



Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Stronger association of polycyclic aromatic hydrocarbons with soot than with char in soils and sediments

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HIGHLIGHTS

- TOC, EC, char, soot, and 12 parent PAHs were measured in sediments and soils.
- Lower concentrations of EC, char, soot and \sum 12PAHs were observed in sediments.
- Differences in transportation and degradation contribute to the relative percentages of char and soot.
- Sorption capacity of soot yields a closer association with PAHs.
- Stronger correlation between PAHs and different carbon fractions occurs in sediments than in soils.

ARTICLE INFO

Article history:

Received 9 July 2013

Received in revised form 24 January 2014

Accepted 4 February 2014

Available online xxx

Keywords:

Relationship

Elemental carbon

Char

Soot

Polycyclic aromatic hydrocarbons

Sorption capacity

ABSTRACT

The knowledge of the association of polycyclic aromatic hydrocarbons (PAHs) with organic matter and carbonaceous materials is critical for a better understanding of their environmental transport, fate, and toxicological effects. Extensive studies have been done with regard to the relationship of PAHs with total organic carbon (TOC) and elemental carbon (EC) in different environmental matrices. The relationship between PAHs and the two subtypes of EC, char (combustion residues) and soot (produced via gas-to-particle conversion) also has been tested in field and laboratory experiments using reference materials. However, a direct comparison of associations of PAHs between with char and with soot in real environmental matrices has to our knowledge not yet been reported because of a lack of methodology to differentiate them. In this study, char and soot were measured using the IMPROVE method to test their associations with 12 EPA priority PAHs measured in topsoil samples ($N = 22$, top 10 cm) collected from the Guanzhong Plain and in surface sediment samples ($N = 32$, top 5 cm) from the Wei River (central China). In both soils and sediments, \sum 12PAHs were more strongly associated with soot than with char, mainly due to the fact that soot and PAHs were produced in the same gas phase during combustion, had a strong affinity for each other, and were transported and deposited together, while char, the combustion residue, was transported differently to PAHs due to its large particle size. Stronger correlations between PAHs and the different carbon fractions (TOC, soot, and char) in sediments than in soils were observed, which is associated with the redistribution of PAHs among the organic matter pools in water because of the processes during soil erosion and sedimentation in the river.

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1. Introduction

Elemental carbon (EC) is produced by incomplete combustion of fossil fuels and vegetation (Gustafsson and Gschwend, 1997; Schmidt and Noack, 2000). It can be formed by two mechanisms.

Char or charcoal is solid residues formed directly from the fuel by pyrolysis, while soot is submicron particles formed via gas-to-particle conversion of molecular precursors in the atmosphere (Schmidt and Noack, 2000). EC is purely of terrestrial origin and ubiquitous in the environment, where it acts as a strong sorbent for many persistent organic pollutants (POPs), including polycyclic aromatic hydrocarbons (PAHs) (Cornelissen et al., 2005, 2006; Agarwal and Bucheli, 2011). The most prominent and ubiquitous

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sources of PAHs in the environment include the incomplete combustion of biomass (such as wood) and fossil fuels (petroleum and coal) (Yan et al., 2005). However, there are also some diagenetic and biological sources (Wilcke, 2000; Lima et al., 2005). High molecular weight PAHs are assumed to be precursors of the macroaromatic structure of soot (Richter and Howard, 2000). Due to co-emission, as well as the high sorption capacities of EC (soot part) for PAHs, it has been suggested that the distribution of PAHs in environmental compartments (e.g. soil or sediments) is related to the distributions of EC (Cornelissen et al., 2006).

Sorption of organic chemicals, especially PAHs, is an important process that controls the fate and ecotoxicological risks of soil and sediment-bound chemicals. The sorption of PAHs to particles can reduce their bioavailability, slowing their biodegradation rates and preserving them in sediments and soils (Lima et al., 2005). Organic matter (OM) and carbonaceous materials (e.g. EC, soot and char, etc.) are the most important sorbents of PAHs in sediments and soils (Jonker and Koelmans, 2002a,b). Previous reports suggest that sorption of organic chemicals to soils and sediments can be described by a “dual-mode sorption mechanism”: absorption in amorphous organic matter and adsorption to carbonaceous materials (Cornelissen et al., 2005). Numerous studies have been conducted to test the relative importance of total organic carbon (TOC) and EC as sorbents for PAHs in soils and sediments. Some studies suggest that sorption of PAHs to EC far exceeds that to TOC (Gustafsson et al., 1997; Persson et al., 2002); while others indicate that concentrations of TOC correlate mainly with those of low molecular weight PAHs (Desaules et al., 2008). There are also studies suggesting that concentrations of higher molecular weight PAHs correlate more closely with those of EC than TOC (Agarwal and Bucheli, 2011; Liu et al., 2011). However, other researchers observed that TOC is the main factor controlling PAH concentrations in organic matter-rich background soils, and concentrations of EC are little correlated with those of PAHs (Wilcke and Amelung, 2000; Rockne et al., 2002; Bucheli et al., 2004; Agarwal and Bucheli, 2011).

Limited studies have been done regarding the comparison of the associations between organic pollutants and the two types of EC, that is, char and soot from real environmental matrices (Jonker and Koelmans, 2002b; Cornelissen et al., 2005; Hauck et al., 2007). Most of these previous studies used standard reference materials of char and soot for sorption experiments (Cornelissen et al., 2005). This may be attributable to the lack of a suitable method to differentiate between char and soot. The chemothermal method (CTO-375), which is a widely used method for EC quantification in soils and sediments, has been suggested to specifically measure soot carbon (Gustafsson et al., 1997), but it removes most of the relatively labile char materials in a pretreatment procedure. Han et al. (2007b) extended the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal optical reflectance (TOR) method, the most popular method for aerosol samples, to measure EC in sediments and soils after chemical acid pretreatment. In a preliminary experiment, Chen et al. (2013) showed that at relatively high EC concentrations the EC recovery was similar for geological samples provided the soil samples were re-suspended and acid pretreated, while for little EC-loaded samples, EC could not be detected without chemical acid pretreatment. This supports the importance and correctness for the extension of the IMPROVE method to soil and sediment samples. The IMPROVE protocol applies programmed progressive heating in different controlled atmospheres and produces four OC fractions (OC1, OC2, OC3 and OC4), three EC fractions (EC1, EC2 and EC3), and one pyrolyzed organic carbon (POC) fraction defined by temperature and oxidation atmosphere. Further studies (Han et al., 2007a) suggested that pure char materials always peak at the EC1 step, while pure soot materials always peak at the EC2 and EC3 steps. A comparison with the

CTO-375 method (Gustafsson et al., 1997, 2001) showed that CTO-375 EC generally shows up in the EC2 and EC3 fractions. Thus, differentiation between char and soot was suggested with the IMPROVE method based on their different refractiveness (Han et al., 2007b). The method has been validated and successfully applied in aerosol studies (Han et al., 2010; Lim et al., 2012) and in soil (Han et al., 2009a) and lake sediment studies (Han et al., 2011). The successful validation and application of this method to soils and sediments facilitates comparative studies of the association of organic pollutants with char and soot in soils and sediments.

