplemental information in Table S1 and S2 (ESM). The soils were air-dried, passed through a 2-mm mesh sieve, and 50 g portions were transferred into plastic containers. The biochar was added in a dry and crushed ($\phi < 300 \mu\text{m}$) state at doses of 5% m/m, based on the research of Koltowski et al. (2016). The soil-biochar mixtures (S1B–S4B) were shaken on a rotary shaker for 24 h. Each soil from trials I and II was contaminated with a mixture of five PAH compounds (Fluorene—Flu, Anthracene—Ant, Phenanthrene—Phe, Pyrene—Pyr, Chrysene—Chr) at 20 mg kg^{-1} of individual compound concentration level. The selection of PAH compounds was based on the differences in their properties (Table S3—ESM).

The aging experiment was carried out in laboratory over 0, 1, 3, 6, and 9 months in darkness, constant air, and water conditions (humidity: 60% full water holding capacity at temperature: $20 \pm 1 \text{ }^\circ\text{C}$). The total PAH content was determined after each time period in dry soil samples and in soil residue containing stable soil organics after removal of the SOM extractable fraction.

2.3 Soil analysis

2.3.1 Physical and chemical properties

The pH was measured potentiometrically in a 1:2.5 (m V^{-1}) soil suspension in 1 mol dm^{-3} KCl solution (PN-ISO10390, 1997). The clay ($\text{fr} < 0.002 \text{ mm}$) and silt ($\text{fr} 0.5\text{--}0.002 \text{ mm}$) contents were analyzed via the aerometric method (PN-R-04032, 1998), while total nitrogen and total carbon were determined in a Macro Cube CN Elementar Analyzer (Elementar Analysensysteme GmbH) after dry combustion. Total organic carbon content was analyzed after sulfochromic oxidation, followed by titration of the excess of $\text{K}_2\text{Cr}_2\text{O}_7$ with $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (PN-ISO 14235, 2003).

2.3.2 Isolation of SOM fractions

The SOM content was expressed by the TOC determination, while the assessment of SOM fractions was based on soil alkaline extraction, which allowed the extractable SOM fraction (E-SOM) to be separated from the stable SOM fraction (S-SOM).

Briefly, the soil was shaken for 24 h with 0.1 M NaOH at $\text{pH} \geq 12$ (soil to liquid ratio = 1:10) according to the International Humic Substances Society method. The supernatant containing E-SOM was removed from the residue by decantation and analyzed for carbon content (Multi N/C 2100/2100S Jena Analytics). The S-SOM fraction expressed as a non-extractable SOM residue was determined by carbon content in dried soil samples after alkaline extraction (Macro cube CN elementar analyzer). The results of S-SOM content were reduced by the amount of biochar applied. E-SOM and S-SOM expressed the transformation of the “natural” organic matter, assuming the negligible biochar mineralization during the experiment. The precision of E-SOM and S-SOM determination expressed as a relative standard deviation (RSD) did not exceed 5% for each sample.

2.3.3 PAH fractions content

The PAHs were analyzed as a total concentration (PAH-tot) and residue fraction bound with S-SOM (PAH-rest), determined after E-SOM was removed from the soil. The first measurements of PAH contents in the soil were determined after 3 days of sample fortification (due to the consideration of equilibrium time) and described as time point “0 month.”

PAHs were extracted with dichloromethane in Accelerated Solvent Extractor (ASE200, Dionex); extraction temperature $100 \text{ }^\circ\text{C}$, static time 5 min, pressure 1200 psi. The extracts were concentrated in hexane (1 ml) and cleaned up on glass columns filled with activated silica gel (1 g) suspended in dichloromethane, and finally eluted with 5 ml of a mixture of $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ (2/3, v/v). PAHs were determined by a triple quadrupole gas chromatograph-mass spectrometer (GC MS/MS; Agilent Technologies, Santa Clara, CA). PAH resolution was achieved on a DB-5 MS fused capillary column with a film thickness of $0.25 \mu\text{m}$, at $250 \text{ }^\circ\text{C}$ splitless injection system temperature.

The quality control included the analysis of soil certified reference material (CRM 131), laboratory control sample and solvent blank sample procedure. The recovery of individual compounds from CRM 131 was within 78–92%, and the precision, expressed as a relative standard deviation (RSD), was in the range of 5–10%. The limit of detection (LoD) for individual PAH compounds fit the range from 0.01 to $0.81 \mu\text{g kg}^{-1}$, while the limit of quantification (LoQ) ranged from 0.02 to $2.10 \mu\text{g kg}^{-1}$.

2.3.4 Spectroscopic properties of soils

Soil samples were scanned in the 350–2500 nm spectral range using a VIS-NIR spectroradiometer PSR-3500® (Spectral Evolution Inc., Lawrence, MA, USA) according to the method described by Ukalska-Jaruga et al. (2018). The spectroradiometer was calibrated using a 99% white NIST reference panel (5 × 5 cm). Four replicate scans were taken for each soil sample, and each replicate was the average of 30 scans. The spectrometer was recalibrated after each soil sample using the white NIST reference panel. Raw spectra were transformed with moving average for smoothing (noise reduction) using Unscrambler X® version 10.3 (Camo As, Olslon Norway).

