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Survey of polycyclic aromatic hydrocarbons (PAHs) in arterial street air of Hangzhou

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Abstract: The presence of particulate and vapor PAHs, SO₂ and NO_x and other interrelated conditions (temperature, traffic intensity and wind velocity) were investigated in the arterial street air of Hangzhou. The concentration of the nine PAHs in the air was mean to 11.7 μg/m³, and the content of benzo(a)pyrene was up to 0.108 μg/m³. The contents of PAHs in the sampling sites were in good relation to the traffic intensity, and would be also affected by the terrain and meteorological conditions. The occurrences of PAHs in ambient air were mainly affected by their physical, chemical characters and temperature. The three- and four-ring PAHs (MW ≤ 228) mainly existed in the vapor phase and the five-ring PAHs (MW > 228) existed predominately in the particulate phase. The fraction of vapor PAHs in the total nine PAHs was 84.2% in the air of the sampling sites. In the morning and evening, the concentrations of PAHs in the arterial street air were higher than that on the noon and the diurnal variation of PAHs was similar to that of the traffic gas NO_x. A conclusion would be drawn that the major source of PAHs in the arterial street air was the traffic. And the results indicated that 75% of BaP would come from traffic source and remaining 25% of BaP would come from non-traffic source.

Key words: polycyclic aromatic hydrocarbons; arterial street; air pollution

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants in the atmosphere. They are generated in the combustion. The major sources identified include fossil fuels, vehicular traffic, industrial processes, smoking and domestic heating (Peltonen, 1995). The occurrences and fates of PAHs in the environment have been studied with great interest because many of them are known to be important mutagens in urban aerosols and contribute much to the cancer of lung in humans (Allen, 1998). And many of them have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) and the European Community. In the United Kingdom, measurements of PAHs in "town air" of the Central London were performed with fluorescence detection as early as 1950s, while more routine monitoring has taken place in Britain and elsewhere over the last 40 years (Waller, 1952; Gordon, 1973; Yamasaki, 1982).

In ambient air, PAHs exists in vapor or particulate phases. For the particulate PAHs are direct mutagenic and/or carcinogenic. So the majority of studies on PAHs were about the particulate PAHs in the last. This has given much information on the multi-ringed heavier PAHs which predominantly exist in particulate phase, but ignored the lighter PAHs which are mostly in vapor phase. Though the lighter PAHs are less mutagenic and/or carcinogenic, they are most abundant in ambient air, and can react with other pollutants, such as NO_x, O₃, in air to generate more toxic derivatives (Arey, 1989). Since 1990s, the PAHs distribution between particulate and vapor phases, the influential factors of PAHs in ambient air have caused people's more attention.

1 Experimental

1.1 Site description

The content of vapor and particulate PAHs in atmosphere was determined at four sites in Hangzhou. Location 1: a crossroads in the culture and education area, which is situated in the west of the city, the traffic intensity was about 3600 motor vehicles per hour. Location 2: a crossroads in the commercial area, which in the central of the city, about 1600 vehicles per hour. Near the two sites, there are many high buildings. Location 3: a crossroads which is in the east but away from the city central, 4000 vehicles per hour or so. Location 4: a site in a campus about 150m

away from the crossroads in the culture and education area. The sites of location 1 and 4 were selected close to each other in order to ensure that the contribution of air pollutants from non-traffic sources, i.e. heating sources and long-range transport was the same at the two site. Consequently any differences in the air pollution level between the two sites should originate only from the differences in the influence of traffic sources.

The street is situated east west. The measuring sites were on the southern side, and 1m to the street. The measuring program was carried out in the autumn. The measurements in the investigation had a mean temperature of 20.8°C. The relative humidity was 80 percent. The local wind direction at all of the sites was from north and west. In the location 1 and 4, the wind speed of the ground was only 0.4 m/s, in location 3 the ground wind speed was up to 4 m/s.

