



## Polycyclic aromatic hydrocarbons in soils of Beijing and Tianjin region: Vertical distribution, correlation with TOC and transport mechanism

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### Abstract

The contents and distribution of 20 polycyclic aromatic hydrocarbons (PAHs) and heterocyclic aromatic hydrocarbons (HAHs) were investigated in 16 soil profiles of Beijing and Tianjin region. Transport of high molecular weight PAHs (HMWPAHs) and the correlation between total organic carbon (TOC) and their concentrations were also discussed. The results indicated that highly contaminated sites were located at urban or wastewater irrigation areas and pollutants mainly accumulated in topsoil (< 40 cm), with a sharp content decrease at the vertical boundary of 30–40 cm. Total PAHs/HAHs concentrations in soils from Tianjin were markedly greater than those from Beijing. Even the contents at bottoms of soil profiles in Tianjin were higher than those in topsoils of Beijing soil profile. HMWPAHs dominated the PAH profiles, exhibiting a uniform distribution of pyrogenic origin between topsoils and deep layers. Furthermore, the percentages of HMWPAHs remained relative constant with the depth of soil profiles, which were consistent with the distribution of particulate matter-associated PAHs in the local atmospheric environments. Therefore, HMWPAHs transport with particulates might be the predominant source found in soil profiles.

**Key words:** Beijing and Tianjin region; soil profile; polycyclic aromatic hydrocarbons (PAHs); transport

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### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously distributed in diverse environment matrices such as soil and sediment (Fernández *et al.*, 2000; Krauss *et al.*, 2000; Grimalt *et al.*, 2004; Gocht *et al.*, 2007a, 2007b), which deserve increasing attention for their high stability, low solubility and toxic, carcinogenic and mutagenic effects. It cannot be easily remediated and therefore will persist over long period, causing a long term risk of transport of PAHs to environment such as groundwater.

PAHs are introduced into environmental compartments both from natural (organic matter diagenesis, plant synthesis, forest and prairie fires, volcanoes, etc.) and anthropogenic processes (fossil fuel burning, incomplete combustion of organic matter, petroleum, incineration, etc.). However, the anthropogenic contribution usually outweighs the inputs from natural sources (Fernández *et al.*, 2000) and is responsible for the increase of PAHs over the last 100–150 years (Wickstrom and Tolonen, 1987). Totally, 90% PAHs accumulate in soils (Gocht *et*

*al.*, 2007b), which are also an important reservoir for atmospheric PAHs deposition (Wild and Jones, 1995; Tao *et al.*, 2003) and provide good media to record the historical PAHs burden as a result of anthropogenic activities.

The fate of PAHs in the environment is primarily controlled by the properties of PAHs and the environmental media. Long-term transport and/or transition of PAHs is an explanation of sources in remote area (Fernández *et al.*, 2000) and in deep layer of soils and sediments (Krauss *et al.*, 2000; Ma *et al.*, 2005; Ping *et al.*, 2007). In addition, the PAHs through atmospheric deposition are initially better preserved in the upper soils (Grimalt *et al.*, 2004). Once deposited in soil, PAHs will be subject to various partitions, degradation and transport/mixing processes, which will ultimately control their vertical distribution in soil. Thereby, PAHs not only accumulate in topsoils but also present in deep layer (Ma *et al.*, 2005; Ping *et al.*, 2007). The adsorption, transport and partition mechanisms of organic contaminants in soils and sediments indicate that the fate of hydrophobic organic compounds is determined by the organic carbon content of substrate (Chiou *et al.*, 1998; Tang *et al.*, 2005). Recent

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studies show that black carbon (soot, fly ash, unburned coal, and char) in soils and sediments exhibit a stronger adsorption to PAHs than nonpyrogenic organic carbon (Dachs and Eisenreich, 2000; Vinturella *et al.*, 2004). The sorption capacity was not significantly affected by different black carbon characteristics (Cornelissen *et al.*, 2004). The calculated black carbon partition coefficients for PAHs are one to two orders of magnitude higher than their corresponding organic carbon-normalized distribution coefficients (Vinturella *et al.*, 2004; Cornelissen *et al.*, 2005), explaining the nonlinear isotherm for PAHs sorption onto black carbon (Accardi-Dey and Gschwend, 2002; Cornelissen *et al.*, 2005). Therefore, the sources and distribution pattern of PAHs at diverse sampling sites and different depths of soil profiles (topsoils and deeper layers) require cautious estimation and interpretation.

Soil samples from 100 cm depth profile can reveal more useful information about the influence of compound retention, partitioning, transport, and fate processes in the vertical soil profiles. However, reports on the distribution of PAH in soil section around 100 cm (Ma *et al.*, 2005; Ping *et al.*, 2007) is seldom.

It is also important to investigate the spatial distribution and transferred pathways of PAHs in soil profiles to have a better assessment of the environmental risks of soil contamination with PAHs. A further understanding of the different concentrations and compositions of PAHs between topsoils and deep layers also requires the study of relationship among physic-chemical properties of PAHs and soil types.

Early surveys showed that topsoils in Beijing-Tianjing area, one of the most polluted areas in China, were heavily contaminated by PAHs (Zhen, 2002; Tang *et al.*

*et al.*, 2005; Ma *et al.*, 2005). Vertical distribution patterns and contamination conditions of PAHs have been rarely described. In this study, we reported our studies on PAHs distribution, composition, transport mechanisms and the correlation between total PAHs/HAHs concentrations and TOC in different horizons in soil profiles in this region. The different concentrations and compositions of PAHs in various profiles between topsoils and deep layers were compared and, the possible transport behavior of PAHs in vertical soil profiles was discussed.

## 1 Materials and methods

### 1.1 Sampling

Soil samples were collected from sixteen profiles (B1–B9, T1–T7) at different sites with different soil types and different geographic conditions in Beijing and Tianjin areas. The sampling sites and the environmental distinction are shown in Fig. 1 and Table 1. Composite samples were taken from five locations in an area of 100 m<sup>2</sup> in grid in each site. From the surface downward in each location, there are ten sects: 0–5, 5–10, 10–15, 15–20, 20–25, 25–30, 30–40, 40–50, 50–75, and 75–100 cm, respectively. Soil samples were wrapped in pre-cleaned aluminum foil, air-dried at room temperature, ground in mortar and sieved through a sieve (80 mesh) after removing stone and residual roots, and then frozen until analysis.