2.4 PAH dissipation rate constants

Rate constants of PAH losses were estimated assuming the pseudo first-order kinetics, on the basis of Eq. (1a, 1b) while the half-life times of PAHs were calculated from Eq. (2):

$$\ln\left(\frac{C}{C_0}\right) = k \cdot t \quad (1a)$$

$$k_{PAH} = \left[\left(\frac{\ln\left(\frac{C}{C_0}\right)}{t_0} \right)_{t_0} \cdot \left(\frac{\ln\left(\frac{C}{C_0}\right)}{t_1} \right)_{t_1} \cdot \left(\frac{\ln\left(\frac{C}{C_0}\right)}{t_3} \right)_{t_3} \cdot \left(\frac{\ln\left(\frac{C}{C_0}\right)}{t_6} \right)_{t_6} \cdot \left(\frac{\ln\left(\frac{C}{C_0}\right)}{t_9} \right)_{t_9} \right] \div 5 \quad (1b)$$

$$T_{1/2} = \frac{\ln(2)}{k_{PAH}} \quad (2)$$

where k apparent reaction rate constant (day^{-1}); k_{PAH} average apparent reaction rate constant calculated for individual compound (day^{-1}); C_0 initial concentration of a given PAH in soil induced and non-induced by biochar addition (mg g^{-1}); C PAH concentration after time t_0, t_1, t_3, t_6, t_9 (mg g^{-1}); and t_0, t_1, t_3, t_6, t_9 time after 0, 1, 3, 6, 9 months of PAHs aging.

2.5 Statistical analysis

The Statistica software (Dell Statistica, version 13.3) was used for statistical analysis. Basic statistical parameters such as mean, median, extreme values (min, max), and coefficient of variation (CoV) were calculated. The chi-squared test was used for checking the normal distribution of the results. One-way analysis of variance (ANOVA) with the Tukey post hoc test multidimensional analysis of variance (MANOVA) with the Lambda Wilks test were applied for testing the significance of differences between aging time and PAH concentrations in soils varying by the addition of biochar. Statistical significance was accepted at $p \leq 0.05$.

3 Results and discussion

3.1 Effect of ERCM-biochar application on soil spectral properties

The impact of biochar application to soils was clearly demonstrated by the differences in VIS-NIR spectroscopic characterization (Fig. 1). The soil samples without biochar treatment had reflectance spectra typical of the upper layer of mineral soils (Debaene et al. 2017). Usually, a higher SOC content means a lower reflectance but this is not the case here. This is probably due to differences in soil texture having a significant impact on spectra (Debaene et al. 2014; Hermansen et al. 2017). The small peak observed in natural soils at 390 nm can be attributed to humic acids (Ouatmane et al. 2000). The two peaks at 1400 and 1900 nm are related to water (O–H bonds). The 2200 nm peak is also related to water (hygroscopic) and clay minerals (Ladoni et al. 2010). The highest reflectance is obtained at 2130 nm and is related to N–H and C=O combination region bands, originating from humic substances (Ladoni et al. 2010). The peaks at around 2300 nm are due to methyl groups derived from aromatic SOM structures. The obtained results indicated that the natural samples were characterized by spectral properties typical for Polish agricultural soil (not published research) and may constitute a broader reference to other soils from temperate climatic conditions. Moreover, spectroscopic properties indicate molecular diversity within soil components, including SOM, and therefore a high sorption potential to the analyzed hydrocarbons.

Soil S4 without biochar application presented the highest reflectance in the predominant range of the spectrum, followed by soil S3 that presented lower reflectance (before 1600 nm), and sample S2 that showed the lowest reflectance (before 1300 nm). After the addition of 5% biochar, there was a significant decrease of the soil reflectance of about 50%, but the reflectance increased proportionally between soils as follows: S3B < S2B < S1B < S4B. In the soil samples with the biochar treatment, the typical spectral features are less evident (e.g., the 1400-nm peak from water is invisible) and the disparity between samples was also less clear. The VIS-NIR region between 700 and 1800 nm becomes featureless. The use of 5% biochar is sufficient to remove the effect of texture on the spectra by intensifying the influence of the carbon fraction and its individual components.

3.1.1 Effect of ERCM-biochar application on SOM content

The SOM analyses in soil samples from trials I (S1–S4) and II (S1–S4B) were performed after the end of the experiment (9 months). The results showed significant quantitative differences between soils treated and untreated with biochar (Table 1) with regard to the carbon content of SOM and their individual fractions. TOC concentrations in soils S1–S4 were

