Polycyclic aromatic compounds (PAHs, oxygenated PAHs, nitrated PAHs and azaarenes) in soils from China and their relationship with geographic location, land use and soil carbon fractions

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HIGHLIGHTS

- PAHs and their derivatives were determined in topsoils from four climate zones.
- Concentration of PACs were highest in the temperate zone and lowest in the tropics.
- ≥4-ring PAHs and <4-ring PAHs were dominant in temperate and tropical zones, respectively.
- Longitude correlated with concentrations of PAHs and NPAHs and latitude with those of NPAHs.
- Concentrations of carbon fractions only correlated sometimes with those of PACs in soils.

GRAPHICAL ABSTRACT
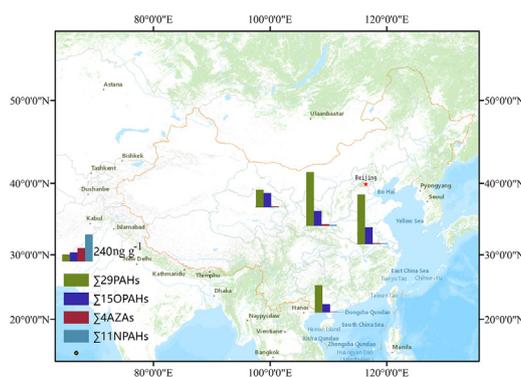
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ABSTRACT

The assessment of risks arising from polycyclic aromatic compounds (PACs), particularly from the polar PACs [azaarenes (AZAs), oxygenated PAHs (OPAHs), nitrated PAHs (NPAHs)] requires us to understand the drivers of their spatial distribution. We determined the concentrations of 29 PAHs, 4 AZAs, 15 OPAHs and 11 NPAHs and their relationships with land use (urban vs. rural and forest vs. agriculture), climate (Qinghai-Tibetan plateau, temperate, sub tropical and tropical) and three C fractions (soil organic C, char, soot) in 36 mineral topsoils (0–5 cm) of China. The average concentrations±standard deviation of the Σ29PAHs, Σ16PAHs, Σ4AZAs, Σ15OPAHs and Σ11NPAHs were 352 ± 283, 206 ± 215, 5.7 ± 3.7, 108 ± 66.8 and 3.2 ± 3.4 ng g^{-1}, respectively. PAH, OPAH, NPAH and AZA concentrations were frequently not correlated within or across the regions reflecting

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different sources and turnover of PAHs and their derivatives. Temperate urban soils showed the highest and tropical rural soils the lowest concentrations of PACs. Forest soils had higher PACs concentrations than agricultural soils. Longitude correlated positively with the $\sum$29PAHs concentrations, because of increasing emissions of PAHs from East to West. The tropical and plateau regions with the lowest PAH concentrations, were dominated by low molecular weight PAHs (LMW-PAHs) with LMW/high molecular weight (HMW)-PAHs ratios >1, while the other two climatic regions with more industrial sites showed the opposite. Latitude correlated with NPAHs likely because of enhanced formation by photochemical reactions during transport in the atmosphere. The concentrations of the $\sum$29PAHs, $\sum$4AZAs, $\sum$15OPAHs, $\sum$11NPAHs and their individual components were only occasionally correlated with those of carbon fractions (soil organic C, soot and char) suggesting a small role of soil C pool properties in driving PACs concentrations. Our results demonstrate that the strongest drivers of PACs concentrations are land use and distance to PAC emission sources followed by climate and size and properties of the soil organic C pool.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent and toxic organic pollutants that occur in environmental matrices worldwide (Wilcke 2000, 2007). Azaarenes (AZAs) are a group of heterocyclic PAHs containing one nitrogen atom in place of a carbon atom in the aromatic ring (Bleeker et al. 1999), while oxygenated PAHs (OPAHs) and nitrated PAHs (NPAHs) are PAH derivatives with hydrogen on the aromatic ring substituted by carbonyl- and nitro-functional groups, respectively (Atkinson and Arey 1994; Lundstedt et al. 2007; Bandowe and Meusel 2017; Idowu et al. 2019). These polycyclic aromatic compounds (PACs) are formed and released into the environment mainly from incomplete combustion of fossil fuel, biofuel and biomass (Anyanwu and Semple 2015; Bleeker et al. 1999; Karavalakis et al. 2011; Shen et al. 2013a; Alves et al. 2016; Bandowe and Nkansah 2016; Lui et al. 2017; Vicente et al. 2016; Wei et al. 2015a, 2015b). Furthermore, spillage of fossil fuel products (coal, tar, oil, refined petroleum) during their exploration, transport, processing, and usage is an additional source of PACs (Bandowe et al. 2014a; Idowu et al. 2019). OPAHs and NPAHs are also formed from transformation of PAHs by biodegradation, thermal degradation and photochemical oxidation (Atkinson and Arey 1994; Lundstedt et al. 2007; Bandowe and Meusel 2017; Idowu et al. 2019). Some PAHs (e.g. naphthalene (NAPH), phenanthrene (PHEN) and perylene (PERY) as well as AZAs have natural biological sources (Bandowe et al. 2009; Bleeker et al. 1999; Michael, 2008; Mumbo et al., 2016; Wilcke 2007).

Soils are important in the global cycling of PACs. They receive PACs via dry and wet deposition from the atmosphere, which can also occur indirectly via litterfall from vegetation (Cousins et al., 1999; Thomas et al. 1998; Wilcke, 2000). Soils have a substantial storage capacity for PACs, which is a function of their carbon concentration, because soil organic matter is the major sorbent of PACs in soils (Nam et al. 2008a). Usually, the degree of contamination of soils with PACs depends on the proximity of their sources with generally higher concentrations in urban and industrial than in rural areas (Bandowe et al. 2010; Bandowe and Wilcke 2010; Wilcke 2000). Gas/particle partition, sorption-desorption, volatilization, abiotic degradation, biodegradation, leaching and bioaccumulation are important dissipation processes that affect the concentrations and spatial distributions of PACs in soils (Bandowe et al. 2011; Harner et al. 1995; Semple et al. 2003). These processes are affected by the physico-chemical properties of the PACs like the octanol-water partition coefficient (K_{OW}), octanol-air partition coefficient (K_{OA}), molecular weight, etc. (Wei et al. 2015a, 2015b), while soil properties like soil C concentrations, moisture content, texture, structure, mineralogy, porosity, enzymatic and microbial properties are also important for the fate of PACs (Bandowe et al. 2014b; Cousins et al. 1999; Wei et al. 2015a; Wilcke et al. 2014a).

