



Black carbon in soils from different land use areas of Shanghai, China: Level, sources and relationship with polycyclic aromatic hydrocarbons



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ABSTRACT

Black carbon (BC) in soils plays a key role of carrying hydrophobic pollutants like polycyclic aromatic hydrocarbons (PAHs). However, little is known about the spatial distribution, sources of BC and its relationship with PAHs in urban soils. We studied BC, total organic carbon (TOC) and PAHs concurrently in 77 soils collected from downtown area, suburban and rural area and industrial area of Shanghai, China. BC was determined by both chemical oxidation (dichromate oxidation, BC_{Cr}) and chemo-thermal oxidation (CTO-375, BC_{CTO}). BC sources were identified qualitatively by BC/TOC concentration ratios and BC-cogenerated high molecular weight (HMW) PAH isomer ratios and quantitatively by principal component analysis followed by multiple linear regression (PCA-MLR). Results showed that BC_{Cr} concentration (4.65 g/kg on average) was significantly higher than BC_{CTO} (1.91 g/kg on average) in Shanghai soils. BC_{Cr} concentrations in industrial area were significantly higher than those in other two. Stronger correlation was found between PAHs and TOC, BC_{Cr} than that between PAHs and BC_{CTO} , which indicates the possibility of PAHs being carried by charcoal and other organic matters thus negating its exclusive dependence on soot. Charcoal was therefore suggested to be taken into account in studies of BC and its sorption of PAHs. BC/TOC ratios showed a mixed source of biomass burning and fossil fuel combustion. PCA scores of BC-cogenerated HMW PAHs isomer ratios in potential sources and soil samples clearly demonstrated that sources of BC in urban soils may fall into two categories: coal and biomass combustion, and traffic (oil combustion and tire wear). PCA-MLR of HMW PAHs concentrations in soil samples indicated that coal and oil combustion had the largest contribution to BC in urban soils while tire wear and biomass combustion were important in downtown and rural area, respectively, which indicated they were main sources of HMW PAHs and presumably of BC.

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1. Introduction

Black carbon (BC) is the carbonaceous residue (e.g., charcoal) or condensate (e.g., soot) generated from incomplete combustion of fossil fuels and biomass. A quantity of 62–294Tg BC were produced per year, of which 80–90% were deposited directly in soils (Druffel, 2004) and the rest were emitted into atmosphere followed by further deposition after transportation. BC in soil may adsorb hydrophobic organic compounds (HOCs) and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs) (Koelmans et al., 2006) and by carrying toxic pollutants, it results in potential human health risk.

BC in agricultural soil, forest soil and grassland soil has been widely investigated and studied in last decades (Skjemstad et al., 2002; Rumpel et al., 2006; Czimczik et al., 2003; Yin et al., 2009;

Ansley et al., 2006; Dai et al., 2005). However, little was known about BC in urban soil especially in metropolises. In an ancient city of China, He and Zhang (2009) investigated BC concentrations in soil profiles from an ancient residential area (0.91 g/kg on average) and a present industrial area (8.62 g/kg on average) and found that BC in the surface layer of soils was mainly from diesel emission while in cultural layers BC was from historical coal use. A study of soot BC in soils from Phoenix, Arizona showed that BC concentrations ranged from 0.2 to 5.4 g/kg and were higher in urban soils than in desert or agricultural soils (Hamilton and Hartnett, 2013). Similarly, concentrations of BC from urban roadside topsoil (a median of 21.8 g/kg) were significantly higher than local background value (3.8 g/kg) in Xuzhou, China (Wang, 2010). Given its complexity of sources and potential risk to residents' health, BC in urban soil should receive more attentions.

BC in soil can be determined by several methods (Hammes et al., 2007). Thermal oxidation (e.g. CTO-375) and chemical oxidation (e.g. Cr_2O_7 oxidation) were representative methods to isolate the most resistant fractions of BC continuum (Masiello, 2004). As

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each method detected different parts of BC continuum, the results varied widely. BC concentrations varied by a factor of up to 500 when different analytic methods were applied to the same soil sample (Schmidt et al., 2001). To eliminate such uncertainty and enhance the reliability of interpretation, method comparison was used in a method study (Roth et al., 2012) as well as environmental monitors (Brändli et al., 2009; Sánchez-García et al., 2013).

PAH was regarded as the precursor of soot, a type of BC, generated during incomplete combustion (Vander Wal et al., 2007). The environmental behaviors and bioavailability of PAHs were strongly affected by BC (Gustafsson et al., 1997; Koelmans et al., 2006). However, among the numerous studies of PAHs in urban soils, few took BC into account. Liu et al. (2011) reported a significant correlation between concentrations of BC and PAHs in the urban area in Beijing, China and there was no such significant correlation found in the rural mountainous area. Ray et al. (2012) observed significant correlations between PAHs and BC in Delhi, India and suggested similar sources of PAHs and BC. Furthermore, most researches of BC and PAHs analyzed BC by method CTO-375 (Liu et al., 2011; Mai et al., 2003). It is soot that the method isolates from BC continuum, while charcoal is oxidized during the analytical procedure. Neglect of charcoal may result in incomprehensive understanding about the relationship between BC and PAHs, since studies have proved that biochar, a type of charcoal, may carry considerable amount of PAHs (Hale et al., 2012; Hilber et al., 2012; Keiluweit et al., 2012).