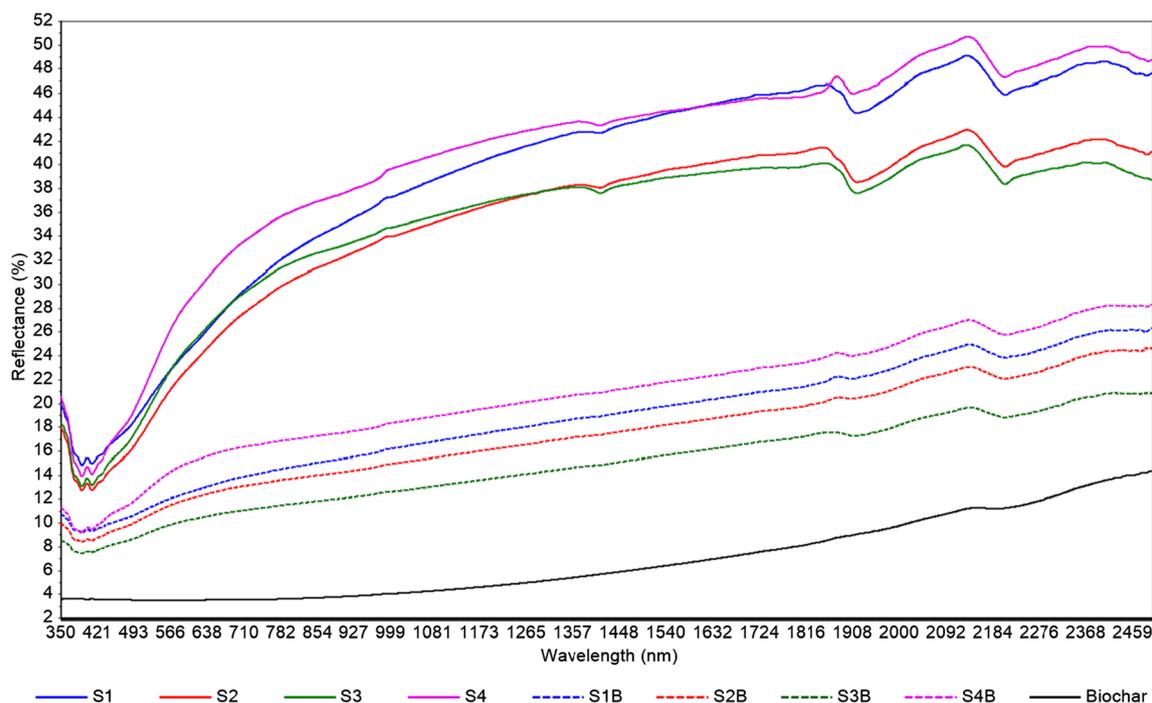


Fig. 1 Spectra in VIS-NIR range of soils treated and untreated with biochar

in the range from 8.8 to 14.3 g kg⁻¹, while their content significantly increased from 38.8 to 49.8 g kg⁻¹ after biochar addition at 5%. Biochar is a very C-rich substrate, and it is also resistant to decay due to the aromatic structure. Therefore, biochar application can increase C stock in soil (Lehmann et al. 2006). According to the literature data, biochar also affects C cycling (Bolan et al. 2012), accelerates nitrogen (N) dynamics (Nelissen et al. 2012) and, in some cases, reduces organic N turnover (Prommer et al. 2014). However, the changes in total SOM after biochar application are gradual because SOM is a heterogeneous mixture that contains numerous compounds with varying degradability and turnover rates (Stevenson 1994). Therefore, the investigation of individual SOM fractions is more informative in practice.

The content of E-SOM and S-SOM fractions varied between soils (Fig. 2). The differences were caused by the properties of individual soils and biochar addition. The E-SOM fraction content was low (median = 4.70 g kg⁻¹ and 5.92 g kg⁻¹) and diverse (CoV = 9% and CoV = 24%), respectively, for soils without and with biochar addition. The S-SOM exhibited relatively comparable concentration (median = 5.15 g kg⁻¹ and 5.05 g kg⁻¹) and higher variance (CoV = 26% and CoV = 39%) in soils without and with amendment. The biochar addition significantly ($p < 0.05$) increased the content of E-SOM fraction (Fig. 2a), while it did not cause changes in the content of the S-SOM fraction. The percentages and proportions of individual organic matter fractions characterize the overall SOM transformation in soils. The S-SOM to E-SOM ratio describes the predominant processes of organic matter transformation and reflects the

mobility and quality of SOM (Guimaraes et al. 2013; Tan 2014; Liu 2016; Ukalska-Jaruga et al. 2019a). In our study, the statistically significant ($p = 0.023$, $F = 7.73$) higher proportions of S-SOM/E-SOM ratio in soils without biochar (1.02 to 1.46) compared to soils with biochar addition (0.42 to 1.20) suggest that biochar may reduce the degree of SOM humification and polymerization. This is also confirmed by the flattening of VIS-NIR spectra (Fig. 1). Demisie et al. (2014) and Lin et al. (2012a) indicated that biochar amendment increased the dissolved organic C content, microbial biomass C compared with un-amended soil. Specifically, the microbial biomass was up to 43–125% higher in biochar-rich soils than in biochar poor adjacent soils (Lehmann et al. 2011). It can be assumed that under the experimental conditions, changes in SOM content could be favored by microorganism activity, but it has not been measured in this study. Wardle et al. (2008) observed the active role of microorganisms in SOM dynamics and transformation in terms of its mineralization after biochar addition. A number of studies also reported a decrease in SOM content after biochar addition (Lehmann et al. 2006; Wardle et al. 2008; Prommer et al. 2014).

3.2 Effect of ERCM-biochar on PAH dissipation

Dissipation profiles of five individual PAHs in the four soils treated and untreated with biochar, determined on the basis of experimental data, are presented in Fig. 3. The amounts of PAHs-tot in the soils without biochar (S1-S4) after period of 6 months decreased by an average of over 67% for Flu-tot, 58% for Ant-tot, 49% for Phe-tot, 46% for Pyr-tot, 14% for

Table 1 Statistical evaluation of SOM content and fractional composition in soils

	Soils S1-S4 (n = 4)			Soils S1B-S4B (n = 4)		
	Minimum	Maximum	Median	Minimum	Maximum	Median
TOC (g kg ⁻¹)	7.00	14.30	12.71	38.78	49.82	45.94
E-SOM (g kg ⁻¹)	3.37	6.59	4.70	5.23	7.93	5.92
S-SOM (g kg ⁻¹)	4.70	7.84	5.15	4.61	7.95	5.05
E-SOM/TOC	0.35	0.55	0.43	0.53	0.68	0.55
S-SOM/TOC	0.48	0.56	0.52	0.48	0.56	0.51
S-SOM/E-SOM	1.02	1.39	1.18	0.77	1.00	0.91

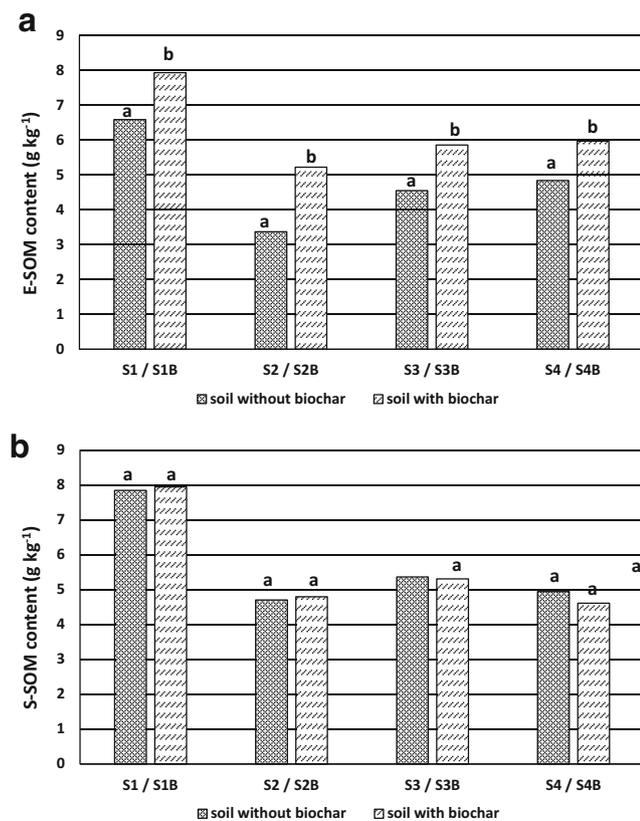
TOC total organic carbon, E-SOM extractable soil organic matter, S-SOM stable soil organic matter (g kg⁻¹)

