



## Characterization and distribution of polycyclic aromatic hydrocarbon in sediments of Haihe River, Tianjin, China

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### Abstract

In this study sediment samples were collected from 13 sites of Haihe River in Tianjin City, China, sixteen of priority polycyclic aromatic hydrocarbons (PAHs) listed in USEPA were analyzed by means of GC-MS. The total concentrations of PAH ranged from 774.81 to 255371.91 ng/g dw, and two to four rings of PAHs were dominant in sediment samples. Molecular ratios, such as phenanthrene/anthracene, fluoranthene/pyrene and low-molecular-weight PAH /high-molecular-weight PAH, were used to study the possible sources of pollution. It indicated a mixed pattern of parolytic and petrogenic inputs of PAHs in sediments in Haihe River. The petrogenic PAHs may be mainly derived from the leakage of refined products, e.g., gasoline, diesel fuel and fuel oil vehicle traffics or gas stations from urban area. The pyrolytic PAHs might be from the discharge of industrial wastewater and the emission of atmospheric particles from petrochemical factories. In addition, the levels of PAHs in the urban and industrial areas are far beyond the values reported from other rivers and marine systems reported. This situation may be due to polluted discharging from some petrochemical industrial manufactories and worse traffic conditions in Tianjin.

**Key words:** PAHs; Haihe River; sediments; Tianjin

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely ubiquitous in the environment, having properties of persistence, high bioaccumulation and mutagenesis, and carcinogenesis potentials (Hites *et al.*, 1977; Blumer, 1976). Contamination of PAHs is very harmful to environments (Fernades *et al.*, 1997). Two sources, the anthropogenic and natural processes, contributed to the PAH input in environments. Anthropogenic input was regarded as the main source for the elevated concentration of PAHs in the environmental matrix including the incomplete combustion, oil spills, urban runoff, domestic and industrial wastewater discharges, atmospheric fallout of vehicle exhaust and industrial stack emission and so on (Doong and Lin, 2004; Simpson *et al.*, 1996; Zakaria *et al.*, 2002). All of these severely aggravate the ecological systems, especially the aquatic environment. For these reasons, it is imperative to investigate the origins and distribution of PAHs in the aquatic environment.

Located in northern China, Tianjin is the third largest industrial and commercial city in China with an area about 11200 km<sup>2</sup> and has a population of 10 million. Being one of the important limnetic reservoirs to Tianjin City, Haihe River has a vital action in maintaining the rapid

industrialization and urbanization of Tianjin City. However, Haihe River is becoming a stagnant river, its branches are almost dry because of the drought and is severely polluted by persistent organic pollutants in recently years (Tianjin Environmental Protection Bureau, 2001; Tao *et al.*, 2003). As organic contaminants, PAHs normally exist in aquatic systems in several forms including the free dissolved phase, the phase bounded to dissolved organic matter, adsorbed to suspended particulate matter, and associated with sediments (Readman *et al.*, 1984; Zhou *et al.*, 1998). As for a stagnant river, the sediment is the receiver for these pollutants. The Haihe River water has been used to irrigate in some suburban areas for more than 40 years because of water shortage in agriculture. It is more fearful that the sludge dredged from Haihe River has also been used to fertilize farmlands in Tianjin suburbs (Tianjin Environmental Protection Bureau, 1996, 2001; Wang *et al.*, 2002). PAHs can be accumulated in human bodies through food-chains, using the water and sludge in Haihe River will be greatly harmful to our health and environments (Doong *et al.*, 2004; Shi *et al.*, 2005). Up to now, there are no detailed studies on the PAHs distribution in Haihe River, so, the purpose of the present work was to investigate the distribution and possible sources of PAHs in sediments of Haihe River and to provide useful information for correlative institutions.

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## 1 Materials and methods

### 1.1 Sample collection, storage, and preparation

To understand the contamination and distribution of PAHs in sediments of the entire Haihe River, sediments were collected from 13 random sites along Haihe River in April, 2004 and the sampling sites are illustrated in Fig. 1.

The sediment samples collected with a stainless steel grab sampler were placed on ice after sampling, immediately transferred to the laboratory and kept in the refrigerators at  $-18^{\circ}\text{C}$  before analysis. Each of the samples was about 400 g.