BC in urban soil may come from both natural and anthropogenic burning of biomass and fossil fuels. Source identification of BC in urban soil is challenging but important. Several methods have been employed to identify the source of BC in soils and sediments, including the use of ^{14}C analysis, ^{13}C analysis, BC/OC ratio, PAH isomer ratio, particle size, morphological characteristics and benzene polycarboxylic acid (BPCA) ratio (Wang, 2012). Despite the higher

reliability of radiocarbon and isotopic analysis, other methods were more widely used for their credibility and less cost. BC/OC ratio method was based on the fact that simultaneous emission of BC and other organic compounds from combustion caused certain BC/OC ratio in aerosol (Gatari and Boman, 2003; Novakov et al., 2000). The ratio was later successfully applied for BC source identification in urban soil and forest soil (Liu et al., 2011; Yin et al., 2009). Some PAH especially high molecular weight (HMW) PAH isomer ratios were believed to reflect combustion sources for the isomer signatures remain when the compounds enter environment (Dickhut et al., 2000). The HMW PAH isomer ratios were used as indicators of sources of PAHs and cogenerated BC during combustion (Mittra et al., 2002).

This paper (i) studies the level and distribution of BC analyzed by two different methods; (ii) identifies BC sources by various methods; and (iii) shows the relationship between BC and PAHs in metropolitan soils under different land use categories.

2. Materials and methods

2.1. Study area and soil sampling

Shanghai is the biggest city and one of the most important industrial centers of China. According to Shanghai Statistical Yearbook (Shanghai Bureau of Statistics, 2012), Shanghai had a population of 23.5 million with a population density of 3702 per square kilometer in 2011. In the same year, Shanghai's vehicle parc reached 3.29 million units and its energy end-use consisted of 9.58 million tons of raw coal, 7.06 million tons of coke, 10.06 million tons of gasoline and diesel oil and 12.46 million tons of other petroleum products.

Soil samples were collected in 2012 (Fig. 1). Seventy-seven sampling sites covered three kinds of land use in Shanghai: downtown

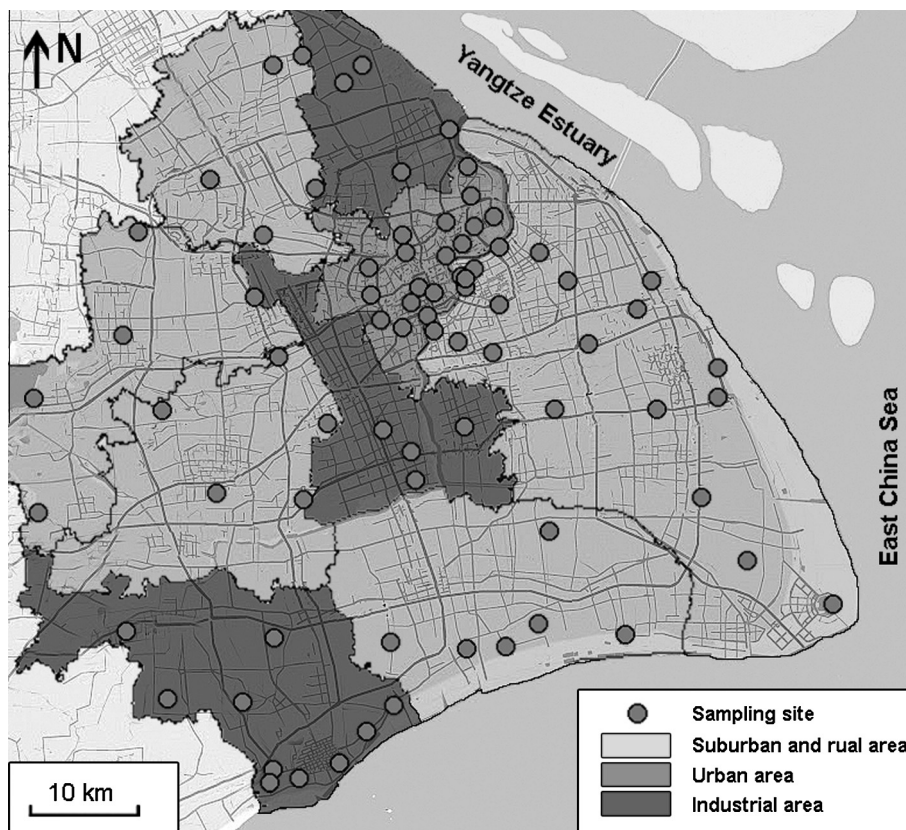


Fig. 1. Schematic map of study area and sampling sites in Shanghai, China.

area, including nine districts characterized by dense population and heavy traffic; suburban and rural area, including five districts where low density of residential areas were connected by highways which passed farmlands; and industrial areas, represented by three districts where steel mills, equipment manufactories, power plants, petrochemical and coal chemical plants were densely located.