Chry-tot, while the decreased in soil with biochar (S1B-S4B) was as follows: Flu-tot = 78%, Ant-tot = 79%, Phe-tot = 78%, Pyr-tot = 77%, Chry-tot = 28%. In soils without biochar, PAH-tot declined rapidly after 1 month of aging and achieved a plateau after 3 months. In soils with biochar, after the decrease in hydrocarbon content in the first 3 months, its increase in 9 months was unexpectedly observed (Fig. 3). We assume that increasing the PAH-tot content at the end of the experiment may result from the release of these contaminants from biochar structures. Similar finding was also observed by Cornelissen et al. (2005), and Rhodes et al. (2010) and Dutta et al. (2017) who found that even a small degradation of a biochar causes the discharge of PAHs to the soil. Interesting results of research on the desorption kinetic of freshly bound Phe in soil were presented by Marchal et al. (2013) who observed that after 14 days, as much as 41% of Phe adsorbed on biochar added to soil may undergo desorption. They highlighted that PAH degradation depends on time and the presence of co-metabolites (bacteria, fungi, and other microorganisms) in soils which enhance this process.

The average rate of individual hydrocarbon decomposition after the experimental time (9 months of incubation) was consistent with the following order: Flu-tot (97–99%) > Ant-tot (97–98%) > Pyr-tot (96–98%) > Phe-tot (96–98%) > Chry-tot (19–89%) and Ant-tot (20–64%) > Flu-tot (24–67%) > Pyr-tot (13–53%) > Phe-tot (10–55%) > Chry-tot (13–23%), respectively, for soils without and with biochar addition. Despite much higher PAHs content in the first few days in the soils with biochar addition than in ones without, after 9 months, these proportions were reversed, and finally, PAH losses in relation to the total content did not exceed 67% of their initial concentration. A significantly lower overall decrease of PAHs-tot concentration in soils with biochar indicate that PAHs are rapidly absorbed by biochar as a result of possible occlusion in its porous structure, while in soils without biochar addition, PAHs are easier decomposed and/or to get slowly bound by soil components during the experimental time. The highly porous biochar structure favors physical protection of occluded compounds against microbial decomposition and chemical extraction (Pignatello et al. 2012; Qi et al. 2017).

Organic compounds may be retained inside small pores of ERCM structure as a result of capillary forces, the vapor pressure, and liquid solubility (Pignatello 1998). This can cause condensation of PAHs, depending on the compound, its concentration, and pore size. Furthermore, the force field inside confining pores, i.e., pores whose width is two sorbate molecular diameters or less, is stronger than on a flat surface because of multiple interactions with the walls (Pignatello 1998; Qi et al. 2017). Nevertheless, the interaction of biochar particles with soil components may lead to pores blocking and closing the PAHs present there. For example, Pignatello et al. (2006) demonstrated that dissolved organic matter may transiently block the pores of biochar particles under certain conditions. Such mechanical locking processes inhibit the process of PAH transport outside of biochar particles, contributing to their temporary accumulation in the soil and to the reduced biodegradation and release—visible at the ninth month of the experiment. This indicates that the sorption of contaminants on ERCM materials does not immobilize contaminants permanently.

The PAH concentration varies between soils over time, which also implies a significant effect of soil properties in the PAH bonding processes (Table 2, Table S4—ESM). Among soil properties (excluding organic matter), particle size distribution has dominant effect on PAH dissipation in soils but only in soils non-induced by biochar addition. This indicates that biochar disturbs the impact of soil properties on soil contamination. Krauss and Wilcke (2002) recognized that PAH sorption affinity expressed by soil organic carbon-water partition coefficients (K_{OC}) depending upon size of the associated soil particles. Mean K_{OC} values of individual PAHs are highest in silt (fine particles), followed by clay and then sand. Despite that, all the soils had a similar particle size distribution (Table S1—ESM) and the analyzed PAHs differed in the partitioning coefficient (Table S3—ESM); Flu-tot, Ant-tot, Phe-tot, Pyr-tot exhibited similar dissipation trends, while Chry-tot was slightly outside of the rest of the analyzed compounds. This may result from its properties, i.e., the highest molecular weight, the highest hydrophobicity, and the lowest solubility than other analyzed compounds. Moreover, Chry



*a, b significant differences at $p < 0.05$

Fig. 2 Comparison of the E-SOM (a) and S-SOM (b) fractions contents in soils

has the largest diameter of the molecule, which may affect the possibility of its occlusion in the structure of SOM or ERCM. Chrysene residue was the least susceptible to degradation, so it was characterized by the highest stability in soil. Generally, the highest rate of decomposition of individual PAHs increased with a decrease in their molecular mass, as also observed by Luo et al. (2012) and Yang et al. (2012).

