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Research of the pollution characteristics of PAHs in air particulate pollutants

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) exhibit a slightly positive correlation. Results showed that PAHs and PM2.5 occurred in the following order of areas: urban > suburban > rural. The light-ring PAHs accounted for higher percentage than the heavy-ring ones in PM2.5. Coal burning, human activities, and industrial pollutants were major sources of PAHs in the urban area according to the ratio of specific toxic PAH compounds. Traffic release and coal burning were predominant integrative sources in suburban areas. In rural areas, the contribution of PAH pollution may originate from coal burning and human activities as the result of long-range transportation from urban and suburban areas.

1. preface

Particulate matter $(PM)_{2.5}$ comprise atmospheric particles that measure less than or equal to 2.5 μm in diameter; these particles can enter the lungs. Although $PM_{2.5}$ account for only a small part of the earth's atmosphere, $PM_{2.5}$ cause considerable impact on air quality and visibility. $PM_{2.5}$ feature a small particle size, are rich in toxic and harmful substances, stay in the atmosphere for long periods, and are transported in long distances. These factors significantly impact human health and quality of the atmospheric environment. Polycyclic aromatic hydrocarbons (PAHs) are strongly toxic, carcinogenic, mutagenic and persistent organic pollutants; studies have shown that most PAHs in the atmosphere are absorbed as tiny particles of $PM_{2.5}$ (also known as lung particles) [1–3], and they can be transported to other long-distance areas [4].

PAHs are cyclic aromatic hydrocarbons, consisting of two or more benzene rings and dioprene, with direct chain, angular, or cross arrangement; they are by-products of incomplete or high-temperature pyrolysis of organic compounds. PAHs are widely found in oil and coal and feature potential teratogenicity, carcinogenicity, and genotoxicity; their toxicity increases with the increase in the number of PAH benzene ring, for example, benzopyrene is a known highly carcinogenic organic compound. As PAHs exhibit very low water solubility and are difficult to eliminate in the environment, they are identified as the first to be controlled by the US Environmental Protection Agency and the European community. Sixteen of these compounds are used as monitoring parameters for environmental pollution.

Studies show that almost all PAHs in the atmosphere adsorb on inhalable PM_{10}, and most of them are adsorbed on fine $PM_{2.5}$. $PM_{2.5}$, which is also known as "accessible lung particles," can enter the

human alveoli and blood system. $PM_{2.5}$ are considerably more harmful to humans than coarse particles [5-8]. PAHs adsorbed on $PM_{2.5}$ can migrate to other regions over long distances. Industrial areas consume large amounts of fossil fuel, resulting in serious pollution by PAHs in the atmosphere [9-10]. The present study aimed to determine the PAH pollution characteristics of air particulate pollutants in a region of Tianjin.

2. Experimental materials and methods

2.1. Sampling instrument

A medium-flow four-channel intelligent sampling instrument (Wuhan Tianhong Instrument Co., LTD.) was used to sample atmospheric particulates (th-16a type), with a sampling flow of 16.7 L/min. Quartz fiber filter paper (diameter: 47 mm) was used as sampling filter film.