Two hundred and fifty grams of every sample was centrifuged (3000–4500 r/min, Centrifuge TDL-5, China), freeze dried (EYELA-FDU-830, Japan), manually removed from stones, ground to granular powder in the quartz mortar to pass through a 70-mesh sieve, and prepared for the extraction and cleanup procedure.

### 1.2 Extraction and cleanup for analysis of PAHs

In these procedures the analysis programs were mainly based on EPA method 3545 (pressurized fluid extraction), 3630C (silica gel cleanup), 3660B (sulfur cleanup) and 8270C (GC/MS quantitation) etc. which were published by USEPA in 1986 and we had a modification here. After 20 g of sediment samples from the sampling procedure were mixed with anhydrous sodium sulfate (1:5 ratio of sediment to sodium sulfate) and activated copper powder (1:1, to desulfurize the extracts), the samples were extracted by accelerated solvent extraction (ASE300, Donex) with *n*-hexane and dichloromethane (1:1 v/v) for 10 min for two static cycles. The extraction temperature was  $125^{\circ}\text{C}$  and pressure was 1500 psi. And then the extraction supernatants were concentrated down to 1–2 ml by rotary evaporator and subsequently purified by the chromatographic column. The chromatographic column was filled with 8 g activated silica gel in *n*-pentane environment, and 1 g anhydrous sodium sulfate overlaying the silica gel. Twenty-five milliliters of *n*-pentane solvent was firstly used to wash the column in order to remove non-

PAHs impurities from the column, and then another 25 ml mixed solvent of dichloromethane and *n*-pentane (2:3 v/v) was used to wash the column for the second time. The second effluent containing PAHs from the samples was collected and concentrated by a rotary evaporator. Finally, the effluent was reduced to a final volume of about 0.1–1.0 ml under a stream of purified  $\text{N}_2$  for the next procedure.

### 1.3 Determination of PAHs

The separation and identification of all samples were analyzed on a Thermo Finnigan trace gas chromatograph equipped with a trace mass selective detector (MSD) (Trace GC 2000-Trace MS, Finnigan, USA). One microlitre of each of extraction samples was injected in a splitless model into the GC-MS equipped with a column which was a 30 m HP-5MS (0.25 mm i.d, 0.25  $\mu\text{m}$  film thickness) (Agilent, USA). Helium was used as carrier gas at a constant flow rate of 1 ml/min. Before injecting samples, the column temperature was programmed from an initial temperature of  $50^{\circ}\text{C}$  (5 min hold) to  $200^{\circ}\text{C}$  (5 min hold) at the rate  $10^{\circ}\text{C}/\text{min}$ , and then followed to  $260^{\circ}\text{C}$  (15 min hold) at the rate  $6^{\circ}\text{C}/\text{min}$ . The MSD was operated in the electron impact mode at 70 eV. The transfer line and ion trap manifold were set at  $280^{\circ}\text{C}$  and  $230^{\circ}\text{C}$ , respectively. Quantification was performed by the external standard method by using a 16 PAHs standard mixture (PPH-10JM, Chem Service Inc., USA). This standard was also performed in the identity and retention time procedures. The mass range scanned was from 50 to 450 amu under full scan acquisition mode. The 16 PAHs detected in sequence were: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (An), fluoranthene (Fla), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InD), dibenz [a,h]anthracene (DahA), benzo[ghi]perylene (BghiP).

Analyzing the individual PAHs composition can be used as an indicator to assess the possible pollution source and illustrated the fate and transport of PAHs in environment