At each site, soils (0–10 cm) were collected with a stainless steel shovel from three to five profiles selected randomly in a 10 m * 10 m square and then mixed as a single composite sample. After being transferred to laboratory, soils were air-dried in a separate dark storage room followed by a hand-picked cleanup to remove stones and roots. Samples were then sieved to pass a 1 mm sieve-mesh and stored at –20 °C.

2.2. Chemical analyses

2.2.1. Black carbon (BC) and total organic carbon (TOC)

BC was determined by method CTO-375 (BC_{CTO}) and Cr₂O₇ oxidation (BC_{Cr}). BC_{CTO} was determined based on Gustafsson et al. (2001). Briefly, acidification of 1 M HCl was applied repeatedly to remove carbonate before oxidation at 375 °C for 24 h. According to the calculation of sample mass and inner volume of furnace, the oxygen was excess so that charring was believed not to have happened.

BC_{Cr} was determined based on Lim and Cachier (1996) with modification. Approximately 0.8 g oven-dried soil was added to a centrifugal tube. After the soil was wetted with distilled water, 1 M HCl was added into the tube twice at an interval of 1 h. Then the tube was dried at 60 °C in an oven. The acidification was repeated until effervescence upon acid addition ceased. The dried remains was spiked with 15 mL 0.1 M K₂Cr₂O₇:2 M H₂SO₄ (1:1, v:v) and the reaction lasted 60 h at 55 °C. During the reaction, K₂Cr₂O₇ was added according to the color change to keep the oxidant in excess, and distilled water was also added several times to keep the volume of solution. The organic carbon content in the residue was regarded as BC.

The BC contents of the residues which survived after thermal and chemical oxidation were determined with a CHNS elemental analyzer (Vario MICRO cube, Elementar Inc., Germany). Soil TOC was determined by wet oxidation under heating with dichromate-sulfuric acid followed by titration with ferrous sulfate (Bao, 2000).

2.2.2. PAHs

Soil samples were Soxhlet-extracted with acetone-dichloromethane (1:1, v/v) for 24 h at 65 °C (U.S. EPA Method 3540C, 1996). The extracts were then concentrated, exchanged to hexane and cleaned-up over amorphous sodium sulfate-alumina-silica gel columns. The eluates were then concentrated and solvent exchanged. The concentrated extracts were analyzed for 16 EPA priority PAHs by GC/MS (Agilent 7890A/5975C).

The GC equipped with a DB-5 polysiloxane polymer column (30 m * 250 μm * 0.25 μm) and helium as the carrier gas. The oven temperature was held at 55 °C for 2 min, heated to 280 °C at a rate

of 20 °C/min and held for 4 min, and then heated to 310 °C at a rate of 10 °C/min and held for 5 min. The injection volume was 1 μL in splitless mode.

The experimental procedure was tested for recoveries by analyzing spiked blanks with 16 PAHs standards, and the recoveries of 16 PAHs ranged from 70% to 110%. A deuterated PAH mixture standard solution containing d₈-naphthalene, d₁₀-acenaphthene, d₁₀-phenanthrene, d₁₂-chrysene and d₁₂-perylene each at a concentration of 10 mg/L was added to each sample prior to extraction. All samples were determined in duplicate. The relative standard deviations (RSDs) and relative average deviations for each compound were on average 10.6% and 7.5%, respectively. Two blanks and two standards (a mixture of 16 EPA PAHs and 5 deuterated PAHs) were carried out every 10 samples. Furthermore, method blanks were determined for any background contamination. The blanks were always negligible. All samples were corrected for both blanks and recoveries.

2.3. Statistical analysis

Relative standard deviations and relative average deviations were calculated using Excel 2003. One-way analysis of variance (ANOVA) was conducted using OriginPro 7, and the means were considered significantly different for *p*-value was less than 0.05. Correlation analysis, principal component analysis (PCA) and multiple linear regression (MLR) were performed using SPSS 19.0 (SPSS Inc., USA). The correlation coefficients were starred when the correlation was statistically significant (one asterisk for 0.01 ≤ *p* < 0.05 and two for *p* < 0.01).

3. Results and discussion

3.1. BC concentrations and distribution in Shanghai soils

Concentrations of BC_{Cr} and BC_{CTO} in Shanghai soils on average are 4.65 ± 2.49 g/kg and 1.91 ± 0.79 g/kg, respectively (Table 1). The mean of BC_{Cr} concentrations in Shanghai soils is comparable to that of campus soil (4.12 g/kg) (Table 2), lower than in roadside soil (13.67 g/kg) but higher than in residential and suburb soils (1.60–1.85 g/kg) of Nanjing city (He and Zhang, 2006). BC_{CTO} concentration in Shanghai soils is comparable to that of Phoenix metropolitan area (Hamilton and Hartnett, 2013), and lower than that of Beijing (Liu et al., 2011) and Xuzhou (Wang, 2010).