1.2 Sampling and analysis

The vapor and particulate phases PAHs were sampled simultaneously using mini-volume air samplers. The flows was 1.0 L/min. Before and after the sampling, the flow was corrected, and the derivation of flow was less than 1%. The sampling programs were lasted three or six hours each time, so the sampling volumes were in the range of 180–360L. The particulate PAHs were collected with 25 mm glass fibre filters (GF, Whatman, U. K.) which were thermally treated at 500°C for 6h prior to use to remove organic contaminants. The vapor PAHs was defined as that associated with XAD-2 (Supelco, U. S. A) which was extracted with dichloromethane until no peaks interfering with the compounds of interest were found in the extractions. The samplers were all lifted to a height of 1.5–2.0m above the ground, which were above average height of personal vehicles (Eskinja, 1996).

After the sampling, the filters were cut into pieces, placed in a clean vial and covered with 10 ml dichlormethane. The XAD-2 resins were poured into an clean vial, covered with 20 ml mixture of dichlormethane and acetonitrile ($V_{CH_2Cl_2} : V_{CH_3CN} = 3 : 2$). All of the vials were sealed with parafilm "M". Then the samples were sonicated for 30 minutes. During the sonication, the water in the ultrasonic bath was replaced every 8 minutes to prevent overheating (Miguel, 1998). Then, 5 ml extracts of the filter was transferred into another vial and 30 μ l dimethyl sulfoxide was injected into the 5 ml extracts as fixity. So did the extracts of XAD-2 resins. The 5 ml extracts were concentrated to dryness under a gentle nitrogen stream at room temperature and press. Residues were dissolved with 970 μ l HPLC-grade methanol. All of the sample solutions were filtered through 0.22 μ m PTFE filters (Millipore, U. K.) into the amber vials. The vials were sealed and stored in a refrigerator (-18°C) until the analysis.

The PAHs extraction of the sample was analyzed by high performance liquid chromatography (Hitachi L-7000 series HPLC) system. The column was a 4.6 mm \times 250 mm C_{18} column (Wakosil). The mobile phases were HPLC-grade methanol and water in a linear gradient program. The flow rate of the mobile phase was kept at 1.0 ml/min, the temperature of the column oven was 40°C. The sample solution (100 μ l) was injected into the HPLC system by a L-7200 autosampler and determined with a fluorescence detector of which excitation and emission wavelengths were automatically set by a time program (Zhu, 1997). The following PAHs determined are listed in Table 1.

1.3 Quality control

A strict regime of quality control was operated in the experiment. Before the onset of the sampling program, PAHs recovery studies were undertaken to demonstrate the availability of the method. A working standard solution was made up from a stock solution premeditated from solid PAHs purchased from Aldrich (U. K.), Wakosil (Japan). Seven separate XAD-2 and seven filters were spiked with the working solution including all the nine PAHs, then extracted and analyzed in the same way as the samples. The recoveries of each PAHs were determined from both

Table 1 Characters and detect limits of PAHs

No.	PAHs	Abbreviation	Formula	Rings	Molecular weight	Carcinogenicity	Detection limits, pg
1	Fluorene	FLU	C ₁₃ H ₁₀	3	166	0	0.53
2	Phenanthrene	PHEN	C ₁₄ H ₁₀	3	178	0	2.95
3	Anthracene	AN	C ₁₄ H ₁₀	3	178	0	3.58
4	Fluoranthrene	FLUR	C ₁₆ H ₁₀	4	202	0	29.13
5	Pyrene	PY	C ₁₆ H ₁₀	4	202	0	14.43
6	1-methyl-pyrene	1-Me-PY	C ₁₇ H ₁₂	4	216		4.80
7	Chrysene	CHRY	C ₁₈ H ₁₂	4	228	0/+	4.83
8	Benzo(e)pyrene	BeP	C ₂₀ H ₁₂	5	252	0/+	3.00
9	Benzo(a)pyrene	BaP	C ₂₀ H ₁₂	5	252	++	3.42

the XAD-2 and the filters. The results indicated that the recoveries of each PAHs from the XAD-2 and the filters were all over 90%, and the relative standard deviations of the recoveries of each PAHs were less than 2.64%.