The objectives of the present study were to (1) determine the concentrations and distributions of TOC, EC, char, soot and 12 EPA-PAHs in surface bed sediments of the Wei River (WR) and its surrounding surface soils in the Guanzhong Plain (GZP), China; (2) assess the relationship between PAH concentrations and those of TOC, EC, char and soot; and (3) study the influence of the different carbon pools on the sediment/pore-water distribution coefficient and its implications on toxicity and fates of PAHs.

2. Experimental

2.1. The study area

The WR is the largest tributary of the Yellow River, the second longest river in China. It flows through the Chinese Loess Plateau (CLP) and carries a large amount of fine-grained calcareous silts, coloring the river yellow. The annual sand transport from north and west of the CLP is about 0.17 billion tons (Wang and Wang, 2004). The river also passes through several large cities such as Baoji and Weinan, and the mega-city of Xi'an. The WR and GZP (Fig. S1, see Supplementary Information, SI) are surrounded by the CLP, where soils are formed from these aeolian deposits (i.e. loess). The Guanzhong Plain hosts a population of ~30 million. The mean annual temperature in this region is ~6–13 °C, the mean annual precipitation 500–800 mm, and the mean annual evapotranspiration 1000–2000 mm (based on observations since the 1950s).

2.2. Sampling

We collected 22 soil samples from the GZP along the riverbank (top 0–10 cm of the mineral soil) using a steel shovel in September 2010. The GZP is located in the clayey loess zone (Liu, 1985), with soil types of Orthic Anthrosols and Mollisols mainly used for agricultural cultivation. Furthermore, 32 sediment samples were collected from the top 5 cm sediments of the Wei River in July, 2011. Sampling sites were located using a Global Positioning System (GPS) (Fig. S1, SI). All samples (~500 g for each one) were freeze-dried. The dried samples were passed through a 2-mm sieve to remove large plant roots and gravel-sized materials, and then stored in a freezer at –4 °C until analysis.

2.3. EC, char and soot quantification

Approximately $\sim 150 \pm 50$ mg of each ground (<63 μm) and homogenized sample was weighed for stepwise acid pretreatment. The details of the procedure have been described by Han et al. (2007b, 2009b). In brief, hydrochloric acid (HCl), hydrofluoric acid (HF) and their mixture were used to remove carbonate, metal oxides and minerals. The remaining residues were filtered through a 47 mm quartz filter (0.4 μm pore size, Whatman) and air-dried in a baking oven at 35 °C.

The EC analysis was conducted following the IMPROVE protocol (Han et al., 2007b). A 0.526 cm² circular punch from the filters was stepwise heated to 120, 250, 450 and 550 °C in a pure He environ-

ment, and four organic carbon (OC) fractions (OC1, OC2, OC3, and OC4) were successively volatilized and oxidized to CO₂ and then reduced to CH₄ for detection with a flame ionization detector. Thereafter, the oven temperature was further raised to 550, 700 and 800 °C in a 2% O₂/98% He atmosphere, volatilizing three EC fractions (EC1, EC2, and EC3). In this procedure, the pyrolyzed organic carbon (POC) produced in the inert He atmosphere was monitored with a laser, such that it could be returned into the OC fraction. Thus, the IMPROVE protocol defines the sum of all three EC fractions minus POC as EC. Han et al. (2007a) further divided EC into char, which is defined as EC1 minus POC (EC1 – POC), and soot, which is defined as the sum of EC2 and EC3 (EC2 + EC3).

2.4. PAHs, TOC, and TN quantification

The procedures for extraction from soil or sediment and purification with silica gel columns have been described extensively elsewhere (Mai et al., 2003; Guo et al., 2007), and only a brief description is given here. We spiked ~5 g soil or sediment samples with a mixture of five deuterated-PAHs (naphthalene-D₈, acenaphthene-D₁₀, phenanthrene-D₁₀, chrysene-D₁₂ and perylene-D₁₂, as surrogate standards) and extracted with dichloromethane in a Soxhlet extractor for 24 h. The extract was concentrated and cleaned-up using a silica gel-alumina column. A known amount of hexamethylbenzene (HMB) was added as internal standard before analysis.

The concentrations of PAHs were determined by an Agilent 7890A gas chromatography equipped with a 5795C mass spectrometer detector (GC-MSD) in the full scan monitoring mode, and chromatographic separation was provided by a 30 m × 0.25 mm × 0.25 μm HP DB-5MS capillary column. The column temperature was programmed as follows: initially held at 60 °C for 5 min, and then increased to 290 °C at a rate of 3 °C min⁻¹, held for 15 min. PAH concentrations were quantified by internal standard calibration based on a five-point calibration function for each individual component. Final PAH concentrations were corrected via the recovery of surrogate standards. Recoveries of the internal standards were 7 ± 4% for naphthalene-D₈, 28 ± 10% for acenaphthene-D₁₀, 76 ± 16% for phenanthrene-D₁₀, 83 ± 13% for chrysene-D₁₂, and 92 ± 14% for perylene-D₁₂. 12 PAHs in EPA priority with recoveries between 72% and 125% were reported in this study. Blanks were included in each batch of 10 samples. Reported PAH concentrations were blank-corrected. Limit of detection (LOD) defined as amount of target compounds that produce a signal to noise ratio of 3:1 was reported in Table S1.

All samples were subjected to HCl pretreatment to remove carbonates and TOC and total nitrogen (TN) were determined using a CHNOS elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Hanau, Germany).

2.5. Quality control/quality assurance

All glassware used in sample preparations were washed using an ultrasonic cleaner and baked at 450 °C in a muffle furnace for 6 h. All solvents used for extraction and analysis were pesticide residue grade. The carbon analyzer was calibrated daily with known quantities of methane. We used in-house standard reference materials of aerosols from the Desert Research Institute (DRI) for calibration of the IMPROVE method. For TOC and TN quantification, three acetanilide standards were included in each batch of 20 samples. Every tenth sample was measured in duplicate. Relative standard deviations (RSD) of duplicate analyses were <10% for EC, char and soot, <3% for TOC and TN and 1–26% for PAHs. Recoveries of spiked PAHs in the extracted solids ranged from 72% to 125% for the 12 target PAHs.