The BC/TOC ratios on average are 0.35 ± 0.10 and 0.15 ± 0.05 for BC_{Cr} and BC_{CTO}, respectively. Ratio of BC_{Cr}/TOC is generally higher in Shanghai soil than in Nanjing soils (0.12–0.22) except for roadside soil (He and Zhang, 2006). BC_{CTO}/TOC is lower in Shanghai soil than in Beijing (0.12–0.37, Liu et al., 2011) and Phoenix (0.20–0.29, Hamilton and Hartnett, 2013).

Although the means of BC concentration (BC_{Cr}) is significantly different (*p* < 0.05) among the three kinds of land use categories, there is no significant difference among BC/TOC ratios. The unexpected low BC/TOC ratios in industrial area soils may be due to the high level of TOC concentrations in this area.

Table 1
Concentrations of TOC, BC_{Cr} and BC_{CTO} in soils and TN (total nitrogen) contents in components after thermal and chemical oxidation of soils from different land use areas of Shanghai.

Samples	TOC (%)	BC _{Cr} (g/kg)	BC _{Cr} /TOC	BC _{CTO} (g/kg)	BC _{CTO} /TOC	TN in components after chemical oxidation (g/kg)	TN in components after thermal oxidation (g/kg)
Downtown area (n = 24)	1.25 ± 0.52 ^a	4.36 ± 1.56	0.37 ± 0.11	1.93 ± 0.60	0.17 ± 0.05	0.36 ± 0.10	0.11 ± 0.05
Suburban and rural area (n = 34)	1.29 ± 0.48	4.17 ± 1.64	0.33 ± 0.07	1.80 ± 0.69	0.15 ± 0.05	0.40 ± 0.13	0.12 ± 0.05
Industrial area (n = 19)	1.54 ± 0.64	5.89 ± 4.01	0.37 ± 0.12	2.06 ± 1.12	0.14 ± 0.05	0.43 ± 0.13	0.14 ± 0.05
Total (n = 77)	1.34 ± 0.54	4.65 ± 2.49	0.35 ± 0.10	1.91 ± 0.79	0.15 ± 0.05	0.40 ± 0.12	0.13 ± 0.04

^a Mean ± SD.

Table 2

BC concentrations and BC/TOC ratios in soils of different cities with different sampling areas, depths and quantification methods.

Cities	Sampling areas	Depth (cm)	Method	BC (g/kg)	TOC (g/kg)	BC/TOC	References
Nanjing, China	Roadside	10	Cr ₂ O ₇	13.67	29.09	0.45	He and Zhang (2006)
	Campus	10	Cr ₂ O ₇	4.12	17.00	0.22	
	Residential	10	Cr ₂ O ₇	1.85	11.19	0.16	
	Suburb	10	Cr ₂ O ₇	1.60	14.14	0.12	
Phoenix, USA	Urban	10	CTO375	2.5	14	0.27	Hamilton and Hartnett (2013)
	Agricultural	10	CTO375	1.4	9	0.20	
	Desert	10	CTO375	0.8	9	0.29	
Beijing, China	Urban	20	CTO375	5.83	15.2	0.37	Liu et al. (2011)
	Rural plain	20	CTO375	3.31	9.33	0.31	
	Mountain	20	CTO375	3.52	28.5	0.12	
Shanghai, China	Agricultural	10	CTO375	2.73	16.13	0.17	Cheng (2009)
Xuzhou, China	Roadside	10	CTO375	29.2	–	–	Wang (2010)
	Background	10	CTO375	3.8	–	–	
Drammen, Norway	Urban	–	CTO375	5.1	25.0	0.21	Brändli et al. (2008)
Delhi, India	Urban	–	–	0.82	13.6	0.06	Ray et al. (2012)
	Rural	–	–	0.64	11.6	0.06	
	Background	–	–	0.47	8.82	0.05	

The BC_{CTO}/TOC ratios in Shanghai soils are very similar to those in the atmospheric fine particles. The annual average element carbon (EC)/OC ratios in PM_{2.5} at urban and suburban sites in Shanghai ranged from 0.18 to 0.20 (Feng et al., 2009). The main organic component in BC_{CTO}, known as soot carbon, is coincident with EC (Hammes et al., 2007). The similar ratio of coincident carbon suggests strongly that BC in Shanghai soils is closely related to deposited atmospheric particles.

The large-scale deposition of BC particles may be partly responsible for homogeneous distribution of BC/TOC. Carbonaceous particles emitted from agricultural fires in adjacent provinces were proved to have significant impact on the air quality of Shanghai during the harvest season (Li et al., 2010). The immigrated particles, plus the ones emitted from local industrial activities, finally deposit in soils of the city through dry and/or wet deposition. Because of the particles' fine sizes and strong ability to be transported, the deposition happens in a large scale and similar reflection of the influence should be observed in different areas.

