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Distribution and Source of Polycyclic Aromatic Hydrocarbons (PAHs) on Dust Collected in Shanghai, People's Republic of China

Y. Ren, Q. Zhang, J. Chen

Center for Environmental Chemistry Study, Department of Environmental Science and Engineering, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China

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Dust is one of the main atmospheric components in the urbanized area (Hildemann et al., 1991). The distribution and concentration of polycyclic aromatic hydrocarbons (PAHs) coated to the dust are paid special attention because of their mutagenic and carcinogenic properties, and consequently have been put into the list of priority monitoring pollutants (Bouzige et al., 1999). Mainly generated during the incomplete combustion of fossil fuels, PAHs are ubiquitous in the atmospheric environment and result in more serious pollution near urban centers than rural areas. With the fast development of population and motors during the last decades, the atmospheric pollution has become one of the main issues in Shanghai. However, few investigations have been conducted to address the distribution of PAHs in dust in Shanghai, not even in China (Qi et al., 2001; Wu et al., 2005). The carcinogenic activity of extractable organic matter from airborne particles in Shanghai is mainly related to the PAHs fraction (Zhao et al., 2003). In the Reports of Environmental Quality of Shanghai in 2003, dust is identified as the most abundant pollutant in urban, suburban and rural areas. But by now, the research on distribution and source of PAHs concentrations of dust in this megacity remains scarce.

The objective of the present work is to measure EPA 16 priority PAHs pollution in dust collected from thirteen sites in Shanghai, China. This study is to investigate the concentration, distribution and source of PAHs in dust of Shanghai for the first time. It is hoped that the results from this study will provide a basic reference to the research of PAHs in dust for the Yangtze River delta database, and for regulatory action to improve environmental quality in Shanghai.

MATERIALS AND METHODS

Sets of stainless steel plates (area 60×40 cm^2, height 5 cm, flat bottom) for collecting bulk deposition (dry and wet depositions mixed together) were placed at thirteen sites in Shanghai urban area from Nov 12, 2004 to Dec 15, 2004. The sampling sites are shown in Figure 1 and described in Table 1. The height of all sampling sites to the ground is less than 1 m. Dust particles were wiped off from the bottom of plates with a brush, dried in a desiccator for 24 h, and then sieved (200 mesh). The samples were stored in a refrigerator at -18 °C before extraction.

Correspondence to: J. Chen

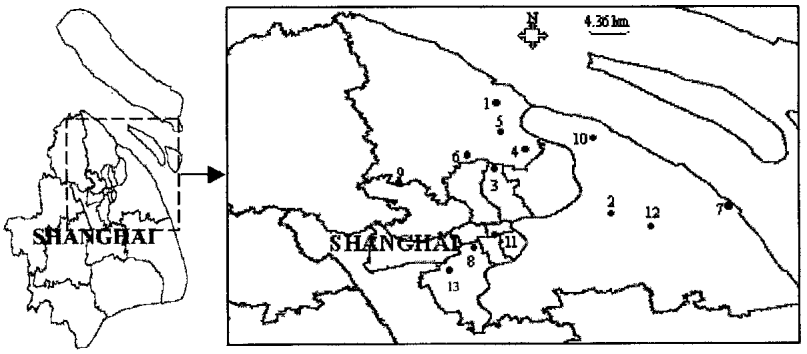

Figure 1. Sampling Sites of dust in Shanghai. The number corresponds with that in Table 1.

Residue grade dichloromethane was purchased from Sigma-Aldrich Lab (Milwaukee, WI, USA). SFE-grade CO_2 was obtained from Shanghai Yunguang Co.. A PAHs mixture containing 16 compounds in methanol was purchased from Chem. Service (West Chester, PA, USA). The compounds contained in the mixture are Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flo), Anthracene (Ant), Phenanthrene (Phe), Fluorathene (Flu), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (InP), Dibenz[a,h]anthracene (DbA) and Benzo[g,h,i]perylene (BgP). A semi-volatile internal standard mixture (2000 μg mL^{-1}) in methylene chloride containing Acenapthene-d10 (Ace-d10), Chrysene-d12 (Chry-d12), Naphthalene-d8 (Nap-d8), Perylene-d12 (Per-d12) and Phenanthrene-d10 (Phe-d10) was purchased from Supelco (Bellefonte, PA, USA). Pyrene-d10 (Py-d10) as surrogate standard was purchased from Sigma-Aldrich (Miamisburg, USA).