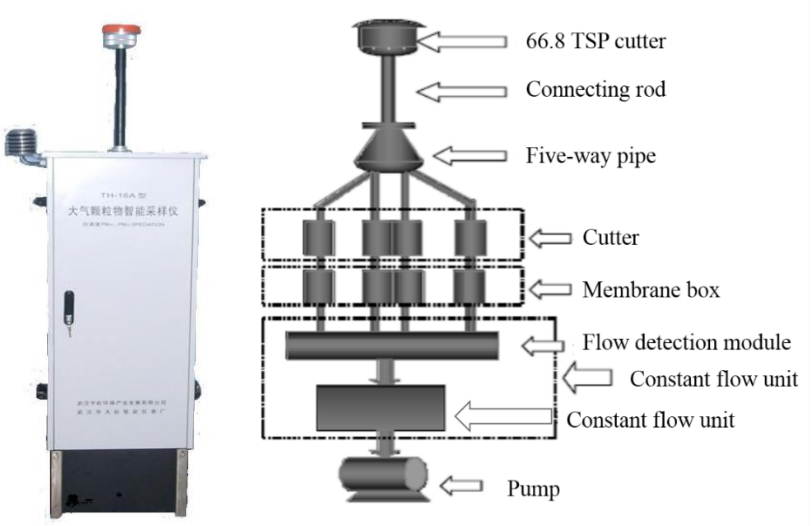

Figure 1. Sampling instrument diagram

2.2. Sampling time

Sampling period: November 12, 2016 to November 17, 2016 (6 days in total).

Sampling status: Samples were collected in the central city for 11.12–11.14 days, at the cleaning point for 11.15 days, and at the industrial point for 11.16–11.17 days. PM10 and PM2.5 samples were collected simultaneously, and two films were used for the day (8:00 AM to 8:00 PM) and night samples (8:00 PM to 8:00 AM).

A total of 48 samples, including 24 PM10 samples and 24 PM2.5 samples, were collected in the first phase.

3. Results and discussion

3.1. PM concentration

Atmospheric particulate pollution is the key problem of air pollution, and quality concentration is the most basic physical quantity that can characterize the pollution characteristics of various air pollutants. Table 1 shows the maximum, minimum, and average mass concentrations of PM_{10} and $PM_{2.5}$ at different sampling points during the first phase of the study. PM_{10} concentrations in the central city, industrial point, and clean point varied by 114–289, 91–254, and 8–110 g/m^3, respectively, with mean values totaling 197, 170, and 59 g/m^3. $PM_{2.5}$ concentrations in the central city, industrial, point, and clean point measured 79–237, 17–50, and 8–45 in • g/m^3, respectively, with mean values reaching 150,

32, and 27 g/m^3, respectively. The results showed that the concentrations of PM_{10} and $PM_{2.5}$ were the highest at the Environmental Protection Bureau, followed by the industrial and clean points.

Table 1. Concentration levels of PM_{10} and $PM_{2.5}$

Varieties of sampling		central city	industrial estate	clear area
PM_{10}/μg/m^3	maximum	289	254	110
	least value	114	91	8
	average value	197	170	59
$PM_{2.5}$/μg/m^3	maximum	237	50	45
	least value	79	17	8
	average value	150	32	27

3.2. PAHs pollution characteristics

In the present study, 16 types of PAHs with optimal control were detected in PM10, and almost all PAHs, except Ind, Dib, and BghiP, can be detected in PM2.5. Tables 2 and 3 provide the PAH concentrations of 12 samples in PM10 and PM2.5. PAH concentrations in PM10 and PM2.5 ranged from 21.07 ng/m3 to 118.23 ng/m3 (mean: 73.42 ng/m3) and from 38.47 ng/m3 to 113.94 ng/m3 (mean: 62.88 ng/m3), respectively. The lowest value was observed in the industrial point and peaked at the city center. In general, similar distributions of 16 kinds of PAHs were observed in PM10 and PM2.5; the concentration of Acy was the lowest, and that of Ant was the highest. One sample exceeded the national atmospheric standard gb3095-1996 by 10 ng/m3, and the rest remained below the standard. However, TSP differs from PM10 and PM2.5 in terms of aerodynamic diameter, whereas PAHs and atmospheric particulates are correlated to a certain extent. This correlation changes with the concentration of atmospheric particulates and increases the comparability.