3.2. Comparison between BC_{Cr} and BC_{CTO}

The C/N ratio of BC_{CTO} (16.1 ± 7.2) is significantly higher ($p < 0.001$) than that of BC_{Cr} (12.0 ± 5.2), which indicates the difference between substances gained by the two methods. Its higher C/N ratio, suggesting less hetero atoms in the aromatic ring and higher degree of aromatization, characterizes BC_{CTO} as soot. Actually, method CTO-375 was developed to determine soot in environmental matrices (Gustafsson et al., 1997). As to BC_{Cr}, lower C/N ratio suggests it includes not only soot but also other substances with lower degree of aromatization, like charcoal. It has been demonstrated that chemical oxidation (e.g. method Cr₂O₇) separated soot and charcoal from BC continuum (Masiello, 2004; Hammes et al., 2007).

The charcoal detected by BC_{Cr} is, analogous to soot, pyrogenic and stable carbon. Due to its higher microporosity and active surface area, charcoal is even more active than soot (Cornelissen et al., 2005). Therefore, the charcoal should not be ignored in the discussion on stability of soil carbon as well as sorption of organic pollutants like PAHs. We did find a stronger correlation of PAH with BC_{Cr} than with BC_{CTO} (see Section 3.4) in Shanghai soils. Chemical oxidation, and whichever method detecting charcoal like BPCA (Glaser et al., 1998), should be taken into account together with method CTO-375 in the study of BC in soils, especially in those soils with a high level of charcoal.

3.3. PAHs concentrations in Shanghai soils

The concentrations of Σ16 EPA PAHs are 3400.8 ± 4342.0 μg/kg, 1371.8 ± 1348.2 μg/kg and 11582.4 ± 14258.1 μg/kg in downtown, rural and industrial areas, respectively. PAHs in all kinds of land use categories are dominated by HMW PAHs especially PAHs with 4 rings (Fig. 2).

3.4. Correlations between TOC, BC and PAHs

As is shown in Table 3, there are no significant correlations between PAHs with TOC and BCs in downtown area. However, if the extra-high value of PAHs at site 69 is excluded, the correlations of PAHs with both BCs are significantly enhanced ($p < 0.01$ for BC_{Cr} with total and HMW PAHs; $p < 0.05$ for BC_{CTO} with total and HMW PAHs). In suburban and rural area, there are significant correlations between the three kinds of organic carbons and total PAHs as well as HMW PAHs, while LWM PAHs show weak correlations with TOC and BCs. The situation in industrial area is similar to suburban and rural area, except that 3-ring PAHs show significant correlations with TOC and BC_{Cr} while 6-ring PAHs get low values in correlations with TOC and BCs.

Generally, volatile naphthalene shows a significant correlation with TOC rather than with BCs, which is coincident with the study in Beijing (Liu et al., 2011). However, it is surprising that 6-ring PAHs show no significant correlations with BCs in industrial area. TOC shows significant correlations with all PAHs. Although it loses two asterisks in the correlations with 2-ring and 6-ring PAHs (Table 3), BC_{Cr} is better than BC_{CTO} which loses other two asterisks in 3-ring and LWM PAHs. Therefore, not all PAHs are associated

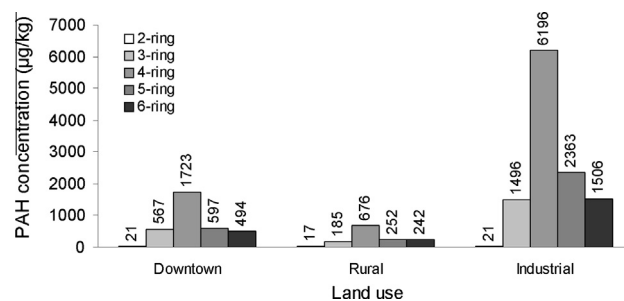


Fig. 2. PAHs components in different land use areas of Shanghai.

Table 3
Linear correlation coefficients (r) between TOC, BC and PAHs.