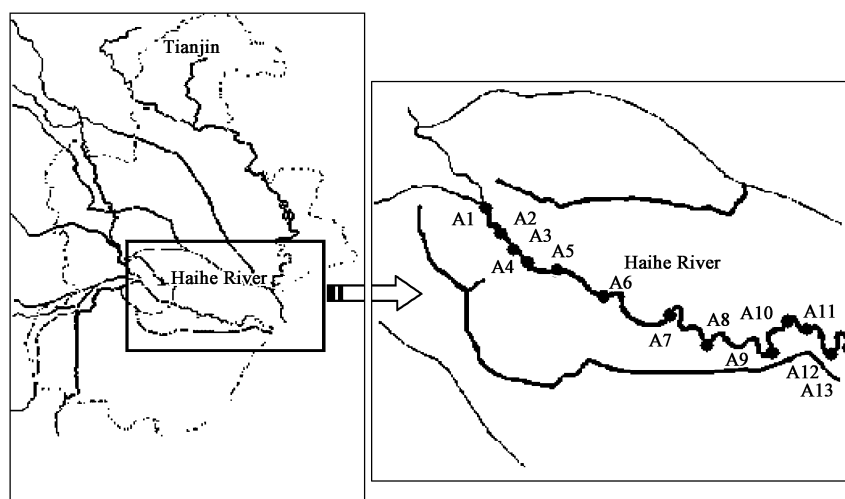


Fig. 1 Sampling area and locations.

(Gigliotti *et al.*, 2002). In this study, several molecular ratios of Ph/An, Fla/Py and LPAH/HPAH (LPAH: containing 2- and 3-rings PAHs; HPAH: containing all of the 4- to 6-rings PAHs) have been developed to interpret PAH compositions and infer the possible sources of PAHs (Soclo *et al.*, 2000; Fernandes *et al.*, 1997; Budzinski *et al.*, 1997). The above ratios were calculated using the average concentrations of individual PAH compounds collected from different stations. For example, phenanthrene and anthracene are two structural isomers of which phenanthrene is a more thermodynamically stable compound than anthracene, and fluoranthene and pyrene have the same condition as phenanthrene and anthracene. Therefore, the values of Fla/Py and Ph/An ratios are related to pyrolytic origins as the value of Fla/Py greater than 1 and that of Ph/An less than 10 at the same time, while the value of Fla/Py less than 1 and that of Ph/An greater than 10 at the same time should be attributed to a petrogenic source (Sirece *et al.*, 1987; Budzinski *et al.*, 1997). In addition, LPAH/HPAH ratios were used to distinguish PAHs of various origins. For instance, low temperature pyrolytic processes such as coal combustion are enriched in the LPAH, whereas coke emissions were done in the higher molecular weight (containing 5- to 6-rings) PAHs (Mai *et al.*, 2002; Schneider *et al.*, 2001). Therefore, the PAHs derived from petrogenic origins if the value of LPAH/HPAH is greater than 1, while from pyrolytic origins if the value of LPAH/HPAH is smaller than 1.

#### 1.4 Analytical quality controls

The method detection limits (MDLs) of PAHs were determined as the concentrations of analytes in a sample which gives rise to a peak with a signal-to-noise ratio of 3. The MDLs here ranged from 1 to 50 ng/g dw. A procedural blank and spike sample consisting of all reagents were run to check for interference and cross contamination for every set of samples. Here the spiked PAH concentrations were 2000 ng/g dw. In this study the recovery of PAHs ranged from 75% to 122%. The methods in this study are qualified for analyzing 16 priority parent PAHs in sediments.

## 2 Results and discussion

### 2.1 PAHs concentrations in sediment

The 16 priority PAHs were detected in all of the sediment samples (Table 1). The PAH concentrations showed wide variation range of 0.154–74433.66 ng/g dw. For individual PAHs, the concentrations were between 186.09 and 11206.45 ng/g dw for naphthalene (2-ring PAHs), 14.46–74433.66 ng/g dw for acenaphthylene, acenaphthene, luorene, phenanthrene and anthracene (3-ring PAHs), 0.85–58345.33 ng/g dw for fluoranthene, pyrene, benz[a]anthracene and chrysene (4-ring PAHs), 0.15–6314.93 ng/g dw for benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenz[a,h]anthracene (5-ring PAHs), and 6.74–3426.90 ng/g dw for indeno[1,2,3-cd]pyrene and benzo[ghi]perylene (6-ring PAHs). 2-, 3- and 4-ring PAHs occupied about 7.6%, 44.4% and 41.2% of the total PAH

Table 1 Concentrations of PAHs in sediment samples from Haihe River at different sampling stations (ng/g dw)