2.6. Sediment–porewater distribution coefficient (K_d) calculations

Knowledge on the relative distribution of PAHs between the solid and liquid phases of environmental matrices such as soil and sediment is required to predict their bioavailability, environmental fate, behavior and toxic effects (Bucheli and Gustafsson, 2000). Solid–water distribution coefficient (K_d) in sediment is usually estimated by the equilibrium partitioning model between TOC and solution (Eq. (1)):

$$K_d = f_{\text{TOC}} \cdot K_{\text{TOC}} \quad (1)$$

where f_{TOC} and K_{TOC} are the fraction of TOC in the solid (kg organic carbon/kg total solid) and TOC normalized distribution coefficients ((mol kg⁻¹ organic carbon)/(mol L⁻¹ solution)), respectively. This model usually underestimate the K_d in real field samples (Bucheli and Gustafsson, 2000; Jonker et al., 2003; Hawthorne et al., 2006, 2007) and thus it is revised and calculated by the combined effects of OC and EC. Both linear (Gustafsson et al., 1997) and nonlinear (Cornelissen et al., 2005) isotherms have been utilized in the combined OC and EC partitioning model. In this study, the linear isotherm was applied (Eq. (2)), because we focused on the research of solid PAHs as well as their relations with EC, char and soot and because we did not avail of measured pore-water PAH concentrations (Gustafsson et al., 1997):

$$K'_d = f_{\text{OC}} \cdot K_{\text{OC}} + f_{\text{EC}} \cdot K_{\text{EC}} \quad (2)$$

where f_{OC} and f_{EC} are the different fractions of OC and EC in the solid, while K_{OC} and K_{EC} are OC and EC normalized distribution coefficients. As EC equals to the sum of char and soot, Eq. (2) can be extrapolated to Eq. (3):

$$K''_d = f_{\text{OC}} \cdot K_{\text{OC}} + f_{\text{char}} \cdot K_{\text{char}} + f_{\text{soot}} \cdot K_{\text{soot}} \quad (3)$$

where f_{char} and f_{soot} are the fraction of char and soot in the solid, respectively, and K_{char} and K_{soot} are char and soot normalized distribution coefficients.

In this study, the pore-water concentrations of PAHs (C_w) are estimated using the equation below for the above three partitioning models, i.e. the TOC, OC + EC, and OC + char + soot models:

$$C_w = C_s / K_d \quad (4)$$

where C_s is the concentration of PAHs in sediments. We use C_w, C'_w, and C''_w to represent the pool-water concentrations calculated using the TOC, OC + EC, and OC + char + soot model, respectively.

Octanol–water, carbon normalized partition coefficient used in this study and proposed toxicity values of PAHs (Neff et al., 2005) for comparison are presented in Table S2.

2.7. Statistical analysis

In this study, IBM SPSS Statistics 20 (SPSS Inc., USA) was utilized for the multivariate statistical analysis and for descriptive and correlation analyses. Origin 7.0 (OriginLab Corporation, USA) was used for figure plot. All parameters are Kolmogorov–Smirnov tested using the Lilliefors modification for normal distribution before correlation analysis.

3. Results and discussion

3.1. TOC and EC in GZP soils and WR sediments

TOC concentrations in GZP soils ranged from 1.5 to 17.1 mg g⁻¹ (Table 1), which were comparable with those from the CLP, China (Fang et al., 2012). TN concentrations in GZP soils varied between 0.33 and 1.91 mg g⁻¹, and showed good correlation with TOC (Fig. S2, SI). The TOC and TN concentrations in WR sediments

Table 1
Polycyclic aromatic hydrocarbon concentrations (PAHs, in ng g^{-1}) and concentrations of carbon fractions (in mg g^{-1}), as well as some ratios used in this study from surface soils of the Guanzhong Plain and the surface bed sediments of the Wei River.

	Soils				Sediments			
	Minimum	Maximum	Mean	STD	Minimum	Maximum	Mean	STD
Phe	10.87	75.90	33.10	19.98	9.33	137.64	38.05	29.25
Ant	0.96	9.18	2.95	2.12	0.77	15.16	3.77	3.36
Fla	4.75	80.13	16.57	16.44	2.60	63.49	15.19	16.35
Pyr	2.32	22.29	8.46	6.08	2.03	58.03	13.10	14.85
BaA	1.38	22.99	5.48	6.01	0.89	23.11	5.13	5.38
Chr	1.83	43.13	10.23	11.46	0.78	61.22	10.17	12.99
BbF	3.58	70.90	17.60	17.59	0.55	59.99	10.84	14.72
BkF	0.95	19.43	4.61	4.60	0.41	17.30	3.20	4.00
BaP	1.56	20.40	6.38	5.70	0.17	38.47	5.37	8.47
IcdP	2.07	44.24	14.79	11.44	0.44	26.23	4.47	5.69
DahA	0.39	47.54	7.78	10.42	0.09	9.91	1.54	2.25
BghiP	2.66	45.16	13.39	11.54	0.37	33.29	5.33	7.77
$\sum 12\text{PAHs}$	48.40	440.01	141.34	105.98	24.35	507.98	116.16	116.46
LMW	11.84	82.29	36.05	21.52	10.34	152.8	41.82	32.44
HMW	24.35	400.71	105.29	94.75	9.51	355.18	74.34	86.58
HMW/LMW	0.87	10.20	3.24	2.26	0.48	3.58	1.50	0.79
$\sum\text{COMB}$	23.64	353.17	97.52	85.63	9.42	345.27	72.80	84.67
$\sum\text{COMB}/\sum 12\text{PAHs}$	0.46	0.85	0.66	0.12	0.32	0.76	0.55	0.12
TOC	1.46	17.12	7.17	3.76	0.33	13.68	2.78	3.12
TN	0.33	1.91	0.91	0.39	0.20	1.43	0.49	0.30
OC	1.13	15.26	6.13	3.38	0.21	12.68	2.40	2.94
EC	0.22	1.87	1.04	0.53	0.11	1.00	0.38	0.22
EC/TOC	0.05	0.30	0.16	0.05	0.05	0.47	0.22	0.11
Char	0.12	1.57	0.73	0.46	0.04	0.59	0.21	0.15
Soot	0.10	0.68	0.32	0.13	0.07	0.59	0.17	0.11
Char/soot	0.63	5.18	2.30	1.32	0.33	2.91	1.32	0.64

Abbreviations: Phe: phenanthrene, Ant: anthracene, Fla: fluoranthene, Pyr: pyrene, BaA: benzo[a]anthracene; Chr: chrysene; BbF: benzo[b]fluoranthene, BkF: benzo[k]fluoranthene, BaP: benzo[a]pyrene, IcdP: indeno[1,2,3-cd]pyrene, DahA: dibenz[a,h]anthracene, BghiP: benzo[ghi]perylene, $\sum\text{COMB}$: sum of Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP and BghiP, LWM: sum of 3-ring PAHs (Phe and Ant), HMW: sum of 4-, 5- and 6-ring PAHs.

ranged from 0.3 to 13.7 mg g^{-1} and from 0.2 to 1.4 mg g^{-1} , respectively, which were comparable with, but a little lower than those in the GZP soils.

EC concentrations in the studied soils and sediments were positively correlated with the corresponding TOC concentrations (Fig. S3, SI). A similar strong correlation between TOC and EC concentrations was also observed by others using different methods such as CTO-375 for soils (Nam et al., 2008a; Agarwal and Bucheli, 2011; Liu et al., 2011) and aerosols (Cao et al., 2003; Chow et al., 2005; Han et al., 2008, 2010), and was linked to the co-emission of EC and TOC by combustion of vegetation and fossil fuels. From urban to remote regions, biomass burning-derived carbon and the formation of secondary OC from the volatile OC increases, resulting in increasingly poor relations between the concentrations of TOC and EC in aerosols (Han et al., 2008). The stronger correlation between EC and TOC concentrations in sediments ($r = 0.92$, $p < 0.0001$) than in soils ($r = 0.81$, $p < 0.0001$) may be related to carbon sources and transport modes in the two compartments. Sediments are more likely to experience water-controlled mixing processes homogenizing the sediments, while soils are more heterogeneous with respect to vegetation-derived TOC concentrations.