### 1.2 Sample extraction

The detailed procedure of the clean-up method was presented previously (Zhang *et al.*, 2008). The extraction was undertaken by placing 100 g soil sample into Soxhlet

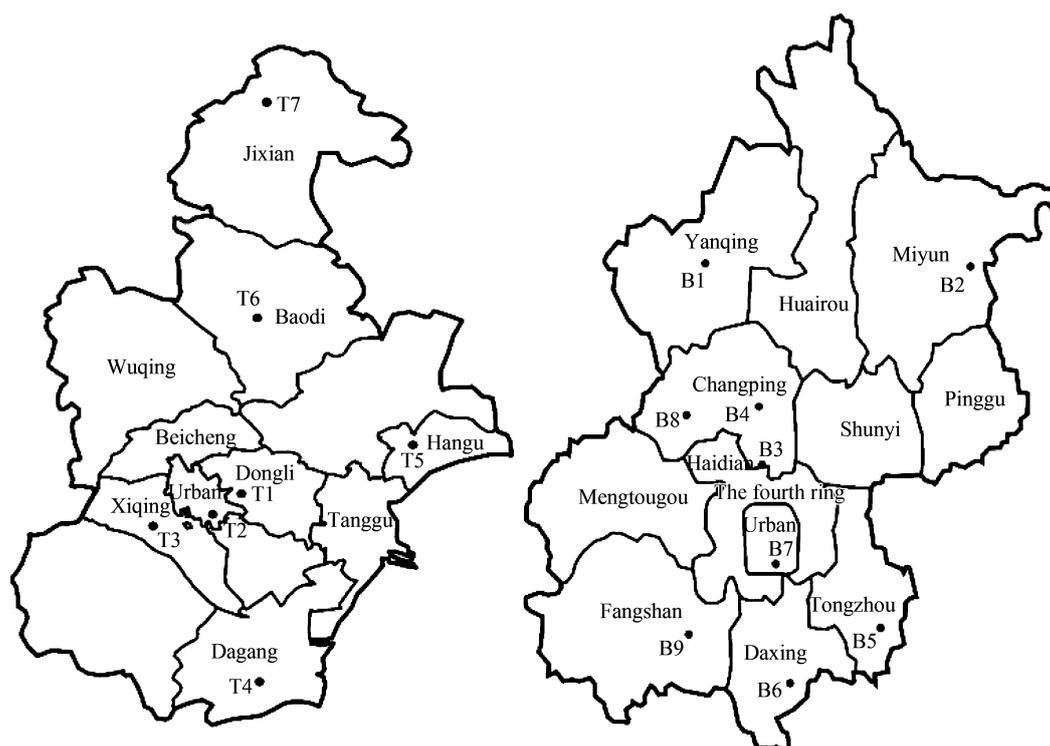


Fig. 1 Map of the study area in northern China and distribution of sampling sites in Tianjin (left) and Beijing (right), respectively

**Table 1** Descriptions of sampling sites

Profile	No. Soil property	Land using	Contamination class <sup>a</sup>	Profile No.	Soil property	Land using	Contamination class <sup>a</sup>
B1	Clay, brown	Farmland/hurst	II	B9	Sand	Industrial estate	II
B2	Silty clay	Hurst	I	T1	Saline soil	Badland	IV
B3	Clay	Farmland	I	T2	Saline soil	Deserted farmland	IV
B4	Clay	Orchard	I	T3	Swamp soil	Cornfield	IV
B5	Sandy silty	Farmland	II	T4	Saline soil	Cornfield	II
B6	Silty clay	Farmland	II	T5	Swamp soil	Grassland	II
B7	Silty clay	Urban grassland	IV	T6	Brown clay	Farmland	I
B8	Brown clay	Paddyfield	IV	T7	Brown soil	Badland	II

<sup>a</sup> Maliszewska-Kordybach, 1996. Classes I–IV of soil contamination were unpolluted, weakly polluted, moderately polluted, and severely polluted, respectively.

apparatus and was performed after adding the deuterated recovery standards, with solvent mixture of redistilled dichloromethane/acetone (1:1, V/V) in 65°C water bath for 36 h. Activated copper powder was added to remove sulfur during the extraction process. The extracts were concentrated by rotary evaporator to about 1 mL, then dried (< 40°C) and being placed into a desiccator. The extracts were separated by a solid-phase combination of aluminum oxide (2 g) and silica gel (3 g) into saturated hydrocarbon, aromatic hydrocarbon (including PAHs) and resin (non-hydrocarbon) using 30 mL petroleum ether, 30 mL dichloromethane/petroleum ether (1:1, V/V) and 25 mL dichloromethane/methanol (9:1, V/V) as eluent, respectively. Aromatic hydrocarbons contain PAHs and HAHs (heterocyclic aromatic hydrocarbons), therefore it was reconcentrated to around 0.2 mL under steam of pure nitrogen and prepared for GC/MS analysis.

### 1.3 TOC analysis

TOC was measured using a WR112 Leco carbon determinator (LECO Corp., Michigan, USA). Micronized samples (ca. 0.2 g) were weighed and placed into crucible. Carbonate minerals removal was performed using 7 mol/L HCl in 60°C water bath for 1 h. The residue was washed by distilled water until the solution pH reached neutral, and then the sample was oven dried at 70°C for 8 h. The residue powder was analyzed in the LECO instrument. The sample was combusted and all organic matter was converted to CO<sub>2</sub>. The amount of elemental carbon in the total CO<sub>2</sub> measured by an infrared detector was calculated and normalized to the original sample weight.