2 Results and discussion

2.1 Results from the sampling

It was regarded that an increase in PAHs (vapor and particulate phase) emission was due to fuel PAHs input. The increase was linearly dependent, giving a term which can be interpreted as the PAHs formed during the combustion process. And a major part ($\geq 50\%$) of emitted PAHs was formed in the combustion process (Westerholm, 1988). Some measurements indicate that diesel-derived aerosols are mostly enriched in lower molecular weight PAHs, whereas higher molecular weight PAHs are principally associated with gasoline engine-derived aerosol (Venkataraman, 1994; Hering, 1984; Benner, 1989). The PAHs emission factors from different fuels investigated are in the ranges of about 35–430 $\mu\text{g}/\text{km}$ and 124–286 $\mu\text{g}/\text{km}$, respectively. Because of the heavy traffic intensity and jammed driving conditions in the sampling sites, the pollution of PAHs was serious. The particulate and vapor phases PAHs measured in the sites are listed in Table 2. The concentrations of ΣPAHs in the street air were varied from 3.04–16.45 $\mu\text{g}/\text{m}^3$ and the mean was up to 11.7 $\mu\text{g}/\text{m}^3$. Benzo(a)pyrene which is regarded as a strong carcinogen to human body was mean to 0.2 $\mu\text{g}/\text{m}^3$ in the arterial street air. It is about fifty times higher than that in central Copenhagen (Nielsen, 1996).

The levels of primary air pollutants depend very much on the traffic intensity, the location of the sampling site and the meteorological conditions. This makes it very difficult to compare the results from different investigations. Nevertheless, the differences may be explained in some way. For example, in this investigation the traffic intensities of location 1 and 2 were heavier than that of location 3, so the PAHs concentrations of the two were mostly higher than that of location 3. However, as far location 1 and 2 were concerned, though the traffic intensity of location 2 was a little heavier than that of location 1, the PAHs concentration of location 1 was a little higher than that of location 2. This was mainly because of the influence of wind. In location 1 during the sampling, the ground wind speed was only 0.2 m/s. In location 2, it is up to 4 m/s, and there is few high building nearby, much PAHs emitted by the vehicular was diffused by the wind. So the PAHs of location 1 was a little higher than that of location 2.

2.2 The content variations of PAHs

In urban atmosphere, NO_x has been regarded as traffic gas and has peaks in the rush hours 8–10 a. m., 4–6 p. m. and minimum in the lunch hour, 0–2 p. m. SO₂ whose emissions can be attributed to industry, power generation and heating showed a totally different diurnal variation with a peak in the lunch hour 0–2 p. m. and a very small variation in the day hours (Nielsen, 1996). The results of the investigation indicated that during the different sampling periods in Hangzhou, for the affect of traffic intensity, the concentration of ΣPAHs at noon was a little lower

Table 2 The concentrations of PAHs measured in the arterial street air of Hangzhou, $\mu\text{g}/\text{m}^3$