The EC concentrations in the GZP soils varied from 0.22 to 1.87 mg g^{-1} (accounting for 5–47% of TOC), which fall into the lower range of the reported values around the world (Table S3, SI). As different methods for EC quantification in soils and sediments can lead to differences of up to two orders of magnitude for an individual sample (Schmidt et al., 2001; Hammes et al., 2007), the EC method should be considered when comparing EC data. The IMPROVE-measured EC usually produces intermediate values when compared to the other methods for EC quantification (Hammes et al., 2007). The EC concentrations in GZP soils were similar to those in Xi'an soils (0.17–2.11 mg g^{-1}) measured using the same method (Han et al., 2009a). However, they were lower than those in Beijing (Liu et al., 2011), Xuzhou (Wang, 2011), and Nanjing

(He and Zhang, 2009) measured using the CTO-375 method. This may be either associated with the relatively lower industrialization in the GZP region or the different EC methods, as sometimes without rigid pretreatment, the CTO-375 method can produce higher EC concentrations due to the survival of some organics (Zhan et al., 2013b).

EC concentrations in the WR sediments varied between 0.11 and 1.00 mg g^{-1} , which were lower than those in the surrounding GZP soils (Table S3, SI; Fig. 1B). This may indicate that the influence of modern atmospheric transported EC deposition exceeded the water entrained EC pollutants in the GZP since $\text{PM}_{2.5}$ EC in this area is among the highest in China (Cao et al., 2007; Han et al., 2009c). In addition, this may also be associated with the topography of the CLP. The CLP consists of a thick aeolian deposit accumulated during the past several million years (Liu, 1985). While the studied soils developed on top of these layers, the sampled river stretch was located in the lowest part of the region and its sediments were likely fed by deeper parts of the loess deposit. EC concentrations decreased significantly in deeper parts of the CLP soils (Zhou et al., 2007; Zhan et al., 2013a), with sharp decreases occurring at ~ 10 m lower than the surface of the loess tableland (~ 160 ka ago). Thus, the combination of lower layer loess sediments and surrounding soil inputs would lead to relatively lower EC concentrations than its surrounding soils. The EC concentrations in the WR were also lower than those measured in the sediments from the Changjiang River estuary and from the shelf of the East China Sea measured using the CTO-375 method (Wang and Li, 2007). The EC/TOC concentration ratios in the sediments ranged between 0.05 and 0.47, which were comparable to those in the GZP soils.

3.2. Char and soot in GZP soils and WR sediments

Char concentrations in the GZP soils ranged from 0.12 to 1.57 mg g^{-1} (Table 1), which contributed 39–84% to total EC

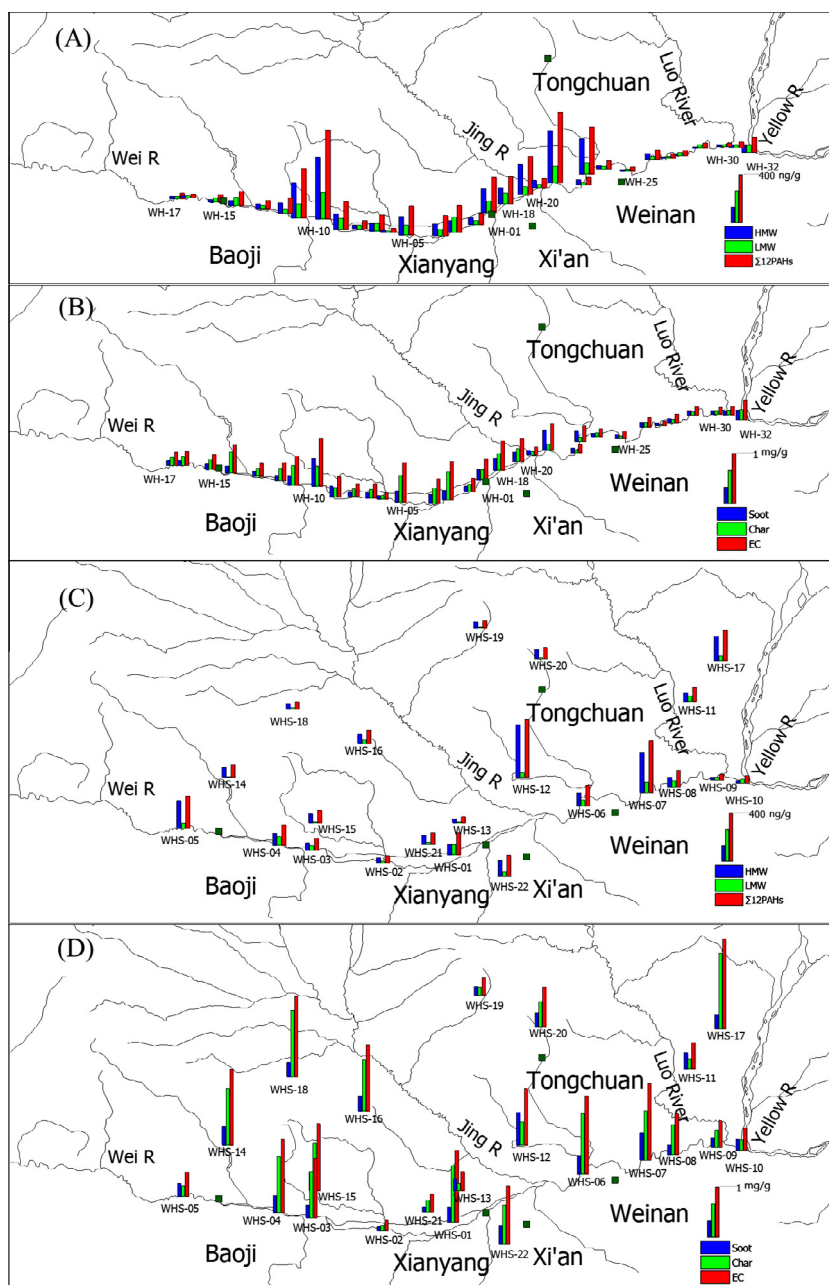


Fig. 1. Spatial distributions of (A and C) $\Sigma 12$ PAHs (total polycyclic aromatic hydrocarbons concentrations), low molecular weight (LMW) and high molecular weight (HMW) PAHs (ng g^{-1}), as well as (B and D) total EC, char and soot (mg g^{-1}) in the surface sediments of the Wei River (A and B) and in its surrounding soils of the Guanzhong Plain (C and D).

