



Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons

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Abstract

Purpose The objective of this study was to evaluate the mutual relations between the soil organic matter (SOM) fractions: fulvic acids (FA), humic acids (HA), humins (HN), black carbon (BC) and the polycyclic aromatic hydrocarbons (PAH) accumulation level in agricultural soils influenced by historical and actual anthropopressure. The research allowed to indicate which fractions of SOM are the major sequestration sinks for PAHs after they are naturally introduced into the soil.

Materials and methods Soil samples were collected from the upper layer of agricultural soils ($n = 41$), and basic physicochemical properties (pH_{KCl} , total carbon, total nitrogen and clay content) were determined. The SOM was characterised by the total organic carbon content and humic substances, including HA, FA and HN, determined by an adapted method recommended by the International Humic Substances Society. The extracts of HA and FA were analysed for carbon content using a liquid CN analyser, while HN constituted the soil carbon in the residue after FA and HA extraction. The content of BC was analysed by dry combustion at 375 °C for 24 h (CTO375); the remaining carbon was determined via combustion in an elemental analyser.

Results and discussion In all soils, significant positive relations between PAH concentrations and TOC content ($r = 0.73$, $p < 0.001$) as well as HN ($r = 0.71$, $p < 0.001$) and BC ($r = 0.86$, $p < 0.001$) were noted. Relations among PAHs, HN and BC were statistically significant only in soils with TOC content $\geq 12 \text{ g kg}^{-1}$, while they were not observed for soils with TOC content $< 12 \text{ g kg}^{-1}$. The links between HN and PAHs were stronger for low-molecular (two and three rings)-weight PAHs ($r = 0.77$, $p < 0.05$) than for high-molecular (\geq four rings) PAHs ($r = 0.68$, $p < 0.05$). Contrary to HN, the BC fraction showed higher correlations with high-molecular-weight PAHs ($r = 0.92$, $p < 0.001$). FA and HA showed no significant relationship with hydrocarbons.

Conclusions Different SOM fractions might possess divergent binding capabilities and dissimilar binding strengths to PAHs. The different proportions and sorption capacities of BC and HN in relation to PAHs of different molecular weight are the result of varying structure, i.e. polar and non-polar functionalities in sorption domains and pore-size structures of these fractions. The high correlation between BC and higher-molecular PAHs may be a result of their co-emission, while the stronger relationships between HN and lower-molecular PAHs are directly related to their higher mobility and easier diffusion to stable SOM fractions.

Keywords Antropopressure · Black carbon · Fulvic acids · Humic acids · Humin · Organic contaminants · Soil · Humic substances

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) exhibit recalcitrant properties in soils, and some of them are potentially

mutagenic/carcinogenic and teratogenic for human beings (Agarwal et al. 2009). The PAHs emitted into the atmosphere are ultimately deposited (dry or wet deposition processes) onto soils (Maliszewska-Kordybach et al. 2009; Duan et al. 2015; Wang et al. 2015; Klimkowicz-Pawlas et al. 2017; Bielińska et al. 2018) and sediments (Luo et al. 2006; Wang et al. 2014; Aemig et al. 2016), where they tend to accumulate. PAH diagnostic ratios may provide an important tool for the identification of pollution emission sources. These ratios mainly based on molecular proportions between parent PAHs and show intrasource variability and intersource similarity (Tobiszewski and Namiesnik 2012). They distinguish PAH pollution originating from petroleum products,

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petroleum combustion and biomass or coal burning. The compounds involved in each ratio have the same molar mass, so it is assumed they have similar physicochemical properties (Mostert et al. 2010; Tobiszewski and Namiesnik 2012). Numerous studies show that diagnostic ratios change in value to different extents during phase transfers and environmental degradation (Pies et al. 2008; Ravindra et al. 2008; Zhang et al. 2008; De La Torre-Roche et al. 2009; Akyüz and Çabuk 2010; Katsoyiannis et al. 2011; Klimkowicz-Pawlas et al. 2017). In soil, PAHs are subjected to numerous physicochemical and biological processes contributing, albeit to various extents, to their loss or accumulation. Those processes include sorption/desorption, transportation, leaching, volatilisation, photochemical oxidation, biological uptake and biodegradation (Ehlers and Loibner 2006; Nam et al. 2008; Yang et al. 2012; Kuppasamy et al. 2017). The majority of PAHs are characterised by a high persistence in the terrestrial environment due to their low water solubility and high sorption affinity to soil components (Ehlers and Loibner 2006). Soil organic matter (SOM) is the main factor influencing the fate of PAHs in the soil environment (Maliszewska-Kordybach et al. 2009; Luo et al. 2012; Klimkowicz-Pawlas et al. 2017). According to Ni et al. (2008), Li et al. (2010), Wang et al. (2012), Yang et al. (2012), Pignatello (2012), Liu (2016), Luo et al. (2013), Ukalska-Jaruga et al. (2015), Klimkowicz-Pawlas et al. (2017) and Bielińska et al. (2018), both the amount and composition of SOM potentially affect the retention of those contaminants in soils.

Soil organic matter consists of a diversity of components with various molecular weights, functional groups and polarities, which control the dynamics of contaminants in the soil through hydrophobic interactions, electrostatic interactions or the formation of chemical bonds (Pignatello 2011; Pignatello 2012; Chen et al. 2017; Bejger et al. 2018; Ukalska-Jaruga et al. 2018). According to Pignatello (2011, 2012), the main components of SOM are humic substances (HS) and black carbon (BC), and based on their molecular structure, they may significantly impact PAH concentration. Humic substances are defined as the organic substances remaining after biomass transformation and include three colloidal fractions: fulvic acids (FA), humic acids (HA) and humins (HN) (Stevenson 1994; Tan 2014). Black carbon consists of exogenous carbonaceous by-products containing char, charcoal and soot from natural fires, land clearing, crop residue burning and fossil fuel combustion (Bucheli et al. 2004; Pignatello 2011, 2012; Hamilton and Hartnett 2013; Liu et al. 2011; Luo et al. 2013).