### 1.4 GC/MS analysis

PAHs and HAHs were analyzed by Thermo-Finnigan Trace-DSQ (Finnigan, USA), with a HP-5 fused silica capillary column (60 m, 0.25 mm i.d., 0.25 µm film thickness) and helium (purity 99.999%) was used as the carrier gas. The injection temperature was maintained at 300°C. The chromatographic column was programmed from 50 to 120°C at 20°C/min, to 250°C at 4°C/min, then to 310°C at 3°C/min and held for 30 min. The GC/MS analyses were performed by electron impact ionization with electron energy of 70 eV with an ion source temperature of 200°C.

### 1.5 Identification and quantification

Soil extracts were analyzed for a set of USEPA 16 priority PAHs including: acenaphthylene (Acy),

acenaphthene (Ace), naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), fluorine (Flu), benzo[a]anthracene (B[a]A), fluoranthene (Fla), pyrene (Pyr), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene (I[1,2,3-cd]P), dibenz[ah]anthracene (DB[ah]A) and benzo[ghi]perylene (B[ghi]P), benzo[e]pyrene (B[e]P), dibenzofuran (DBF), dibenzothiophene (DBT) and perylene (Per). The first nineteen were measured quantitatively whereas perylene was analyzed qualitatively according to chromatograph peak areas. Identification and quantification of the target compounds were performed by matching their retention time with standards and by comparison of peak areas with standards spiked to the extract prior to injection. To facilitate comparison among all detected PAHs profiles, all their peak areas prior to statistical analysis were normalized, which have been done by dividing the peak for individual PAH by the maximum peak of all 20 PAHs or HAHs in each horizon in different soil profiles.

The deuterated recovery standards (phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub>, concentration 3966, 4000, and 4000 µg/mL, respectively; purity 99.1%, 100%, and 100%, respectively), internal standard (terphenyl-d<sub>14</sub>, concentration 499.6 µg/mL, purity 99.8%), external standards (16 PAHs solution mix, purity 98%–100%, certified analyte concentration 196.6–201.2 µg/mL), were supplied by AccuStandard Inc., USA. Procedural blanks with each set of twenty samples and a duplicate with each of soil profile (ten samples) were processed by performing the entire analytical procedures. The concentrations of the blank samples ranged from 3.9 to 7.1 ng/g for 19 PAHs/HAHs. To determine the recoveries of the compounds identified, recovery standards (1.5 µg) were used to spike all the soil samples prior to extraction. Average recoveries of phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub> were 69%, 92%, and 86% for B1–B9, 73%, 81%, and 76% for T1–T7, respectively. The limits of detection based on *s/n* of 3 were in the range of 0.1 to 0.8 ng/g for dry soils. A standard solution was prepared with external standards and internal standards using dichloromethane as diluting solvent. The linear range was established by six point calibration curve in the range of 0.25–3.5 µg/mL.

## 2 Results and discussion

### 2.1 Total PAHs/HAHs concentrations in topsoils

The sum of 19 PAHs/HAHs concentrations in topsoils

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(0–30 cm) ranged over 2 orders from 17.8 to 8357.2  $\mu\text{g}/\text{kg}$ , which is greatly in excess of the endogenous PAHs concentrations (1–10  $\mu\text{g}/\text{kg}$ ) in soils (Edward, 1983) and higher than those (mean  $318.2 \pm 148.2$  ng/g) in agricultural soils from subtropical regions in China (Hao *et al.*, 2007). However, it is lower than concentrations present in soils in Dalian (219–18727  $\mu\text{g}/\text{kg}$ ) (Zhen *et al.*, 2007), wastewater irrigated area of Shenyang (181.4–5004.2  $\mu\text{g}/\text{kg}$ ) (Song *et al.*, 1997) and the Yangtze River Delta region (8.6–3881 mg/kg) (Ping *et al.*, 2007) in China, and Estonian urbanized areas (2200–12300  $\mu\text{g}/\text{kg}$ ) (Trpido, 1999). A recent survey of topsoils in Beijing (Ma *et al.*, 2005) and Tianjin (Zhen, 2002) gave comparable PAHs concentrations (16–3884  $\mu\text{g}/\text{kg}$  and 200–5190  $\mu\text{g}/\text{kg}$ , respectively).

According to four classes, unpolluted, weakly polluted, moderately polluted and severely polluted of soil contamination with PAHs proposed by Maliszewska-Kordybach

(1996), surface soils (0–15 cm) from 12 out of 16 sampling sites (except for B2, B3, B4, and T6) could be considered as polluted, five sites (B7, B8, T1, T2, and T3) as severely polluted. The most heavily polluted sites B7, T2, and T3, with content of PAHs  $\geq 3000$   $\mu\text{g}/\text{kg}$ , are either urban or wastewater irrigation area.

## 2.2 Vertical distribution

As shown in Fig. 2, in each profile, the total PAHs/HAHs concentrations accumulated dominantly in topsoils (0–40 cm), which were greater than those in deep layers (> 40 cm) where the average concentration was below 50  $\mu\text{g}/\text{kg}$  in Beijing area, which was lower than the mean concentration (359  $\mu\text{g}/\text{kg}$ ) in subsoil (1.5–1.8 m) from Beijing outskirts (sampling sites were located around the Forth Ring Road) (Ma *et al.*, 2005). However, PAHs concentrations in deep layers of Tianjin area (except for