Supercritical Fluid Extraction (SFE) was performed with a SFXTM 220 SFE System (Isco, Inc. USA) using high purity CO_2. Each 100.0 mg dust sample was extracted in a 10 mL extraction cell. Collection of the extracted analytes was carried out in a test tube filled with approximately 10 mL dichloromethane. SFE was carried out in the following procedure: a 5-min period on static mode, followed by 30-min dynamic extraction at 80 °C and 4500 PSI. Supercritical fluid flow rate on dynamic step was held at 1.5 mL min^{-1} by a variable-flow restrictor. After extraction, all solutions were evaporated and adjusted to 200 μL in dichloromethane under a gentle stream of clean nitrogen. The analysis was performed on GC-MS spectrometer (Agilent, USA). A HP-5MS (J & W Scientific, USA), 30 m × 0.25 mm I.D., fused-silica capillary column, of 0.25 μm film thickness was used. The carrier gas was high purity helium (1.0 mL min^{-1}). The temperature program was from 80 °C (1 min) to 150 °C at 15 °C min^{-1}, then from 150 °C to 200 °C at 5 °C min^{-1}, and finally from 200 °C to 300 °C (8 min) at 10 °C min^{-1}. The injector temperature was set at 250 °C and 1 μL analyte was injected in splitless mode. The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The quantitative analysis was processed

through the selective ion mode (SIM). In the methods of this study, the PAHs had recoveries between 59-119% with the majority falling in the range of 80-120%, except Nap (59%), Acy (72%) and Ace (76%). Relative standard deviations of the recoveries of each PAH were in the range of 2-10%. In addition, Py-d10 as surrogate standard was added in the 16 PAHs mixture, the average recovery of which was 81%. The blank tests did not show any significant levels of any of the PAHs, and thus, contamination from the experimental procedure can be excluded.

Table 1. Sample sites and environmental data for dust in Shanghai.

Number	Site codes	Sample site	Representative environment
1	B	BaoSteel	Industrial region of steel
2	C1	Century Park	Park
3	C2	Crossover of main roads	Area of heavy traffic
4	F	Fudan University	Educational area
5	J	Jiang Wan	Traffic zone
6	R	Residential quater	Residential area
7	S1	San Jia Gang	Outskirts
8	S2	Shanghai Normal University	Educational area
9	T	Tao Pu	Logistic center
10	W	Wai Gao Qiao	Industrial region of chemical plants
11	X	Xu Jia Hui	Shopping center
12	Z	Zhang Jiang	Industrial region of Electronic Industries
13	G	Outside of Guilin Park	Near one main road

RESULTS AND DISCUSSION

The average concentration ($\mu g\ g^{-1}$) of the individual PAH, and their sums were showed in Table 2. There were 6 sites in Table 2, the concentrations of which were lower than the mean value (8.48 $\mu g\ g^{-1}$ see Table 4). The total concentration of PAHs at Site S1 was the lowest, which was near the sea, and far away from the downtown area, and the level of everyday activity (traffic, fossil fuel combustion, cooking and heating, etc.) in the area was low. The most serious polluted sites were Site C2 and G, in which C2 lies at the crossover of two main roads, and sample G was collected from the outside of Guilin Park which is near one main road. The concentrations of most PAHs of two sites were maximal in all values measured. The concentrations of other sites such as Site B, J and R were higher than 9.00 $\mu g\ g^{-1}$. Around those sites the main surroundings were industrial area, traffic zone and residential areas, in which combustion was the very important activities of human beings. The observation above emphasized that locations with heavy traffic burden, large industrial point sources and contributions to the domestic heating resulted in higher levels of PAHs.

In recent years, the amount of coal has been decreased and the quality of coal

Table 2. The concentrations (μg g^{-1}) of priority PAHs in dust from 13 different regions in Shanghai.