The behaviour of HS and BC in soils differs depending on their structural properties (Pignatello 2011). Humic substances have a considerably high sorption capacity due to their abundant hydrophobic carbon domains, including macromolecular aliphatic chains and aromatic carbon components, and a

significant amount of flexible pores, facilitating the retention of organic contaminants in soils (Stevenson 1994; Schaumann 2006a, b; Pignatello 2012). Due to their structural heterogeneity, HS are characterised as a “three-dimensional phase” consisting of rubbery (relatively high flexibility and mobile) and glassy (metastable state) sorption/partition domains (Schaumann 2006a, b; Pignatello 2011, 2012). The composition and properties of BC depend on feedstock and formation conditions. BC is a strong adsorbent of organic compounds due to its abundant microporosity and the hydrophobic nature of its fundamental structural unit, polyaromatic sheets, which are characterised by a glassy state related with excess free volume of sorption pores (Pignatello 2011, 2012). The carbon-normalised distribution coefficient of a compound between raw BC and water (K_{BC}) can be 10^1 – 10^4 times greater than the corresponding value between non-pyrogenic soil organic matter such as HS and water (K_{OC}), and the difference increases with decreasing solute concentrations (Ni et al. 2011). Based upon these findings, sorption mechanisms of PAHs to different fractions of SOM have been investigated (Yang et al. 2010, 2012; Wang et al. 2011, 2012; Luo et al. 2012; Sun et al. 2012, 2013; Chen et al. 2017). So far, such research was mainly based on laboratory sorption experiments (batch studies) carried out at a stable temperature to obtain a relatively short equilibrium time between the contaminant and the studied SOM fraction (mainly HA). However, such conditions exclude the effects of various environmental processes and conditions in soil, influencing PAHs-SOM interactions.

In this context, the objective of this study was to evaluate the mutual relations between the SOM fractions FA, HA, HN, BC and the concentration of PAHs in soils from an area with high anthropogenic pressure (current and historical). The overall aim was to determine which SOM fraction represents the major sequestration sink for PAHs.

2 Material and methods

2.1 Site description and soil sampling

The soil organic matter fractions and the polycyclic aromatic hydrocarbons were isolated from soils subjected to long-term and strong industrial anthropogenic pressure, resulting in a potential high PAH concentration. The sampling points ($n = 41$) were located in the Czerwionka-Leszczyny municipality (area, 115 km²; population density, 366 persons km⁻²; dust emission, 6827 kg year⁻¹ km⁻²; dust emission from industrial sources, 1084 kg year⁻¹ km⁻²) in southwestern Poland (Silesia Voivodeship). The research area combines districts of typical urban/industrial character and agricultural areas. Soil contamination in the area is mainly a result of fuel combustion, road transport and other industrial activities dealing with the disposal of environmentally harmful mining waste, producing

bituminous masses, and the mining industry. Rybnik industrial district, which has been active for numerous years, has strongly transformed the area, resulting in the occurrence of numerous waste dumps and storage sites for metallurgical wastes.

The samples were collected from the surface layer (0–30 cm) of agricultural soils located at different distances from potential PAH emission sources. The sampling sites were chosen to reflect the variability of land use and soil properties influencing differences in organic matter content and its composition. The samples were air-dried, passed through a 2-mm mesh sieve and stored in the dark at 12–16 °C until analysis.

2.2 Properties of soil materials

Most of the collected soils exhibited a high acidity, with a pH_{KCl} value ranging from 3.8 to 7.8, maximum carbonate content of 1.7% and low clay content ($\text{fr} < 0.002$ mm) with a mean value of 1.0% ($\text{CoV} = 101\%$). Concentrations of TC and TN were in the range of 8.5–167.2 g kg^{-1} ($\text{CoV} = 143\%$) and 0.8–11.7 g kg^{-1} ($\text{CoV} = 109\%$), respectively (data are described in more detail in Ukalska-Jaruga et al. 2018). The TC/TN ratio showed diversified values from 6.7 to 15.3, which indicates a varying degree of organic matter decomposition in soils from the studied area (Stevenson 1994; Tan 2014). Considerable differences were observed for TOC contents ($\text{CoV} = 131\%$), ranging between 7.0 and 130.2 g kg^{-1} , indicating the various degrees of supply inflow and accumulation of organic matter in agricultural soils.

2.3 Soil analysis

2.3.1 Physical and chemical soil characterisation

The measured characteristics included pH_{KCl} , clay content, total nitrogen, total carbon and total organic carbon concentrations. The pH was measured potentiometrically in a 1:2.5 (m V^{-1}) soil suspension in 1 mol L^{-1} KCl solution (PN-ISO10390, 1997). The clay content ($\text{fr} < 0.002$ mm) was analysed via the aerometric method (PN-R-04032, 1998), while total nitrogen (TN) and total carbon (TC) were determined in a vario Macro cube CN elemental analyser (Elementar Analysensysteme GmbH) after dry combustion. Total organic carbon (TOC) content was determined after sulfochromic oxidation followed by titration of the excess $\text{K}_2\text{Cr}_2\text{O}_7$ with $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (PN-ISO 14235, 2003). The carbonate content was analysed by the Scheibler method, which determines the volume of carbon dioxide separated from the decomposition of carbonates.