Sample	Nap	Acy	Ace	Fle	Ph	An	Fla	Py	BaA	Chr
A1	11206.45	1773.23	8121.44	13650.05	74433.66	17851.28	58345.33	32533.34	8461.17	10125.44
A2	5471.03	362.74	596.65	1375.19	6088.85	1417.00	4561.28	2445.43	551.79	810.02
A3	2243.57	280.64	864.54	1294.31	5212.30	1421.04	4118.10	3105.03	581.22	729.51
A4	902.07	360.77	800.80	1329.11	5535.47	1450.31	3708.63	2800.96	582.73	655.46
A5	3110.92	391.17	432.07	862.14	2534.39	831.89	2619.07	1611.62	331.94	470.52
A6	186.09	59.62	100.28	46.69	51.44	48.70	108.77	72.34	10.33	9.49
A7	211.98	41.52	72.33	100.22	38.51	34.78	175.59	47.27	1.66	0.85
A8	296.21	70.18	30.02	77.21	44.32	53.20	105.83	49.17	10.18	8.11
A9	306.47	88.22	14.46	81.13	52.16	48.26	165.61	52.85	12.27	9.47
A10	451.12	102.66	318.98	285.43	117.83	54.54	371.02	180.31	20.52	14.66
A11	854.31	227.01	280.50	906.30	1062.44	983.09	1522.74	967.02	67.67	56.60
A12	1302.51	242.49	55.91	572.12	186.20	78.95	1065.49	683.45	42.36	26.02
A13	235.12	132.14	47.56	25.65	80.53	38.32	134.00	79.11	6.51	4.02
Sample	BbF	BkF	BaP	InD	DahA	BghiP	∑PAHs			
A1	6314.93	1542.80	3361.40	3426.90	1882.77	2341.73	255371.91			
A2	419.74	81.47	201.04	247.71	123.41	110.06	24863.43			
A3	400.02	52.02	210.79	224.46	69.23	90.77	20897.54			
A4	337.02	59.24	210.95	226.81	90.81	107.40	19158.54			
A5	257.72	37.61	193.92	148.27	60.00	106.31	13999.59			
A6	3.47	0.15	0.79	8.97	12.55	55.12	774.81			
A7	3.47	0.98	0.37	17.52	54.84	35.15	837.01			
A8	1.40	0.35	1.75	14.52	16.34	13.62	792.41			
A9	0.82	0.65	0.36	9.11	7.51	8.45	857.81			
A10	6.93	0.99	0.16	9.69	45.33	6.74	1986.91			
A11	25.02	10.75	11.56	16.74	25.55	95.74	7113.04			
A12	21.52	11.51	8.99	13.27	27.26	85.33	4423.38			
A13	2.46	6.23	4.51	10.12	18.02	62.35	886.65			

Nap: naphthalene; Acy: acenaphthylene; Ace: acenaphthene; Fle: fluorine; Ph: phenanthrene; An: anthracene; Fla: fluoranthene; Py: pyrene; BaA: benz[a]anthracene; Chr: chrysene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BaP: benzo[a]pyrene; InD: indeno[1,2,3-cd]pyrene; DahA: dibenz[a,h]anthracene; BghiP: benzo[ghi]perylene.

concentration, respectively, showing that two to four rings PAHs were the most abundant in the sediment samples. In addition, the concentrations of all individual PAHs were also various in the study area. The proportion of each of the individual PAHs in the total PAH concentration are shown in Fig.2. It can be obviously seen that phenanthrene and fluoranthene have higher concentrations among the 16 PAHs in the sediment samples, occupying approximately 27.12% and 21.88%, respectively.

Table 2 illustrates the concentration levels of the total PAH in different riverine and marine sediments in the reports (Ashley and Baker, 1999; Khim *et al.*, 2001; Baumard *et al.*, 1998; Zakaria *et al.*, 2002; Pereira *et al.*, 1996; Witt, 1995; Valette-Silver *et al.*, 1999; Zhou *et al.*, 2000). The total concentrations of PAH in different sediments from Haihe River ranged from 774.81 to 255371.91 ng/g dw. The mean value of the total PAH concentrations in Haihe River was 27074.08 ng/g dw that was 2.7- to 225.6-fold greater than the reported ones in Fig.2.