Table 2. The concentration distribution of PAHs in PM_{10} (ng/m^3)

PM_{10}	Ud1	Un1	Ud2	Un2	Ud3	Un3	Sd1	Sn1	Sd2	Sn2	Bd	Bn
NaP	7.65	1.70	6.72	6.86	6.22	4.26	4.99	1.97	7.70	6.63	5.06	6.00
Acy	2.01	2.18	1.27	0.23	1.79	N.D.	3.53	N.D.	1.66	0.84	0.23	N.D.
Ace	3.79	4.95	6.99	0.36	6.70	2.75	1.35	N.D.	5.66	1.07	0.43	N.D.
Flu	15.64	10.67	12.86	1.55	11.98	2.50	5.26	1.18	11.67	3.91	2.50	1.20
Phe	14.83	11.12	11.17	6.31	12.21	5.60	3.60	3.98	10.60	10.87	8.44	4.31
Ant	15.43	11.91	11.90	6.56	12.86	5.88	3.77	4.90	14.19	14.00	8.60	4.57
Fluo	11.83	5.68	6.46	8.85	13.75	3.25	2.15	3.45	9.98	4.88	7.91	2.85
Pyr	8.89	4.23	5.20	8.41	11.28	3.35	2.80	2.43	9.27	5.01	6.50	2.77
BaA	1.62	1.68	1.70	3.20	3.91	4.02	1.83	N.D.	2.24	N.D.	1.05	N.D.
Chr	3.07	6.41	6.47	9.28	12.55	6.80	0.29	N.D.	6.22	N.D.	6.87	N.D.
BbF	2.55	0.39	0.47	3.27	3.78	5.96	0.14	0.61	1.93	N.D.	2.92	N.D.
BkF	2.95	0.39	0.92	6.43	7.45	10.15	0.78	0.98	2.75	N.D.	5.75	N.D.
BaP	7.11	N.D.	N.D.	4.16	8.77	1.48	1.23	1.56	5.14	N.D.	6.72	N.D.
Ind	1.92	N.D.	N.D.	2.31	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dib	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.66	N.D.
BghiP	N.D.	N.D.	N.D.	1.55	4.97	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

PM_{10}	Ud1	Un1	Ud2	Un2	Ud3	Un3	Sd1	Sn1	Sd2	Sn2	Bd	Bn
PAHs	99.28	61.28	72.14	69.34	118.23	56.00	31.71	21.07	89.01	47.22	67.64	21.70

Note: U= central city ,S= industrial estate, B= clear area, d= daytime, n=night.N.D.=not detected.

Table 3. The concentration distribution of PAHs in $PM_{2.5}$ (ng/m^3)

$PM_{2.5}$	Ud1	Un1	Ud2	Un2	Ud3	Un3	Sd1	Sn1	Sd2	Sn2	Bd	Bn
NaP	2.98	N.D.	6.67	4.07	1.35	2.93	4.67	3.08	1.84	1.74	4.82	3.36
Acy	N.D.	2.35	2.11	0.64	2.59	3.83	2.67	N.D.	N.D.	3.36	1.03	N.D.
Ace	N.D.	5.21	6.74	N.D.	5.26	7.26	6.40	N.D.	N.D.	5.91	2.51	N.D.
Flu	1.91	12.09	11.21	1.72	11.79	9.77	8.64	3.07	3.71	9.37	10.48	1.42
Phe	9.92	12.33	11.04	8.37	14.89	11.20	17.13	4.85	9.03	10.16	8.19	7.46
Ant	11.28	12.99	11.59	8.80	15.42	14.09	18.04	6.01	9.50	12.72	8.56	7.92
Fluo	16.52	12.10	10.02	12.46	13.20	8.70	12.84	7.19	13.83	9.24	5.27	6.53
Pyr	14.66	6.41	8.93	10.37	13.10	6.35	7.78	3.63	14.64	6.59	2.79	4.10
BaA	14.61	0.86	4.29	4.81	8.25	1.88	0.83	5.28	5.88	N.D.	0.52	6.24
Chr	5.23	3.61	14.76	14.09	7.01	1.22	2.17	1.65	11.45	N.D.	0.67	N.D.
BbF	N.D.	0.60	2.17	5.40	5.11	0.22	2.36	0.49	2.11	N.D.	0.81	2.79
BkF	N.D.	1.18	4.27	10.64	7.33	0.26	3.01	0.55	4.17	N.D.	1.59	N.D.
BaP	N.D.	1.38	5.01	12.48	8.63	1.65	N.D.	2.71	4.89	N.D.	2.06	2.70
Ind	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dib	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BghiP	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PAHs	77.10	71.10	98.82	93.83	113.93	69.37	86.53	38.47	81.06	59.08	49.28	42.50