2.3.2 Isolation of SOM fractions

The assessment of SOM fractions included the separation of humic substances (HS) and black carbon (BC). HS were

fractionated by exhaustive extraction of humic acids (HA) and fulvic acids (FA), according to the IHSS method and ISO 12782-4 (2012) while humins were determined as a residue after humic acid extraction. This method uses the high solubility of FA in acidic and alkali solution and the high solubility of HA only in alkali solutions. Briefly, 10 g of soil was acidified in 0.1 M HCl to pH 1–2 to obtain a 1:10 w/v soil to solution ratio, shaken for 1 h in a laboratory shaker and centrifuged (10 min, 3000 rpm). The supernatant containing the first extract of FA1 was removed from the residue by decantation, and the residue was then rinsed 2–3 times with distilled water, shaken and centrifuged. The remains of the soil sample were neutralised with 0.1 M NaOH and extracted with 1 M NaOH to obtain a 1:10 w/v soil to solution ratio and a pH > 12 to ensure high HA solubility. The suspension was equilibrated overnight by continuous shaking, and the supernatant containing extracted FA2 + HA was decanted. The alkaline solution was acidified with 6 M HCl to gravimetrically precipitate HA.

Concentrations of organic carbon in the separated fractions, namely FA1, FA2 and HA were measured after each extraction step via a CN analyser (Multi N/C 2100/2100S Jena Analytics). The total fraction of FA was expressed as the sum of FA1 and FA2. Humic contents were determined in soil residues after the extraction of FA and HA in a CN analyser (vario Macro cube CN elemental analyser).

The BC content was measured via chemo-thermal oxidation at 375 °C for 24 h (CTO-375), according to Gustafsson et al. (1997). The soil sample was heated in a muffle furnace with air access, and subsequently, the carbon residue was determined by combustion in an elemental analyser (vario Macro cube CN; Elementar Analysensysteme GmbH). Prior to BC analysis, carbonates were determined, and their contents were subtracted from the C contents.

2.3.3 Determination of soil PAH concentrations

The analysis of PAHs comprised 16 individual compounds from the US EPA list (US EPA 1995). Prior to extraction, soil samples were ground to obtain a grain size ≤ 0.10 mm and spiked with 10 μl of an internal standard solution containing five deuterated PAHs: d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene and d12-perylene; the final concentration of each compound ranged between 1 and 5 $\mu\text{g cm}^{-3}$. The PAHs were extracted with dichloromethane in an accelerated solvent extractor (ASE200, Dionex Co.) under the following conditions: extraction temperature 100 °C, static time 5 min and pressure 1200 psi. The extracts were then 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 $\text{CH}_2\text{Cl}_2/n$ -hexane (2/3, v/v) mixture. The PAHs concentrated in *n*-hexane were determined by gas chromatography with a mass

spectrometer (GC-MS) (Agilent Technologies, Santa Clara, CA); PAH resolution was achieved in a DB-5 MS-fused capillary column with helium as carrier gas. Data were collected in SIM mode. The quality control included the analysis of certified reference material (CRM 131), a laboratory control sample and a solvent blank sample. The recoveries for individual compounds from CRM 131 were within 62–84%; precision expressed as a relative standard deviation (RSD) was in the range of 5–12%. The limit of detection (LoD) for individual PAH compounds ranged from 0.01 to 0.81 $\mu\text{g kg}^{-1}$, while the limit of quantification (LoQ) ranged from 0.02 to 2.10 $\mu\text{g kg}^{-1}$.

2.4 Statistics

The software package Statistica (Dell Statistica, version 13.1) was used for statistical analysis. Basic statistical parameters such as mean, median, extreme values (min and max), lower (LQ) and upper quartile (UQ), 5th and 95th percentiles, coefficient of variation (CoV) and skewness were analysed. The chi-squared test was applied for checking the normal distribution of the results, and Pearson's correlation was used to assess simple relations among physicochemical soil parameters and SOM fractions. Statistical significance was accepted at $p \leq 0.05$. Principal component analysis (PCA) was used to provide an overview of the distribution pattern of PAHs in SOM fractions and soil properties. PCA was used to examine the interrelations among a set of measured variables in order to identify the underlying structure of those variables. PCA as a non-parametric statistical technique used for not normally distributed results allowed for a unique and independent response about PAHs, HS and soil property relations in analysed soils. PCA used an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components (PC 1–PC 3 for all data set and group of soil with $\text{TOC} \geq 12 \text{ g kg}^{-1}$; PC 1–PC 4 for group of soil with $\text{TOC} < 12 \text{ g kg}^{-1}$). The first component (PC 1) accounted the largest part of data variability, and each succeeding component accounted the remaining variability of the data set. The number of significant PC was determined based on the screen plot.

3 Results and discussion

3.1 SOM content and fractional composition

The results showed significant quantitative differences in the contents of individual SOM fractions: FA, HA, HN and BC (Table 1). Carbon concentrations were 0.36–7.55 g kg^{-1} for FA, 0.61–13.8 g kg^{-1} for HA, 0.15–122.9 g kg^{-1} for HN and 0.23–45.29 g kg^{-1} for BC (Table 1). The BC (CoV = 287%) and HN (CoV = 231%) fractions were characterised by the

highest diversity, while HA (CoV = 43%) exhibited the lowest differentiation. The share of individual TOC fractions (median value) followed the overall trend $\text{BC} < \text{FA} < \text{HN} < \text{HA}$ (Fig. 1).

The percentages and proportions of individual HS fractions are considered as parameters characterising the overall SOM transformation in soils. The HA to FA ratio describes the predominant processes of organic matter transformation that reflects the mobility and quality of SOM (Guimaraes et al. 2013; Tan 2014; Liu 2016; Paul 2016). In our study, the relatively high proportions of HA/FA ranging from 0.30 to 18.23 (Table 1) is in agreement with Liu (2016), Guimaraes et al. (2013) and Bieleńska et al. (2018), who found that HS occurs mainly in high-polymerised organic forms. Moreover, Chen et al. (2017) found that in soil freshly contaminated with PAHs, the equilibrium between humic acids can be disturbed resulting temporary changes in soluble organic matter concentrations.

