

# Polycyclic aromatic hydrocarbons contamination in subsoil from outskirts of Beijing, People's Republic of China

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## Abstract

Forty-five pooled subsoil samples, collected from the outskirts of Beijing at the depths of 1.5–1.8 m, were analyzed for 17 polycyclic aromatic hydrocarbons (PAHs) using gas chromatography and mass spectrometry (GC–MS) to determine their total contents and distribution patterns. The sum of 17 PAHs concentrations varied from not detected to 0.982  $\mu\text{g g}^{-1}$  in subsoil. The higher total contents of PAHs were observed in the southeast areas where there are some industries. PAHs in most of the subsoil were lower than those in the topsoil (0.016–3.884  $\mu\text{g g}^{-1}$ ). PAHs concentrations displayed no relationship with the organic materials. In subsoil, the dominated PAHs were perylene>benzo(a)pyrene>benzo(g,h,i)perylene>indeno(1,2,3-cd)pyrene. It was notable that the content of 8 carcinogenic PAHs represented 47% of the total priority PAHs and the concentration of benzo(a)pyrene in the subsoil was comparable to that in the topsoil, which was much higher. The distribution of target compounds especially perylene and the fluoranthene/pyrene ratio shows that the sources in the subsoil are characterized by combustion such as traffic and incorporation of the diagenetic PAHs.

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**Keywords:** Polycyclic aromatic hydrocarbons; Subsoil; Beijing; Leaching; Traffic emission

## 1. Introduction

Recently, environmental contamination relating to persistent organic compounds has become a matter of great concern. Polycyclic aromatic hydrocarbons

(PAHs) have been of interested focus due to the carcinogenic as well as mutagenic properties (Perera, 1997). Sixteen PAHs (naphthalene—Na; acenaphthylene—Acy; acenaphthene—Ace; fluorene—Fl; phenanthrene—Ph; anthracene—An; fluoranthene—Flu; pyrene—Pyr; benz(a)anthracene—BaA; chrysene—Chr; benzo(b)fluoranthene—BbF; benzo(k)fluoranthene—BkF; benzo(a)pyrene—BaP; indeno(1,2,3-cd)pyrene—InP; dibenz(a,h)anthracene—DBA; ben-

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zo(*g,h,i*)perylene—yBghiP) were listed as priority pollutants by the US Environmental Protection Agency (US EPA). PAHs are introduced into the environment primarily due to the incomplete combustion of fossil fuels and other organic materials. Comparatively stable molecular structure, slow rates of photochemical decomposition and biodegradation contribute to the persistence of PAHs in the environment.

Soil system seems to be the important repository for atmospheric PAHs (Wild and Jones, 1995). Once deposited, they can reside for longer than 20 years (Wild et al., 1990), and the accumulation may lead to contamination of food chains (Kipopoulou et al., 1999; Samsøe-Petersen et al., 2002). However, PAHs are not static and recalcitrant. They are subject to redistribution and transformation processes. PAHs generally accumulate in organic matter-rich horizons because of their persistence and affinity for soil organic matter (Matzer, 1984; Smith et al., 1993; Wilcke et al., 1996). According to the reports (Berteigne et al., 1988; Pichler et al., 1996), the concentrations of PAHs frequently increase from the horizon consisting of little decomposed organic material to the lowermost organic horizon which directly overlay the uppermost mineral soil. On the other hand, the organic material and preferential flow can enhance the transport of organic pollutants to the deeper layer. If the upland soil are frequently irrigated or saturated with water for a significant part of the year, there is an increased likelihood of leaching of PAHs from the zone of contaminated sites to the deeper layers to endanger the groundwater quality (Weigand et al., 2001). Leaching of PAHs may be more significant where there is ground contaminated with solvents. Therefore, a wide investigation for soil contamination with PAHs is needed to avoid any food production risk and to restrict the deleterious effect of these contaminants on the ecosystem.

Up to now, most knowledge on the distribution of PAHs in the environment is derived from studies in “western world” (Edwards, 1983; Jones et al., 1989; Wilcke et al., 1999; Wilcke, 2000). There is a lack of more information on the state of the contamination of the environment especially in soils with PAHs in China (Chu et al., 2003; Ma et al., 2003; Tao et al., 2004; Wang et al., 2003). Beijing, the capital of China, is one of the economic and culture center of China. The high population (over 13 million) and

rapid industrialization during the last decades have resulted in a lot of environmental problems. The increasing vehicle traffic associated with population growth in metropolitan areas can be responsible for increasing PAHs concentrations and consequent degradation of air, soil and watershed quality (Van Metre et al., 2002). It was reported that the PAHs concentration calculated in terms of the total suspended particles in atmosphere was  $178 \mu\text{g g}^{-1}$  in summer and  $749 \mu\text{g g}^{-1}$  in winter in this city (Okuda et al., 2002). This may result in high concentrations of PAHs in soils. Up to now, only limited attentions on a small scale were paid to the accumulation and distribution of PAHs in Beijing soils (Chu et al., 2003; Ma et al., 2003). In 2001, the Chinese government carried out a systematic and tremendous investigation to assess the state of soil contamination on the outskirts of Beijing where there are undergoing great changes due to the rapid urbanization and industrial development. The survey covers an area of approximately  $1000 \text{ km}^2$  and the discussion here is one part of the project (the program is still going on now).