(mean: 64.4%). These concentrations were similar to those in Xi'an soils ($0.07\text{--}1.12 \text{ mg g}^{-1}$) (Han et al., 2009a) and soils from the CLP ($0.03\text{--}4.19 \text{ mg g}^{-1}$) (Zhan et al., 2013a), but lower than those in Xi'an urban dusts ($1.3\text{--}16.5 \text{ mg g}^{-1}$) measured using the same method (Han et al., 2009a). Soot concentrations in the GZP soils were generally lower than char concentrations, ranging from 0.10 to 0.68 mg g^{-1} , which contributed 16–61% to total EC (mean: 35.6%). Also they were again comparable to those in Xi'an soils, but lower than those in Xi'an urban dusts (Han et al., 2009a). Similar to EC (Table S3, SI), char and soot concentrations in the WR sediments were again lower than those in its surrounding GZP soils (Table 1). The percentage of char and soot in total EC in the WR sediments were similar (mean: 54% vs. 46%). This means there was a higher percentage of soot in total EC in sediments than in

soils (p values of 0.006 in t -test). Zhan et al. (2013a) found that char concentrations decreased with soil depth in the CLP, while soot concentrations showed little variation with depth and they suggested this may be due to the different degradability of char and soot. Furthermore, spatial distribution of char and soot in the CLP surface soils showed lower char and soot concentrations and higher soot/char ratios occurring in the northwest part (the upper reach of the WR) than in the southeast part (the lower reach of the WR) (Zhan et al., 2013a). Thus, as sediments of the Wei River are in the lower geographical locations relative to its surrounding soil samples, both the inputs of old layer silts and soil inputs from the upper reach can contribute to the higher fractional contribution of soot to total EC concentrations in sediments (46%) than in its surrounding soils (36%).

In general, the IMPROVE method-derived soot concentrations were comparable to those measured using the CTO-375 method with rigid pretreatment (Han et al., 2011). Compared with those from worldwide soils measured using the CTO-375 method (Table S3, SI), our soot concentrations in the GZP soils were generally lower. However, the soot concentrations in the WR sediments were in general comparable with those from Lake Washington, Washington coastal slope (Dickens et al., 2004), and the Swedish continental shelf (Sanchez-Garcia et al., 2010), but lower than those in river sediments from USA (Grossman and Ghosh, 2009) and Norwegian harbors (Oen et al., 2006), and considerably lower than those from the Changjiang River estuary and the shelf of the East China Sea measured using the CTO-375 method (Wang and Li, 2007).

3.3. PAH patterns in soils and surface sediments of the Wei River

The total concentrations of 12 EPA-PAHs ($\Sigma 12\text{PAHs}$) in GZP soils ranged from 48.4 to 440.0 ng g⁻¹ (mean: 141.3 ng g⁻¹), which were a little higher than those in WR sediments (range of 24.4–508.0 ng g⁻¹ and mean of 116.2 ng g⁻¹) (Table 1). The observation of higher concentrations in soils than in sediments was similar to that for EC, char and soot concentrations in these two matrices, which we attribute to the dilution effect of the inputs of old layer silts from the CLP to the river sediments. The $\Sigma 12\text{PAH}$ concentrations (for both soils and sediments) in our study were at the lower end of the range of PAH concentrations in soils and sediments of China (Table S4, SI).

The PAH mixtures in the GZP soils and WR sediments had a similar molecular distribution (Fig. 2). Similar to previous studies (e.g. see summary from Wilcke (2000)), most individual PAH concentrations in GZP soils and WR sediments were significantly positively correlated with each other (Table 2). Wilcke (2000) reported that the composition of PAH mixtures throughout the temperate zone were similar, which may be associated with the “weathering” of PAHs, e.g. transformation during atmospheric transport. On average, the PAH composition in both soils and sediments was dominated by phenanthrene (Phe) and fluoranthene (Fla) with the lowest contribution from anthracene (Ant), benzo(k)fluoranthene (BkF) and dibenzo(a,h)anthracene (DahA). The similarity in composition pattern suggests that the main sources of PAHs in the two matrices (soils and sediments) of the GZP area were similar. However, the detailed comparison showed that GZP soils had a relatively high percentage of high-molecular-weight (HMW) PAHs (4–6 rings) such as benzo(g,h,i)perylene (BghiP), DahA, indeno(1,2,3-cd)pyrene (IcdP), and benzo(b)fluoranthene (BbF), while in the WR sediments, low-molecular-weight (LMW) PAHs (3 rings) such as Phe were more abundant (Fig. 2A).

The HMW/LMW ratio averaged 1.50 (range: 0.48–3.58) in the WR sediments and 3.24 (range: 0.87–10.20) in its surrounding topsoils (Table 1), and the difference between sediments and soils was significant (p value in t -test < 0.001). Generally, fossil fuel combustion produces more HMW-PAHs, while petrogenic sources of PAHs contain more LMW-PAHs. Unburned fuels predominantly contain LMW-PAHs, which can enter rivers via street/storm water runoff. In addition, as soil is the source of sediments, erosion inputs also deliver relatively higher concentrations of LMW-PAHs due to their higher water solubility (Zakaria et al., 2002).

The concentrations of $\Sigma 12\text{PAHs}$, LMW- and HMW-PAHs showed very similar spatial distributions with EC, char and soot in sediments, with high concentrations close to the cities of Xi'an and Xi'an (Fig. 1). This pattern was also similar to those of potentially hazardous elements in this river (Han et al., 2012) and were consistent with the population distribution and anthropogenic influences.

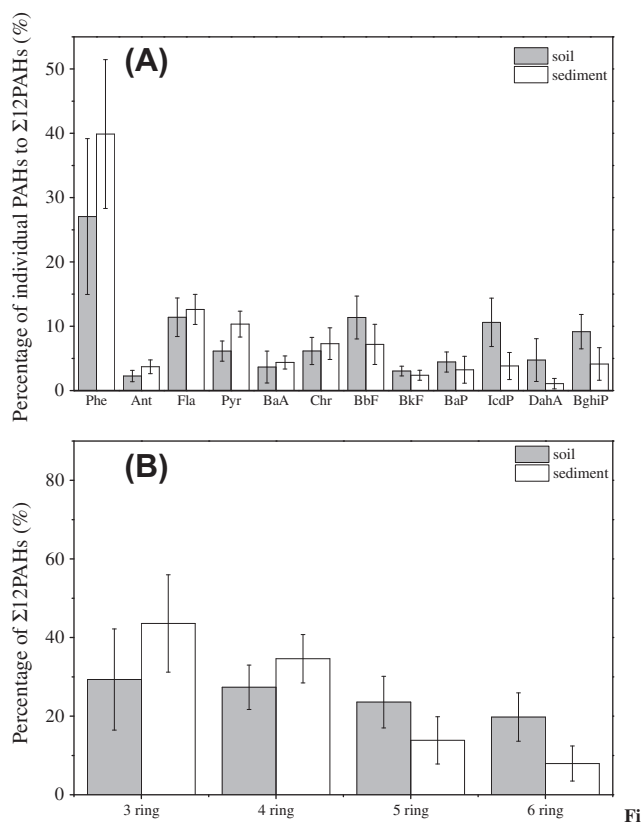


Fig. 2. Comparisons of distribution patterns of (A) the 12 individual EPA-PAHs (polycyclic aromatic hydrocarbons) and, (B) 3-, 4-, 5-, and 6-ring PAHs in the surface sediments of the Wei River (white color) and its surrounding topsoils (gray color) of the Guanzhong Plain. Error bars represent standard deviations of all soil ($N = 22$) and sediment samples ($N = 32$).