Black carbon is considered as the chemically and biologically inactive part of organic matter (Pignatello 2011). In the soils of the studied region, BC constituted a significantly smaller part of the TOC, approximately 8% (Table 1). Only 25% of the soils were characterised by a BC content above 1.5 g kg^{-1} , while the remaining soils exhibited values below 0.9 g kg^{-1} . These findings are consistent with the study of Bucheli et al. (2004), Li et al. (2010), Liu et al. (2011), Ni et al. (2008, 2011), Luo et al. (2013), Oktaba et al. (2018), Duan et al. (2015) and Wang et al. (2014), who also found highly diverse BC concentrations from areas under strong anthropogenic pressure. According to Oen et al. (2006), Nam et al. (2008) and Liu et al. (2011), the BC/TOC ratio may be used as an indicator of a potential pollution source of BC. A BC/TOC ratio near or below 0.11 indicates biomass burning, while a high value (near 0.5) often points to a pyrogenic fossil fuel source. In our study, the BC/TOC values ranged from 0.02 to 0.39 (Table 1), with the most predominant values of 0.03–0.19 (5th–95th percentile), suggesting on BC origin from biomass combustion. Wang et al. (2014) reported that soils from agricultural areas showed relatively homogeneous BC/TOC values below 0.5 and concluded that BC emissions were a product of mixed sources. Our BC/TOC ratio was lower compared to those reported by Nam et al. (2008) (0.09–227) and Liu et al. (2011) (0.22–0.52). However, our values were similar to those reported by Hamilton and Hartnett (2013) and Wang et al. (2014), namely 0.2–0.29 and 0.12–0.37, respectively. According to literature data, the obtained relatively low and homogeneous BC/TOC ratio confirms the agricultural character of the studied soils with significant anthropogenic impacts. The BC content of the soils of our area has also been described by Klimkiewicz-Pawlas et al. (2017).

Table 1 Statistical evaluation of the SOM fractional composition in soils ($n = 41$)

	Mean g kg^{-1}	Median	Min	Max	LQ	UQ	Percentile 5th	Percentile 95th	CoV %
FA	2.05	1.63	0.36	7.55	1.37	2.53	0.85	3.70	65
HA	6.90	6.36	0.61	13.81	5.08	7.98	3.30	11.77	43
HN	11.64	3.76	0.15	122.91	2.26	5.25	0.73	61.93	231
HA/FA	4.07	3.69	0.30	18.23	3.20	4.33	1.60	7.24	65
BC	2.43	0.90	0.23	45.29	0.73	1.57	0.64	3.67	287
BC/TOC	0.10	0.08	0.02	0.39	0.06	0.11	0.03	0.19	75

Min, minimum; *Max*, maximum; *LQ*, lower quartile; *UQ*, upper quartile; *CoV*, coefficient of variation

3.2 Compositional profile and identification of PAHs sources

The concentrations of 16 PAHs at individual sampling points exhibited a rather high variability, ranging from 381.7 to 224,133.9 $\mu\text{g kg}^{-1}$, with a median of 1253.0 $\mu\text{g kg}^{-1}$ (Table 2), although 75% of the soil samples were characterised by a 16PAHs content below 2022.96 $\mu\text{g kg}^{-1}$. Since the values were not normally distributed, the median value was considered appropriate for the assessment of the average PAH content in further evaluations.

Generally, the presented results are significantly higher compared to other values reported for the top layer of agricultural soils from non-industrial areas in Poland by Oleszczuk and Pranagal (2007), 105–290 $\mu\text{g kg}^{-1}$; Maliszewska-Kordybach et al. (2008, 2009), 80–7264 $\mu\text{g kg}^{-1}$ as well as in Japan, 52.9–2810 $\mu\text{g kg}^{-1}$ (Chen et al. 2017); China, 176.1–563.3 $\mu\text{g kg}^{-1}$ (Lang et al. 2015) and 103.6–5872 $\mu\text{g kg}^{-1}$ (Jiao et al. 2015) and Norway, 9–11,000 $\mu\text{g kg}^{-1}$ (Nam et al. 2008). Our values even exceed the values of other areas subjected to significant anthropogenic pressure, e.g. China, 247–1410 $\mu\text{g kg}^{-1}$ (Duan et al. 2015) and the Czech Republic, 139.4–24,360 $\mu\text{g kg}^{-1}$ (Holoubek et al. 2009).

A comparable level of contamination has been observed in India (Agarwal et al. 2009; Suman et al. 2016), and exhaustive information on the contents of 16 PAHs in agricultural soils of Poland has been provided by Maliszewska-Kordybach et al. (2008, 2009), who indicate that the average contents of 16 PAHs in the soils of the country is 395 $\mu\text{g kg}^{-1}$. Maliszewska-Kordybach et al. (2008, 2009) have shown that the degree of industrialisation/urbanisation is one of the basic factors determining the level of soil pollution. Soils of typical agricultural areas studied by Maliszewska-Kordybach et al. (2008, 2009) were characterised by a considerably lower content of contaminants (median for $\Sigma 16$ WWA = 355 $\mu\text{g kg}^{-1}$) in relation to non-agricultural areas under the direct influence of industrial activity (median for $\Sigma 16$ WWA = 545 $\mu\text{g kg}^{-1}$). The highest concentrations, above 100 $\mu\text{g kg}^{-1}$, were noted for five dominating hydrocarbons: fluoranthene, pyrene, benzo(b) fluoranthene, phenanthrene and chrysene, while their contributions to $\Sigma 16$ PAH varied in the range of 8.2–21.1%. The lowest abundances corresponded to acenaphthylene, anthracene and dibenz(a,h) anthracene (0.3–0.7% of the sum of 16 WWA) (Table 2).