Site codes		B	C1	C2	F	G	J	R	S1	S2	T	W	X	Z
PAHs	N / n	3	3	5	6	7	5	3	4	7	6	4	4	4
Nap	2	0.34	0.57	0.32	0.29	0.57	0.28	0.58	0.30	1.31	0.36	0.21	0.22	0.10
Acy	2	Nd	Nd	Nd	Nd	0.55	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Ace	3	0.08	0.06	0.10	0.07	0.22	0.06	0.58	0.08	0.05	0.11	0.11	0.02	0.03
Flo	3	0.17	0.17	0.19	0.26	0.50	0.15	0.19	0.12	0.16	0.18	0.22	0.08	0.08
Phe	3	1.67	1.05	1.92	1.92	3.58	1.44	1.89	0.53	1.33	1.43	1.58	0.96	0.62
Ant	3	0.19	0.14	0.22	0.18	0.37	0.20	0.17	0.09	0.16	0.17	0.23	0.12	0.11
Flu	4	0.34	0.16	0.35	0.28	0.56	0.22	0.26	0.11	0.32	0.21	0.23	0.13	0.16
Pyr	4	1.50	0.61	2.12	1.23	2.98	1.60	1.40	0.30	1.05	1.27	1.16	0.74	0.53
BaA	4	0.55	0.26	0.82	0.44	1.05	0.46	0.48	0.16	0.40	0.43	0.59	0.25	0.20
Chry	4	0.81	0.42	1.84	0.71	1.27	1.10	0.95	0.26	0.79	0.85	0.94	0.46	0.38
BbF	5	0.56	0.35	1.44	0.58	1.12	0.79	0.69	0.21	0.66	0.61	0.72	0.36	0.44
BkF	5	0.49	0.27	1.08	0.41	1.00	0.58	0.55	0.18	0.46	0.48	0.53	0.29	0.35
BaP	5	1.86	0.51	1.92	0.86	1.61	0.99	0.95	0.31	0.86	0.73	1.02	0.51	0.84
DbA	5	0.17	0.16	0.28	0.19	0.25	0.20	0.19	0.17	0.19	0.17	0.19	0.15	0.22
InP	6	0.34	0.26	0.93	0.42	0.82	0.58	0.43	0.20	0.43	0.36	0.55	0.26	0.30
BgP	6	0.23	0.21	0.68	0.34	0.64	0.43	0.34	0.16	0.35	0.27	0.46	0.21	0.28
sum		9.30	5.20	14.21	8.18	17.09	9.08	9.65	3.18	8.52	7.63	8.74	4.76	4.64

Note: n : the number of rings of PAHs; N : the number of testing; Nd: Not determined;
Site codes were listed in Table 1.

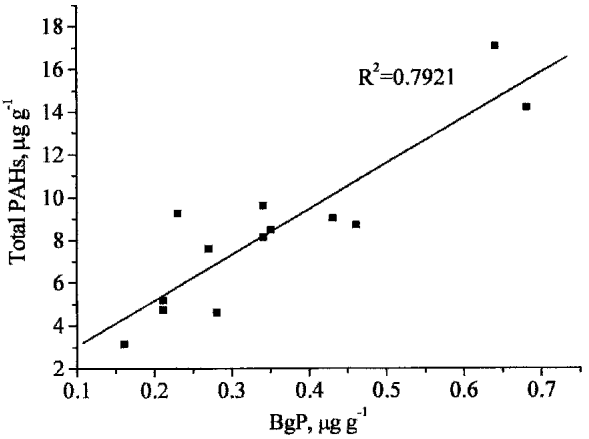

Figure 2. Correlation between BgP and Total PAHs.

improved gradually in Shanghai under the severe control. However, the motor vehicle in Shanghai has grown rapidly. The investigation showed that the vehicle has grown at an average rate of 23% per year from 1992, and exceeded 2.0 million in 2004. This means that exhaust of the vehicle will be the main sources of PAHs in Shanghai. As shown in Table 2, the concentrations of Bap and Chry were almost highest at Site C2. In addition, Site G, J and T were near heavy traffic roads where the concentrations of some PAHs (e.g. Phe, Chry, BaA and Pyr) were very high. Some results of calculation were shown in Table 3. The values of InP/(InP + BgP) in the 4 sites were 0.58, 0.56, 0.57 and 0.57, which were in the range (0.35-0.70) for diesel engine emission (Fang et al., 2004). And the values of Flu/(Flu + Pyr) and InP/BgP were similar at these sites. And there was a good correlation between BgP concentration and the total PAHs concentration in the dust (Figure 2). Since BgP was associated with the vehicular emission (Zheng et al., 2000; Omar et al., 2002), which suggested that the vehicular emissions was the main source of dust PAHs in Shanghai. The mean BaA/Chry (0.57 ± 0.11) and BbF/BkF (1.28 ± 0.16) values in the dust samples were comparable to those in the automobile combustion source samples (0.53 ± 0.06 and 1.26 ± 0.19, respectively) (Dickhut et al., 2000). Taken together, the above compositional analysis affirmed that the vehicular emission from fossil fuel combustion appeared to be the predominant source of combustion-derived PAHs in dust of Shanghai. The exhausts of the vehicle, especially the traffic jams resulting in the slow-down of the vehicle, a large amount of PAHs was emitted from the incomplete combustion of petroleum fuel.

Table 3. Concentrations ratios of PAHs in dust from 4 sampling sites.