Sampling time		FLU		PHEN		AN		FLUR		PY		1-MePY		CHRY		B(e)P		B(a)P		ΣPAHs
		V*	P	V	P	V	P	V	P	V	P	V	P	V	P	V	P	V	P	
10:16	1	2.10	0.05	5.34	0.13	0.64	0.04	2.13	0.31	0.65	0.02	0.29	0.25	0.83	0.33	0.03	0.78	0.02	0.21	14.15
7:00-	2	1.67	0.06	5.03	0.23	0.46	0.03	1.95	0.30	0.46	0.01	0.39	0.22	0.87	0.31	0.02	0.64	0.01	0.23	12.89
10:00	3	1.47	0.06	4.66	0.24	0.39	0.03	1.37	0.24	0.51	0.02	0.18	0.16	0.85	0.29	0.02	0.51	0.02	0.28	11.30
	4	0.28	-	2.33	-	0.23	-	0.27	-	0.09	-	0.08	0.02	0.06	0.01	-	0.09	-	0.11	3.55
11:00	1	2.20	0.04	4.12	0.13	0.41	0.03	2.71	0.39	0.35	0.01	0.30	0.22	0.99	0.37	0.05	0.78	0.03	0.34	13.47
-14:00	2	1.83	0.05	5.82	0.18	0.37	0.03	2.64	0.42	0.32	0.02	0.27	0.20	0.89	0.25	0.01	0.69	0.01	0.36	12.02
	3	1.88	0.04	3.98	0.16	0.49	0.02	1.78	0.31	0.35	0.01	0.30	0.19	0.82	0.28	0.04	0.63	0.04	0.32	11.64
	4	0.44	-	2.29	-	2.52	0.07	0.24	-	0.26	-	0.05	-	0.04	0.02	0.10	0.12	-	0.11	4.36
15:00-	1	2.09	0.06	4.78	0.29	0.47	0.02	2.49	0.45	0.42	0.01	0.31	0.20	0.81	0.21	0.03	0.73	0.03	0.41	13.81
18:00	2	2.33	0.09	6.28	0.27	0.57	0.01	2.67	0.61	0.51	0.02	0.38	0.16	0.95	0.35	0.02	0.48	0.06	0.38	14.70
	3	1.43	0.07	4.74	0.29	0.36	0.01	2.10	0.37	0.37	0.02	0.27	0.17	0.71	0.13	0.03	0.74	0.02	0.17	12.00
	4	0.21	-	2.43	-	0.17	-	0.16	-	-	-	0.07	-	0.14	0.04	0.01	0.11	-	0.11	3.71
10:17	1	2.12	0.07	6.39	0.16	0.63	0.04	3.25	0.51	0.38	0.02	0.30	0.18	0.89	0.31	0.02	0.94	0.01	0.23	16.45
7:00-	2	1.56	0.05	4.99	0.18	0.58	0.04	2.97	0.47	0.42	0.03	0.34	0.17	0.81	0.31	0.04	0.64	0.03	0.21	14.14
10:00	3	1.56	0.07	4.52	0.11	0.48	0.03	2.33	0.39	0.46	0.04	0.32	0.17	0.88	0.30	0.03	0.79	0.05	0.42	12.95
	4	0.32	-	2.10	0.15	0.11	-	0.33	-	0.02	-	0.08	-	0.07	-	-	0.09	-	0.10	3.04
11:00-	1	1.81	0.06	5.57	0.29	0.47	0.03	2.18	0.44	0.31	0.02	0.36	0.19	0.76	0.20	0.02	0.84	0.02	0.20	13.77
14:00*	2	1.59	0.05	4.38	0.11	0.61	0.05	1.64	0.31	0.37	0.02	0.31	0.17	0.93	0.29	0.03	0.52	0.01	0.37	11.76
	3	1.95	0.04	5.67	0.32	0.30	0.04	2.64	0.58	0.59	0.08	0.36	0.16	0.67	0.18	0.01	0.52	0.03	0.41	14.55
15:00-	1	2.17	0.04	5.74	0.26	0.58	0.05	2.05	0.59	0.53	0.07	0.36	0.20	0.70	0.30	0.03	0.84	0.04	0.29	14.84
18:00	2	1.88	0.06	5.23	0.25	0.65	0.05	1.84	0.61	0.50	0.05	0.37	0.19	0.69	0.30	0.04	0.83	0.03	0.30	14.08
	3	1.58	0.05	4.49	0.13	0.47	0.04	2.25	0.66	0.38	0.03	0.31	0.18	0.55	0.21	0.02	0.55	0.02	0.21	12.13
	4	0.24	-	2.34	-	0.18	-	0.01	0.31	0.07	-	0.10	0.01	0.11	0.03	-	0.10	-	0.11	3.66

*. in this sampling the sample of the location 1 was given up; * *. V is the vapor phase PAHs; P is the particulate phase PAHs

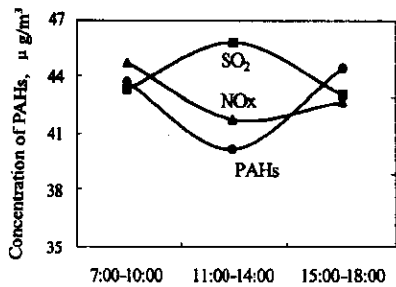


Fig.1 Variations of NOx, SO₂(10 times) and ΣPAHs during the sampling period in Hangzhou

than in the morning and evening (Fig. 1). And the variation was similar to NO_x, but contrary to SO₂. Both NO_x and SO₂ were measured simultaneously with the PAHs. It is known that traffic contributed much to the content of PAHs in the arterial streets, so a conclusion can be deduced that the PAHs in the Hangzhou arterial street air was mainly from the traffic.