Climate (e.g. temperature, precipitation, monsoon cycles, solar insolation) also has a fundamental effect on the above processes, and thus concentrations and composition patterns of PACs in soils. For those

PACs (like OPAHs and NPAHs), that are additionally formed from post-emission transformation of PAHs, this implies that their concentrations and spatial distribution in soils cannot be predicted from the degree of anthropogenic activity. Our understanding of the influence of biogeochemical and climatic factors on the distribution and fate of PACs are largely based on studies of the hydrophobic PAHs. AZAs, OPAHs and NPAHs, with their more reactive and polar functional groups are bound to behave in ways which could be fundamentally different from the hydrophobic PAHs. Most published studies focus on PAHs at contaminated sites (higher anthropogenic impact) (Arp et al. 2014; Wilcke 2007) and also a series of articles draw attention to the role of background soils (Nam et al. 2008b; Wilcke et al. 2003; 2014). Several studies have been reported about PAHs in soils of China (Cai et al. 2008; Wilcke 2007), but minimal work has been reported on their derivatives (OPAHs, NPAHs and AZAs), even though substantial quantities of these compounds can occur in emission sources, air and dust from China (Bandowe et al., 2014a, 2016; Bandowe and Meusel 2017; Shen et al., 2011, 2012, 2013b; Wei et al. 2015a, 2015b). With the realization that significant portions of the (eco)toxic effects in extracts from soil can be attributed to these PAH derivatives (Arp et al. 2014; Bandowe and Meusel 2017; Wincent et al. 2015), there is an urgent need to understand the sources, levels and fate of PAH derivatives in soils and identify the processes that drive their spatial distribution in the environment.

Elemental carbon (EC, also referred to as black carbon), similar to PACs, is also ubiquitous in the environment and mainly originates from a range of incomplete combustion processes of carbon-containing materials (Goldberg 1985; Han et al. 2010). EC can be subdivided into char and soot based on the difference in their formation temperatures and processes (Han et al. 2010). Char is a carbonaceous material formed by the pyrolysis of organic substances and contains incomplete burning residues, while soot refers to fine carbon particles formed at higher temperature via gas-to-particle conversion processes. EC and PACs are emitted together from various combustion sources, are co-sorbed, co-transported, and co-deposited into various environmental compartments including soils (Arp et al. 2014; Bucheli et al. 2004; Cornelissen et al. 2005; Lohmann et al. 2004). Because of its larger particle size, char tends to be deposited at locations closer to their point source, while soot is transported far from their emission sources and deposited in rural and remote regions along with especially the most volatile PACs (Nam et al. 2008a; Wania and MacKay 1996). The sources, transport, and fate of PACs are therefore strongly connected to those of elemental carbon fractions (EC, char and soot), but this link is little investigated for the PAH derivatives such as AZAs, OPAHs and NPAHs (Arp et al. 2014; Wei et al. 2015a).

In this study, we sampled 36 mineral topsoils (0–5 cm) from four different climate zones of China, i.e. temperate (TE), plateau (PL), subtropical (SU) and tropical (TR) and determined the concentrations of PACs (OPAHs, NPAHs, AZAs and PAHs) and carbon fractions. We examined the relationship between PAC distribution in mineral topsoils and

[1] land-use (urban vs. rural and forest vs. agricultural), [2] climate and [3] soil organic C (SOC) and EC (char and soot) concentrations in soil. We aimed to elucidate the importance of the different drivers of the spatial PACs distribution in soils.

2. Materials and methods

Thirty-two mineral topsoil samples (0–5 cm) (Table S1) were collected at rural sites of Qinghai Lake Basin, Xi'an, Chao Lake Basin and Zhanjiang, which represent the plateau (PL), temperate (TE), subtropical (SU) and tropical climates (TR), respectively in China (Fig. 1). Fig. S1 informs about the climatic conditions of the various climatic zones. In addition to these rural soils, four urban top soils (0–5 cm) from the city of Xi'an in TE were also collected (Table S1). All samples were freeze-dried, after removal of plant residues and gravel-sized materials. The freeze-dried soils were then ground and sieved (<75 μm), and preserved in a freezer at −20 °C until analysis. The concentrations of 29 PAHs and alkyl-PAHs, 15 OPAHs, 4 AZAs and 11 NPAHs (Table 1) were determined in all soils, following methods described in previous studies and supplementary information (Bandowe et al. 2014a; Wei et al. 2015a; Wilcke et al. 2014a). In brief, the samples were extracted with organic solvents by pressurized liquid extraction on an accelerated solvent extractor (ASE 200). Extracts were then cleaned up and fractionated into a PAHs-containing fraction and a polar-PACs containing fraction by column chromatography. The identification and quantification of target compounds in extracts from each sample was accomplished with a gas chromatograph coupled to a mass spectrometer (GC–MS) operated in selected ion monitoring mode. Further details including quality control procedures are described in the supplementary information. A summary of the original data is given in Table S2.

Soil total carbon (TC), inorganic carbon (IC), organic carbon (OC), total nitrogen (TN) and total sulfur (TS) concentrations were determined using a CNS Analyzer (Elementar vario EL cube, Elementar Analysensysteme GmbH, Hanau, Germany) (Wei et al. 2015a; Wilcke et al. 2014a). EC, char and soot concentrations were quantified using the thermal optical IMPROVE protocol with acid pretreatment (Table 2, Han et al. 2007; Wei et al. 2015a; Zhan et al., 2015). Details of the sampling, analytical procedures and quality assurance/control are further explained in the supplementary materials and previous papers (Bandowe and Wilcke 2010; Lundstedt et al. 2014; Wei et al. 2015a).