The content distribution of optimal control PAHs was consistent among different samples with different ring numbers. According to physicochemical properties, PAHs can be divided into two types: (1) low-molecular-weight aromatic hydrocarbons, such as NaP, Acy, and Ace, with 2 to 3 benzene rings; they are volatile and exhibit certain toxicity to aquatic organisms; (2) high-molecular-weight aromatic hydrocarbons, such as Pyr, BaP, and Ind, with 4–6 benzene rings. These compounds feature high boiling point and are non-volatile but exert carcinogenic and mutagenic effects. Compound stability increases with increasing number of aromatic rings in the structure. To further understand the distribution of PAHs, this study divided PAHs into two groups according to the number of different cyclic PAHs, including NaP, Acy, Ace, Flu, Phe, Ant, and Fluo, which possess less than 4 rings and are called light rings. Pyr, BaA, Chr, BbF, BkF, BkF , BaP, Ind, Dib, and BghiP possess more than four rings in one set (double rings). Figure 2 shows the proportions of PM10 and PM2.5 in the total PAHs at different sampling points, light rings, and heavy rings. The proportions of 2, 3, 4, and 5–6 rings in total PAHs are subdivided.

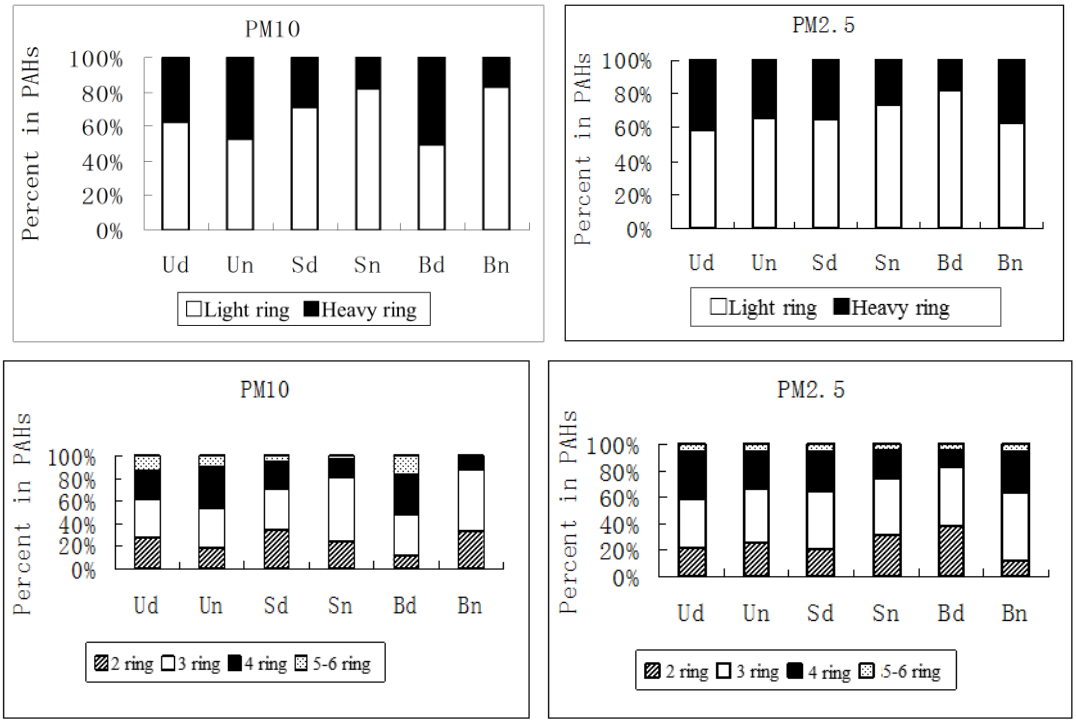

Figure 2. PAHs distribution of different rings in PM_{10} and $PM_{2.5}$

In the first phase of the study, the concentration changes of PAHs among the samples are due to the high percentage of light-ring compounds, which mainly comprise three- and four-heavy-ring PAHs. The form of PAHs in air is mainly related to their physical and chemical properties and environmental temperature. Although the Henry constant of high-molecular-weight PAHs is observed at a low steam pressure, these PAHs are naturally stable and mainly exist as particles; thus, the content of particles with generally high-molecular-weight