Pollution Characteristics of Environmental Hormone Phthalates in the $PM_{2.5}$ in Haidian, Beijing

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Abstract
Phthalates contaminants in $PM_{2.5}$ were analysed qualitatively and quantitatively. A total of 15 phthalates were detected. Some of them are documented by the U.S. Environmental Protection Agency priority pollutants list, which were identified as environmental hormones. The higher content of phthalates in summer is mainly caused by the higher temperature. On the other hand, coal combustion has less influence on it.
Key words: *phthalates; environmental hormones; $PM_{2.5}$*

1 Introduction

Phthalates (PAEs) are a class of environmental endocrine disruptor, [1-2] and its estrogenic effects can lead to spermatozoa atrophy and sperm distortion, [3]especially affect children in their developmental stages. In recent years, toxic PAEs have drawn much attention[4-6] but few related reports can be retrieved due to complicated pre-treatment and analysis procedures. It is wildly known that Beijing city, the capital of China, has suffered air pollution problem for a long time. Although the atmospheric environmental quality has been greatly improved due to a vigorous renovation recently, but the future is still not optimistic. In this paper, air pollution in Beijing was selected as the example to study the characteristics and resources of phthalates in the $PM_{2.5}$ of environmental pollution.

2 Experimental

2.1 Sampling

$PM_{2.5}$ samples were collected by using the United States Thermo 2025i instrument. The flow of sampler was set at 16.7 L/min; the instrument consists of filter, sampling clip, exhaust fan, flow recorder, timer and control system, shell and other components. Sampling site was selected at Haidian road intersection on behalf of the typical urban pollution in Beijing. The sampling was performed in 2014, details are shown as follows: 4 days in winter (16, 17, 18 and 19 in January), 4 days in spring (14, 15, 16 and 17 in May), 4 days in summer (17, 18, 19 and 20 in July), and 4 days in Autumn (17, 18, 19 and 20 in October), 7 days during the Asia-Pacific Economic Cooperation(APEC) (5, 6, 7, 8, 9, 10 and 11 in November). Air qualities were classified as excellent, good, light pollution, moderate pollution, heavy pollution and serious pollution.

The collected samples were extracted with rectified chloroform using Soxhlet's extractor for 72 hours. The crude extractive was filtered, concentrated and dried, followed by the precipitation of asphaltenes using n-hexane and the separation of PAEs by silica gel-alumina column chromatography. The detection limits were 0.01~0.1 mg.

Qualitative and quantitative analysis of PAEs were performed by Finnigan TSQ70B GC-MS which equips a DPX-35 capillary column (0.25 mm × 30 m). The data were

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analyzed by MassLab workstation. The ionization voltage was 70 eV and the temperature program was 70-300 ℃, 3 ℃/min, and the detection limit was 1.0×10^{-12} g (1.0 pg) to 1.0×10^{-11} (10 pg), as well as the detection limit of this method 0.001-0.01 ng/m^3. The accuracy and accuracy of this method were certified by QC/QA test, which was in accordance with the requirements of U.S.EPA. No phthalates were detected in the blank reference.

Since the response value of each kind of PAEs to the instrumentation system is differential, so it is necessary to divide the standard sample into a series of concentration gradient to eliminate the effect of the corresponding value. By a gradient of standard sample solution, a quantitative curve for PAEs was generated, and the concentration of PAEs in each sample was quantified by this standard PAEs quantitative curve.

3 Results and discussion

3.1 Concentrations of PAEs in the atmosphere of Beijing

Table 1 shows the kinds of PAEs detected in $PM_{2.5}$ samples that were collected in a certain monitoring point Haidian District, Beijing. 15 kinds of PAEs were detected including DEP, DMP, DBP, DOP and DEHP.

Table 1 – Detected atmospheric $PM_{2.5}$ of phthalates in Haidian Beijing

Num.	Phthalates	Num.	Phthalates
1	Dimethyl phthalate * (DMP)	9	Dicyclohexyl phthalate *
2	Diethyl phthalate * (DEP)	10	Di (2-ethylhexyl) phthalate * (DEHP)
3	Dipropyl phthalate *	11	Decyl hexyl phthalate
4	Di-n-butyl phthalate * (DBP)	12	Dioctyl phthalate (DOP)
5	Butyl isobutyl phthalate	13	Diisooctyl phthalate
6	Diisobutyl phthalate *	14	Decyl octyl phthalate
7	Diamyl phthalate *	15	Butyl benzyl phthalate *
8	Dihexyl phthalate *		