	Σ16PAHs	LMW ^a	HMW ^b	2-Ring	3-Ring	4-Ring	5-Ring	6-Ring
<i>Downtown area (n = 24)</i>								
TOC	0.089	−0.077	0.133	−0.175	−0.075	0.100	0.218	0.156
BC _{Cr}	0.172	0.014	0.214	−0.150	0.017	0.193	0.266	0.225
BC _{CTO}	0.051	−0.100	0.093	−0.224	−0.098	0.058	0.161	0.147
<i>Suburban and rural area (n = 34)</i>								
TOC	0.380	0.224	0.400*	0.364*	0.194	0.372*	0.400*	0.482**
BC _{Cr}	0.344*	0.118	0.376*	0.214	0.100	0.354*	0.356*	0.464**
BC _{CTO}	0.398*	0.249	0.416**	0.227	0.234	0.392*	0.414**	0.482**
<i>Industrial area (n = 19)</i>								
TOC	0.453*	0.460*	0.444*	0.414*	0.457*	0.371	0.570**	0.203
BC _{Cr}	0.546**	0.404*	0.561**	0.213	0.402*	0.518*	0.731**	0.004
BC _{CTO}	0.402*	0.207	0.428*	0.173	0.205	0.426*	0.585**	−0.205
<i>Total (n = 77)</i>								
TOC	0.353**	0.294**	0.358**	0.238*	0.292**	0.317**	0.419**	0.245*
BC _{Cr}	0.522**	0.378**	0.539**	0.147	0.378**	0.508**	0.655**	0.173
BC _{CTO}	0.319**	0.166	0.341**	0.119	0.165	0.335**	0.441**	−0.017

^a LWM: low molecular weight.

^b HMW: high molecular weight.

* 0.01 ≤ p < 0.05.

** p < 0.01.

with soot (BC_{CTO}). Charcoal and other organic matters may play important roles in carrying PAHs. This conclusion is supported by the findings that considerable PAHs were detected in charcoal. Jonker and Koelmans (2002) determined a concentration of 43.2 mg PAHs/kg in a bark charcoal and Hilber et al. (2012) reported a quantity of 9–335 mg PAHs/kg in biochars. The recalcitrant charcoal and biochar had a long turnover time (Kuhlbusch, 1998; Lehmann et al., 2009) and the PAHs carried and protected by charcoal may still remain in soils when land use changed from agricultural lands and forests to towns and factories.

3.5. BC sources identification

3.5.1. 1BC sources revealed by BC/TOC

BC/TOC concentration ratio has been used to identify the source of carbonaceous aerosols over the Indian Ocean, with a hypothesis that biomass burning and fossil fuel-caused aerosols had a typical BC/TOC ratio of 0.11 and 0.50, respectively (Novakov et al., 2000). Initially used in atmospheric particles researches, the ratio was also successfully applied in urban soils. The BC_{CTO}/TOC ratio was found to have declined from urban soils (0.37) to rural plain soils (0.31) and rural mountainous soils (0.12) in Beijing, which matched the intensity of anthropogenic activities (Liu et al., 2011). Higher values of BC_{Cr}/TOC in roadside soils (0.45) were quantified than those in park, campus, residential area and rural agricultural soils (0.12–0.26) in Nanjing (He and Zhang, 2006). The ratios of BC concentrations measured by method BPCA to TOC were found to have decreased with increasing distance from a major urban highway, from 0.07 in soils next to the highway to 0.03 in the background soil at 500 m distance (Glaser et al., 2005).

Two different BC/TOC ratios (Table 1) in Shanghai soils are gained, depending on analytical methods. Both ratios of BC_{Cr}/TOC (0.35 ± 0.10) and BC_{CTO}/TOC (0.15 ± 0.05) indicate a mixed source of biomass burning and fossil fuel. Because it is finer in size and more easily transported than BC_{Cr}, BC_{CTO} is more like the BC in the initial method. Therefore, BC_{CTO}/TOC is used to identify BC source. However, the proportion of fossil fuel in sources is more than it is assumed to be. Due to the attenuation of native soil organic carbon, biomass burning should result in BC/TOC ratios even smaller than 0.11 in soils. In brief, biomass burning and fossil fuel together contribute BC in Shanghai soils.

3.5.2. BC sources indicated by cogenerated PAH ratios

By using HMW PAH isomer ratios, Mirta et al. (2002) identified BC source in suspended sediments of the Mississippi River based on the fact that BC and PAHs are cogenerated during the combustion process. Therefore, we used Fl/Py, BaA/Chry and InP/BghiP isomer ratios in Shanghai soils to indicate sources of cogenerated BC. Although results from Kim et al. (2009) showed that 4–6 rings PAH ratios changed much less than LWM PAHs ratios 100 h after being exposed to simulated sunlight, PAH ratios were adjusted for photo-degradation in this paper to restore the initial values by using the following equation (Dickhut et al., 2000):

$$\text{Ratio}_{\text{initial}} = \text{Ratio}_{\text{observed}} \exp((\lambda_1 - \lambda_2) * t) \quad (1)$$

where λ_1 and λ_2 are the average photo-degradation rate constants on “gray group” particles (Behymer and Hites, 1988) of the PAH in the numerator and denominator of the same ratio, respectively. t is the duration (hours) of photo-degradation, estimated by assuming an aerosol residence time of 5 days (Warneck, 1999) and 12 h of sunlight per day.