The study here mainly described the contents and distribution of 17 PAHs in the subsoil. The comparison of PAHs in topsoil with subsoil was also concerned. The objective was to determine to what extent deep soils are contaminated with PAHs in this region. The compositional patterns, and molecular indices of selected PAHs, were used to indicate the possible PAHs sources.

## 2. Materials and methods

### 2.1. Materials and reagents

The standard solutions including perylene and 16 unsubstituted EPA-PAHs (priority pollutants according to the US Environmental Protection Agency, EPA) at the concentration of  $1000 \mu\text{g ml}^{-1}$  for each compound were obtained from Supelco (Bellefonte, PA, USA). 2-Fluorobiphenyl and 2,4,5,6-tetrachloro-*m*-xylene were purchased from Aldrich chemical company. The standards were further diluted with isooctane to prepare working standards. Silica gel (100–200 mesh; Qingdao Haiyang Chemical Company, China) was activated at  $130 \text{ }^\circ\text{C}$  for 12 h.

All the solvents (Beijing Chemical Factory, China) were of analytical purity and redistilled in all-glass system prior to use. The glassware was cleaned successively in the following order: washed with detergent and water, soaked in 5%  $K_2Cr_2O_4$  sulfuric acid solution overnight, washed with water and distilled water in turn, dried in an oven and rinsed with acetone just before use.

## 2.2. Collection and preparation of soil samples

Beijing is located at the northwestern border of the Great North China Plain at  $39^{\circ}48'N$  latitude and  $116^{\circ}28'E$  longitude at an altitude of 44 m above mean sea level. The Yanshan Mountain range is to the northeast, and the Bohai Sea is 160 km to the southeast. It is cold and dry in winter with the lowest temperature of  $-15^{\circ}C$ , while it is hot and humid in summer with the highest temperature up to  $40^{\circ}C$ . The average annual precipitation is about 600 mm. The physiognomy of northwest is higher than that of southeast. The southeast area used to be industrial center with a few chemical plants and the northwest areas have several tour sights such as the Summer Place Park. The investigation area is around the Fourth Ring Road on the outskirts of Beijing, with 5 km to the east, 14 km to the south, 7 km to the west and 6 km to the north. The soil was collected in April 2001 and the location of sampling sites is shown in Fig. 1.

For topsoil sample (5–30 cm), multiple cores covering about  $1\text{ km}^2$  were collected to get one subsample with stainless steel drill firstly and then 16 vicinal subsamples were mixed fully to obtain one pooled topsoil sample representing  $16\text{ km}^2$  areas. For subsoil (1.5–1.8 m), multiple cores covering about  $1\text{ km}^2$  included in the  $16\text{ km}^2$  were collected. In addition, a deep soil was collected at depths of about 10 m to be used as matrix blank. Each fully mixed sample was air-dried in dark at room temperature ( $10\text{--}15^{\circ}C$ ), well ground, passed through  $<1\text{-mm}$  sieves and then was stored in glass bottles at  $-4^{\circ}C$  until analysis. The selected subsoil properties are given in Table 1. The content of organic matter (OM) varied between 1.6 and  $13.9\text{ g kg}^{-1}$ . The pH is above 7 (7.86–8.95) indicating alkali soils. The remaining water content in the soil was determined gravimetrically after drying individual subsample in an oven at

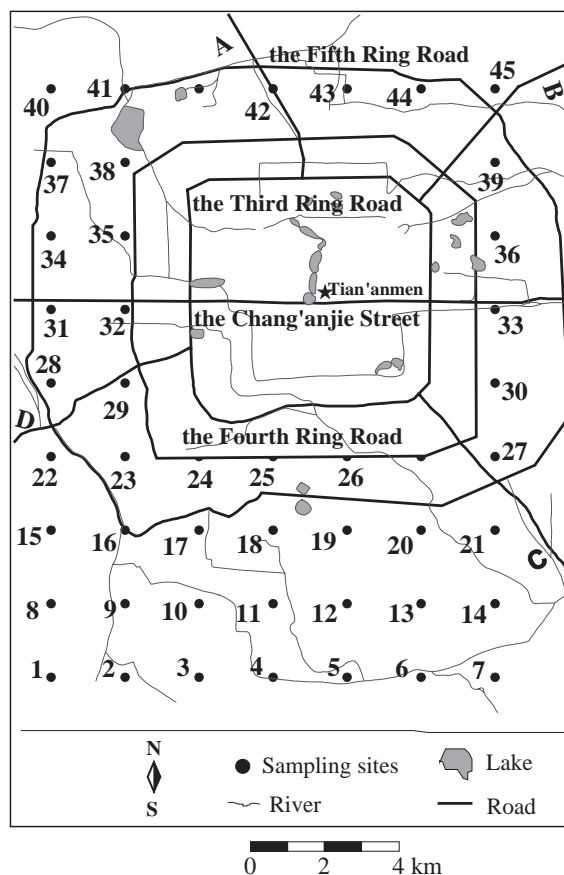


Fig. 1. Map of sampling site on the outskirts of Beijing. (A) Jing-Chang highway; (B) Beijing Capital Airport Expressway highway; (C) Jing-Jin highway; (D) Jing-Shi highway.