3. Results

3.1. Concentrations of carbon fractions in soil

The concentrations of TC, IC, TOC, TN and TS were on average ± standard deviation, 27.7 ± 17.2 (range: 3.45–77.9), 3.95 ± 4.94 (0.09–19.9), 23.8 ± 17.7 (2.72–73.8), 2.26 ± 1.61 (0.29–7.19) and 0.40 ± 0.28 (0.07–1.58) mg g^{-1}, respectively. The average concentrations of TC, TN, TS and OC in soils of PL were nearly double those of TE, SU and TR, while the IC concentrations decreased with decreasing latitude from PL to TR (Table 2).

The concentrations of EC, char and soot averaged 1.68 ± 1.88 (range: 0.19–9.13), 1.13 ± 1.42 (0.07–5.46) and 0.55 ± 0.67 (0.06–3.67) mg g^{-1}, respectively. The highest concentration of soot occurred at urban sites of TE and of char in soils of PL (Table 2). The lowest concentrations of char and soot occurred in the soils of TR.

3.2. Concentrations and composition pattern of PAHs

The concentration of Σ29PAHs and Σ16EPA-PAHs in mineral topsoils averaged 320 ± 207 (range: 45–957) and 179 ± 140 (26–610) ng g^{-1}, respectively (Tables 2 and S3). The average concentrations of Σ16EPA-PAHs showed similar spatial trends as the concentrations of Σ29PAHs. The highest concentration of Σ29PAHs was found in the urban area of TE, followed by SU, TE (rural), TR and PL, in decreasing order (Tables 2 and S3). In TE, the concentration of Σ29PAHs was clearly higher in the urban than rural area (Fig. S2). In TE, forest soils showed the highest average concentrations of Σ29PAHs (335 ng g^{-1}), followed by soils from river shores (283 ng g^{-1}) and cropping fields (263 ng g^{-1}, Fig. S3). The concentration of Σ29PAHs in SU was also higher in forest than agricultural soils (Fig. S4).

There were slight differences in the composition patterns of the PAH mixtures of the various climatic zones (Figs. 2, S5). The contribution of individual PAHs to the ∑29 PAHs in TE decreased in the order PHEN > B(BJK) > RET > 1,3-DMNAPH (Fig. 2). At the urban locations of TE, the highest contributions to the ∑21PAHs were from PHEN, B(BJK) and PYR, while at the rural locations, the dominant parent-PAHs were
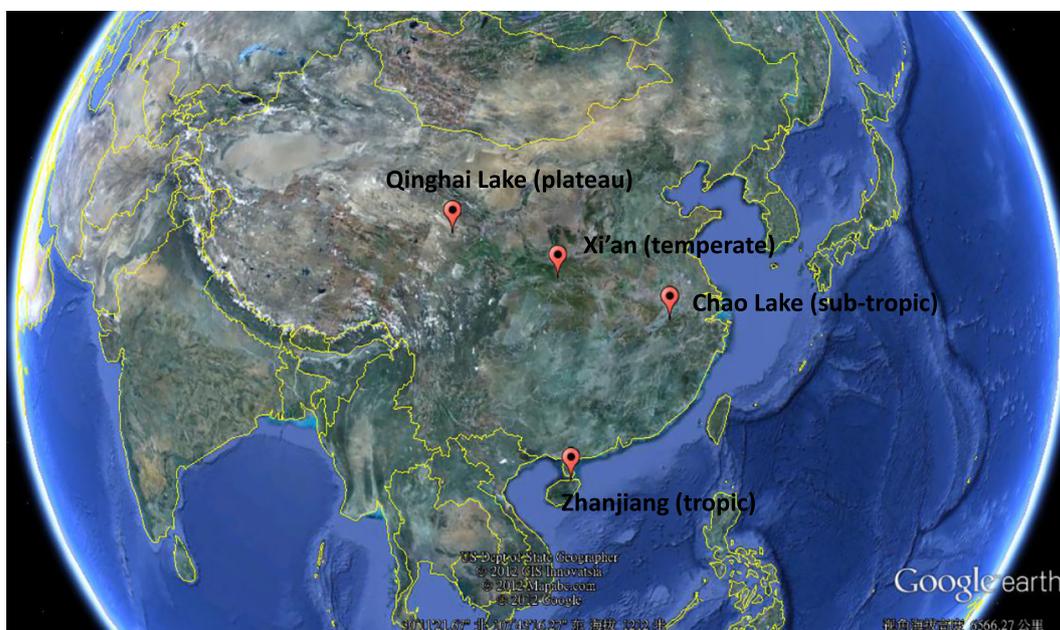

Fig. 1. Sampling sites of surface soil in plateau, temperate, subtropical and tropical areas in China. Details of individual sampling sites are shown in Table S1.

Table 1
The names and abbreviations of the PACs analyzed in this study.