Overall, the higher-molecular hydrocarbons contributed more pronouncedly to the total content of PAHs than the lower-molecular ones; the groups with more than four rings accounted

Fig. 1 Percentage of individual SOC fractions in TOC content ($n = 41$). SOM: soil organic matter, BC: black carbon, FA: fulvic acids, HA: humic acids, HN: humins

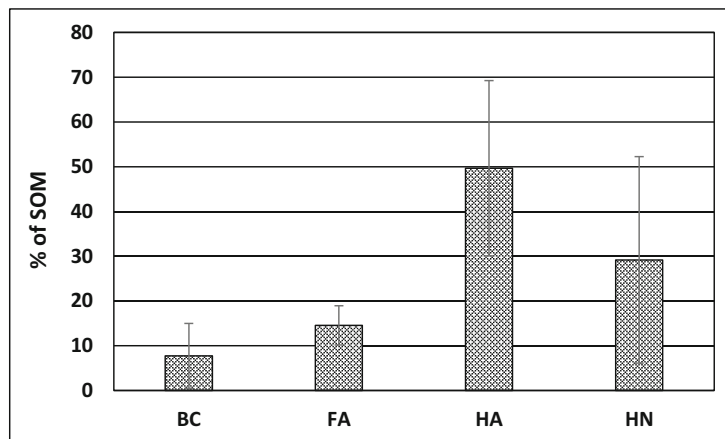


Table 2 Statistical evaluation of the concentrations and contributions of individual PAHs in soils ($n = 41$)

PAHs	Abbreviation	Number of rings	Total concentration of PAHs ($\mu\text{g kg}^{-1}$)				Percentage in 16 PAHs			
			Median	Min	Max	CoV	Median	Min	Max	CoV
Naphthalene	Nap	2	66.5	34.1	5430.4	303	5.7	1.1	30.1	71
Acenaphthylene	Acy	3	3.8	1.3	1375.5	447	0.3	0.1	1.1	46
Acenaphthene	Ace	3	12.9	6.1	1484.2	346	1.1	0.5	1.9	36
Fluorene	Fl	3	13.0	6.3	2455.8	374	1.1	0.5	2.1	29
Phenanthrene	Phe	3	130.1	56.6	20,481.1	351	11.4	6.1	28.5	29
Anthracene	Ant	3	9.2	2.5	4647.2	425	0.7	0.5	2.1	40
Fluoranthene	Fla	4	285.3	71.3	41,635.6	374	21.1	5.1	26.0	17
Pyrene	Pyr	4	209.0	48.6	29,515.9	374	14.8	7.3	17.6	17
Benzo(a)anthracene	BaA	4	70.0	15.4	18,916.3	405	5.0	3.1	8.6	22
Chrysene	Chr	4	107.4	32.3	17,017.4	371	8.2	6.4	11.4	10
Benzo(b)fluoranthene	Bbf	5	160.6	31.4	22,999.2	377	10.7	3.9	16.0	19
Benzo(k)fluoranthene	BkF	5	51.3	9.3	20,009.5	473	3.6	0.7	8.9	30
Benzo(a)pyrene	BaP	5	74.1	9.8	16,618.6	396	5.4	2.3	7.9	24
Indeno(1,2,3-cd)pyrene	IcdP	6	57.3	10.6	15,753.1	418	4.3	0.6	7.7	30
Dibenz (a,h)anthracene	DahA	6	8.4	1.5	1185.9	355	0.7	0.3	1.5	37
Benzo (ghi)perylene	BghiP	6	59.9	13.8	11,844.1	394	4.3	2.6	7.5	22
$\Sigma 16$ PAHs	–	–	1253.0	381.7	224,133.9	371	–	–	–	–
Carcinogenic PAHs ^a	–	–	563.1	151.0	123,158.2	398	41.7	23.5	60.7	15
2 + 3-ring PAHs	–	–	249.8	107.2	33,996.8	341	21.0	10.1	63.8	38
4-ring PAHs	–	–	665.4	168.9	102,331.8	375	49.3	24.3	55.9	13
5 + 6-ring PAHs	–	–	412.8	82.9	87,805.2	402	29.5	11.9	45.6	20

Min, minimum; *Max*, maximum; *CoV*, coefficient of variation (%)

^a According to Nadal et al. (2007)

for 78%, while low-molecular PAH compounds (two and three rings) accounted for almost 21% of the total concentration of contaminants (Table 2). There were also differences in the distribution of the selected groups in the total sample pool. In the case of PAHs with two and three rings, in nearly 90% of soils, their percentage was below 30%, while the percentage of PAHs with more than four rings was never below 20%. The mean concentration of carcinogenic PAHs was $563.1 \mu\text{g kg}^{-1}$ (Table 1), and their contributions to $\Sigma 16$ PAHs were rather uniform, with a median value of 41.7%. The observed fingerprints of $\Sigma 16$ PAHs are in agreement with other data reported in the literature for agricultural areas (Oleszczuk and Pranagal 2007; Ravindra et al. 2008; Duan et al. 2015; Suman et al. 2016).

Polycyclic aromatic hydrocarbons can originate from natural processes such as biomass burning, volcanic eruptions and diagenesis (Pies et al., 2008; Ravindra et al. 2008; Akyüz and Çabuk 2010; Katsoyiannis et al. 2011; Wang et al. 2015). However, in urban or industrial regions, the majority of these compounds are from anthropogenic sources: coal and wood burning, petrol and diesel oil combustion and industrial processes (Ravindra et al. 2008; Akyüz and Çabuk 2010; Katsoyiannis et al. 2011; Tobiszewski and Namiesnik 2012). The PAH diagnostic ratios of selected individual

compounds may provide an important tool for the identification of their pollution sources, and the PAH emission profile of a given source depends on the processes producing the PAHs. During low-temperature processes (e.g. wood burning), low-molecular-weight PAHs are usually formed, whereas high-temperature processes, such as the combustion of fuels in engines, emit higher-molecular-weight PAH compounds (Pies et al. 2008; Mostert et al. 2010; Tobiszewski and Namiesnik 2012). At high temperatures, organic compounds are cracked to reactive radicals, which react to form stable PAHs during pyrosynthesis. These PAHs are less alkylated, and their molecules contain more aromatic rings than petrogenic PAHs (Ravindra et al. 2008; Katsoyiannis et al. 2011; Tobiszewski and Namiesnik, 2012). Several markers allow to differentiate between pyrogenic and petrogenic sources of PAHs (Table 3). Our results indicate that the majority of identified PAHs originated from mixed sources, pyrogenic and petrogenic, which is in line with general trends in Poland (Maliszewska-Kordybach et al. 2008; Maliszewska-Kordybach et al. 2009). The majority of soils in our study exhibited high levels of high-molecular-weight PAHs (Tables 2 and 3), which confirms the industrial character of the region; the use of coal for industrial and individual