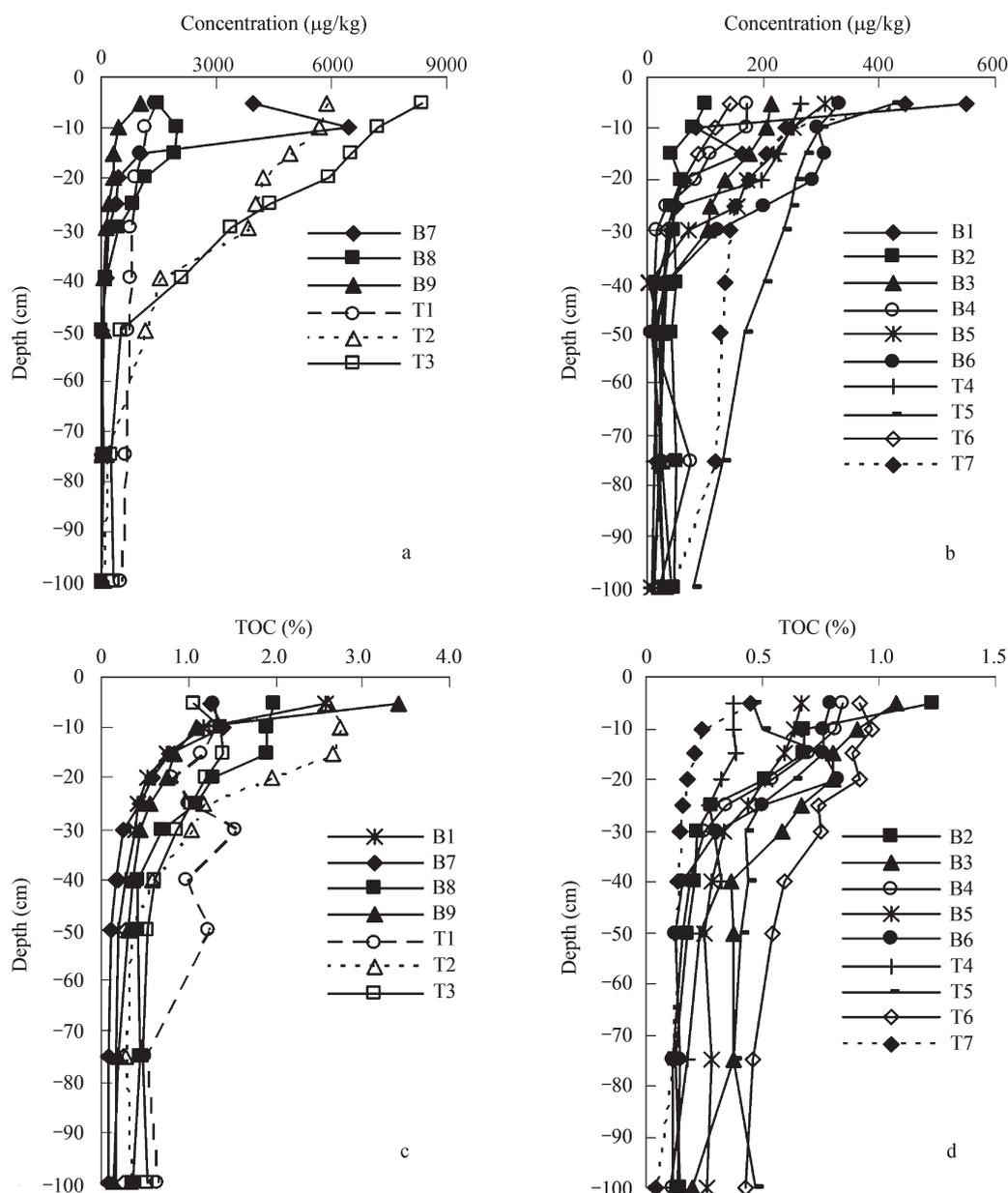


Fig. 2 Vertical distribution of total PAHs/HAHs concentrations (a, b) and TOC (c, d).

T4) compared to the report by Ma *et al.* (2005) were greater than the counterparts of Beijing, especially at the bottom profile of T1, T2 and T3, where the concentrations were higher than those in topsoils of Beijing area with the exception of B7 and B9. At the depth of 30–40 cm, namely the boundary between the humic layers and the mineral soil or around plough layer, a sharp decrease in PAHs concentration occurred, which was in agreement with previously published PAHs concentrations in rural soil and forest soil (Krauss *et al.*, 2000; Gocht *et al.*, 2007a; Ping *et al.*, 2007).

Figure 2 shows the similar trend of the vertical distribution of the total PAHs/HAHs concentrations in soil profiles from the two areas. However, the concentrations in the whole profile of Tianjin are generally higher than those of Beijing, which can be explained by three reasons. First, with a large industrial area, Tianjin suffers from heavier pollution in atmosphere (Wu *et al.*, 2004b) and topsoil (Ma *et al.*, 2005); second, wastewater irrigation and sludge application have been commonly practiced for at least 40 years (Wang *et al.*, 2002a, 2002b) at the rate of billion tons per year (TEPB, 2001); third, different to Beijing the soils are mainly swamp soil or saline soil which may facilitate to the transport of PAHs from topsoil into deep layer.

### 2.3 PAHs/HAHs profiles

The distribution patterns (fingerprints) of PAHs/HAHs were evaluated to compare their constitutional differences for different soil horizons. Normalization has been done by dividing the maximum peak of PAHs or HAHs in each horizon in different soil profiles. The normalized distribution patterns are showing in Fig. 3. These are similar in different soil horizons of all samples, with dominant PAHs being  $\Sigma$ COMB (the sum of combustion specific PAHs), as typical combustion/pyrogenic origin PAHs which can be represented by the sum of HMWPAHs (HMWPAHs, 4–6 rings) (Fla, Pyr, Chr, B[a]A, B[b]F, B[k]F, B[e]P, B[a]P, I[1,2,3-cd]P, and B[ghi]P) (Prah and Carpenter, 1983; Hwang *et al.*, 2003), and phenanthrene. When grouped according to concentrations, it is evident that  $\Sigma$ COMB become fractionated during transport through soil profiles with relatively low concentrations (Fig. 3), whereas this phenomenon is not present in the heavily polluted sampling sites (T1, T2, and T3). The depth of delamination is different with the change of total organic carbon (TOC), such as 0–10 cm for (B1, B2), 0–30 cm (B3, B4, B9, T4, and T5), indicating that TOC content influences PAHs distribution and transport of HMWPAHs less readily than the low molecular weight PAHs (LMWPAHs).