Results of MANOVA confirmed the significant influence of aging time and soil organic matter content on the PAH-tot concentration in soils (Table 2). Organic matter is recognized as one of the main components that determine the sorption of organic contaminants (Pignatello 2012; Klimkowicz-Pawlas et al. 2017; Qi et al. 2017; Ukalska-Jaruga et al. 2019b). Our results confirmed that native organic matter actively involved in the binding of organic contaminants even after introducing exogenous organic matter (such as ERCM) into the soil (Fig. 2; Table 2, Table S4—ESM). A crucial role in this process is played by S-SOM and E-SOM fractions, which represent the most ubiquitous and widespread natural non-living organic materials such as humic substances (Pignatello 2012; Chen et al. 2017). The content of the PAH-rest fraction remaining after E-SOM extraction and related with freely dissolved PAHs was also changed over time (Fig. 3b). Generally, the

amount of PAH fraction bound by the S-SOM after 9 months of incubation varied from 0.9 to 3.5% and 0.2 to 1.3% of the total initial PAH concentration, respectively, for soils non-induced and induced by the addition of biochar. The low level of PAH accumulation in S-SOM proves that the E-SOM fraction played a dominant role in hydrocarbon association in this experiment. The different degree of PAH sorption by S-SOM probably depends on the chemical and structural heterogeneity of SOM (Pignatello et al. 2006; Pignatello 2012; Chen et al. 2017; Qi et al. 2017). This effect has been more described in detail in our previous publication (Ukalska-Jaruga et al. 2019b).

Results of MANOVA also pointed out that biochar, which significantly affects the change of soil spectroscopic properties, also modifies PAH behavior and aging processes in the soil. The literature data prove that the strength of this impact may depend on biochar properties. Many studies indicate that the addition of biochar to the soil caused the immobilization of PAHs (Cornelissen et al. 2005; Rhodes et al. 2010) affecting the decrease of its freely dissolved forms over time (Oleszczuk et al. 2012; Koltowski et al. 2016). According to Dutta et al. (2017), Tag et al. (2016), Beesley et al. (2011), and Chen et al. (2008), increasing the biochar pyrolysis temperature increases the degree of carbonization, which extends the surface sorption area but reduces the abundance of amorphous organic matter. The highly specific surface area of biochar affects the capability to adsorb organic contaminants, causing their retention and immobilization in the soil (Sharma et al. 2004; Dutta et al. 2017). The O/C ratio is a function of production conditions and is often used as an indicator of biochar aromaticity and reactivity. Low values of O/C ratio (< 0.6) indicate its higher aromaticity and lower reactivity directly related to its molecular structure (Spokas 2010). In our study, the O/C ratio was 0.15 (Table S2—ESM) and pointed high reactivity of biochar and potentially high sorption surface. Generally, biochar is made up of clusters of hydrogen and oxygen-condensed polyaromatic ring structures with few polar O-containing functional groups at the rim (Knicker 2011; Hale et al. 2016). Aromatic structures cause biochars to be highly condensed and more stable (Hammes et al. 2007) but at the same time deprived of many reactive functional groups. According to Streubel et al. (2011), two physical features of biochar provide sorption sites for a wide variety of non-polar organic molecules. The oxygen-rich surface functional groups contribute largely to the high pH, CEC, hence sorption potential of biochars and the aromatic ring structure, which affords a recalcitrant chemical and biological nature (Streubel et al. 2011; Lin et al. 2012b; Qi et al. 2017). Although adsorption to biochars is predominantly fast due to their highly reactive surface area, its sorption sites could be overcome by other compounds, e.g., inorganic

Fig. 3 Dissipation of five individual PAHs in soils. Data are presented as total (a) and residual (b) content of individual PAHs