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## 2.2 Spatial distribution of PAHs

Fig.3 illustrates the total PAH concentrations were signi-

ficant differences in all of the sampling locations ranged from 774.81 ng/g dw to 255371.91 ng/g dw. The highest concentration occurred at the location A1, approximately 10–330 fold higher than from other locations. It is possible that the site A1 is the junction of four highly polluted branches in the last years which are Beiyunhe, Nanyunhe, Xinkaihe and Ziyahe Rivers, these rivers should give the most contributions to the concentration of the station A1. High concentrations of the total PAHs still occurred in the sites of A1 to A5 in urban and industrial regions and ranged from approximately 13999.59–255371.91 ng/g dw with a mean value of 66858.20 ng/g dw. Low concentrations occurred at sites of A6 to A13 in suburban regions in the range of 774.81–7113.04 ng/g dw with a mean value of 2209 ng/g dw. Relatively high concentrations in urban and industrial regions (A1 to A5) may be attributed to the high emissions of both atmospheric deposits from petrochemical factories located along Haihe River in the past decades and automobiles in these regions. In addition, because there was little water from branches in recent years for the drought weather, the water in Haihe River is almostly stagnant. Consequently, the suspended particulate matter with PAHs, which mainly derived from the urban and industrial areas, was gradually deposited locally and had almost no transport in the Haihe River due to less hydrodynamic conditions. Obviously the stagnant water may further give rise to the higher concentrations of PAH in the urban and industrial areas than that in the suburban areas (Koh *et al.*, 2002; Tianjin Environmental Protection Bureau, 1996, 2001).

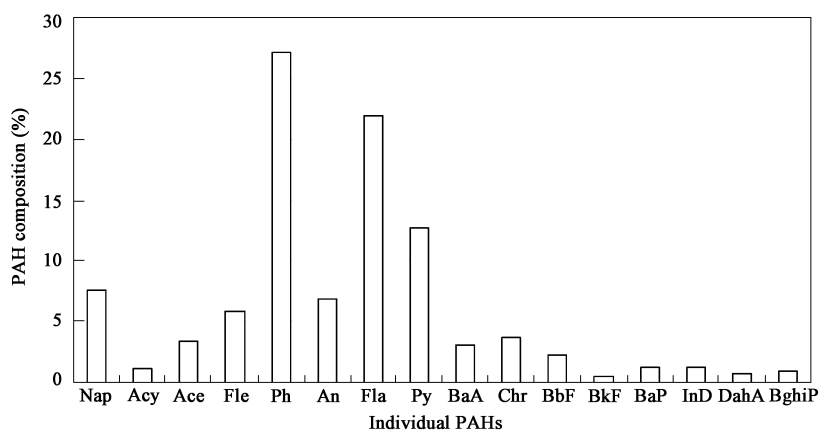


Fig. 2 Sixteen individual PAHs proportion in the total PAH concentration.

Table 2 Total PAHs in sediments from different locations

Locations	Sample number	$\Sigma$ PAHs (ng/g dw)		Reference
		Mean	Range	
Haihe River, China	13	27074	775–255372	This study
Baltimore Harbor, USA	80	10030	89–46200	Ashley and Baker, 1999
Ulsan Bay, Korea	30	339	10–3100	Khim <i>et al.</i> , 2001
West Mediterranean Sea	22	2306	1.5–20440	Baumard <i>et al.</i> , 1998
Malaysia	21	187	4–924	Zakaria <i>et al.</i> , 2002
San Francisco Bay, CA.	16	8195	2944–29590	Pereira <i>et al.</i> , 1996
Baltic Sea	15	1200	720–1900	Witt, 1995
Beaufort Sea, Alaska	11	275	159–1092	Valette-Silver <i>et al.</i> , 1999
Xiamen Harbor, China	9	367	247–480	Zhou <i>et al.</i> , 2000

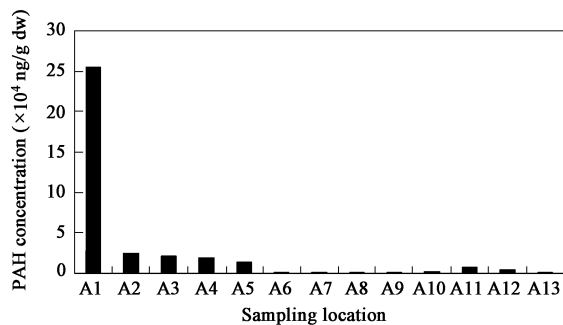


Fig. 3 Total PAH concentrations in sediments at different locations from Haihe River. A1 to A13 represents sampling locations.