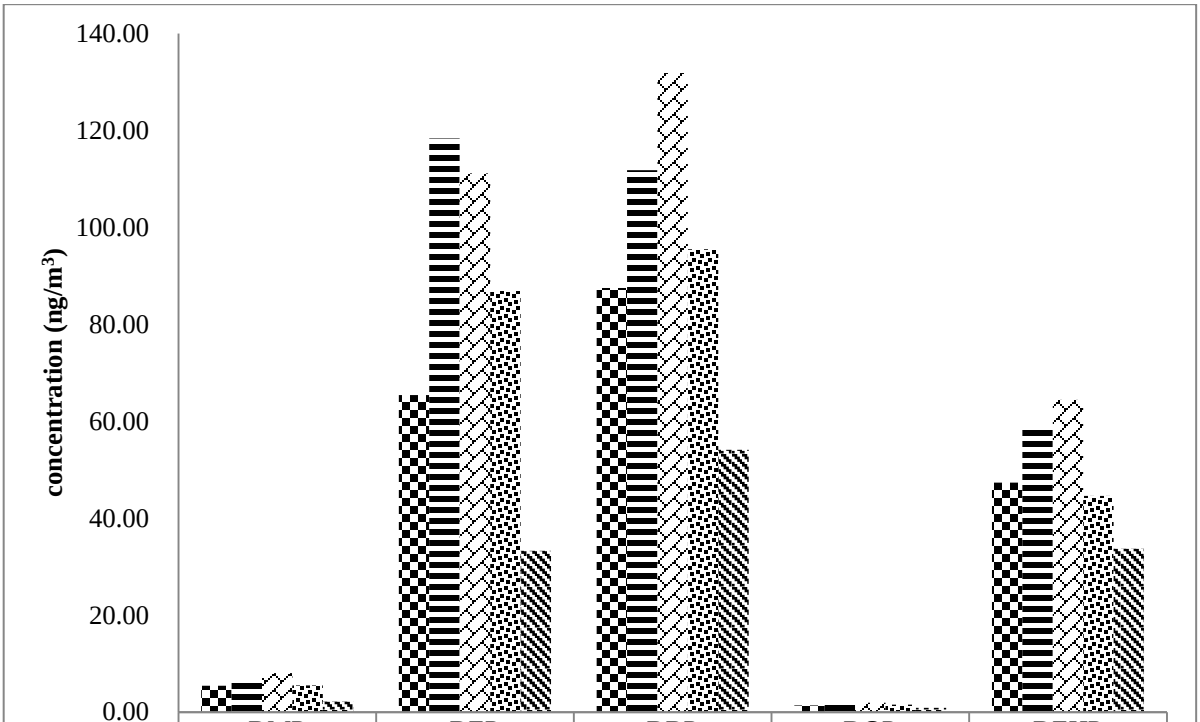
* The ordinary phthalates environmental hormone in the atmosphere

3.2 Toxicity and pollution source of PAEs

Table 2 shows the concentrations of 5 PAEs on a busy traffic intersection in different seasons in Beijing. These results show that the concentration of pollutants in summer was relatively high, but during the APEC, the concentration of pollutants was relatively low due to a series of policies adopted by the government. According to the concentrations of 5 PAEs in the atmosphere shown in Fig. 1, it was found that the concentration of PAEs in summer was much higher than that was in spring, autumn and winter. Among them, the average concentration of five phthalates in summer is more than twice than the APEC period, and is more than 1.5 times of that in winter. In the summer, the concentration of 5 PAEs was the same to that in the winter when the air quality was seriously polluted. We think that the concentration of PAEs in the $PM_{2.5}$ is less related to the combustion of coal.

In the days of January 18, May 16, July 17 and October 17, the air quality was mild pollution, but the total amount of 5 phthalates was different. In summer, the total amount of 5 PAEs was above 1.5, 1.3, and 2.6 times than that in winter, autumn and APEC period, respectively. The concentration of DEP in summer was above 3.3 times than that in the APEC period, and the average concentration of $PM_{2.5}$ was lower than that of APEC during the four days in summer, but the amount of PAEs was much higher than that of APEC,

and the average concentration of five PAEs in summer was higher than that in winter, indicating that coal combustion was not the main contributors to PAEs. We postulated that this may be attributed to the high temperature in summer, which leads to the volatility of PAEs generated by the exposure of plastic products to the sunlight.