Table 3 Application of molecular diagnostic ratios for evaluation of PAHs contamination sources

PAH ratio	Reference value	Potential source	Reference	Range values in the current study
FL/(FL + PYR)	< 0.5 > 0.5	Petrol emissions Diesel emissions	Ravindra et al. 2008; Klimkowicz-Pawlas et al. 2017	0.03–0.22
ANT/(ANT + PHE)	< 1 > 1	Petrogenic Pyrogenic	Pies et al. 2008	0.03–0.20
FLA/(FLA + PYR)	< 0.4 0.4–0.5 > 0.5	Petrogenic Fossil fuel combustion Grass, wood, coal combustion	De La Torre-Roche et al. 2009	0.41–0.67
BaA/(BaA + CHR)	0.2–0.35 > 0.35	Coal combustion Vehicular emissions	Akyüz and Çabuk 2010; Klimkowicz-Pawlas et al. 2017	0.26–0.53
IcdP/(IcdP + BghiP)	< 0.2 0.2–0.5 > 0.5	Petrogenic Petroleum combustion Grass, wood and coal combustion	Klimkowicz-Pawlas et al. 2017	0.17–0.57
BaP/BghiP	< 0.6 > 0.6	Non-traffic emissions Traffic emissions	Katsoyiannis et al. 2011	0.71–1.72
LMW/ HMW	< 1 > 1	Petrogenic Pyrogenic	Zhang et al. 2008	0.11–1.76

Min, minimum; *Max*, maximum; *CoV*, coefficient of variation (%)

heating processes still represents an important issue and leaves fingerprints in terms of soil contamination.

3.3 Relationship between PAH accumulation in soil and SOM fractional composition

Soil characteristics, affecting the processes controlling the persistence of PAHs (Maliszewska-Kordybach et al. 2009; Mostert et al. 2010; Suman et al. 2016), were the other variables contributing to the variability of PAH concentrations in soils. Although the content of the clay fraction had no effect on PAH content, and the influence of pH was practically negligible (data not shown), TOC exhibited a significant correlation with all PAH compounds (Table 4). The influence of TOC on PAH sorption is generally known and well described by Nam et al. (2008), Ni et al. (2008), Maliszewska-Kordybach et al. (2008, 2009), Yang et al. (2011, 2012), Mostert et al. (2010) and Chen et al. (2017). Stronger links corresponded to the lower-molecular-weight compounds such as PAHs with two and three rings (Table 4), which is in agreement with the findings of Nam et al. (2008), who argued that more volatile PAHs may easier approach an equilibrium with SOM over a larger spatial scale. For a more detailed analysis of the effect of TOC content on links with PAHs concentrations, the two subgroups of soils with lower (TOC < 12 g kg⁻¹, *n* = 21) and higher (TOC ≥ 12 g kg⁻¹, *n* = 20) TOC content were separated (Table 4).

The most significant effect of TOC on the PAH content was observed in soils with a TOC content above 12 g kg⁻¹, where the concentration of ∑16 PAH increased with the increase in

the stable SOM fractions. This suggests that the direction and stage of transformation as well as the fractional composition of SOM have a significant impact on the retention of these contaminants in the soil.

Our results show that the predominant partitioning medium for PAHs in soil affecting their retention was HN and BC. This impact was particularly evident in soils with higher TOC levels, namely above 12 g kg⁻¹ (Table 4). The PAH content significantly increased with increasing organic carbon of HN and BC, implying that PAHs in various fractions were significantly affected by their abundance as well as physicochemical properties. Correlation coefficient values indicate that BC exhibited the greatest relationship with PAHs (*r* = 0.87 for BC and *r* = 0.73 for HN), despite the lowest contribution in total SOM content. This illustrates that the organic carbon originating from BC and HN might possess a divergent binding capability with the same compounds. Our findings are supported by other sorption-related studies showing that different SOM types had dissimilar binding strengths with PAHs (Schaumann 2006a, b; Yang et al. 2010, 2011; Pignatello 2011; Wang et al. 2011, 2012; Chen et al. 2017). According to Pignatello (2012), the sorption selectivity by SOM fractions has a number of potential causes: (1) preference for particular microdomains within fractions that are envisioned to segregate on the basis of functional group identity (aromatic, paraffinic, carbohydrate domains); (2) preference based on strong functional group interactions, such as hydrogen bonding and (3) preference based on the nature of the thermodynamic physical state of SOM, namely the configurations and conformations of the molecules and strands at microstructural level.