3.4. Association of PAH with TOC, soot, and char

The $\Sigma 12\text{PAHs}$ concentrations in GZP soils correlated significantly with the total pyrogenic carbon (EC), and soot, but not with TOC and char (Table 2). Soot showed the strongest correlation with the $\Sigma 12\text{PAHs}$ concentrations in GZP soils ($r = 0.66$, $p = 0.0009$), suggesting that soot was an important sorbent of PAHs (Fig. 3, Table 2, Table S5-1, SI). Furthermore, in soils EC and soot showed significant correlations with HMW-PAHs, as well as 4-, 5- and 6-ring PAHs (Table 2). This underlines that in the studied soils EC and EC fractions were more important sorbents for PAHs than the soil organic matter. This is also in line with the conclusion from previous studies that the spatial distribution of PAHs is mainly dictated by interactions with EC and EC is considered a ‘super-sorbent’ and responsible for a large part of the sorption/partitioning of some hydrophobic organic compounds in soils and sediments (Cornelissen et al., 2006; Oen et al., 2006).

Associations between PAHs and pyrogenic carbon fractions are attributable to co-emission, co-transport, co-deposition and post-depositional sorption of PAHs in soils and sediments to these materials. There are several possible reasons for the stronger correlations of soot concentrations with $\Sigma 12\text{PAHs}$ concentrations (Fig. 3). Firstly, although the surfaces of both char and soot are porous, soot has a much higher surface to volume ratio than char (Schmidt and Noack, 2000). As a result, soot has a strong affinity to non-polar substances such as PAHs, dioxins, and furans (Gustafsson and Gschwend, 1997). Jones et al. (2005) proposed that soot contains oxygen in its surface layer, enhancing its hydrophilic character, and increases its sorption capacity for many

Table 2
Correlations coefficients of the concentrations of different carbon fractions with those of PAHs in the surface sediments of the Wei River ($N = 32$) and surrounding soils of the Guanzhong Plain ($N = 22$). All data except char/soot and EC/TOC ratios were log-transformed.

		Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	IcdP	DahA	BghiP	Σ 12PAHs	LMW ^a	HMW ^b	3ring ^c	4ring ^d	5ring ^e	6ring ^f
<i>Sediment</i>																				
TOC	Pearson correlation	0.93	0.88	0.91	0.90	0.90	0.91	0.85	0.87	0.84	0.60	0.69	0.55	0.93	0.93	0.89	0.93	0.92	0.85	0.58
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OC	Pearson correlation	0.92	0.87	0.91	0.90	0.90	0.91	0.85	0.87	0.85	0.60	0.68	0.55	0.92	0.92	0.89	0.92	0.92	0.85	0.58
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EC	Pearson correlation	0.89	0.79	0.80	0.79	0.80	0.81	0.75	0.76	0.73	0.62	0.63	0.56	0.84	0.88	0.79	0.88	0.80	0.75	0.59
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Char	Pearson correlation	0.73	0.60	0.60	0.59	0.61	0.64	0.56	0.56	0.54	0.58	0.49	0.52	0.65	0.73	0.60	0.73	0.61	0.56	0.55
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soot	Pearson correlation	0.92	0.89	0.91	0.90	0.89	0.89	0.84	0.88	0.84	0.59	0.71	0.54	0.92	0.92	0.88	0.92	0.90	0.85	0.57
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Char/soot	Pearson correlation	0.20	0.05	0.01	0.00	0.03	0.07	0.02	-0.02	-0.02	0.18	0.02	0.16	0.07	0.18	0.02	0.18	0.03	0.00	0.16
	<i>p</i> value (2-tailed)	0.28	0.78	0.97	0.98	0.87	0.70	0.92	0.91	0.91	0.34	0.93	0.39	0.70	0.31	0.90	0.31	0.89	0.98	0.37
EC/TOC	Pearson correlation	-0.79	-0.76	-0.85	-0.84	-0.84	-0.85	-0.78	-0.81	-0.80	-0.53	-0.61	-0.48	-0.83	-0.80	-0.82	-0.80	-0.85	-0.79	-0.51
	<i>p</i> value (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Soil</i>																				
TOC	Pearson correlation	0.15	0.14	0.42	0.23	0.28	0.24	0.42	0.36	0.40	<u>0.53</u>	0.56	<u>0.50</u>	0.40	0.15	<u>0.44</u>	0.15	0.33	<u>0.46</u>	<u>0.52</u>
	<i>p</i> value (2-tailed)	0.51	0.53	0.05	0.31	0.21	0.28	0.05	0.10	0.06	0.01	0.01	0.02	0.07	0.51	0.04	0.51	0.14	0.03	0.01
OC	Pearson correlation	0.11	0.09	0.40	0.19	0.26	0.21	0.40	0.34	0.40	<u>0.53</u>	0.56	<u>0.49</u>	0.37	0.11	<u>0.43</u>	0.11	0.30	<u>0.45</u>	<u>0.52</u>
	<i>p</i> value (2-tailed)	0.63	0.70	0.07	0.39	0.24	0.35	0.06	0.12	0.07	0.01	0.01	0.02	0.09	0.64	0.05	0.64	0.17	0.04	0.01
EC	Pearson correlation	0.39	<u>0.47</u>	<u>0.51</u>	<u>0.43</u>	0.38	0.40	<u>0.47</u>	0.42	0.39	<u>0.46</u>	<u>0.49</u>	<u>0.45</u>	<u>0.52</u>	0.40	<u>0.49</u>	0.40	<u>0.47</u>	<u>0.48</u>	<u>0.46</u>
	<i>p</i> value (2-tailed)	0.07	0.03	0.01	0.04	0.08	0.07	0.03	0.05	0.08	0.03	0.02	0.04	0.01	0.06	0.02	0.06	0.03	0.02	0.03
Char	Pearson correlation	0.36	0.38	0.40	0.35	0.30	0.30	0.37	0.30	0.30	0.38	0.40	0.35	0.41	0.36	0.38	0.36	0.36	0.38	0.37
	<i>p</i> value (2-tailed)	0.10	0.08	0.07	0.11	0.18	0.18	0.09	0.17	0.18	0.08	0.06	0.11	0.06	0.10	0.08	0.10	0.10	0.08	0.09
Soot	Pearson correlation	0.36	0.57	0.68	0.58	0.55	0.57	0.63	0.62	<u>0.54</u>	0.54	0.59	0.59	0.66	0.40	0.65	0.40	0.65	0.64	0.57
	<i>p</i> value (2-tailed)	0.10	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.07	0.00	0.07	0.00	0.00	0.01
Char/soot	Pearson correlation	0.20	0.11	0.10	0.05	-0.01	0.01	0.08	0.01	0.05	0.15	0.14	0.09	0.11	0.19	0.08	0.19	0.04	0.09	0.12
	<i>p</i> value (2-tailed)	0.36	0.63	0.66	0.84	0.97	0.97	0.74	0.97	0.81	0.50	0.52	0.70	0.64	0.40	0.72	0.40	0.86	0.70	0.59
EC/TOC	Pearson correlation	0.39	<u>0.49</u>	0.06	0.24	0.08	0.21	-0.01	0.03	-0.11	-0.22	-0.20	-0.14	0.13	0.40	-0.02	0.40	0.15	-0.05	-0.19
	<i>p</i> value (2-tailed)	0.08	0.02	0.79	0.28	0.71	0.35	0.96	0.90	0.63	0.32	0.37	0.52	0.58	0.06	0.94	0.06	0.52	0.82	0.40

Bold indicates correlation significance at the 0.01 level (2-tailed).