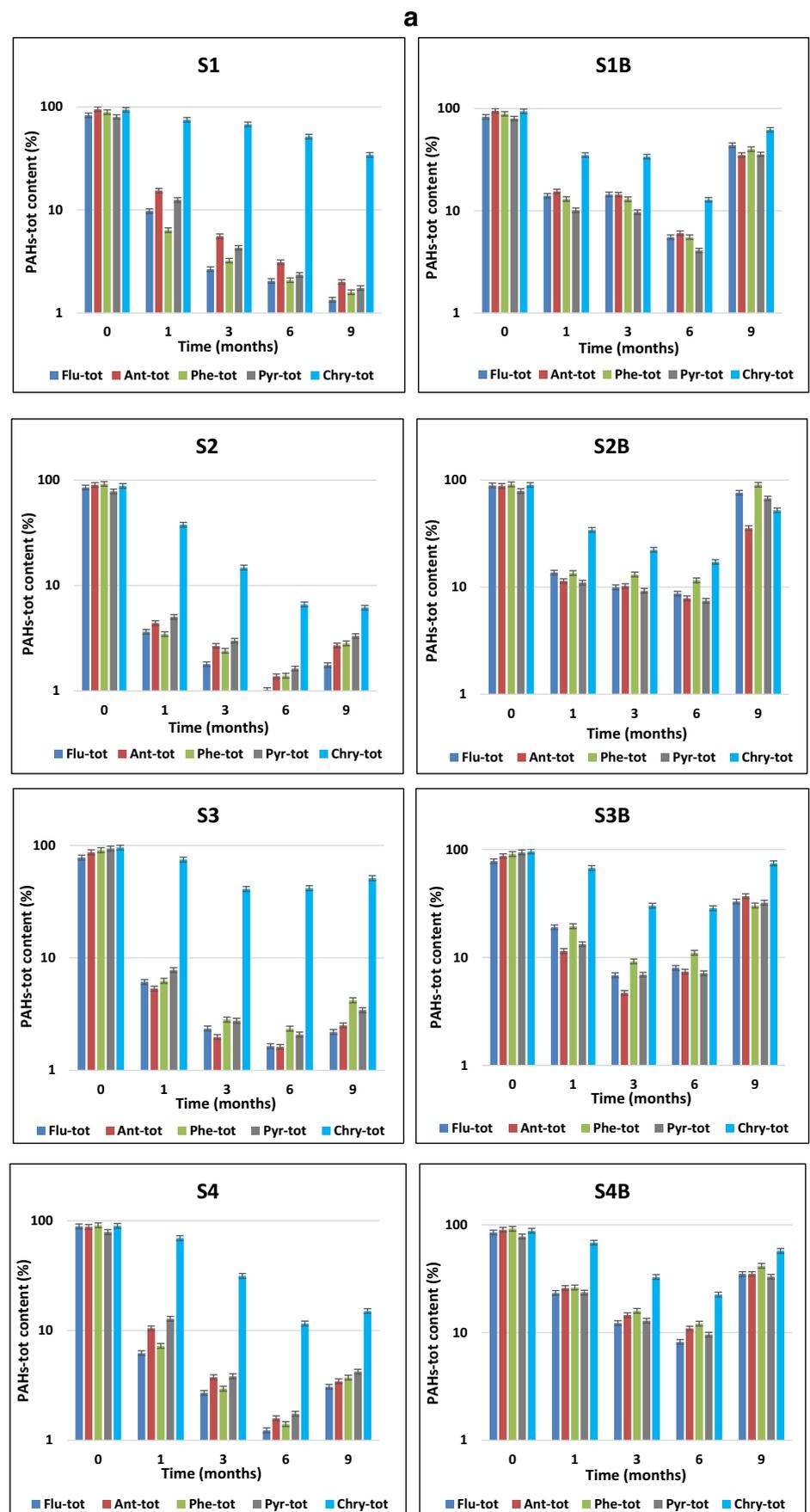


Fig. 3 (continued)

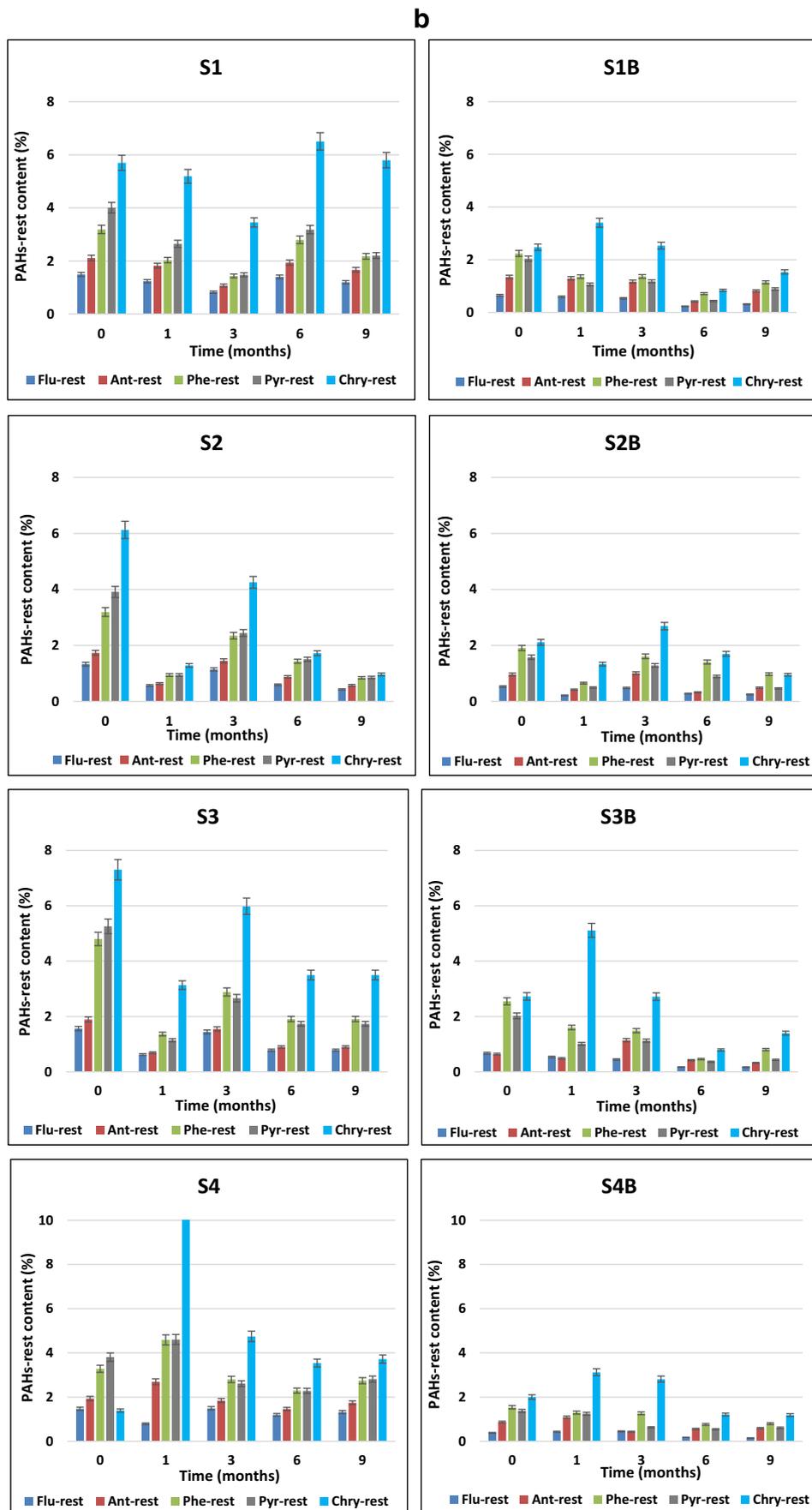


Table 2 Results of MANOVA test presenting the influence of aging time and soil properties on the PAH-tot and PAH-rest changes in soils^a

Source of PAHs variation	Soils S1-S4 (n = 4)		Soils S1B-S4B (n = 4)	
	PAH-tot	PAH-rest	PAH-tot	PAH-rest
Aging time	<i>F = 7.24</i> <i>p = 0.0000</i>	<i>F = 22.49</i> <i>p = 0.0000</i>	<i>F = 4.72</i> <i>p = 0.0001</i>	<i>F = 4.13</i> <i>p = 0.0003</i>
Soil properties	<i>F = 3.63</i> <i>p = 0.0029</i>	<i>F = 5.36</i> <i>p = 0.0002</i>	<i>F = 3.63</i> <i>p = 0.0029</i>	<i>F = 1.56</i> <i>p = 0.1655</i>

Statistical significant F-test values ($p < 0.005$) have been italicized

^a PAH-tot and PAH-rest were analyzed as the sum of individual hydrocarbon change (Flu, Ant, Fen, Pyr, Chry)

contaminants or metal ions occurring in the soil (Beesley et al. 2011). It may be the case that the biochar compete with native organic matter, such as E-SOM and S-SOM, favoring PAH uptake in the soil.