Eight potential sources for BC in Shanghai soils were taken into account (Table 4). Fl/Py, BaA/Chry and InP/BghiP isomer ratios in samples and sources were compressed to two factors by PCA. As is shown in Fig. 3, eight sources naturally fall into four groups: biomass combustion, coal combustion, oil combustion and tire wear. Soil samples spread in a wide range, which suggests mixed sources of BC in urban soils. In all land use areas, PC1 scores of most soil samples surround coal combustion extending to biomass combustion. In downtown and industrial areas, PC2 scores range closer to oil combustion and tire wear; while in suburban and rural area, they cover all the sources which crowd in a narrow range. Therefore, sources of BC in urban soils may fall into two categories: coal and biomass combustion, and traffic (oil combustion and tire wear).

3.5.3. BC sources apportioned by HMW PAH concentrations

Concentrations of BC-cogenerated HMW PAHs in soil samples of each area were used for PCA with varimax rotation. Rotated component matrix and percentage variance explained are shown in Table 5. Four highest values in each column (component) are highlighted.

Organic matters in environments always have multiple sources (e.g. Górká et al., 2014) and some factors from PCA may indicate more than one possible cause (Ravindra et al., 2008). In downtown area,

Table 4
BC-cogenerated HMW PAH isomer ratios in potential sources and soils of Shanghai.

	Fl/Py ^a	BaA/Chry	InP/BghiP
<i>Combustion</i>			
Brown coal	1.25 ^b	0.68	0.86
Bituminous coal	1.13	0.52	0.92
Gasoline	0.79	0.56	0.19
Diesel oil	0.64	0.61	0.54
Wood	1.04	0.85	1.78
Grass	1.38	0.85	1.38
<i>Tire wear</i>			
Summer tire	0.27	0.23	0.17
Winter tire	0.37	0.09	0.16
<i>Soil samples of Shanghai</i>			
Downtown area (n = 24)	1.04 ± 0.27 ^c	1.12 ± 0.19	0.95 ± 0.15
Suburban and rural area (n = 34)	1.27 ± 0.40	0.94 ± 0.21	0.95 ± 0.13
Industrial area (n = 19)	1.20 ± 0.22	0.98 ± 0.34	0.87 ± 0.11
Total	1.18 ± 0.33	1.01 ± 0.25	0.93 ± 0.13

^a Fl: Fluoranthene; Py: Pyrene; BaA: Benz[a]Anthracene; Chry: Chrysene; InP: Indeno[123-cd]pyrene; BghiP: Benzo[ghi]perylene.

^b All ratios of sources were calculated from Yunker et al. (2002) except for brown coal which was from Grimmer et al. (1983) and tires which were from Glaser et al. (2005).

^c PAH isomer ratios (mean ± SD) of soils were adjusted for photo-degradation.

the first component has high correlations with 4–6 ring PAHs. This component is assigned to a combined source (oil and coal combustions). BkF was identified as a marker of diesel emissions

(Venkataraman et al., 1994). BghiP plus BaP was found to be accumulated in traffic tunnels (Larsen and Baker, 2003). InP was also found in vehicle emissions (May and Wise, 1984). High loadings of Py, BaA, Chry are also found in this factor. Py, BaA, Chry were reported as indicators of coal combustion (Simcik et al., 1999). The second component is highly loaded in Fl, BaA, BaP and InP. This component is also indicative of a mix of oil and coal emissions. The third component is predominated by Py, BaA, Chry and BghiP. This component is attributed to tire wear. Abundant Py, Chry and BghiP were found in tire particles (Glaser et al., 2005; Boonyatumanond et al., 2007).

In suburban and rural area, components are interpreted as sources by the same rules as above except for the second component. The second component has high loadings on Fl, Py, Bb/kF and BaP which were believed to relate to biomass and coal combustions (Larsen and Baker, 2003). Therefore, this component is selected to represent biomass and coal combustions.

In industrial area, coal combustion and oil combustion are appointed for component 1 and 2, respectively.

Multiple linear regression (MLR) analysis is performed with PCA scores as independent variables and ΣHMW-PAHs as dependent variable in each area. Excellent correlations ($r^2 > 0.99$, $p < 0.001$) are found between the MLR equation-simulated concentrations of ΣHMW-PAHs and measured values in all areas. The relative contribution of each source to total sources is calculated on the ratio of each component coefficient to the sum coefficients in the equation (Table 5).