$105^{\circ}C$  for 12 h. All results were reported as dried weight basis.

## 2.3. Extraction and clean-up

The detailed procedure of extraction and clean-up was presented in the previous works (Chu et al., 2003; Ma et al., 2003). After 1 ml of 2-fluorobiphenyl ( $4.0\text{ }\mu\text{g ml}^{-1}$ ) was added as surrogate for PAHs analysis and 1 ml of 2,4,5,6-tetrachloro-*m*-xylene ( $0.4\text{ }\mu\text{g ml}^{-1}$ ) for organochlorine pesticides analysis, accurately weighed soil sample (about 10 g) was extracted by ultrasonic in 30 ml acetone/petroleum ether (1:1) thrice during 15 min followed and separated by centrifugation. The combined extract was divided into two portions, one for hydrocarbon analyses and the other one for organochlorine pesticides and

Table 1  
Selected subsoil properties on the outskirts of Beijing city

Site	Land-use	Clay <2 $\mu\text{m}$ (%)	pH	OM <sup>a</sup> (g kg <sup>-1</sup> )	Ntot <sup>b</sup> (g kg <sup>-1</sup> )	Soil type
1	Cornfield	2.2	8.65	2.68	0.15	Sandy
2	Woodland	9.2	8.61	4.38	0.23	Sandy loam
3	Cornfield	31.8	8.56	10.15	0.41	Clay
4	Maize field	8.1	8.76	3.39	0.22	Silt loam
5	Woodland	6.7	8.54	2.43	0.30	Silt loam
6	Maize field	15.9	8.50	5.89	0.36	Silt loam
7	Cornfield	19.8	8.73	7.43	0.42	Silt loam
8	Cornfield	14.2	8.34	12.13	0.59	Silt loam
9	Orchard	8.8	8.47	2.99	0.18	Silt loam
10	Farmland	18.4	8.49	6.18	0.41	Silt loam
11	Cornfield	17.8	8.28	7.84	0.36	Silt loam
12	Cornfield	18.5	8.52	5.68	0.34	Silt loam
13	Maize field	16.1	8.57	3.35	0.24	Silt loam
14	Cornfield	27.3	8.34	11.66	0.72	Silt loam
15	Maize field	10.6	8.15	4.65	0.32	Sandy loam
16	Scrub	13.4	8.47	6.76	0.35	Loam
17	Cornfield	11.7	8.47	2.24	0.17	Sandy loam
18	Riverbed	15.9	8.28	6.84	0.45	Sandy
19	Maize field	8.1	8.62	3.23	0.23	Silt loam
20	Scrub	16.5	8.00	3.49	0.23	Sandy loam
21	Vegetable land	15.8	8.73	4.50	0.31	Silt loam
22	Riverbed	18.5	8.68	4.49	0.20	Loam
23	Woodland	10.9	8.51	4.36	0.27	Sandy loam
24	Woodland	14.4	8.95	2.37	0.18	Sandy loam
25	Woodland	4.5	8.21	4.83	0.31	Silt loam
26	Vegetable land	3.2	8.33	11.33	0.63	Silt loam
27	Farmland	15.1	8.49	2.21	0.23	Loam
28	Vegetable land	15.1	8.72	3.51	0.24	Sandy loam
29	Vegetable land	20.0	8.21	2.47	0.14	Loamy sand
30	Vegetable land	12.5	8.38	4.97	0.31	Sandy loam
31	Foot of the hill	12.7	8.47	3.36	0.24	Sandy loam
32	Tree by the road	7.5	8.36	8.36	0.40	Sandy loam
33	Roadside grassland	13.1	8.29	9.26	0.52	Loam
34	Orchard	9.9	8.41	10.46	0.56	Silt loam
35	Tree by the road	21.2	8.35	10.64	0.52	Silt loam
36	Cornfield	13.5	8.25	5.18	0.78	Loam
37	Orchard	10.9	8.01	6.30	0.35	Loam
38	Orchard	14.4	7.86	13.85	0.67	Silt loam
39	Scrub and riverbed	9.2	8.64	8.73	0.44	Sandy loam
40	Hillside woodland	18.2	8.47	5.74	0.37	Silt loam
41	Roadside woodland	10.3	8.58	11.01	0.76	Silt loam
42	Roadside woodland	10.5	8.38	1.60	0.13	Sandy loam
43	Vegetable land	14.1	8.66	4.46	0.23	Sandy loam
44	Woodland, dump	14.9	8.46	9.25	0.50	Silt loam
45	Vegetable land	22.0	8.57	5.80	0.35	Silt loam
	Minimum	2.2	7.86	1.60	0.13	
	Maximum	31.8	8.95	13.85	0.78	
	Mean (SD <sup>c</sup> )	13.9 (5.8)	8.45 (0.2)	6.05 (5.8)	0.36 (0.2)	

<sup>a</sup> Organic matter.