Underline indicates correlation significance at the 0.05 level (2-tailed).

^a LMW = low molecular weight PAHs.

^b HMW = high molecular weight PAHs.

^c 3-ring = Phe + Ant.

^d 4-ring = Fla + Pyr + BaA + Chr.

^e 5-ring = BbF + BkF + BaP + DahA.

^f 6-ring = IcdP + BghiP.

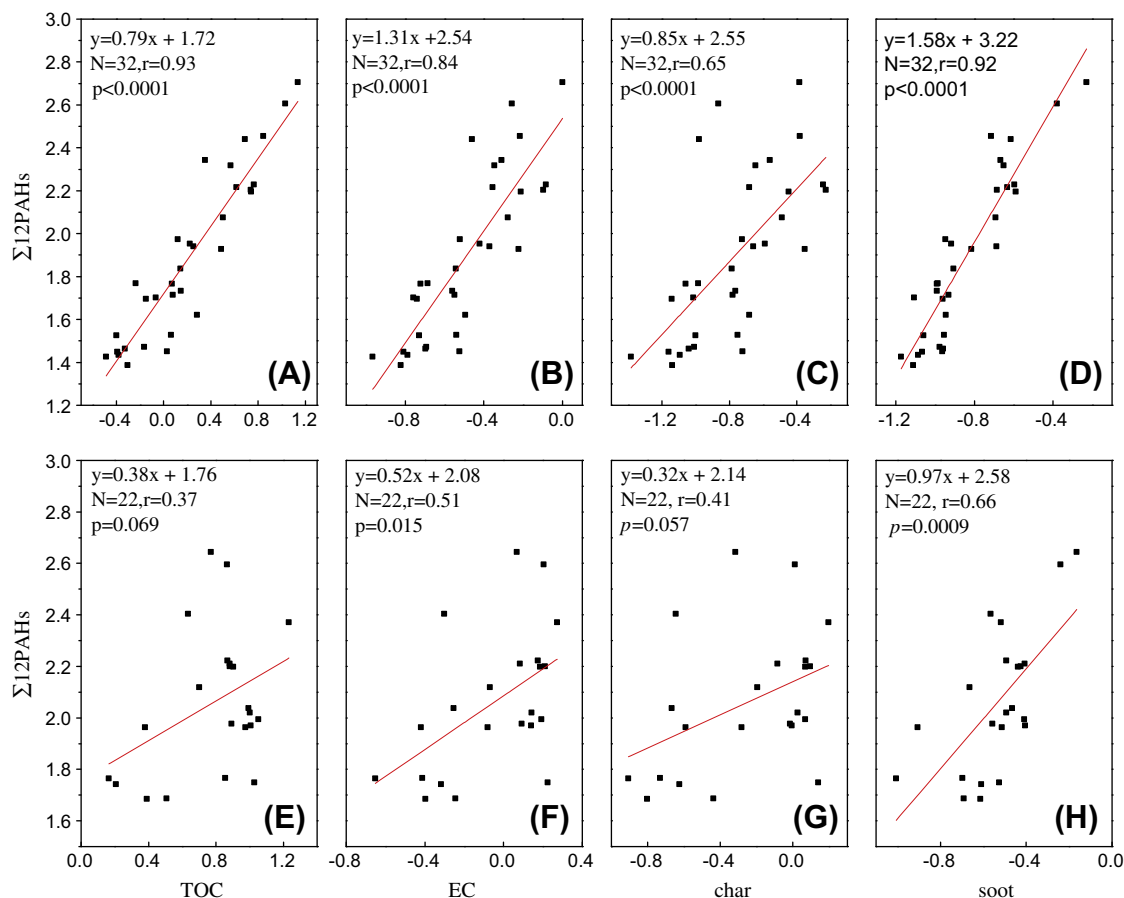


Fig. 3. Relationships between ΣPAHs concentrations (ng g^{-1}) and TOC, EC (sum of char and soot), char and soot concentrations (mg g^{-1}) in GZP surface soils (A–D) and the WR surface bed sediments (E–H). All data were log-transformed. Kolmogorov–Smirnov test (Lilliefors modification not shown) suggests the normal distribution of all these parameters.

compounds. Thus, soot has been frequently proposed as the pool of organic matter in soils with the highest sorption capacity for PAHs (Gustafsson and Gschwend, 1997; Jonker and Koelmans, 2002b; Lima et al., 2005). Secondly, soot has also been suggested to be co-emitted together with PAHs in flames, and the molecular precursors of soot particles are thought to be PAHs with high molecular weights of 500–1000 amu (Richter and Howard, 2000). Char is mainly produced by pyrolysis at low temperature combustion with no gas-to-particle conversion process that consumes PAHs as precursors. In addition, char occurs at a larger particle size, which limits its co-transport with PAHs. Hence, char is less associated with PAHs during co-production/co-emission, and consequently the tendency of char to deposit in situ may also result in a low association with PAHs (Table 2). In our study, HMW-PAHs showed a stronger association with soot than LMW-PAHs for soil samples (Table 2). This may have two reasons. Firstly, HMW-PAHs as molecular precursor of soot (Richter and Howard, 2000) can co-emitted with soot into the atmosphere, and are likely to be co-deposited to soils by particle deposition. Secondly, LMW-PAHs are generally semi-volatile components and more likely enter the soil environment by partitioning from the gas phase, and thus are less associated with atmospheric soot particles.

Unlike in soils, all carbon fractions including TOC are well correlated with PAHs in the sediments, in which soot, OC and TOC concentrations showed the strongest correlations with those of $\Sigma 12\text{PAHs}$ ($r = 0.92\text{--}0.93$, $p < 0.0001$). Significant correlations between each sorbent and all ring sizes of PAHs were also observed. The strongest correlation existed for 3-ring PAHs and the weakest correlation was with the 6-ring PAHs. Compared with TOC, EC and

soot, char had a weaker correlation with $\Sigma 12\text{PAHs}$ ($r = 0.65$, Table 2, Table S5-2, SI), as well as those of with the LMW- and HMW-PAHs. These results were similar to those observed in soils, which confirms the stronger control of PAH retention in soils and sediments by soot than by char. The combined principal component analysis (PCA) (Table S5-3, SI) for all sediment and soil data also supports that soot surpasses char as the main PAH carrier in the study area.

The closer associations between PAHs and different carbon fractions in sediments than in soils may be attributable to the different mechanisms controlling PAHs sorption in soils and sediments. Nam et al. (2008b) suggested that the associations between EC and PAHs are more important in close proximity to combustion sources, while TOC–PAH partitioning is more important in more remote sites. As erosion processes and, especially sedimentation processes in the river bed can result in the same effects as those occurring in the long range atmospheric transport process, it can be expected that the dominant mechanism of sorption of PAHs to organic matter in sediments is absorption. In addition, particle size fractionation may occur during the sedimentation processes as reported by Secco et al. (2005). TOC has been observed to be concentrated in fine particles in the sediments of this river (Han et al., 2012) and has been shown to retain heavy metals in the WR in an absorption-like process. PAHs in sediments mainly originate from wastewater discharges, urban runoff, storm water inflows, soil inputs and water flux mixing with frequent re-suspension and re-transport within the river system, facilitating dynamic redistribution via desorption and absorption of PAHs among the various organic matter pools. However, in soils such a dynamic redistribution is not possible because of the stable contact of PAHs

Table 3

Estimated solid-water distribution coefficient (K_d in kg L^{-1}) and pool-water concentrations of PAHs (C_w in ng L^{-1}) from 3 partitioning models such as TOC, OC + EC, and OC + char + soot model for sediment samples of the Wei River (see Table S2 for octanol–water and carbon normalized partition coefficients used in this study).