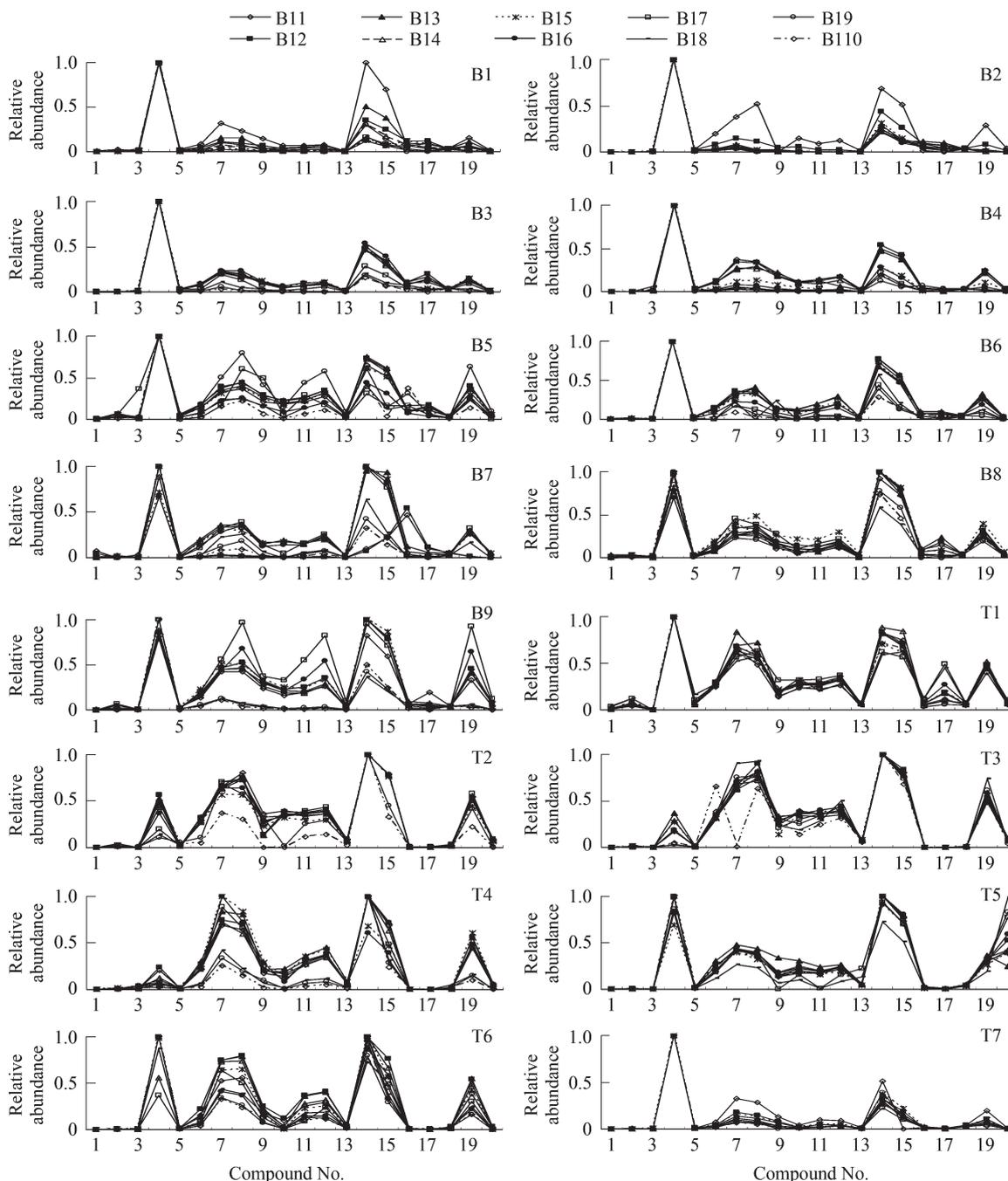
Interestingly, in the case of T5, a different vertical distribution of the relative abundance of Per was observed. Here the relative abundance increased with depth, as opposed to the general trend of other individual PAH and  $\Sigma$ PAHs, which decreases with soil depth. Similar depth distribution of Per has also been observed in other studies (Grimalt *et al.*, 2004; Gocht *et al.*, 2007a). The explanation may be that this type of soil from T5 offers conditions and materials favoring production of Per. Also there are many studies introduced that the formation of Per in deep soils and

sediments suggest that anaerobic/anoxic conditions favor the formation of Per from unknown precursors (Gocht *et al.*, 2007a; Grimalt *et al.*, 2004).

Figure 4 shows a high percentage of  $\Sigma$ COMB in Beijing and Tianjin accounting for average 42% and 85%, respectively, which is comparable to the percentage of  $\Sigma$ COMB in atmospheric particulates in Beijing (65%–84%) and Tianjin (80%–94%) (Zhang *et al.*, 2004, 2006a; Wu *et al.*, 2004a). The  $\Sigma$ COMB predominance pattern is common, usually occurring in atmospheric particulates (Wu *et al.*, 2007; Odabasi *et al.*, 1999) and soils (Maisto *et al.*, 2006; Nam *et al.*, 2007). Here, the pattern is consistent with previously studies, indicating a strong contribution of combustion sources (Prah and Carpenter, 1983; Hwang *et al.*, 2003) and higher contamination in Tianjin than in Beijing. That the percentages for Beijing declined little with depth and are lower than those of Tianjin can be explained by the sources and soil styles. Automotive exhaust is the main source in Beijing, and is contributed by carbon isotopic of PAHs becoming more enriched in  $^{13}\text{C}$  with increasing molecular weight (Okuda *et al.*, 2002). However, in Tianjin, coal contribution accounts for 41% of the total source to the surface soil (Zuo *et al.*, 2007) with the contribution of long history of wastewater irrigation (TEPB, 2001; Wang *et al.*, 2002a, 2002b).

Although the emission patterns of PAHs have great impact on the PAHs profile, long-range transport potential of PAHs changes their compositions. Different physicochemical properties of PAHs may elucidate the concentration gradient and the different composition of PAHs from urban, suburban, and rural soils (Zhen *et al.*, 2007). The PAHs fraction can also occur at the local scale along short-distance transport from point emitters (Wilcke *et al.*, 1996; Meharg *et al.*, 1998). HMWPAHs associated with particulates undergo “single hop” transport behavior, making them prone to rapid deposition and retention close to source regions (Tuháčková *et al.*, 2001; Zhen *et al.*, 2007). Duan *et al.* (2005) divided Tianjin into three zones including industrialized, urban districts, and rural, featuring distinctive PAHs levels and profiles. The T7 site belongs to a rural zone where no wastewater was used for irrigation and which is distant from serious pollution sources. Thus, it may receive atmospheric inputs of PAHs associated with particulate matter or vapor phase. The atmospheric residence time of PAHs is closely related to the behavior of the carrier particulates (McVeety and Hites, 1988; Baker and Eisenreich, 1990) and their transport potential. Since  $\Sigma$ COMB are mainly associated with particulates, they tend to simple sedimentation by dry or wet deposition close to the source during transport into atmosphere, which may explain the low percentage of  $\Sigma$ COMB in T7 than in other sites of Tianjin area.