Name	Abbreviation	Name	Abbreviation
Polycyclic aromatic hydrocarbons	**PAHs**	Acridine	ACR
1,2,3,4 Tetrahydronaphthalene	THNAPH	Carbazole	CBZ
Naphthalene	NAPH	**Oxygenated PAHs**	**OPAHs**
2 Methylnaphthalene	2-MNAPH	1 Indanone	1-INDA
1 Methylnaphthalene	1-MNAPH	1,4 Naphthoquinone	1,4-NQ
Biphenyl	BP	1 Naphthaldehyde	1-NLD
1,3 Dimethylnaphthalene	1,3-DMNAP	2 Biphenylcarboxaldehyde	2-BPCD
Acenaphthylene	ACENY	9 Fluorenone	9-FLO
Acenaphthene	ACEN	1,2-Acenaphthenequinone	1,2-ACEQ
Fluorene	FLUO	9,10 Anthraquinone	9,10-ANQ
Phenanthrene	PHEN	1,8 Naphtalic anhydride	1,8-NAA
Anthracene	ANTH	4H Cyclopenta[d,e,f] phenanthrenone	CPHENone
2 Methylphenanthrene	1-MPHEN	2 Meth 9,10 anthraquinone	2-MANQ
3,6 Dimethylphenanthrene	3,6-DMPHEN	Benzo[a]florenone	B(A)FLUone
Fluoranthene	FLUA	7H Benzo[de]anthracen 7 one	BANTone
Pyrene	PYR	Benzo[a]anthracene 7,12 dione	7,12-B(A)A
Retene	RET	5,12 Naphthacenequinone	5,12-NACQ
Benzo[a]anthracene	B(A)A	6H Benzo[c,d]pyren 6 one	BPYRone
Chrysene + triphenylene	CHRY	*Nitrated PAHs*	*NPAHs*
Benzo[b + j + k]fluoranthenes[a]	B(BJK)	1 Nitronaphthalene	1-NNAPH
Benzo[e]pyrene	B(E)P	2 Nitrobiphenyl	2-NBP
Benzo[a]pyrene	B(A)P	5 Nitroacenaphthene	5-NACEN
Perylene	PERY	2 Nitrofluorene	2-NFLU
Indeno[1,2,3 cd]pyrene	IND	9 Nitrophenanthrene	9-NPHEN
Dibenzo[a,h]anthracene	DIBE	9 Nitroanthracene	9-NANT
Benzo[g,h,i]perylene	B(GHI)	(2 + 3) Nitrofluoranthenes[b]	2+3-NFLA
Coronene	COR	1 Nitropyrene	1-NPYR
Azaarenes	*AZAs*	2,7 Dinitrofluorene	2,7-DNFLU
Quinoline	QUI	6 Nitrochrysene	6-NCHR
Benzo[h]quinoline	BQI		

[a] Sum of benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene.
[b] Sum of 2-nitrofluoranthene and 3-nitrofluoranthene.

Table 2
Summary of soil properties and concentrations of polycyclic aromatic compounds (PACs) in surface soils from four climate zones, China.

Analytes	TE (urban)	TE (rural)	PL	SU	TR
Soil properties					
Water content (%)	15.60 ± 7.02	27.87 ± 41.14	12.15 ± 8.88	27.08 ± 11.31	22.27 ± 3.89
Dry density (g cm^{-3})	1.16 ± 0.10	0.94 ± 0.26	0.96 ± 0.21	1.20 ± 0.22	1.08 ± 0.12
LOI[a] (%)	5.91 ± 0.48	6.90 ± 3.30	11.10 ± 5.07	7.30 ± 3.74	11.01 ± 3.11
TC (mg g^{-1})	22.34 ± 2.05	23.30 ± 12.74	45.78 ± 17.22	20.34 ± 17.39	21.28 ± 9.56
TN[a] (mg g^{-1})	1.23 ± 0.31	1.82 ± 1.30	3.82 ± 2.06	1.79 ± 1.20	1.90 ± 0.76
TS[a] (mg g^{-1})	0.31 ± 0.08	0.31 ± 0.14	0.63 ± 0.42	0.33 ± 0.23	0.36 ± 0.10
IC[a] (mg g^{-1})	8.27 ± 1.54	3.98 ± 4.81	7.08 ± 5.92	1.42 ± 3.52	0.16 ± 0.05
TOC[a] (mg g^{-1})	14.06 ± 3.58	19.33 ± 15.35	38.70 ± 21.57	18.92 ± 16.80	21.12 ± 9.53
OC[a] (mg g^{-1})	11.77 ± 3.56	17.66 ± 13.69	36.59 ± 20.14	17.12 ± 14.24	20.65 ± 9.32
EC[a] (mg g^{-1})	2.29 ± 1.28	1.67 ± 1.72	2.11 ± 1.65	1.80 ± 2.83	0.47 ± 0.29
Char (mg g^{-1})	1.07 ± 0.86	1.11 ± 1.43	1.81 ± 1.61	1.11 ± 1.71	0.19 ± 0.09
Soot (mg g^{-1})	1.22 ± 0.71	0.56 ± 0.35	0.31 ± 0.08	0.69 ± 1.13	0.27 ± 0.24
TC/TN	11.45 ± 1.47	10.22 ± 1.25	10.03 ± 0.61	9.41 ± 2.49	10.98 ± 0.97
Char/soot	1.03 ± 0.55	1.54 ± 1.53	5.54 ± 4.72	1.59 ± 0.66	1.14 ± 0.79
PACs (ng g^{-1})					
∑LMW-PAHs[b]	130 ± 50	82 ± 25	56 ± 23	127 ± 73	67 ± 17
∑HMW-PAHs[b]	306 ± 159	112 ± 69	29 ± 19	187 ± 91	26 ± 13
∑Comb-PAHs[b]	297 ± 153	107 ± 65	28 ± 19	167 ± 100	25 ± 12
∑6Alkyl-PAHs[b]	151 ± 65	90 ± 31	62 ± 28	111 ± 57	125 ± 94
∑16EPA-PAHs[b]	379 ± 180	169 ± 72	81 ± 38	257 ± 153	86 ± 20
∑21PAHs[b]	436 ± 205	194 ± 89	85 ± 41	315 ± 155	92 ± 23
∑29PAHs	602 ± 273	295 ± 118	154 ± 70	437 ± 200	238 ± 133
∑15OPAHs	103 ± 23	76 ± 41	123 ± 98	147 ± 63	70 ± 16
∑4AZAs	5.5 ± 1.4	7.5 ± 4.8	5.7 ± 4.0	5.8 ± 3.6	3.6 ± 2.1
∑11NPAHs	4.6 ± 2.0	4.2 ± 4.8	1.3 ± 1.6	4.6 ± 3.0	2.3 ± 3.7
Retene	62.2 ± 34.8	25.1 ± 20.4	8.6 ± 5.6	28.2 ± 33.8	2.9 ± 0.9
Perylene	9.4 ± 6.1	4.7 ± 6.4	0.8 ± 0.7	20.7 ± 44.4	1.2 ± 0.8