	TOC model				OC + EC model				OC + char + soot model			
	Log K_d		C_w		Log K_d		C_w		Log K_d		C_w	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Phe	1.7–3.3	2.4	52.6–278.9	126.6	2.0–3.4	2.6	45.1–144.0	85.1	2.1–3.5	2.8	28.1–103.7	56.2
Ant	2.3–3.9	3.0	1.3–9.2	3.5	2.6–3.9	3.1	0.8–4.9	2.3	2.9–4.1	3.5	0.3–2.3	1.0
Fla	2.3–3.9	3.0	4.3–25.3	10.4	2.6–4.0	3.2	3.2–17.0	7.0	2.5–4.0	3.1	3.3–19.0	8.0
Pyr	2.3–4.0	3.0	3.0–19.5	8.0	2.6–4.0	3.2	2.1–13.0	5.4	2.6–4.0	3.2	2.2–14.4	6.1
BaA	3.1–4.7	3.8	0.2–1.3	0.6	3.4–4.8	3.9	0.2–0.9	0.4	3.5–4.8	4.1	0.1–0.7	0.3
Chr	3.1–4.7	3.8	0.3–2.0	0.9	3.4–4.8	4.0	0.2–1.3	0.6	3.3–4.8	4.0	0.2–1.4	0.7
BbF	3.4–5.0	4.1	0.1–1.3	0.5	3.7–5.1	4.3	0.1–0.9	0.3	3.8–5.1	4.4	0.0–0.8	0.3
BkF	3.4–5.0	4.1	0.0–0.4	0.2	3.7–5.1	4.3	0.0–0.3	0.1	3.9–5.2	4.5	0.0–0.2	0.1
BaP	3.2–4.8	3.9	0.1–1.4	0.4	3.5–4.9	4.1	0.0–0.9	0.2	4.7–5.9	5.3	0.0–0.2	0.0
IcdP	4.1–5.7	4.8	0.0–0.2	0.1	4.5–5.8	5.0	0.0–0.1	0.0	4.0–5.7	4.7	0.0–0.4	0.1
DahA	3.3–5.0	4.0	0.0–0.3	0.1	3.7–5.0	4.2	0.0–0.2	0.1	3.2–4.9	3.9	0.0–0.4	0.1
BghiP	3.6–5.3	4.4	0.0–0.5	0.2	4.0–5.4	4.6	0.0–0.3	0.1	4.2–5.4	4.7	0.0–0.2	0.1
Σ 12PAHs			70.4–313.6	151.2			54.8–165.5	101.7			36.7–124.0	73.0

with various carbon pools. LMW PAHs released from soot can enter into the gas phase quickly, leaving less/no chance of TOC to adsorb PAHs (Nam et al., 2008a,b). This also partially explains the high HMW/LMW ratios in soils.

3.5. Ecological risk associated with PAH contamination

To assess the possible toxicological effect of PAHs in sediments we compared our measured concentrations to a number of toxicological thresholds (above which adverse biological effects are expected) as defined in various sediment quality guidelines (SQGs, Table S2, SI): effects range-low (ERL), effects range-median (ERM), threshold effects levels (TEL), probable effects levels (PEL), and threshold (TEC), median (MEC) and extreme (EEC) effect concentrations (Long et al., 1995; MacDonald et al., 1996; Swartz, 1999). The results (Table S6, see SI for the evaluation method) indicate that all PAHs and their individual concentrations, except for the cases of Phe and DahA, were lower than the toxicologically relevant threshold limits. This suggests that occurrences of adverse biological effects due to PAHs contamination in the WR are very low. Estimated pore-water concentrations (C_w) in the WR (Table 3) calculated from 3 different partitioning models (TOC, OC + EC, and OC + char + soot model) were also lower than the proposed chronic and acute toxicity values (Neff et al., 2005) (Table S2), further confirming low toxicity occurring in the water system.

Comparison of the estimated solid-water distribution coefficient, K_d , K'_d and K''_d calculated based on TOC, OC + EC, and OC + char + soot partitioning model, respectively, (Table 3) showed that K''_d were the highest while K_d were the lowest for all PAHs from the sediment samples of the WR. This is also the case for all individual PAHs from different sampling sites (Fig. S4A, using Phe as an example). Accordingly, the calculated pool-water concentrations of PAHs from the three different model, C_w , C'_w and C''_w , showed that C_w was the highest while C''_w was the lowest. Again this is the case for all samples from different sediment sampling sites. This suggested that the occurrence of EC, and especially its different fractions of char and soot in sediments can cause more PAHs in solid due to the high sorption capacity of EC or soot to PAHs. Therefore, lower dissolved PAH concentrations in water and less biotic effects to aquatic organisms would be expected with the increase in EC and soot concentrations in sediments.

4. Conclusions

The association of PAHs with two fractions of EC (char and soot) was for the first time investigated in real environmental matrices from both sediments and soils. Stronger relationship of PAHs with

soot than with char in both compartments in a semi-arid region of north China confirms the stronger sorption capacity for PAHs of soot than char. This study highlights the importance to differentiate between char and soot, with formation from combustion pyrolysis and gas-to-particle conversion, respectively, for our understanding of the environmental transport and fate of PAHs. It also confirms the suitability of measuring char and soot using the IMPROVE thermal optical method, which was previously only used for aerosol samples. The formation mechanisms of soot developing from high molecular PAHs as precursor and the specific physico-chemical properties such as the sub-micron size and high surface areas of soot may contribute to the stronger association of PAHs with soot. Closer associations between PAHs and different carbon fractions in sediments than those in soils can be attributed to the different mechanisms controlling PAHs sorption in soils and sediments. Absorption of PAHs in sediments due to water flux mixing with frequent re-suspension and re-transport within the river system results in high correlations of PAHs with all carbon fractions, while adsorption in soils leads to close relations of PAHs with soot or joint deposition of soot and soot-adsorbed PAHs, while there are no relations with char. More EC, especially soot in sediments may lead to low dissolved PAH concentrations in water and less biotic effects to aquatic organisms. Future studies should be extended to more environmental matrices such as aerosols to test the different relationships of PAHs with char and soot.

Acknowledgement

This study was supported by the West Light Foundation of Chinese Academy of Sciences, the NSF of China (41073102, 41273140), the National Basic Research Program of China (2010CB833403, 2013CB955900), the Chinese Academy of Sciences (XDA05100402, KZZD-EW-04), the State Key Laboratory of Loess & Quaternary Geology (LQ0701), the Key Project of the National Research Program of China (2012BAH31B03), and the Swiss National Science Foundation (SNF 200021_131938/1).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.02.021>.

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