	DMP	DEP	DBP	DOP	DEHP
Jan.	5.43	65.42	87.51	1.36	47.36
May	6.59	118.36	111.80	1.80	58.57
July	8.04	111.15	131.85	1.93	64.43
Oct.	5.51	86.86	95.51	1.54	44.59
APEC	2.15	33.28	54.13	0.89	33.71

Fig. 1 –The average of five kinds of pollutants

The sampling time during the APEC was in fall, the content of 5 PAEs was significantly lower than that in the 17, 18, 19 and 20, October, mainly due to the state adopted a series of policies in the APEC, including Beijing within 100 km^2 around. In addition to the thermal power electronic enterprises which reduced 30% emissions of pollutants, steel, coking and other gas-related enterprises were all discontinued, around Beijing 100 to 200 km^2 range, non-compliance of steel, coking and other gas-related enterprises discontinued. Motor vehicles were odd-and-even license plate rule and other emission reduction measures to reduce the concentration of $PM_{2.5}$ to improve air quality and reduce the PAEs emissions.

Tong Qing, et al.[7] said that when the aerodynamic particles are less than 1.1μm, DMP in summer is higher than in winter, which is in accordance with our results. This is partly due to the lower atmospheric vapor pressure of the DMP, which results in the condensation of DMP-containing vapors on the fine particles rather than on the larger particles. Under high temperatures, plasticizer volatilized from the plastic products is easily happened. On the other hand, DMP is wildly used as mosquito repellent in summer, which also increases the DBP content in the air, as well as the industrial emissions. Such facts can explain why DBP content in summer is significantly higher than it in winter. The

content of DEHP in summer is higher than that in winter in Beijing, [8,9] Ji'nan [10] and Hangzhou [11], which indicates that the DEHP in the air is mainly from the plastic products industry emissions, rather than the coal combustion. The widespread use of PAEs in plastics has caused the environmental hormones, and some PAEs contaminants lead to abnormal embryonic growth and development. [12] Therefore, the control of PAEs in plastic pollutants to keep healthy is of great significance.

Table 2 – The levels of 5 kinds of PAEs on a busy traffic intersection in Beijing(ng/m^3)

Pollutant Sorts / Date		DMP	DEP	DBP	DOP	DEHP	Total	$PM_{2.5}$ (μg/m^3)
Winter	Jan. 16	9.48	75.23	97.45	1.43	52.74	233.33	378
	Jan.17	4.32	68.79	99.41	1.39	45.02	218.93	186
	Jan. 18	3.92	56.89	75.94	1.29	44.97	183.01	94
	Jan. 19	3.98	60.75	77.24	1.32	46.71	190	121
Spring	May 14	4.75	87.32	77.57	1.22	49.81	220.67	21
	May 15	8.75	143.52	135.87	2.15	69.85	360.14	98
	May 16	6.89	132.75	113.87	1.96	54.87	310.34	87
	May 17	5.98	109.83	119.89	1.86	59.76	297.32	56
Summer	July 17	9.13	152.87	189.53	2.76	87.65	449.11	98
	July 18	7.32	91.53	103.87	1.57	56.72	261.01	34
	July 19	6.98	87.64	96.59	1.32	49.87	242.4	28
	July 20	8.74	112.57	137.41	2.06	63.47	324.25	38
Autumn	Oct.17	3.89	81.24	86.91	1.29	41.11	214.44	120
	Oct.18	5.98	79.73	103.45	1.43	42.74	233.33	183
	Oct.19	6.18	96.75	102.54	1.76	50.76	257.99	292
	Oct.19	5.98	89.72	89.13	1.69	43.76	230.28	227
APEC	Nov.5	1.87	29.86	48.64	0.81	32.97	84.18	50
	Nov.6	1.29	24.89	42.64	0.65	29.46	98.93	14
	Nov.7	1.89	31.24	53.87	0.88	35.23	123.11	48
	Nov.8	1.98	32.75	56.81	0.87	33.63	126.04	84
	Nov.9	2.87	39.86	61.32	0.98	33.67	138.7	70
	Nov.10	3.24	43.71	64.87	1.13	36.23	149.18	92
	Nov.11	1.94	30.65	50.78	0.94	34.75	119.06	27

4 Conclusions

1. The average concentrations of $PM_{2.5}$ in five different time periods follow the order of autumn>winter>spring>APEC>summer, as well as five kinds of PAEs summer>spring>autumn>winter>APEC, indicating that the concentration of PAEs mainly depends on temperature: the higher the temperature, the higher concentration of PAEs.
2. The highest concentration of the 5 contaminants was DBP, followed by DEP, the least is DOP.
3. The high temperature in summer led to the highest content of PAEs, which has few things to do with coal combustion.

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