The fairly constant percentage of  $\Sigma$ COMB with depth in soil cores suggests that HMWPAHs dominate the PAHs profiles exhibiting a uniform distribution of pyrogenic origin between topsoils and deep layers. The vertical gradient in TOC had only a small influence on PAHs composition, indicating that an insignificant relationship exists between TOC and the HMWPAHs concentrations.



**Fig. 3** Profiles in different soil horizons for 20 compounds. The legend is the same as in B1 in all soil profiles and the number 1–10 represent horizons depth: 0–5, 5–10, 10–15, 15–20, 20–25, 25–30, 30–40, 40–50, 50–75, and 75–100 cm, respectively. (1) Acy; (2) Ace; (3) Nap; (4) Phe; (5) Ant; (6) B[a]A; (7) Chr; (8) B[b]F; (9) B[k]F; (10) B[a]P; (11) I[1,2,3-cd]P; (12) B[ghi]P; (13) DB[ah]A; (14) Fla; (15) Pyr; (16) Flu; (17) DBF; (18) DBT; (19) B[e]P; (20) Per.

#### 2.4 Relationship between TOC and total PAHs/HAHs concentrations

The soil samples contain a wide range of TOC contents (Fig. 2), with the lowest value of 0.4% (T4, Fig. 2c) and the highest 3.5% (T7, Fig. 2c) in the surface soil (0–5 cm), which were lower than reported data in Europe (Maliszewska-Kordybach, 1996). Depth distributions of TOC and total PAHs/HAHs concentrations are similar here, indicating that correlation exists between TOC and total PAHs/HAHs concentrations (Fig. 2).

It has been observed that the high PAHs concentration

in soils is accompanied with high TOC content (Chiou *et al.*, 1998; Wilcke and Amelung, 2000). However, Zhang *et al.* (2006b) concluded that PAHs concentration was not significantly influenced by TOC content until it arrived at a certain level in the weakly polluted soil.

There appeared to be a relationship between the soil organic carbon content and the total PAHs/HAHs concentrations of the soil. Therefore, Pearson correlations and scatter plots were carried out between the two variables, which tend to correlate well with each other at all sites (Fig. 5). The correlation coefficients ( $r$ ) varied between

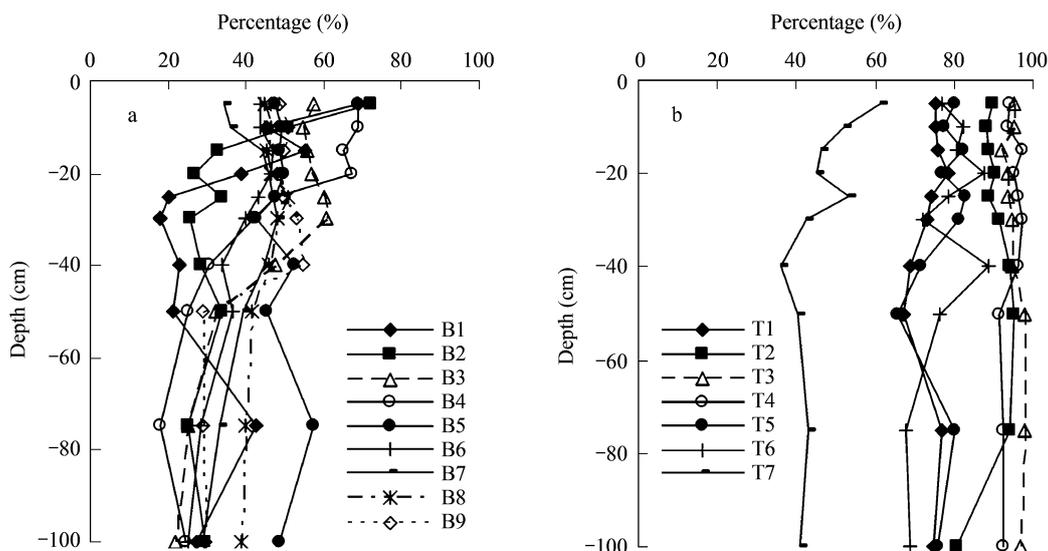


Fig. 4 Percentage of  $\Sigma$ COMB to total PAHs/HAHs concentrations in different soil profiles. (a) Beijing; (b) Tianjin.