The results (Fig. 3b, Table 2) showed that the biochar significantly affects the sorption of PAHs by native organic matter (PAH-rest). Some analogies can be observed, i.e., an increased PAH-rest concentration in some time points in soil without biochar causes a decrease in the content of hydrocarbons in soils with biochar (respectively for the same soil) (Fig. 3). Nevertheless, the highest concentration of PAH-rest was observed in the initial interval (0–3 months) of aging time (Fig. 3). Decreases and increases in the PAH concentration possibly depended on their movement and diffusion between phases of organic matter and biochar. Gao et al. (1998) studied the aging effects on sorption and desorption mechanisms which showed that aging leads to higher retention, a reduced desorption, and to lesser extractability as a result of the greater contaminant sequestration or binding.

Additionally, the mutual proportions between changing PAH-rest and PAH-tot fractions point toward different binding processes for PAHs in soils (Table 3). The share of PAH-rest in PAH-tot increase proportionally only in soil S1 without biochar addition while in the rest of soils, the value of these ratios did not shown any clear tendencies of change. Similarly, the addition of biochar to the same soil modified the sorption properties, significantly reducing the PAH-rest/PAH-tot ratio,

and thus changing the soil sorption potential for hydrocarbons.

A variety of mechanisms can be responsible for the interactions occurring between PAHs and SOM or ERCM. According to Schaumann (2006a, b), Wang et al. (2011), Pignatello (2012), and Chen et al. (2017), aging of PAHs is strongly related with sorption and degradation processes. Sorption may be categorized by the type of intermolecular forces that characterize the sorbate-immobile phase interaction: chemisorption, physisorption, and ion exchange (Kah et al. 2017). Physisorption included adsorption and absorption have the greatest importance in the phenomena of PAHs retaining by SOM and ERCM structures (Pignatello 2011). Adsorption is mainly related with the association of PAH molecule at the surface of the solid biochar particles whose atomic/molecular lattice cannot be penetrated by contaminants. Absorption concerns the intermingling/dissolution of a molecule within the atomic molecular lattice of a solid and is mainly related to the binding of PAHs by SOM structures (Pignatello 2011; Pignatello 2012; Kah et al. 2017). The PAH sorption to SOM is usually described by the dual-model sorption concept (Schaumann 2006a, b; Pignatello 2012). Within this theory, SOM is assumed to be composed of two domains, one displaying linear and non-competitive absorption or partitioning (non-carbonized organic matter) while the other showing non-linear, extensive, and competitive surface adsorption (carbonized organic matter) (Schaumann 2006a, b;

Table 3 PAH-rest to PAH-tot percentage ratio in soil S1

Aging time	Soil without biochar					Soil with biochar				
	Flu-rest/ Flu-tot	Ant-rest/ Ant-tot	Fen-rest/ Fen-tot	Pyr-rest/Pyr- -tot	Chry-rest/ Chry-tot	Flu-rest/ Flu-tot	Ant-rest/ Ant-tot	Fen-rest/ Fen-tot	Pyr-rest/ Pyr-tot	Chry-rest/ Chry-tot
0 month	4.1Aa	3.2Ab	5.5Aa	6.8Aa	4.0Aa	2.7Ab	9.0Ab	9.1Ab	10.2Ab	2.0Bb
1 month	12.7Ba	11.9Ba	31.9Ba	21.2Ba	5.1Aa	4.2Ab	8.4Ab	10.4Ab	10.5Ab	9.7Ab
3 months	31.1Ca	19.3Ca	44.5Ca	34.4Ca	6.1Aa	3.7Ab	8.2Ab	10.6Ab	12.2Ab	7.5Aa
6 months	68.4Da	62.3Da	64.1Da	65.4Da	12.6Ca	4.2Ab	6.9Bb	13.0Ab	10.6Ab	6.5Ab
9 months	89.5Ea	83.4Ea	86.9Ea	86.2Ea	16.9Da	0.7Ab	1.0Cb	1.6Bb	1.3Bb	1.8 Bb

Different lower case letters within the same PAH compound indicate significant differences between soil induced and non-induced by biochar, while uppercase letters differences in aging time between compounds (ANOVA, Mann-Whitney *U* test, $p < 0.05$)

Pignatello 2012). Adsorption to ERCM may encompass several qualitatively different processes: (1) the resting of molecules on discrete surface sites, (2) the partitioning of molecules into an order microscopic hydration phase near the surface, (3) the condensation of the PAHs molecules into a liquid-like state in small pores, and (4) the layering of molecules on the surfaces of water films that coat ERCM (Pignatello 2011). Likewise, absorption PAHs to SOM may involve residence of some molecules within closed pores and/or at specific molecule scale sites within the phase. ERCM may effectively increase sorption capacity of soils but at the same time may disturb sorption processes by natural organic matter accumulated in soil.

Nevertheless, in natural environmental conditions, the processes of PAH sorption to SOM or ERCM (described above) can be modified by other factors affecting the hydrocarbon dissipation, such as transportation to mineral phase, leaching, volatilization, photochemical oxidation, biological uptake, and biodegradation (Ehlers and Loibner 2006).