<sup>b</sup> The total content of nitrogen.

<sup>c</sup> Standard deviation.

phthalate esters analysis, which would be discussed in the other paper. The solvent was evaporated by K–D apparatus and then reduced the volume to about 1 ml by a gentle stream of nitrogen.

The portion for hydrocarbon was fractionated with a silica gel chromatography column (30 cm×10 mm I.D.). After the sample solution was loaded on the column, the analytes were eluted with 25 ml of petroleum ether and followed by 30 ml of petroleum ether/dichloromethane (3:2). The second fraction contained PAHs. The solvents were evaporated and then reduced the solution volume to 0.2 ml for GC–MS determination.

#### 2.4. GC–MS determination

The determination of PAHs was performed on a Hewlett Packard 6890 gas chromatography–5973 mass selective detector (GC–MS) system equipped with a fused silica capillary DB-5 column (30 m×0.25 mm I.D., 0.25- $\mu$ m film thickness; J and W Scientific, Folsom, CA, USA) and the carrier gas was helium. The ionization was carried out in the electron impact mode at 70 eV and the mass range scanned was from 50 to 550 under full scan acquisition mode. The GC temperature program was as follows: initial temperature of 50 °C was held for 2 min, increased at a rate of 4 °C min<sup>-1</sup> to 280 °C, then held for 20 min. 1  $\mu$ l of extract was injected in the splitless mode and the purge time was 1 min. The identification was based on the retention time and mass spectrum with appropriate individual standards.

#### 2.5. Quality control

In order to monitor the sample processing, the matrix blank and procedural blank consisted of the solvents used in all steps of extraction and clean up, with the sample matrix excluded. The result showed that the purity of solvent is satisfied. The result of the soil blank used as matrix for spiking demonstrated that blanks were relatively free of contamination and only several peaks at the same retention times corresponding to several phthalate esters. Thus there is no indication of significant sample contamination during the drying.

The efficiency of the extraction and clean-up procedure was checked by spiked recovery experi-

ments ( $n=5$ ). No background subtraction was used to correct the results. Recoveries of the surrogate exceeded 80%. The recoveries with spiked PAHs in soil ranged from 75 to 115%. The limits of detection (LODs) calculated with a signal-to-noise ratio of 3:1 in blank sample ranged from 0.002  $\mu$ g g<sup>-1</sup> for BaA to 0.042  $\mu$ g g<sup>-1</sup> for Na. The relative standard deviations were less than 10% and the results are presented in Table 3. The method was used to analyze PAHs contaminated soil/sediment certified reference material CR912 (U.S. EPA). All the measurement fell within the given performance interval.

The effect of air-drying on the patterns of PAHs in this work was not tested. As reported by Cousins et al. (1997), no significant trends of loss for compounds were heavier than benzanthracene. For some of the lighter molecular weight compounds, the concentrations in wet analyzed soils were notably higher than in the dried soils. However, the conditions of their experiment could be considered to be the “worst case” because of a small soil mass used, a high percentage of the surface area of the soil particle exposed and a long exposure time. The drying conditions of our study were much better than those of Cousins et al. (1997) and they were similar to those reported by Wilcke and Amelung (2000) with even lower drying temperature in darkness (10–15 °C). In that study (Wilcke and Amelung, 2000), differences between the air-dried and wet samples were within the range of analytical error for most PAHs and polychlorinated biphenyl (PCBs) except for Na and PCB8. For these two compounds, a loss of about 45% of the initial concentrations during drying occurred. Thus the concentrations of Na reported in our study are likely to be low and have to be interpreted with care.

### 3. Results and discussion

#### 3.1. PAHs concentrations

The concentrations below the detection limits were given a value of zero for calculation. The sum of 16 priority PAHs ( $\Sigma$ EPA-PAHs) and the concentration of perylene (Per) in subsoil are presented in Table 2. The total content of 17 PAHs in subsoil ranged from not detected (three sites of 29, 42 and 45) to 0.982  $\mu$ g g<sup>-1</sup> with a mean value of 0.359  $\mu$ g g<sup>-1</sup>. Generally, about

Table 2

The sum of PAHs concentrations ( $\mu\text{g g}^{-1}$ , dried weight) in topsoil and subsoil on the outskirts of Beijing city