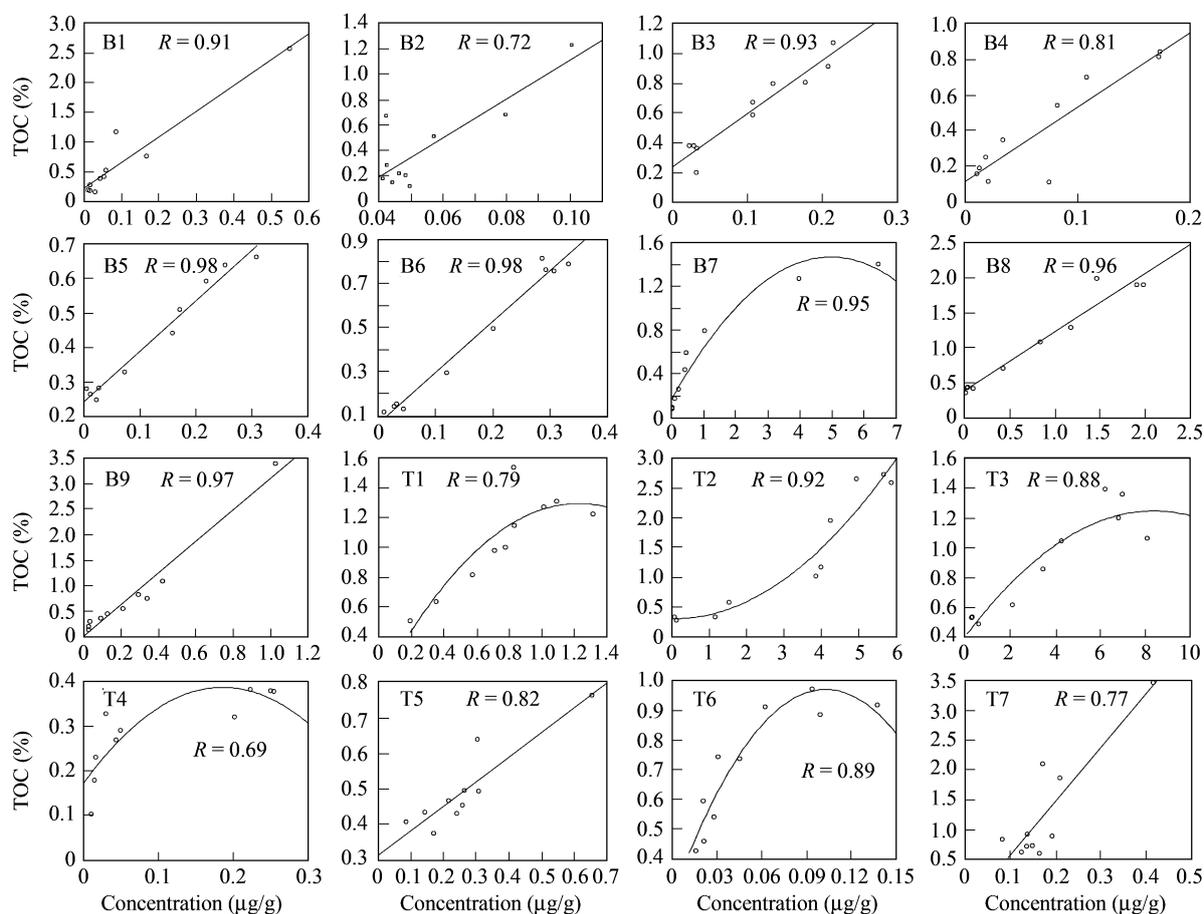


Fig. 5 Correlation between TOC and total PAHs/HAHs concentrations from different sampling sites. The scatter plot and fit line were made using SPSS 11.5.

0.77 and 0.97 which were statistically significant at level of 0.01. The fit line in the scatter plots were made using linear regression and quadratic regression with  $R$  value ranged from 0.69 (T4) to 0.98 (B6). Quadratic regression between PAHs concentration and TOC in this study presents in the sampling site with higher PAHs concentration, and linear regression in the areas with relatively lower PAHs

concentration with the exception of B1, B9, and T7. The two patterns here associate not only with PAHs concentration but with TOC which consist of both autochthonous products (leaf litter, organism debris) and allochthonous inputs from black carbon (soot, char, unburned coal, and organic pollutant) in soils. Soil PAHs concentrations were correlated well with TOC. Beijing soils generally contain-

ing lower PAHs/HAHs concentrations than Tianjin soils. The nonlinear phenomenon of those areas (B7, T1, T2 and T3) with higher PAHs concentration and higher TOC may be explained by the composition of organic matter according to previous investigations (Accardi-Dey and Gschwend, 2002; Cornelissen *et al.*, 2005). They reported that black carbon, as a fraction of organic matter, may explain the nonlinear isotherms for adsorption of PAHs to organic matter. Further investigations, especially the elaboration, for how the compositions of organic matter influence PAHs will be conducted.

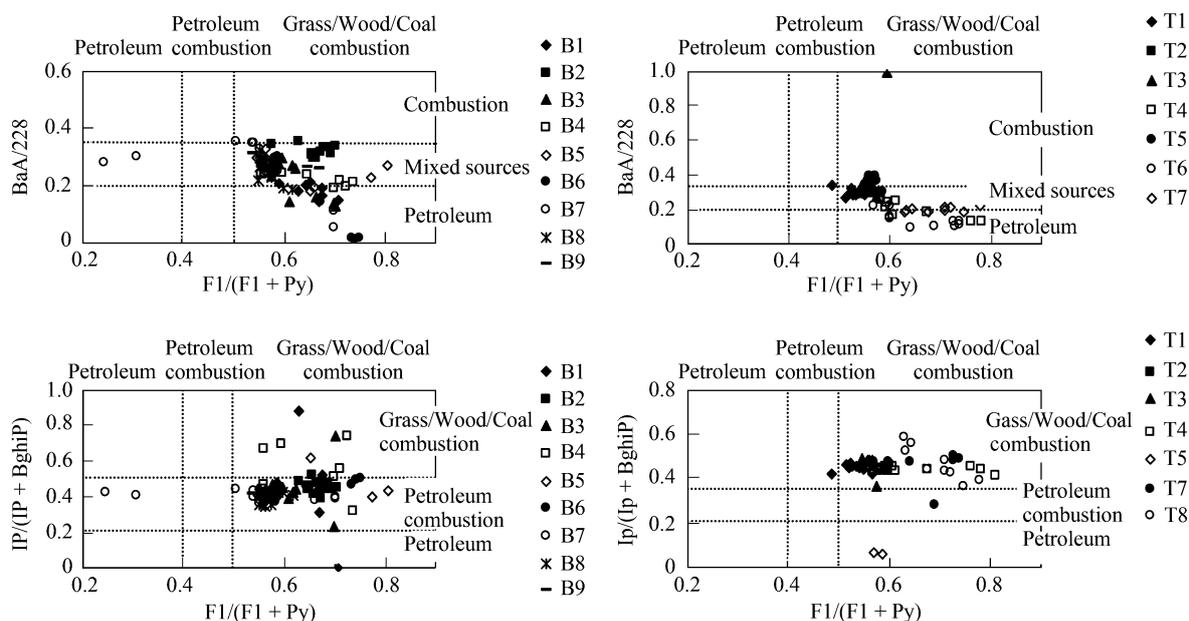
The curve between total PAHs/HAHs concentration and TOC might be due to the strong adsorption of PAH to organic matter in soil, especially allochthonous carbonaceous matter exhibiting adsorption properties much different from autochthonous soil organic matter (Dachs and Eisenreich, 2000). This is confirmed by the PAHs profiles in topsoils (Fig. 3) where relative abundance of HMWPAHs is higher than in deep layers despite the down-core change extent of TOC. Soot and coal dust are common ingredients with a wide range of TOC content in the topsoils of highly industrialized regions (Kuhlbusch, 1998; Accardi-Dey and Gschwend, 2002). Although soot carbon contents are usually lower than organic carbon content in the soil and other environmental matrixes (Dachs and Eisenreich, 2000), the strong adsorption ability lead the soot a major adsorbent for PAHs.