Table 4 Correlation coefficients between the PAHs content and the SOM fractions (g kg^{-1}) depending on the level of TOC content in soils

Level of TOC content in soil	SOM fractions	2 + 3-ring PAHs	4-ring PAHs	5 + 6-ring PAHs	$\Sigma 16$ PAHs
All data ($n = 41$)	TOC	0.81 ^b	0.71 ^b	0.71 ^b	0.73 ^b
	FA	0.16	0.21	0.12	0.17
	HA	0.28	0.29	0.22	0.27
	HN	0.79 ^b	0.68 ^b	0.70 ^b	0.71 ^b
	HA/FA	0.24	0.09	0.13	0.13
	BC	0.83 ^b	0.82 ^b	0.92 ^b	0.86 ^b
	BC/TOC	0.41 ^a	0.43 ^a	0.50 ^a	0.45 ^a
TOC $\geq 12 \text{ g kg}^{-1}$ ($n = 20$)	TOC	0.87 ^b	0.77 ^b	0.77 ^b	0.82 ^b
	FA	-0.26	-0.05	-0.05	-0.13
	HA	0.23	0.24	0.26	0.24
	HN	0.77 ^a	0.69 ^a	0.68 ^a	0.73 ^a
	HA/FA	0.04	0.25	0.26	0.31
	BC	0.82 ^b	0.81 ^b	0.92 ^b	0.87 ^b
	BC/TOC	0.66 ^a	0.69 ^a	0.80 ^b	0.73 ^b
TOC $< 12 \text{ g kg}^{-1}$ ($n = 21$)	TOC	0.11	0.06	0.17	0.10
	FA	0.26	0.02	0.10	0.08
	HA	0.26	0.22	0.13	0.20
	HN	-0.11	-0.05	0.05	-0.02
	HA/FA	0.06	0.20	0.05	0.13
	BC	-0.32	-0.29	-0.38	-0.34
	BC/TOC	-0.31	-0.37	-0.27	-0.32

^a Significant correlations at the level of $p < 0.05$; ^b significant correlations at the level of $p < 0.001$

In our study, HN and BC exhibited potentially different accumulation capacities for PAHs (Table 4). HN were characterised by the strongest relation with low-molecular PAHs ($r = 0.77$ for $\Sigma 2 + 3$ -ring compounds) in contrast to higher-molecular-weight PAHs ($r = 0.69$ for $\Sigma 4$ -ring compounds, $r = 0.68$ for $\Sigma 5 + 6$ -ring compounds), while BC was more strongly associated with high-molecular-weight PAHs ($r = 0.92$ for $\Sigma 5 + 6$ -ring compounds) than with lower-molecular PAHs ($r = 0.81$ for $\Sigma 2 + 3$ -ring compounds). Wang et al. (2011, 2012, 2015) explained these relations with the limited accessibility to microporous domains of HN matrices for the larger-molecular-weight PAHs. The authors observed a lower adsorbed mass of pyrene compared to phenanthrene for the same sorbent, which as most likely related to the structural rearrangement of the HN matrix under slow diffusion into microporous domains pronounced with the adsorption of low-molecular PAHs. Yang et al. (2010), Pignatello (2012), Wang et al. (2011, 2012, 2015) indicated that the HN surface is covered with various polar and apolar functionalities (e.g. C(C-H/C-C), C-O(C-OH/C-O-C), C=O and -COO groups), which may interact with PAHs.

Due to its high microporosity, BC contains a proportionately higher surface area than HN (Pignatello 2011). Although BC is less reactive and more condensed than HN, it possesses backbone structures of aromatic molecule stacks poor in functional groups and the interlayer spacing that decreases as a function of

condensation or maturation. Larger PAHs easily diffuse into the BC pores and are effectively retained via physical interactions (Schaumann 2006a, b). Luo et al. (2012) have suggested that surface characteristic of SOM fractions plays a critical role in interactions with organic contaminants due to the better access to the surface sorption/retention domains in the first stage after they are released into the soil. This implies that the abundance of the surface carbon domains of HN plays an important role in attracting PAHs and in further interactions, possibly via multiple mechanisms such as hydrophobic interactions including alkyl and aromatic carbon domains and p-p interactions with aromatic carbon domains (Pignatello 2011, 2012).

Furthermore, Agarwal and Bucheli (2011) explained that strong BC and PAH associations in industrial areas may be the result of several processes: co-emission of BC and PAH, PAH gas-to-BC particle partitioning during atmospheric transport, PAH air-to-BC soil partitioning and sorption of PAH to BC in the soil after deposition. Also, Li et al. (2010), Duan et al. (2015) and Wang et al. (2014) showed significant correlations between TOC, BC and PAHs and pointed to a critical impact of BC on the long-term retention of PAHs in the soil, especially in industrial areas. The TOC/BC-PAH links in the research area have also been pointed out by Klimkowicz-Pawlak et al. (2017).

Table 5 Factor analysis, factor loading matrix correlation after varimax rotation used to generate the PCA components

	All data set ($n = 41$)			TOC ≥ 12 g kg ⁻¹ ($n = 20$)			TOC < 12 g kg ⁻¹ ($n = 21$)			
	PCA 1	PCA 2	PCA 3	PCA 1	PCA 2	PCA 3	PCA 1	PCA 2	PCA 3	PCA 4
Clay	-0.24	-0.72 ^a	0.39	-0.56 ^a	-0.72 ^a	-0.26	0.35	-0.31	-0.53 ^a	-0.20
pH _{KCl}	-0.03	-0.33	-0.87 ^a	-0.41	-0.40	0.76	0.31	-0.49	0.48	-0.19
TC	-1.00 ^a	-0.02	0.04	-0.99 ^a	-0.05	-0.11	-0.69 ^a	-0.63 ^a	0.26	0.08
TN	-0.84 ^a	0.42	0.01	-0.75 ^a	-0.52	-0.28	-0.88 ^a	-0.33	0.02	-0.21
TC:TN	-0.93 ^a	-0.23	0.1	-0.95 ^a	0.24	-0.03	0.45	-0.49	0.40	0.46
TOC	-0.97 ^a	-0.02	0.15	-0.96 ^a	0.01	-0.24	-0.86 ^a	-0.45	0.05	-0.01
FA	-0.22	0.87 ^a	-0.06	0.12	0.88 ^a	-0.23	-0.58 ^a	0.46	-0.06	-0.14
HA	-0.32	0.77 ^a	0.01	-0.02	0.68 ^a	-0.35	-0.39	0.49	0.68 ^a	-0.05
HN	-0.95 ^a	-0.15	0.15	-0.96 ^a	0.11	-0.19	-0.22	-0.80 ^a	-0.47	0.05
BC	-0.81 ^a	-0.24	-0.32	-0.83 ^a	-0.03	0.44	0.56 ^a	-0.60 ^a	0.36	-0.19
16 PAHs	-0.86 ^a	-0.03	-0.27	-0.85 ^a	-0.23	0.23	-0.25	0.08	-0.11	0.84 ^a
Eigenvalue	6.01	2.29	1.15	6.2	2.3	1.2	3.3	2.8	1.6	1.1
% of variance	54.7	20.8	10.4	56.2	20.9	11.3	30.2	25.0	14.4	10.1
Cumulative %	54.7	75.5	85.9	56.2	77.2	88.5	30.2	55.2	69.6	79.7