[a] LOI, TC, TN, TS, IC, TOC, OC, EC are loss on ignition, total carbon, total nitrogen, total sulfur, inorganic carbon, total organic carbon, organic carbon and elemental carbon concentrations of soil samples, respectively.
[b] ∑LMW-PAHs is sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; ∑HMW-PAHs is sum of fluoranthene, pyrene, benzo[a]anthracene, chrysene + triphenylene, benzo[b + j + k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3 cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and coronene; Combustion-derived PAHs (∑Comb-PAHs) is calculated as ∑HMW-PAHs minus perylene. ∑6Alkyl-PAHs is sum of 2 methylnaphthalene, 1 methylnaphthalene, 1,3 dimethylnaphthalene, 2 methylphenanthrene and 3,6 dimethylphenanthrene; ∑21PAHs is sum of ∑LMW-PAHs and ∑HMW-PAHs mentioned above.
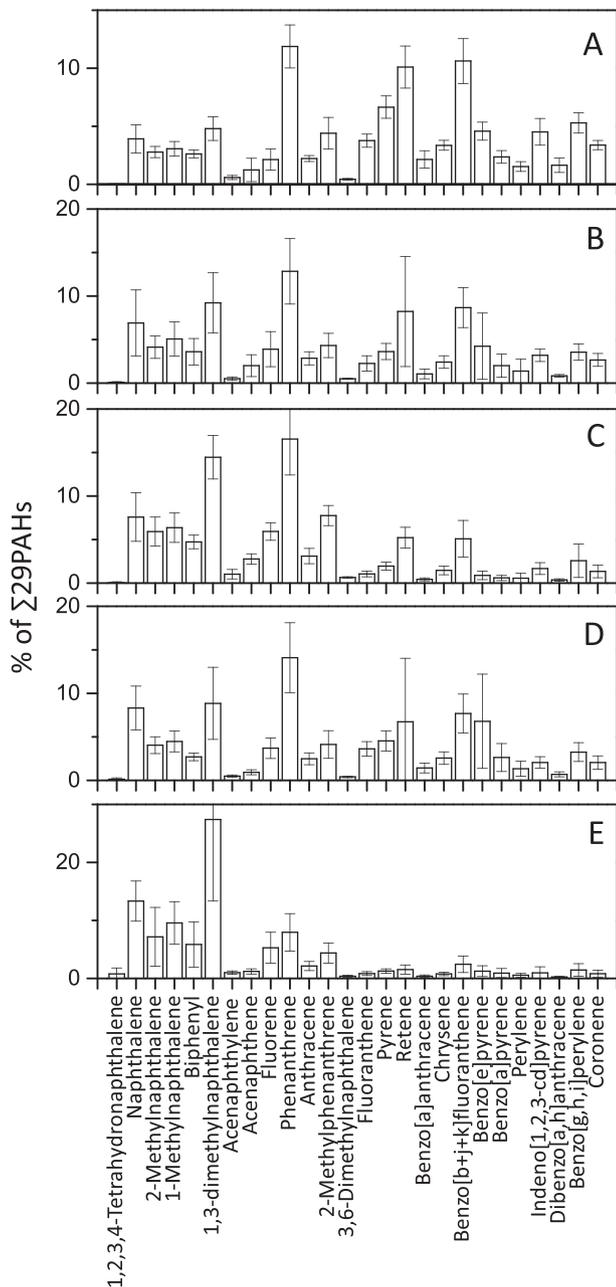
Fig. 2. Mean contributions of individual PAHs to the Σ29PAHs concentrations in soils of the urban [A] and rural sites [B] of the temperate [A, B], plateau [C], subtropical [D] and tropical [E] zones of China.

PHEN, B(BJK) and NAPH (Fig. S5). At both, the urban and rural TE sites, the ∑LMW-PAHs/∑HMW-PAHs was <1, i.e. 0.45 ± 0.09 (at the urban sites) and 0.89 ± 0.38 (at the rural sites) (Table S3).

In PL, the ∑29PAHs mixtures were dominated by PHEN > 1,3-DMNAPH > 2-MPHEN > NAPH (Fig. 2). The three most dominant nonsubstituted PAHs (parent-PAHs) in PL were PHEN, NAPH and FLUO which were all low molecular weight PAHs (Fig. S5). The average ∑LMW-PAHs/∑HMW-PAHs concentration ratio in this region was 2.4 ± 1.1 (Table S3). PHEN, 1,3-DMNAPH, B(BJK) and NAPH were the four most abundant of the mixture of 29 PAHs in SU (Fig. 2). The parent-PAHs in this region were dominated by PHEN, NAPH, B(BJK) and B(E)P with the average ∑LMW-PAHs/∑HMW-PAHs concentration ratio being 2.39 ± 1.12 (Fig. S5, Table S3).

In TR, the 29 PAH mixtures were dominated by LMW-PAHs with major contributions of NAPH and its alkylated derivatives (1,3-

DMNAPH, 1-MNAPH) and PHEN (Fig. 2). When considering only the parent-PAHs (i.e. 21 PAHs), the major contributors were NAPH > PHEN > FLUO (Fig. S5). Higher molecular weight PAHs contributed little to the total PAH concentration in TR. The average ∑LMW-PAHs/∑HMW-PAHs concentration ratio in TR was 3 ± 1, which indicates a dominance of low molecular weight PAHs over high molecular weight ones, similar to PL but different from TE and SU (Table S3).

3.3. Concentrations and composition pattern of PAHs derivatives

The average concentrations ± standard deviation of Σ4AZAs, Σ15OPAHs and Σ11NPAHs in surface soils were 5.7 ± 3.7 (1.6–15.9), 108 ± 67 (27–284) and 3.2 ± 3.4 (not detected – 10.9) ng g^{-1}, respectively (Tables 2 and S2). Similar to the PAHs, the derivatives also showed highest average concentrations in forest soils (10, 105 and 7.4 ng g^{-1} for Σ4AZAs, Σ15OPAHs and Σ11NPAHs, respectively) of TE (Fig. S3). The average concentrations of Σ4AZAs in river shore soils (7.9 ng g^{-1}) was higher than in the cropping soils (4.3 ng g^{-1}), which is similar to the spatial distribution of Σ29PAHs in TE. But the average concentrations of Σ15OPAHs and Σ11NPAHs in the cropping soils (66 and 3.1 ng g^{-1}, respectively) was higher than in the river shore soils (47 and 1.0 ng g^{-1}, respectively) which is opposite to the relationship for Σ29PAHs and Σ4AZAs in TE (Fig. S3). In SU, the highest concentration of PAHs derivatives occurred in forest soils (7.4, 156 and 6.5 ng g^{-1} for Σ4AZAs, Σ15OPAHs and Σ11NPAHs), which is similar to the Σ29PAHs (Fig. S3).