Site	Perylene in subsoil	$\Sigma\text{EPA-PAHs}^a$		$\Sigma\text{Car-PAHs}^b$	
		Topsoil	Subsoil	Topsoil	Subsoil
1	0.023	0.016	0.343	0.006	0.206
2	<0.006	0.337	0.238	0.318	0.038
3	0.011	0.714	0.356	0.079	0.318
4	0.064	0.442	0.098	0.347	0.078
5	<0.006	0.506	0.016	0.128	0.006
6	0.012	0.315	0.279	0.155	0.205
7	0.077	0.085	0.302	0.022	0.178
8	<0.006	0.308	0.307	0.096	0.162
9	0.230	0.047	0.627	0.032	0.513
10	<0.006	0.082	0.062	0.008	0.01
11	0.010	0.472	0.384	0.441	0.049
12	<0.006	0.353	0.215	0.229	0.042
13	0.009	2.146	0.746	1.269	0.502
14	<0.006	0.669	0.255	0.319	0.232
15	<0.006	0.533	0.076	0.235	0.069
16	<0.006	0.470	0.948	0.297	0.906
17	<0.006	0.343	0.982	0.206	0.121
18	<0.006	0.501	0.114	0.209	0.005
19	0.096	1.317	0.222	0.273	0.061
20	0.022	0.874	0.644	0.332	0.617
21	0.064	0.704	0.098	0.308	0.078
22	<0.006	0.568	0.228	0.226	0.195
23	0.340	0.811	0.600	0.257	0.589
24	<0.006	0.353	0.074	0.140	0.052
25	0.012	0.487	0.225	0.176	0.031
26	0.065	3.554	0.857	1.566	0
27	0.250	1.591	0.697	0.675	0.689
28	<0.006	1.473	0.490	0.626	0.194
29	<0.006	3.491	0	1.241	0
30	0.169	0.627	0.398	0.513	0.285
31	0.069	1.918	0.175	0.802	0.169
32	0.214	1.152	0.523	0.456	0.175
33	0.076	0.753	0.370	0.412	0.182
34	0.045	0.821	0.162	0.316	0.08
35	<0.006	1.453	0.032	0.405	0.019
36	<0.006	2.172	0.097	1.325	0.004
37	<0.006	2.361	0.081	1.020	0
38	0.007	1.252	0.144	0.436	0.024
39	0.162	3.884	0.818	1.758	0.578
40	<0.006	1.922	0.028	0.917	0
41	0.132	2.366	0.520	1.036	0.205
42	<0.006	1.321	0	1.249	0
43	<0.006	0.405	0.101	0.260	0.068
44	<0.006	0.278	0.080	0.170	0
45	<0.006	0.185	0	0.101	0
SD <sup>c</sup>	0.09	0.96	0.28	0.45	0.219
Mean	0.094	1.032	0.311	0.475	0.176
Median	0.065	0.669	0.228	0.316	0.078
Minimum	0.007	0.016	0.000	0.006	0.000
Maximum	0.340	3.884	0.982	1.758	0.906

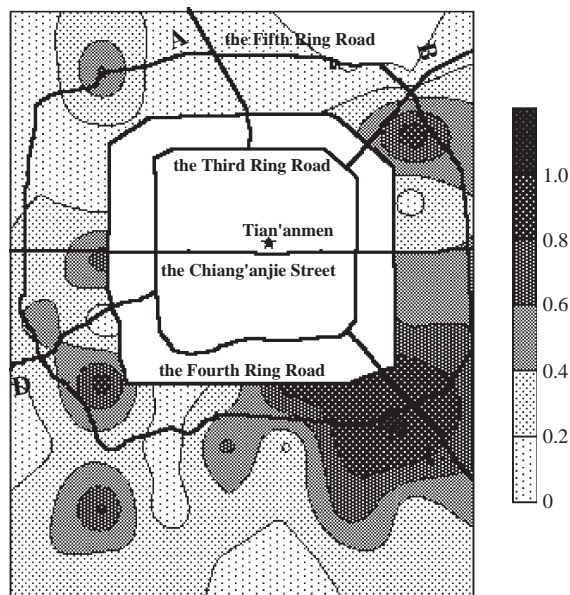


Fig. 2. The contour map of the sum of 17 PAHs ( $\mu\text{g g}^{-1}$ , dried weight) in subsoil on the outskirts of Beijing. The color scale represents the concentration range. The deeper the color, the higher the concentration.

93.3% of the subsoil sample on Beijing outskirts were contaminated with PAHs obviously above the natural level resulting from plant synthesis and fires ( $0.001\text{--}0.010 \mu\text{g g}^{-1}$ ) (Edwards, 1983). A majority of samples in the study was much higher than the target value set by Dutch government for unpolluted soil ( $0.02\text{--}0.05 \mu\text{g g}^{-1}$  dried weight), but no samples exceeded  $4 \mu\text{g g}^{-1}$ —the intervention value set for soil sanitation (Van Brummelen et al., 1996). They were also well below the guideline values for less sensitive land-use with groundwater protection which is  $40 \mu\text{g g}^{-1}$  (SNV, 1996). The highest level was found at the site of 17, which is located in the southwest of Beijing around the Fourth Ring Road. High concentration was also found at the sample of 39, which is located between the Fourth Ring Road and the Fifth Ring Road. The contour map (Fig. 2) about the sum of 17 PAHs shows that subsoil in the southeast of Beijing outskirts was contaminated with relatively higher contents of PAHs. There are many industries in this region and some of

Notes to Table 2:

<sup>a</sup> The sum of 16 priority PAHs.