## 2.5 Transport

To elucidate PAHs transport in the vertical soil profiles, an evaluation of the PAHs sources in topsoils and bottom soil is discussed using PAHs ratios. For both areas of Beijing and Tianjin, the B[a]A/228 (B[a]A/(B[a]A+Chr)) ratio mainly ranged from 0.2 to 0.35, consisting of mixed sources (combustion and petrogenic sources), whereas the large number of samples is assigned to the combustion by

the IP/IP+B[ghi]P (I[1,2,3-cd]P/(I[1,2,3-cd]P+B[ghi]P)) and Fl/Fl+Py (Fla/(Fla+Pyr)) ratios which exhibited less scatter in most samples. The Fl/Fl+Py ratios in soils from Beijing (0.54–0.81) with exception of B7 (0.25–0.70) and Tianjin (0.49–0.81) are similar with slight variation. Different IP/IP+B[ghi]P ratios correspond almost always to Fl/Fl+Py ratio > 0.50 (Fig. 6) supporting the conclusion that different combustion products are important sources for HMWPAHs in all soil samples from the two areas. Most samples from Beijing have IP/IP+B[ghi]P ratios consistent with petroleum combustion, which may be supported by the isotopic trend of PAHs in Beijing affected by automotive exhausts (Okuda *et al.*, 2002), while those from Tianjin have ratios more consistent with coal/wood combustion. In light of obvious reports and the surroundings of the sampling site, wastewater irrigation appears to be another important reason for heavy PAHs pollution in Tianjin (TEPB, 2001; Zuo *et al.*, 2007).

Individual PAHs differ in physical and chemical properties. In general, LMWPAHs are more volatile and water soluble, and less lipophilic than HMWPAHs, which are often combined with black carbon during combustion emissions (Krauss *et al.*, 2000; Nam *et al.*, 2007). These properties substantially influence the environmental behavior of PAHs in environmental compartments such as soil. Much research have investigated the transport and transition behavior of PAHs in soil, presented that bioturbation and leaching from the organic horizons result in PAHs transport into the mineral soil (Krauss *et al.*, 2000) and LMWPAHs (< four rings) are probably mainly transported as true solutes (Krauss *et al.*, 2000), while low solubility and strong affinity to organic matter severely limited vertical transport of HMWPAH with seepage water in soils (Gocht *et al.*, 2007b; Saison *et al.*, 2004). HMWPAHs are transported in association with dissolved organic matter or organic colloids (Maxin and Kögel-Knabner,



**Fig. 6** PAHs cross plots for the ratios of BaA/228 vs. Fl/Fl+Py and IP/IP+B[ghi]P vs. Fl/Fl+Py. Plots on the right are for Tianjin and plots on the left are for Beijing.

1995; Krauss *et al.*, 2000). Gustafsson *et al.* (1997) and Dachs and Eisenreich (2000) have indicated the differences in adsorption PAHs onto soil organic matter and onto black carbon. Therefore, a distinctive mechanisms or other process might exist to explain the transport of  $\Sigma$ COMB.

HMWPAHs have a stronger affinity to soot than to the organic matter in atmospheric particulates, and adsorption onto organic matter accounts for less than 10% of the total PAHs (Dachs and Eisenreich, 2000). Furthermore, PAHs present in soot formed during combustion process are not available for aqueous partitioning (Jonker and Koelmans, 2002). The PAHs profiles exhibit a uniform distribution in bottom and topsoils and a relatively constant percentage of  $\Sigma$ COMB with depth in soil profiles, as compared to the percentage of  $\Sigma$ COMB in local atmospheric particulates (Zhang *et al.*, 2004, 2006a; Wu *et al.*, 2004b), and thus their transport is considered to be associated with the movement of particulates such as soot, unburned coal, and char. Therefore, transport with particles may be the predominant mechanism in soil cores. This is consistent with profiles of particulate-associated PAHs in local atmospheric environment. In the whole soil profile, the  $\Sigma$ COMB percentage changes little with soil depth in Beijing whereas no clear decrease exist in Tianjin, which may be attributed to extensive wastewater irrigation used for 40 years in Tianjin, facilitating transport, or the soil styles favoring transport of particulate-associated HMWPAHs.

### 3 Conclusions

The total PAHs/HAHs concentrations among different soil profiles were obviously different and the most heavily polluted sites were located at urban or wastewater irrigation areas. The PAHs concentrations in Tianjin were markedly greater than those in Beijing, even at the bottom of soil profile in Tianjin area the concentrations were higher than those in topsoils of Beijing soil profile. The target compounds mainly accumulated in topsoils (< 40 cm) and decreased sharply at the boundary of 30–40 cm.

HMWPAHs dominated the PAHs profiles with the relatively constant percentage in the vertical distribution of the soil profiles, which was consistent with the profiles of particulate-associated PAHs in local atmospheric environment. It can be concluded that HMWPAHs in soil profiles were originated from combustion sources.

Although TOC and total PAHs/HAHs concentrations correlated well with each other at all sites, it was not yet to get a conclusion once for all through the different fit modes in the scatter plots (linear regression and quadratic regression) of the correlation between total PAHs/HAHs concentrations and TOC contents. The detail mechanisms of those patterns are investigating in our laboratory.

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