PAHs content is higher than that with low-molecular-weight PAHs. The ring number is less than the 4 for PAHs with high vapor pressure and temperature during sampling at 29 °C (34 °C); these PAHs mainly exist in the form of gas but exist in the solid state at low temperatures. The sampling time of this study was relatively short (November, with a total of 6 days). Thus, a large number of tricyclic PAHs were present in the samples. Based on the interaction of these factors, the granular PAHs that mainly exist in the atmosphere of the studied region possess three and four rings.

3.3. The correlation between PAHs and PM_{10} and $PM_{2.5}$

Figure 3 shows the correlation between PAHs and PM10 and PM2.5. In general, PAHs and PM exhibit a certain but non-significant correlation. The correlation coefficient of PAHs and PM10 is 0.3251, and that of PAHs and PM2.5 is 0.4744. The correlation between PAHs and PM2.5 is higher than that between PAHs and PM10, indicating that PAHs are more prone to be adsorbed on fine particles.

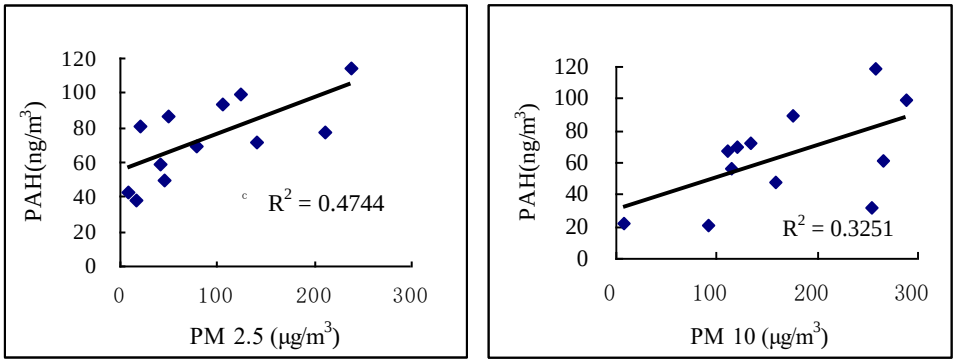

Figure 3. Correlation between PM10, PM2.5, and PAH concentration

Figure 4 shows the changes in PAH concentration in PM_{10} and $PM_{2.5}$ during the day and night at the different sampling points. As PAHs and PM feature a certain relationship, PAH concentration depends on PM concentration to a certain extent. Therefore, the concentration of PAHs and PM were present in the following order: urban > industrial point > clean point. High PAH concentration was observed at the clean point; its pollution is transported in long distances from urban areas. Figure 4 also shows that the concentration of PAHs in PM obtained during the day at different sampling points is higher than that at night, indicating that daily life and work emissions of residents are the main sources of organic pollutants.