### 2.3 PAHs compositions in sediments

In this study the ratios of Fla/Py and Ph/An were in the range of 1.32–3.72 and 0.83–4.30, respectively. Only at the station A8 the ratio of Ph/An was smaller than 1. The result indicated that the PAHs in Haihe River obviously derived from a pyrolytic source. In the past few years, there were many petrochemical industries along Haihe River. The discharge of industrial wastewater and the emission of atmospheric particles from these factories might be the pyrolytic source in this study area (Tao *et al.*, 2003; Tianjin Environmental Protection Bureau, 2001). Although these factories were forced to close by the local government in recent years because of their severe pollution problems, the PAHs in sediments derived from these factories many years ago are still abundant in Haihe River. However, the ratios of LPAH/HPAH in this study ranging from 0.99 to 2.58 with a mean value of 1.61 (Fig.4), which were all greater than 1 except for the station A1 (the value was 0.99), indicated that these sediments were mainly contaminated by petrogenic PAHs. Normally, in big cities like Tianjin City petrogenic PAHs are mainly derived from the leakage of the refined products such as gasoline, diesel fuel and fuel oil from urban vehicle traffics and gas stations. When entering into the environment, they are widely dispersed through atmospheric transport and absorbed to the dust in the air which gradually deposited onto the ground and rivers. After a long time, the street dust absorbed with the PAHs can transport into rivers and become the suspended particulate matter in aquatic systems via surface runoff due to the high and intense rainfall events. At last the PAHs in sediments will be enriched greatly due to the deposition of suspended particulate matter (Readman *et al.*, 1984; Zhou *et al.*, 1998).

The conclusion that the sediments were mainly con-

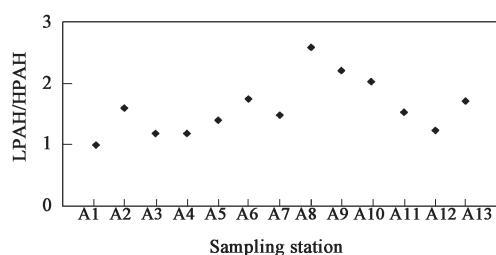


Fig. 4 The LPAH/HPAH ratios in sediments from different stations.

taminated by petrogenic PAHs we have drawn from the LPAH/HPAH is just on the contrary with the result that the PAHs in Haihe River derived from a pyrolytic source drawn from the Ph/An and Fla/Py ratios. These contrary results were not inconsistent but in fact reflected that in Haihe River there were a mixed inputs of pyrolytic and petrogenic PAHs simultaneously. For instance, recently Zakaria *et al.* (2002) reported that the PAH source in Malaysian riverine and coastal sediments contains both petrogenic and pyrolytic PAHs. As many possible contamination sources may be coexistent, samples in this study were characterized as a mixture of pyrolytic and petrogenic contamination that is in good agreement with our results.

### 3 Conclusions

The study showed that concentrations of the total and individual PAHs in sediments from Haihe River were all extraordinarily higher in the world, and PAHs with two to four rings were the most abundant and accounted for about more than 93% of the total PAH concentration. The distribution of PAH concentrations in sediments varied significantly in all of the sampling locations. The PAH concentrations were sharply higher in the stations (A1 to A5) in the industrial or urban areas than in suburban areas, which may be due to the more petrochemical factories and automobiles in the industrial and urban areas but the less ones in suburban areas. According to the ratios of Ph/An, Fla/Py and LPAH/HPAH, we found that the PAHs in sediments in Haihe River simultaneously derived from both petrogenic and pyrolytic sources. The petrogenic PAHs may be mainly derived from the leakage of refined products such as gasoline, diesel fuel and fuel oil from urban vehicle traffics and gas stations. The pyrolytic PAHs may be attributed to the contamination from petrochemical industries along Haihe River in the last years.

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