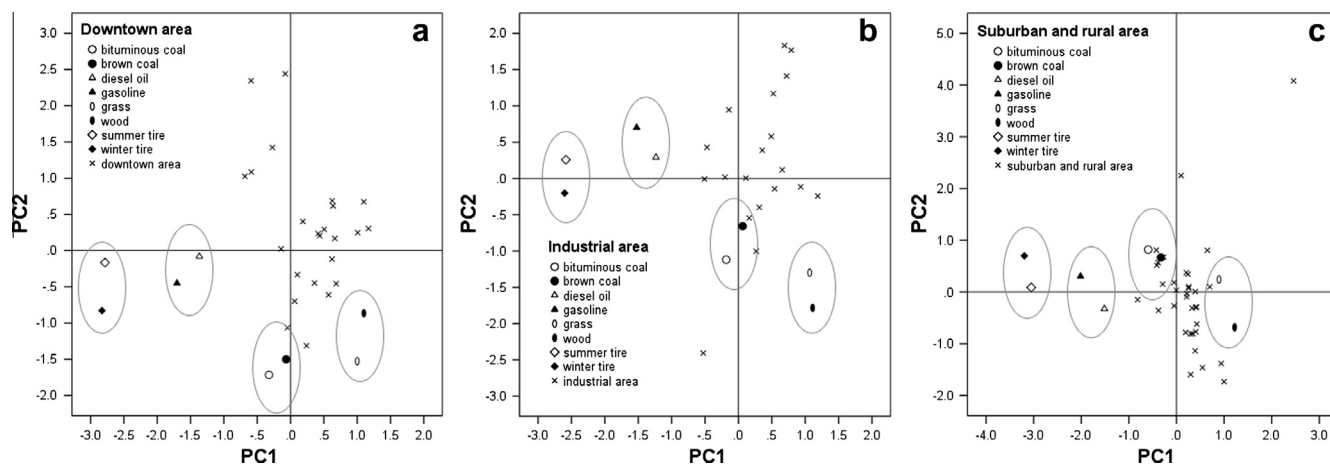


Fig. 3. Principal components analysis of BC-cogenerated HMW PAHs isomer ratios of potential sources and soils in Shanghai ((a) downtown area; (b) industrial area; (c) suburban and rural area). Eight potential sources naturally fall into four groups: biomass combustion, coal combustion, oil combustion and tire wear. The ratios of soils were adjusted for photo-degradation.

Table 5
Component matrix identified by principal component analyses of soils in different land use areas of Shanghai.

Component ^a	Downtown area			Suburban and rural area				Industrial area	
	1	2	3	1	2	3	4	1	2
Variance (%)	38.7	34.6	25.1	36.5	33.3	15.7	13.1	50.7	43.1
Fl	.431	.808	.399	.359	.854	.230	.282	.705	.604
Py	.543	.547	.633	.407	.808	.369	.198	.694	.616
BaA	.530	.622	.562	.532	.398	.699	.255	.940	-.074
Chry	.570	.545	.605	.501	.441	.466	.576	.876	.408
Bb/kF	.654	.569	.484	.538	.605	.222	.536	.966	.238
BaP	.668	.615	.397	.647	.591	.345	.301	.964	.142
InP	.648	.615	.414	.733	.448	.332	.373	.158	.983
DahA	.805	.425	.412	.797	.374	.380	.222	.167	.979
BghiP	.672	.468	.536	.758	.460	.309	.319	.142	.980
Source ^b	O&C	O&C	T	O	B&C	C	T	C	O
Contribution (%)	33.4	36.4	30.3	27.5	35.7	19.1	17.7	62.4	37.6

Bold values are the four highest values in each column (component).

^a Components with eigenvalue more than 1 were selected.

^b B: biomass combustion; C: coal combustion; O: oil combustion; T: tire wear.

Generally, coal and oil combustion have the highest contribution in urban soils while traffic (tire wear) and biomass combustion are found important in downtown and rural area, respectively, which indicates they are main sources of HMW PAHs and presumably BC.

4. Conclusions

BC_{Cr} had significantly higher concentrations (4.65 ± 2.49 g/kg) than BC_{CTO} (1.91 ± 0.79 g/kg) in Shanghai soils. BC_{Cr} concentrations in industrial area soils were higher than those in downtown area while the lowest level was found in suburban and rural area. Relatively lower C/N ratio in BC_{Cr} indicated that the components of BC_{Cr} included not only soot but also less aromatized charcoal. The stronger correlations of PAHs with BC_{Cr} than with BC_{CTO} suggested that not all PAHs were associated with soot (BC_{CTO}) in Shanghai soils as charcoal and other organic matters may play important roles in carrying PAHs. It was therefore suggested that, in the study of BC and its sorption of PAHs, charcoal should be taken into account.

The BC_{CTO}/TOC concentration ratios in soils were very similar to the reported EC/OC ratio in PM_{2.5} at Shanghai urban and suburban sites, which strongly suggested that BC in Shanghai soils was closely related to deposited atmospheric particles. BC sources revealed by BC_{CTO}/TOC ratio were attributed to biomass burning and fossil fuel combustion. By using BC-cogenerated HMW PAH isomer ratios of four categories of potential sources of BC and seventy-seven soil samples (adjusted for photo-degradation), it was clearly demonstrated that coal and biomass combustion along with oil combustion and tire wear were the main sources of BC in Shanghai soils. By using PCA-MLR of concentrations of BC-cogenerated HMW PAHs in soil samples of each area, coal and oil combustion were found the highest contribution in urban soils while tire wear and biomass combustion were important in downtown and rural area, respectively, which indicated they were main sources of HMW PAHs and presumably BC.

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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.apgeochem.2014.04.011>.

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