The highest concentration of Σ4AZAs was found in the rural area of TE and the lowest in TR (Table 2). The spatial distribution of AZAs was similar to that of PAHs as indicated by the significant correlation ($p <$ 0.05) between the concentrations of Σ4AZAs and Σ29PAHs ($r = 0.41$), ∑Comb-PAHs ($r = 0.48$) and ∑LMW-PAHs ($r = 0.45$) for the data from all the sampling sites ($n = 36$, Fig. S6). Carbazole was the most dominant of the four AZAs in each of the four climatic regions (Fig. 3). The individual AZA/related PAH concentration ratio was <1 in all regions. Among the four AZA/parent-PAH concentration ratios, the CBZ/FLUO concentration ratio was the highest (Table S3).

The highest average concentration of Σ15OPAHs occurred in SU and the lowest in TR (Tables 2 and S3). Urban areas in TE had higher average concentration of Σ15OPAHs than rural areas (a difference of ca. 26%). With the data from all locations pooled together ($n = 36$), the concentrations of Σ15OPAHs significantly correlated with those of the ΣComb-PAHs ($r = 0.35$, $p = 0.038$) but not with those of the Σ29PAHs or ΣLMW-PAHs (Fig. S6).

The composition of the OPAHs mixture differed slightly among the different climatic zones (Fig. 3). The four most abundant compounds were BANTone, BPYRone, 9,10-ANQ and 9-FLO at both the rural and urban sites of TE (Fig. 3). In PL, the four most dominant OPAHs included the same three compounds (BANTone, BPYRone, 9,10-ANQ) as in TE but also 7,12-B(A)A. In SU, the dominant OPAHs were BANTone, 9,10-ANQ, BPYRone and 9-FLO. In TR, the OPAH mixture was dominated by BANTone, BPYRone, but also 2-MANQ and 5,12-NACQ (Fig. 3). The individual OPAH to related PAH concentration ratios were sometimes >1, except for 1,4-NQ/NAPH and 1-NLD/1-MNAPH which were always <1. High values (8–90) occurred for the 7, 12-B(A)A/B(A)A ratios in PL, SU and TR (Table S3).

The highest concentration of ∑11NPAHs was found in SU and the lowest in PL (Tables 2 and S3). Including all soils from all locations ($n = 36$), the concentrations of ∑11NPAHs were significantly correlated ($p ≤ 0.001$) with those of ∑29PAHs ($r = 0.77$), ∑Comb-PAHs ($r = 0.55$) and ∑LMW-PAHs ($r = 0.79$) (Fig. S6). The NPAHs mixtures in TE were dominated by 2 + 3NFLA > 9-NPHEN > 1-NNAPH > 2,7-DNFLU. At the rural locations of TE, the four most dominant NPAHs were 1-NNAPH > 2 + 3NFLA > 5-NACEN > 9-NPHEN, which was slightly different from the urban sites (Fig. 3). 1-NNAPH was also the most dominant NPAH in PL with the next three most abundant being 2,7-DNFLU > 9-NPHEN > 5-NACEN. 1-NPYR was the most dominant NPAH in SU

Fig. 3. Mean contributions of individual AZAs, OPAHs and nitro-PAHs to the $\sum$4AZAs, $\sum$15OPAHs and $\sum$11NPAHs concentrations in soils of the urban [A] and rural sites [(B)] of the temperate [A, B], plateau [C], subtropical [D] and tropical [E] zones of China.

while in TR the dominant NPAH was 5-NACEN followed by 9-NPHEN and 2 + 3NFLA (Fig. 3). Hence, there were differences in the composition of the NPAHs mixtures among the four climatic zones as well as differences between the rural and urban sites within TE. The individual NPAH/PAH concentration ratios were much lower than the other ratios of derivative/parent-PAHs (Table S3). The 2 + 3-NFLA/FLA concentration ratio was the highest among the NPAH/PAH concentration ratios and ranged between 0.10 ± 0.06 (urban sites of TE) and 0.58 ± 0.41 (TR, Table S3). The 1-NPYR/PYR concentration ratio in our study decreased in the order, TR > TE_rural > PL > SU > TE_urban (Table S3). The 2 + 3-NFLA/1-NPYR concentration ratio which is often used as an indicator of the degree of photochemical formation of NPAHs in air samples (Bandowe and Meusel 2017) ranged between 1.4 (TR) and 3.8 (urban sites of TE, Table S3).

Longitude correlated significantly with the concentrations of $\sum$29PAHs ($r = 0.53$, $p < 0.001$) and $\sum$11NPAHs ($r = 0.39$, $p = 0.02$), but not with those of $\sum$15OPAHs or $\sum$4AZAs (Figs. 4, S7). Latitude correlated significantly negatively with the concentrations of $\sum$11NPAHs ($r = -0.38$, $p = 0.027$), but not with those of any other PACs group (Figs. 4, S8).

The LMW-PAHs concentrations in soils correlated significantly with those of OC ($r = 0.36$, $p = 0.030$), EC ($r = 0.40$, 0.017), char (0.34, 0.043) and soot (0.51, 0.002), while those of the HMW-PAHs correlated significantly with those of EC (0.37, 0.026) and soot (0.57, <0.001), but not OC and char (Table S4, Figs. S9–S10). The $\sum$15OPAHs concentrations did not significantly correlate with those of carbon fractions, while the $\sum$11NPAHs concentrations mainly correlated with the OC concentrations ($r = 0.42$, $p = 0.011$, Table S4). Nevertheless, there were many individual OPAHs and NPAHs concentrations which correlated significantly with those of carbon fractions, such as 1,4-NQ, 1-NLD, 9-FLO, 9,10-ANQ, CPHENone, 2-MANQ, B(A)FLUone, 1-NNAPH, 5-NACEN, 2-NFLU, 9-NANT ($r = 0.35$–0.62, $p < 0.038$), suggesting their similar sources and fates. The $\sum$4AZAs concentrations significantly correlated with those of most carbon fractions in all samples ($r = 0.34$–0.47, $p = 0.004$–0.043).