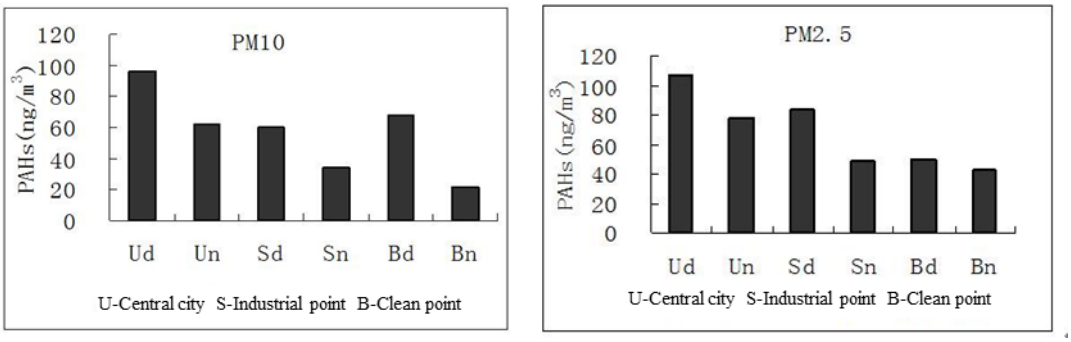

Figure 4. Changes in PAHs concentration and diurnal variations at sampling points in PM_{10} and $PM_{2.5}$

4. Conclusion

The main sources of PAHs include natural and man-made sources. Natural sources of PAHs comprise combustion (Forest fires and volcanic eruptions) and biosynthetic processes (Sediment diagenesis, bioconversion, and gases in tar pits). PAHs originate from industrial processes, oxygen combustion, garbage incineration and landfill, food production, and direct traffic emissions. In addition, as tires wear, dust particles and road surface wear of the asphalt road increase, and their quantities significantly increase along with the development of industrial production, contributing most of the total PAHs in the environment. Oil spills have also become a part of the PAH anthropogenic process. These compounds form in biological degradation, hydrolysis, and light elimination approaches such as cracking. The content of PAHs in the environment constantly shows a dynamic balance and is maintained at low concentration levels. However, with the intensification of human activities in recent years, the dynamic balance in the environment changed, and an environment of PAHs developed. Therefore, speeding up the elimination of PAHs in the environment and reducing the environmental pollution caused by PAHs have attracted increasing attention.

The relative relation of PAH concentration may provide source information. A Pyr/BaP ratio of 2–6 indicates a typical traffic pollution, whereas a ratio of less than 2 characterizes coal burning and

domestic pollution [11]. When Fluo/Pyr ratio or pollutant sources were considered, a 1.4 PAH ratio was observed for coal combustion, 1 for wood combustion sources; a ratio of less than 1 indicates oil sources of PAH input.

Table 4. PM ratios of characteristic PAHs compounds

$PM_{2.5}$	Pyr/BaP	Fluo/Pyr	PM_{10}	Pyr/BaP	Fluo/Pyr
U	1.98	1.29	U	1.92	1.20
S	4.30	1.32	S	2.46	1.28
R	1.45	1.71	R	1.38	1.16

Note: U= central city ,S= industrial estate, R= clear area,

Table 4 shows the ratios of different PAH compounds at different PM regions. At the city center point, Pyr/BaP yielded PM2.5 and PM10 values of 1.98 and 1.98, both of which are less than 2, whereas Fluo/Pyr values totaled 1.29 and 1.20, both of are less than 1.4 and higher than 1, respectively. When the ratios were integrated, they can be assumed as central city PAHs originating from coal combustion, human activities, and industrial pollution. At the industrial point, Pyr/BaP ratios of 4.30 and 2.46 were observed, which between the 2–6 value for pollution sources; these values can be considered to be caused by traffic pollution. Fluo/Pyr ratio in PM2.5 ranged from 1.32 to 1.4, whereas that of PM10 ranged from 1.4 to 1.28, indicating that coal as source cannot be ignored. Near-traffic pollution may be due to the industrial bulk cargo logistics center, with a considerable contribution coming from automobile exhaust. The clean point values of Pyr/BaP reached 1.45 and 1.38, respectively, both of which are less than 2. Fluo/Pyr values totaled 1.71 and 1.71, indicating that pollution can be characterized as coal burning and further originate from the city center and industrial points at long distance transports.

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