3.3 Half-life time of PAHs

Loss profiles of individual PAHs in the four soils of different properties, determined on the basis of experimental data, and Eq. (2) are presented in Table 4. Due to the very broad ranges of half-life times encountered in the literature, any direct comparison with experimental data can only have the character of an approximation.

In soils without biochar addition, compounds, i.e., Flu, Ant, Phe, Pyr, exhibited a relatively similar $T_{1/2}$ in range from 43 to 59 days, while Chry was characterized by much higher and broader $T_{1/2}$ value than other hydrocarbons, from 67 to

280 days. The highest $T_{1/2}$ for Chry was observed in the soil S3, while the lowest in the soil S2, differing in the clay content and pH which could affect the observed divergences. Lower molecular PAHs, such as Flu, Ant, Phe, and Pyr (molecular weight from 178 to 202 mol dm³), are characterized by relatively high volatility and solubility in water, and hence, greater and easier degradability (Agarwal et al. 2009). Compared to the readily degradable compounds, Chry (228 mol dm³ molecular weight) is more hydrophobic and less water-soluble (Agarwal et al. 2009). The strong affinity of Chry to biochar (strong sorption) together with physicochemical features caused its lower bioavailability and biodegradability. The biodegradation is also inhibited by the greater chemical stability of the higher molecular PAHs (Agarwal et al. 2009; Kuśmierz et al. 2016).

The biochar addition to the soils significantly influenced changes in the half-life time of all PAHs, irrespective of soil type. The higher changes have been noted for Phe—an average 14-fold increase of $T_{1/2}$, and the lowest for Flu—an average sevenfold increase (Table 4). $T_{1/2}$ for other compounds have changed from 9 to 12 orders of magnitude. The effect of biochar on the increase in the half-life of PAHs confirms its specific role in its retention and aging time. According to the literature data, in the case of the loss rate of those compounds, the half-life time differences within individual PAHs may reach even several years. The half-life times given by Shuttleworth and Cerniglia (1995) for Pyr ranged from 133 to 317 days, and the value determined by Kuśmierz et al. (2016) was 122–150 days, while the time-frame given in Oleszczuk and Baran (2003) spans the period from 117 to 492 days. An even more extensive time-frame, ranging from 527 to 1133 days, for Chry was determined by Kuśmierz et al.

Table 4 Rate constants k (1 day⁻¹) and half-life times $T_{1/2}$ (days) of PAHs degradation in examined soils

	Soil without biochar							
	S1		S2		S3		S4	
	k	$T_{1/2}$	k	$T_{1/2}$	k	$T_{1/2}$	k	$T_{1/2}$
Flu	1.60×10^{-2}	43	1.50×10^{-2}	46	1.41×10^{-2}	49	1.29×10^{-2}	54
Ant	1.45×10^{-2}	48	1.34×10^{-2}	52	1.37×10^{-2}	51	1.25×10^{-2}	56
Phe	1.53×10^{-2}	45	1.32×10^{-2}	53	1.17×10^{-2}	59	1.22×10^{-2}	57
Pyr	1.50×10^{-2}	46	1.26×10^{-2}	55	1.25×10^{-2}	56	1.17×10^{-2}	59
Chry	4.01×10^{-3}	175	1.03×10^{-2}	67	2.50×10^{-3}	280	7.0×10^{-3}	99
	Soil with biochar							
	S1B		S2B		S3B		S4B	
	k	$T_{1/2}$	k	$T_{1/2}$	k	$T_{1/2}$	k	$T_{1/2}$
Flu	3.05×10^{-3}	227	1.01×10^{-3}	685	4.10×10^{-3}	169	3.39×10^{-3}	204
Ant	0.82×10^{-3}	843	3.83×10^{-3}	181	2.42×10^{-3}	286	1.59×10^{-3}	435
Phe	1.32×10^{-3}	526	3.70×10^{-4}	1873	2.93×10^{-3}	237	2.10×10^{-3}	330
Pyr	1.29×10^{-3}	539	5.06×10^{-4}	1370	2.78×10^{-3}	250	2.02×10^{-3}	343
Chry	5.12×10^{-4}	1353	7.41×10^{-4}	936	3.40×10^{-4}	2037	9.5×10^{-4}	730

Flu fluorene, Ant anthracene, Phe phenanthrene, Pyr pyrene, Chry chrysene

(2016). Nevertheless, the conducted research is mainly of predictable nature and the real half-life time and behavior of PAHs in soil depend on many environmental factors.

4 Conclusions

The addition of ERCM such as biochar to the soils significantly affected their spectroscopic properties, related mainly to SOM component. This caused also a change in content and mutual proportion between SOM fractions. Significant decrease in the stable fraction and increase in the extractable fraction of SOM after biochar addition suggest that biochar significantly reduce the degree of SOM humification and polymerization.

The results indicated that, in spite of the presence of a strong sorbent in the soil, such as ERCM-biochar, and thus an expected increase in the persistence of PAHs, a more rapid loss of PAHs from the soil induced by biochar is possible, mainly in the first 3 months. However, it is still not fully known whether this is the effect of physical protection of PAHs occluded in biochar structures by creating non-extractable bound-residue fraction or PAH degradation. Usually, the amount of PAH fraction bound by the native stable SOM fraction was about four times higher in the soils without ERCM-biochar than with ERCM-biochar addition, which confirms the literature evidence of a high sorption potential of biochar to PAHs. Nevertheless, the lack of a clear trend in the process of PAH-rest accumulation suggests a different efficiency of PAH binding in the soil and the high importance of aging time in these processes. The ERCM addition to the soils also influenced the change in the half-life time of PAHs, affecting an increase in their persistence and residence time. Our research proves that ERCM significantly modifies dissipation and sorption processes of PAHs in soil.

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