Fig. 4. Relationship between longitude and concentration of $\sum$29PAHs [A] and $\sum$11NPAHs [B] and between latitude and concentrations of $\sum$11NPAHs [C] in the soil samples.

4. Discussion

4.1. Carbon fractions in soil

The OC and EC concentrations in the studied soils were similar to those reported in other studies from China (Table S6). The probable reason for the high organic matter concentrations in the Qinghai-Tibet plateau is the cool and humid climate (Table 2, Fig. S1A) resulting in lower microbial activities and thus slower organic matter turnover similar to boreal forests in the northern hemisphere (Goulden et al. 1998). Furthermore, the steppe conditions in PL with its dry summers favor the formation of Mollisols associated with a pronounced carbon sequestration (Frank 2002; Wang et al. 2002, 2008). The IC concentrations decreased with increasing latitude, probably because of the reverse relationship between precipitation and latitude in our study (Fig. S1B).

The highest concentration of soot occurred at the urban sites of TE, but this was not the case for char (Table 2). The reason is probably that soot is mainly formed via higher temperature processes like coal and oil combustion while char is mainly formed in lower temperature processes (e.g. biomass burning, Han et al. 2010). The soils of PL showed the highest concentration of char, probably due to grassland fires and domestic burning of cow dung and sheep droppings (Han et al. 2015a). The lowest concentrations of char and soot occurred in the soils in TR which suggests lower emissions of EC in this region.

4.2. Land use as a driver of PACs concentrations

The highest concentrations of the Σ29PAHs, Σ4AZAs, Σ15OPAHs and Σ11NPAHs in soils of our study were consistently lower than those in soils of contaminated sites in the western industrialized regions (coking sites, traffic areas and urban waste deposit sites, Tables S7-S10). On the other hand, the PAHs and OPAHs concentrations in our study were higher than those in soils from remote regions of developing/less industrialized regions, which may be explained by the higher emissions from combustion of fossil fuel for household heating, power plants, transport and industries in China (Wilcke 2000; Wilcke et al. 2014a). The concentrations of $\sum$4AZAs and Σ11NPAHs were similar to background concentrations reported from other regions. The Σ11NPAHs concentrations in our study were lower than in agricultural soils of eastern, China (50 ± 45 ng g^{-1} for Σ11NPAHs, Sun et al. 2017).

The significant correlation of the concentrations of $\sum$4AZAs and Σ11NPAHs with those of the Σ29PAHs is an indication of similar sources of PAHs, AZAs and NPAHs (Table S5). The concentrations of $\sum$15OPAHs concentrations only correlated significantly with those of the $\sum$comb-PAHs but not with those of the $\sum$29PAHs or LMW-PAHs (Table S5). This finding contrasts with the strong correlations between soil concentrations of PAHs and OPAHs found in previous studies (Bandowe et al. 2010, 2011, 2014a; Sun et al. 2017). In air samples in northern China, the total PAHs concentrations were also significantly correlated with OPAHs concentrations (Li et al. 2014, 2015). Our findings therefore suggest that sources and fates of the OPAHs and PAHs are different. For example there might be additional biological degradation of both OPAHs and PAHs in the soils which could occur at different rates because of differences in bioavailability of the two compound groups (Wilcke et al. 2014b). Transport (volatilization and leaching) of OPAHs and PAHs could also occur at different rates because of the differences in physico-chemical properties.

In TE and SU, the $\sum$LMW-PAHs/$\sum$HMW-PAHs concentration ratios were <1, which indicates that the sources of PAHs in these two regions are dominated by high temperature fossil fuel (coal, oil) combustion. This is further backed by the individual alkyl-PAH/parent-PAH ratios (<1, Table S3), which is also considered as strong indicator of the dominance of high temperature pyrogenic sources (Lima et al. 2005). In PL and TR with the lowest PAHs concentrations the LMW-PAHs/HMW-PAHs concentration ratios were >1, which we interpret as indication of higher contributions from low temperature biomass burning, higher

impact of diffuse sources, as well as specific biological sources which are known to have relative higher emissions of low molecular weight PAHs and their alkylated derivatives (Daly et al. 2007; Lima et al. 2005; Wilcke 2007).

The urban sites of TE showed the highest concentrations of PAHs (Table 1), which indicate a higher intensity of activities that produced PAHs (fossil fuel utilization for heating, industries, vehicular transport, etc., Table S2). The higher concentrations of PAHs in forest sites in the SU and TE regions than the grassland sites can be explained by the "forest filter effect" that scavenges and deposits higher amounts of atmospheric pollutants into soils (Bandowe et al. 2018; Horstmann and McLachlan 1998; Matzner 1984).

The correlation of longitude with the concentrations of Σ29PAHs and Σ11NPAHs (Fig. 4) is in line with the increasing anthropogenic activities from west (PL, 100°E) to east China (SU, 118°E).

4.3. Relationship between PACs concentrations and latitude

The PACs concentrations were consistently the lowest in TR which can be partly attributed to the fact that tropical regions are affected by more pronounced loss processes including higher microbial, thermal and photolytic activity, which will often cause the degradation of PAHs as well as their transport to colder locations (Wilcke 2000, 2007; Bandowe et al. 2014a; Wilcke et al. 2014a). Moreover, this tropical region in China has lower levels of industrial activity than the other regions (TE and SU) (National Bureau of Statistics of China 2018).