<sup>b</sup> The sum of 8 carcinogenic PAHs.

<sup>c</sup> Standard deviation.

them are discharging black smokes, which could be potential atmospheric sources for PAHs.

There are no previous data about PAHs in the subsoil in Beijing or other region in China, and then no comparison could be made for the temporal and spatial variation. As reported by [Atanassova and Brümmer \(2003\)](#), the average content of 15 PAHs in the deep soils layers (1.52–1.58 m) was  $0.571 \mu\text{g g}^{-1}$ , which was higher than the data here. For our project, topsoil was also sampled which would be discussed in details in another paper. The  $\Sigma$ EPA-PAHs in topsoil is listed in [Table 1](#), which ranged over two orders of magnitude from 0.016 to  $3.884 \mu\text{g g}^{-1}$  with a mean of  $1.032 \mu\text{g g}^{-1}$ . The levels were lower than those in UK urban soil ( $4.395 \mu\text{g g}^{-1}$ ). In comparison to the other limited data reported in China, the topsoil PAHs concentrations in Beijing suburban were slightly higher than those in topsoil from Tianjin next to Beijing ( $0.20\text{--}5.19 \mu\text{g g}^{-1}$  with the mean value of  $0.82 \mu\text{g g}^{-1}$ ) ([Zhen, 2002](#)). In 33% samples of the concentrations fell into the range ( $1\text{--}3 \mu\text{g g}^{-1}$ ) of those of urban background in highly industrialized countries ([Meharg et al., 1998](#); [Weiss et al., 1994](#)). The concentrations of PAHs in most of subsoil were lower than those in the topsoil. However, the content of PAHs in subsoil at the sites of 1, 7, 8, 9, 16 and 17 were comparable or higher than those in the topsoil. Except for the site of 7, the other five sites are all located in the Beijing southwest. As investigated, the topsoil in the southwest and the north of the studied area is mainly sandy loam ([Ma, 2004](#)). The leaching of PAHs from the topsoil into the subsoil in such area would be easier. In addition, the outskirts of Beijing are undergoing rapidly urbanized and industrialized and then burying of some contaminated soil materials during the construction is another big possibility. It must be pointed out that each topsoil sample represented an area of  $16 \text{ km}^2$  covering a large scale of land usage while each subsoil sample only represented an area of  $1 \text{ km}^2$ . Therefore, the comparison of the levels of PAHs in the two different layers needs to be treated with caution.

It was notable that BaP, the most potent carcinogenic PAHs, was from not detected to  $0.579 \mu\text{g g}^{-1}$  with a mean value of  $0.051 \mu\text{g g}^{-1}$  in subsoil, which was similar to those in the topsoil ( $0.005\text{--}0.270 \mu\text{g g}^{-1}$  with a mean value of  $0.055 \mu\text{g g}^{-1}$ ). A review reported that the median concentration of BaP was from 0.01 in grassland to  $0.088 \mu\text{g g}^{-1}$  in urban soils ([Wilcke,](#)

[2000](#)). The data in our study fell in this range. The total content of eight carcinogenic PAHs, e.g., BaA, Chr, BbF, BkF, BaP, DBA, InP and BghiP ( $\Sigma$ Car-PAHs; [Menzie et al., 1992](#)) in the subsoil for each site were  $0\text{--}0.906 \mu\text{g g}^{-1}$  with a mean value of  $0.177 \mu\text{g g}^{-1}$ , which represented on average 47% of the total priority PAHs. The mean content ( $0.475 \mu\text{g g}^{-1}$ ) of  $\Sigma$ Car-PAHs in topsoil which varied from 0.006 to  $1.758 \mu\text{g g}^{-1}$  is about 2.67 times higher than that in the subsoil.

### 3.2. PAHs patterns

The average concentration of individual PAHs in subsoil is presented in [Table 3](#). The detectable frequency (DF) varied from 4% for BaA to 82% for Fl. Per>BaP>BghiP>InP were the most abundant compounds. The ratio of 2 and 3-: 4-: 5 and 6-ring PAHs was 7:1:12 and the composition of PAHs in subsoil was characterized with high molecular weight compounds known to be carcinogenic. Abundant four and five rings compounds were also observed in airborne particulate from local urban areas of Beijing ([Simoneit et al., 1991](#)), which could deposit into the topsoil. We analyzed the correlation values ( $r$ ) among 17 individual PAHs, the sum of 17 PAHs ( $\Sigma$ PAHs), soil organic matter (OM) and the total content of nitrogen (N<sub>tot</sub>) in subsoil. There was no good relationship among most of the PAHs except for Per, DBA and InP ( $r>0.8$ ). Unlike other compounds, Per ( $r=0.63$ ), DBA ( $r=0.57$ ) and InP ( $r=0.52$ ) also gave strong correlation with  $\Sigma$ PAHs. [Jones et al. \(1989\)](#) found that soil OM content has some controlling influence on the PAHs concentration in soils—the higher the OM content the higher the PAHs concentration. However, in this study, no correlations were found between PAHs concentration, organic matter content and the soil properties. For example, sample 17 had relatively low OM content, but the  $\Sigma$ PAHs concentrations in soil were high. The result suggests that the PAHs patterns in Beijing soils are not controlled by the organic matter content.