	C2	G	J	T
InP/InP+BgP	0.58	0.56	0.57	0.57
Flu/Flu+Pyr	0.14	0.16	0.12	0.14
InP/BgP	1.37	1.28	1.35	1.33

From the figures of all selected sites, the most serious species were BaP, Phe and Pyr, the maximal values of which were 1.92, 3.58, and 2.98 μg g^{-1}, respectively. The concentrations of Nap, Ace, Flo, DbA, and Ant were relatively low. The total contribution of BaP, Phe, BaA, Chry, Pyr, BbF and BkF in all PAHs were in the range of 61-80%, the highest of which was 12.61 μg g^{-1} at Site G, followed by 11.14 μg g^{-1} at Site C2. However, Acy, Ace, Flo, DbA and Ant had relative low concentration in dust, below 0.25 μg g^{-1} in most cases, many of which have less than 3-ring in their structures. It indicated that in urban dust of Shanghai, PAHs owning 3-ring, 4-ring and 5-ring were the primary components, some of which were the main genotoxic PAHs to humans. Although the storage of samples will cause the partial evaporation of low-molecular-weight (LMW) PAHs, this result may be mainly related to the long deposit time of dust, which resulted in the volatilization of LMW PAHs such as Nap, Ace and Acy. It was similar with the investigation of aerosol collected from Beijing (Xie et al., 2003) and Hong Kong (Zheng et al., 2000). LMW PAHs tended to be concentrated in the vapor phase while high-molecular-weight (HMW) PAHs were often associated with particulates.

Table 4. Comparison of PAHs measurements (μg g^{-1}) in dust collected in different regions in the world (Shanghai: this study; Kurashiki City: Oda et al., 2001; Macao: Qi et al., 2001; Berlin: Frommer et al., 2004).

Cities	Shanghai[1]			Kurashiki City[2]		Macao[3]		Berlin#[4]	
	Mean	Med.	Max	Mean	Max	Mean	Max	Med.	Max
Nap	0.53	0.32	1.31	Nd	nm	0.07	0.14	0.20	1.90
Acy	0.18	Nd	0.55	nm	nm	0.05	0.09	0.03	0.10
Ace	0.33	0.08	0.58	nm	nm	0.02	0.02	0.05	0.26
Flo	0.39	0.17	0.50	nm	nm	0.06	0.15	0.09	0.24
Phe	1.64	1.44	3.58	2.60	2.90	0.66	1.62	0.96	2.11
Ant	0.38	0.17	0.37	0.46	0.57	0.12	0.37	0.07	0.21
Flu	0.52	0.23	0.56	5.50	6.50	1.34	4.24	0.96	3.19
Pyr	1.46	1.23	2.98	6.90	7.80	1.96	6.15	0.67	2.28
BaA	0.72	0.44	1.05	0.83	1.20	0.45	1.20	0.29	1.41
Chry	1.06	0.81	1.84	1.70*	1.90*	1.92	4.00	0.55	2.00
BbF	0.97	0.61	1.44	1.20**	1.40**	0.88	1.88	0.54	1.90
BkF	0.83	0.48	1.08	0.22	0.28	0.39	0.92	0.37	1.91
BaP	1.28	0.86	1.92	0.35	0.49	0.30	0.70	0.29	1.39
DbA	0.54	0.19	0.28	Nd	nm	0.20	0.52	0.05	0.29
InP	0.85	0.42	0.93	0.38	0.54	0.64	1.51	0.33	2.11
BgP	0.76	0.34	0.68	0.74	nm	1.60	3.20	0.35	1.28
sum	8.48	8.52	17.09	17.98	23.58	10.66	26.71	5.80	22.58

Note: #: values of household dust; *: sum of Triphenylene and Chrysene; **: sum of Benzo[b]fluoranthene and Benzo[j]fluoranthene; Nd: Not determined; nm: not mentioned in the reference.

1. Dust from outdoor in Shanghai; 2. Dust from a roadway tunnel in Japan; 3. Dust from outdoor in Macao; 4. Dust from inside of apartment in Berlin.

Results from Site B, C2, G, J and T exhibit higher fractions of HMW PAHs (80%, 78%, 74%, 77% and 76%) than those from Site C1 and S1 (67% and 61%). The former five sites were close to various sources of pollution (e.g., steel plant, traffic zones), while the latter two sites were far away from them. It indicated that a large proportion of HMW PAHs was a typical character of dust collected from the sources of severe pollution considered as combustion origin products (Budzensiki et al., 1997; Masclet et al., 1987). The ratio of the sum of major combustion specific compounds (ΣCOMB, Flu, Pyr, Chry, BaA, BbF, BkF, InP and BgP) to the sum of 16 PAHs was less than 0.5 in park at Site C1, and more than 0.6 at Site C2 and J, indicating that there were more extensive combustion activities at the latter two sites.

As shown in Table 4, many PAHs concentrations measured in this study were similar to those reported elsewhere. The maximal values of most PAHs were lower than those in other reports. Compared to the results of Macao (Qi et al., 2001) and Kurashiki City in Japan (Oda et al., 2001), which were mainly obtained from traffic zones, the sum of PAHs concentration in dust of Shanghai was low, but the concentrations of some PAHs were high or of the same level, such as BaP, BbF, BkF InP and Phe.

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