^a Loadings > 0.5 . TC, total carbon; TN, total nitrogen; TOC, total organic carbon; FA, fulvic acids; HA, humic acids; HN, humins; BC, black carbon; 16 PAHs, the sum of 16 polycyclic aromatic hydrocarbons

Ehlers and Loibner (2006) and Wang et al. (2011) proved that the affinity of PAHs to SOM depends on the SOM-PAH contact time, described as “ageing”. Ageing is an important determinant of the sorption characteristics of PAHs in the soil under long-term anthropopression. Gao et al. (1998) study the ageing effects on mechanism-specific sorption and desorption which showed that ageing time leads to higher retention and reduces desorption and lessens extractability as a result of the greater contaminant sequestration or binding. The “ageing effect” is attributed to the slow relaxation of glassy macromolecules comprised of HN or BC. Wang et al. (2011) proposed the theory of sequential bonding of pollutants by SOM, which proceeds in the following steps: (step 1) capturing the fraction of fresh pollutants by FA (weak hydrogen bonds with PAH, facilitating the migration in the soil profile); (step 2) bounding by HA (metastable sorbent states, inclusion by HA micellar forms) and (step 3) slow sorption of contaminants into the glassy HN structures (process ageing). The significant positive correlations between HN and PAHs noted for the area with long-term historical deposition of PAHs in the soil (Table 4) confirm this theory. Moreover, our results indicate that, in such areas, even low percentages of black carbon may substantially modify sorption capacity and persistence of PAHs in soils.

For further insights into the relationship among PAHs and soil physicochemical properties, factor analysis based on the principal components method (PCA) was applied. This approach allowed a detailed analysis of the dependence of individual parameters (also those that are not noticeable by ordinary correlations) and excluded the influence of outliers. The PCA

(with varimax rotation) was performed using the following parameters: $\sum 16$ PAHs, clay content, pH_{KCl}, TOC, TN and TC/TN as well as FA, HA, HN and BC. The total data variations within the data set were exemplified by three PCA components (Table 5). Three factors were extracted for the total data set as well as for soils with TOC contents above 12 g kg⁻¹, accounting for 85.9 and 88.5% of the total variation, respectively. For soils with TOC contents below 12 g kg⁻¹, four principal components were extracted, explaining 79.7% of the total variation. The first factor (54.7% of variation for all data sets) confirmed the highly positive correlation with the $\sum 16$ PAHs and SOM fraction loadings such as BC ($r = -0.81$) and HN ($r = -0.95$) as well as soil parameters directly reflecting the quality of SOM: TOC ($r = -0.97$), TC ($r = -1.00$), TN ($r = -0.84$) and TC:TN ($r = -0.93$). The first component described the effect of anthropogenic pressure, confirming that among the different SOM fractions, HN and BC affect PAH accumulation in the soil. Factor two (20.8%) reflected the lower reverse impact of FA ($r = 0.87$) and HA ($r = 0.77$) on PAH retention in the soil, which was also related to clay content ($r = -0.72$), while factor three indicated the slight (only 10%) importance of soil acidity on that process. In the soils with TOC ≥ 12 g kg⁻¹, the three first factors explained 88.5% of the variability of PAHs and were strongly correlated with the same loading as for the entire data set. However, in soils with TOC < 12 g kg⁻¹, four significant factors explained 79.7% of the data variation, of which the first factor (30.2% of variation) was correlated with TC ($r = -0.69$), TOC ($r = -0.86$), TN ($r = -0.88$), BC ($r = 0.56$) and FA ($r = -0.58$), while the second factor (25% of variation) was correlated with TC ($r = -0.63$), BC ($r = -0.60$) and HN ($r = -0.80$). The third

factor exhibited a significant effect of HA ($r = 0.63$), while the fourth factor described soil contamination by PAHs; both factors accounted for almost 24.5% of the variation. The results of the PCA indicate that SOM fractional composition is responsible for most of the variation in the extracted PAHs, determining PAH accumulation and persistence.

4 Conclusions

Different SOM fractions might possess divergent binding capabilities and different binding strengths to PAHs, depending on the TOC content. The BC and HM fractions were most strongly related to the amounts of PAH in the soil, while HA and FA were of less importance. The different sorption capacities of BC and HN in relation to PAHs of different molecular weight are a result of physicochemical characteristic related with various structures, i.e. polar and non-polar functionalities in sorption domains and pore size structures of these fractions. The high BC correlation with higher-molecular PAHs may arise from their co-emission, while the stronger relationships of HN with lower-molecular PAHs are directly related to their higher mobility and easier diffusion to stable SOM fractions. These findings are significant for our understanding of the environmental fate of PAHs in the soils of industrialised areas and the associated mechanisms, especially considering that the predominant HN and BC fractions of SOM are responsible for an increased retention and persistence of PAHs, thereby reducing their biodegradability.

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