The average patterns of individual 16 PAHs in topsoil and subsoil are given in the bar diagram ([Fig. 3](#)). On average, the concentration of individual PAHs in topsoil was higher than that in the subsoil. It was clearly to be seen that unlike in the subsoil, the PAHs mixtures in the topsoil were on average dominated by Flu>Pyr>Na>BkF>Ph. The concentra-

Table 3  
Concentrations ( $\mu\text{g g}^{-1}$  dry mass) of individual PAHs in subsurface soils on the outskirts of Beijing

	Abbr.	Mean	Range <sup>a</sup>	DF <sup>b</sup> (%)	LODs <sup>c</sup>	R (%)
Naphthalene	Na	0.028	ND–0.166	40	0.042	75
Acenaphthylene	Acy	0.005	ND–0.148	11	0.011	98
Acenaphthene	Ace	0.009	ND–0.132	31	0.006	95
Fluorene	Fl	0.035	ND–0.522	82	0.003	89
Phenanthrene	Ph	0.019	ND–0.480	31	0.016	110
Anthracene	An	0.026	ND–0.216	49	0.006	95
Fluoranthene	Flu	0.009	ND–0.087	42	0.005	103
Pyrene	Pyr	0.004	ND–0.065	49	0.003	98
Benz(a)anthracene	BaA	0.002	ND–0.051	4	0.020	90
Chrysene	Chr	0.003	ND–0.051	33	0.002	106
Benzo(b)fluoranthene	BbF	0.006	ND–0.052	49	0.004	101
Benzo(k)fluoranthene	BkF	0.021	ND–0.303	44	0.003	115
Benzo(a)pyrene	BaP	0.051	ND–0.579	58	0.004	96
Perylene	Per	0.048	ND–0.340	51	0.006	101
Dibenz(a,h)anthracene	DBA	0.028	ND–0.278	49	0.007	85
Indeno(1,2,3-cd)pyrene	InP	0.035	ND–0.375	47	0.006	90
Benzo(g,h,i)perylene	BghiP	0.030	ND–0.765	36	0.011	96
$\Sigma$ 2- and 3-ring PAHs		0.122	0–0.851			
$\Sigma$ 4-ring PAHs		0.018	0–0.153			
$\Sigma$ 5- and 6-ring PAHs		0.220	0–0.940			

<sup>a</sup> Not detected.

<sup>b</sup> Detectable frequency.

<sup>c</sup> Limits of detection.

tions of Fl, BaP and InP in the subsoil were comparable or higher than those in the topsoil. The PAHs contamination process in the soil is complex. Generally, low molecular weight PAHs tend to evaporate to air or leach into deep soil and are also more susceptible to biotic and abiotic degradation (Wilson and Jones, 1993) while higher molecular weight PAHs are relatively less loss from the surface soil and also resist to degradation (Bossert and Bartha, 1986). Therefore, the distribution patterns

of PAHs in soil would shift to higher molecular weight PAHs in top layer and to lower molecular weight PAHs in deep soils. However, in this study, high molecular compounds as discussed above dominated the profile of PAHs in subsoil. We presume that such results may attribute to two possibilities: one is during the construction some topsoil contaminated with high molecular weight PAHs were moved to the deep layer; the other is there is unknown PAHs sources in the subsoil.

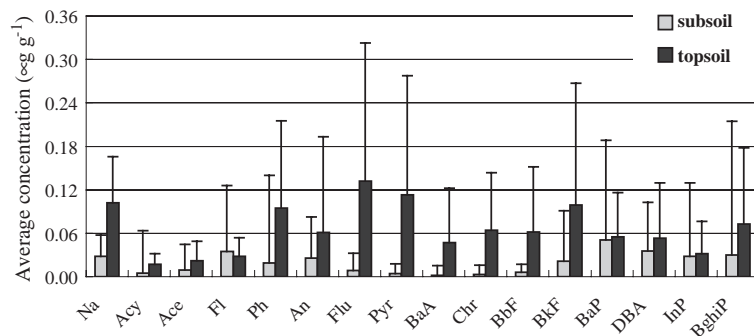


Fig. 3. The average concentration of the individual PAHs in subsoil and topsoil on the outskirts of Beijing. Bars represent means and vertical lines represent standard deviations, respectively.