The contribution of the individual PAHs to the Σ21PAHs concentrations were highly variable among the studied areas resulting in a site- and region-specific composition of the mixtures of PAHs (Figs. 2, S5). PHEN was one of the three dominating compounds in all areas (Figs. 2, S5), which is similar to previous studies (Han et al. 2015b; Wei et al. 2015a; Wilcke et al. 2014a). The most or second most abundant of the 21 parent-PAHs in TR, SU and PL was NAPH, which is in line with observations from other studies in tropical and remote regions, reflecting higher impact from vegetation burning, low temperature combustion of solid fuels (straw, household wood and coal combustion), inputs from long-range transport and biological sources (Cabrerizo et al. 2011, 2012; Daly et al. 2007; Wilcke 2007; Wilcke et al. 2003, 2014a). The fact that besides NAPH, the methyl-NAPHs were also the dominating alkyl-PAHs in TR and PL suggested that methyl-NAPHs may also have biological sources (Wilcke et al. 2014a).

Carbazole, which was the most dominant AZA in all climatic zones (Fig. 3) has recently be classified as a possible human carcinogen (IARC 2013). The finding that the CBZ/FLUO concentration ratio was the highest (Table S3), was similar as in urban soils of Bangkok, in A horizons of forest soils near an Al smelter in Slovakia (Bandowe et al. 2018; 2014a) and in emissions from simulated household combustion of coal in the Xuanwei region, China (Lui et al. 2017). Azaarenes such as carbazole are frequently identified as markers of coal combustion (Bandowe et al. 2014a).

In the few studies, in which four OPAHs were measured in soils of China, the dominant OPAHs were BANTone and 9,10-ANQ in eastern China (Sun et al. 2017), while 9-FLO an 9,10-ANQ dominated in suburban soils of Xi'an in western China (Wei et al. 2015a). Furthermore, studies of the gas and particle phase of air at a rural site in Pearl River Delta, China identified 7H benzo[de]anthracene 7 one as the dominant OPAH (Huang et al. 2014), while a study in northern China detected 9-FLO, 9,10-ANQ and BANTone as the dominant OPAHs in air (Li et al. 2015), which is similar to the dominating OPAHs in our study.

The 2 + 3-NFLA/1-NPYR concentration ratio in air samples is used as indicator of the sources of NPAHs (i.e. either from combustion or post-emission formation by free radical reactions, which increases the ratio) in air samples but it is uncertain whether this proxy can be applied to soils (Bandowe and Meusel 2017). The fact that the 2 + 3-NFLA/1-NPYR concentration ratios were <5 at all locations (Table S3) suggested that most of the NFLAs originated from primary sources

(Bandowe and Meusel 2017). The highest 2 + 3-NFLA/1-NPYR concentration ratio (i.e. 3.78 ± 1.09) occurred in the urban area of TE, which might be interpreted as indicative of high amounts of precursors (fluoranthene and NOx) in the urban area that promote the formation of NFLAs (Table S3). The individual NPAH/parent-PAH concentration ratios were not always varying in the same direction among the four climatic zones, indicating that a multiplicity of sources (primary and secondary) and fate processes might be affecting these ratios in soils (Table S3). Hence, a strict application of these ratios in soil might not be robust. For instance, the 1-NPYR/PYR concentrations ratio suggests that TR is most affected by high-temperature combustion sources (diesel particulate emissions from vehicles and power plants) while the urban area of TE is most affected by emissions of low-temperature combustion processes (e.g., emissions from wood stoves) (Bandowe and Meusel 2017). Such an interpretation contrasts with the known sources of pollution in the considered regions and also the conclusions drawn from the well-known and validated alkyl-PAH/parent PAH ratios (Lima et al. 2005).

The finding that the Σ11NPAHs concentrations showed a close correlation with latitude probably indicates more pronounced photochemical formation of NPAHs from northern (PL, 37°N) to southern China (TR, 21°N, Fig. 4).

4.4. Organic C and EC as driver of PACs concentrations

The correlations between OC, char and soot concentrations with those of PACs were not consistent (Table S4, Figs. S9–S10). Associations between HMW-PAHs and soot can be attributed to co-emission, co-sorption, co-deposition and similar post-emission transport and fate (Han et al. 2015b; Wei et al. 2015a). There are several reasons for the different relationships among the concentrations of LMW-PAHs and HMW-PAHs with those of the carbon fractions: 1) LMW-PAHs are more present in the gaseous phase and are likely to undergo equilibrium partitioning between the air and soil organic matter; 2) soot has a higher surface value than char and thus soot has a strong affinity to non-polar substances like PAHs; 3) HMW-PAHs are molecular precursor of soot and can be co-emitted with soot into the atmosphere, and subsequently co-deposited to soils (Richter and Howard 2000; Schmidt and Noack 2000; Wei et al. 2015b).

5. Conclusions

Land use showed the most pronounced effects on the concentrations of all PACs groups with higher concentrations in urban than rural soils and forest than agricultural soils, illustrating the multitude of sources of all PACs in urban areas and the scavenging effect of forests. Another important control of PACs concentrations was distance to the sources as illustrated by the relationship between some PACs (PAHs and NPAHs) concentrations and longitude. The latitudinal location also influenced the concentrations and compositions of some PACs with higher concentrations in TE and SU than TR and PL. The lower concentrations in TR and PL went along with the dominance of low- molecular weight compounds. The lower level of industrial activity, dominance of low temperature combustion processes, biological sources and higher level of dissipation processes (in tropical regions) are some factors that may explain the relatively lower concentrations of PACs and higher proportion of LMW-PAHs in the TR and PL than TE and SU regions. The size of the OC pool in soil and the composition of the EC pool (i.e. the soot and char concentrations) played a minor role for PAHs concentrations mainly limited to low molecular weight PAHs. Our results suggest that PACs concentrations and composition patterns in soils are influence by land-use, distance to PACs emission sources, latitudinal location, and the size and properties of the soil organic C pool.

Appendix A. Supplementary data

The material mentioned in this study are presented in supplementary materials, including materials and methods, Tables S1–S10, and Figs. S1–S10. Supplementary data to this article can be found online at doi:https://doi.org/10.1016/j.scitotenv.2019.07.022.

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