### 3.3. Sources of PAHs

In the studied area, the unsubstituted PAHs were the most abundant components, which suggested combustion or pyrolysis process was dominant for the PAHs (Benner et al., 1990). Moreover, at low to moderate temperature, as in the wood stove (Lake et al., 1979), or as from the combustion of coal (Lafamme and Hites, 1978), low molecular weight parent PAH compounds are abundant. At high temperature, such as in the vehicle emissions, the high molecular weight parent PAHs compounds are dominant (Lee et al., 1977). Samples from the outskirts of Beijing exhibited significantly higher fraction of high molecular weight PAHs, suggesting the pyrolysis at high temperature such as vehicle emission was the predominated source in subsoil.

Some fingerprints could be also used in the sources identification (Khalili et al., 1995). It was reported that the ratios of Ph/An and Flu/Pyr were usually selected to distinguish petrogenic and pyrogenic sources of PAHs. A Ph/An ratio of less than 10 and a Flu/Pyr ratio of greater than 1 suggest strong pyrogenic sources (Sicre et al., 1987). In the area studied, Ph/An varied from 0.04 to 12 with a mean value of 3.11 and Flu/Pyr varied from 0.29 to 8.23 with a mean value of 2.38. Ph/An ratios plotted vs. Flu/Pyr ratios in subsoil are presented in Fig. 4. The cross plot analysis shows that in 67% samples fall into the pyrogenic zone (I) and there are three sites indicating the mixture (II) of pyrogenic and petrogenic sources of PAHs. In 26% sites with Ph/An<10 but Flu/Pyr<1 (III) were excluded from the two categories for which

it is difficult to verify the PAHs from various pollution sources just by the selected ratios.

For the three most abundant compounds in the present study, BaP is usually emitted from automobiles (Rogge et al., 1993a,b). InP and BghiP is a tracer of automobile exhausts combustion (Baek et al., 1991; Fraser et al., 1997; Li and Kamens, 1993). Another important indicator is the unsubstituted PAHs: Per. In the subsoil, Per was found at more than a half of all stations. At these samples containing Per, the average contribution is about 18%. According to Tisser and Salot (1981), a Per content of more than 10% indicates a diagenic process. In the temperate topsoil, this compound may be from pyrolysis of the fossil fuels (Wilcke et al., 2002) while in soils/sediments (not in very surface) Per is mostly derived from nature diagenesis process (Silliman et al., 1998, 2000). Vertical profile of Per concentration in a sediment core was completely different from that of other PAHs concentration in the same core (Meyers and Ishiwatari, 1993). In addition, many previous studies reported that Per is less abundant PAHs in atmospheric particles. According to Thiele and Brümmer (2002), bioformation of nearly all PAHs including DBA can take place under reducing conditions in the presence of humic substances and decomposable plant material with appropriate PAHs precursors. In the subsoil, there are strong relationships among Per, DBA and InP ( $r>0.8$ ). Therefore, the occurrence of the three high molecular weight compounds in subsoil may be biological formation partly or totally although their contents in topsoil probably originate in from anthropogenic sources.

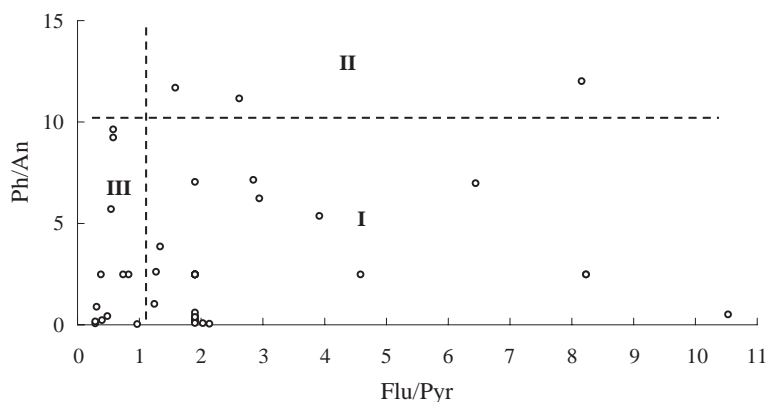


Fig. 4. Cross-plot of fluoranthene/pyrene (Flu/Pyr) vs. phenanthrene/anthracene (Ph/An) ratios in soils on Beijing outskirts.

#### 4. Conclusions

Both topsoil and subsoil on the outskirts of Beijing have been contaminated by PAHs. The overall level of PAHs is not high compared to other nation-wide and /or world-wide systems. They were characterized with high molecular weight PAHs known to be carcinogenic. The level of PAHs in subsoil was obviously lower than that in the topsoil except for several sites. It is notable that the concentration of BaP in two layers was comparable indicating the traffic influence on both soils. No correlations were found between PAHs concentration, OM and the subsoil properties. The combustion, especially the traffic emission, has a great effect on the soil PAHs contamination. Some high molecular weight compounds such as Per, DBA and InP may be biological formation.

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