2.3 Distribution of PAHs in the arterial street air

In atmosphere, the occurrences of PAHs were mostly affected by their own physical and chemical characteristics. It has been shown that experimentally measured gas phase concentrations of PAHs in urban

samples correlate well with their subcooled liquid vapor pressures (Pankow, 1987). PAHs vapor pressures are strongly correlated with molecular weight. With the increase of molecular weight, the estimated sublimation pressure will bring down correspondingly. For example, the estimated sublimation pressures at 25°C are 1.6×10^{-2} , 6.0×10^{-4} and 1.9×10^{-10} Pa for phenanthrene (M = 178), pyrene (M = 202) and coronene (M = 300), respectively (Murray, 1974; Sonnefeld, 1983). Other studies have been found that the fraction of PAHs in the gas phase increase with temperature (Yamasaki, 1982). In the investigation most PAHs determined were three- and four-ring PAHs whose molecular weights were all less than 228, the mean temperature during the sampling period were 20.6°C. So the three- and four-ring PAHs were mostly in vapor phase, and the contribution of vapor PAHs to the total PAHs was up to 81.3%. The five-ring PAHs were mostly in particulate phase, and contributed little to the total PAHs (Fig.2 and 3). The results

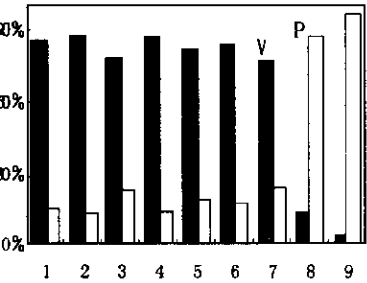


Fig.2 Distributions of PAHs in vapor and particulate phase of Hangzhou

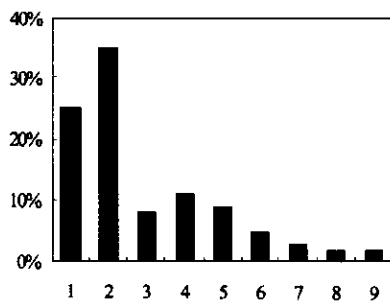


Fig.3 Percentages of PAHs in the total sum of the two sampling sites

were consistent with other studies (Halsall, 1994).

2.4 Traffic contribution of BaP

In order to measure the composition of PAHs from the vehicular exhaust, the samples were collected in a roadway tunnel, which is a 1313m long, 10m wide, one tube system, and the traffic intensity was about 750 motor vehicles per hour. The site was in the middle of the tunnel. And about 350m away the tunnel, a background was set. It appears reasonable to assume that the contributions from long-range transport, power plants and heating sources are the same or almost the same in the air of the two sampling sites. Because the distance between the two sites is only a few hundred meters. If one can neglect the

influence of atmospheric chemical processes, deposition and resuspension processes, the only difference at the two sites was the traffic sources. Though the PAHs composition differs from car to car and is dependent on driving conditions, fuel, lubricant and engine conditions (Pedersen, 1980). The waste gas from vehicular can be assumed as the exclusive source in the tunnel and the PAHs composition of a car exhaust has so far been determined by measuring the exhaust trapped in the traffic tunnel.

Benzo(a)pyrene was usually selected as a reference compound, because it is a strong mutagen and relatively stable in the atmosphere. Other studies indicated that there lay good correlation with other PAHs (Jiang, 1988). Fig. 4 shows that there lay good correlation between $\Delta\Sigma$ PAHs and $\Delta\Sigma$ BaP ($r=0.89$). Fig. 5 shows the accuracy of determined Δ PAHs/ Δ BaP ratios. The accuracy of the determined Δ PAHs/ Δ BaP ratio varied from 16 % of fluorene to 33 % of benzo(e)pyrene with an average of 25 %.

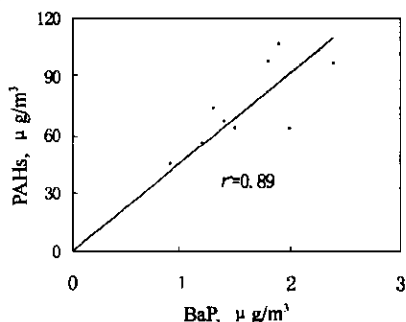


Fig. 4 Correlation between the concentrations of Δ BaP and Σ PAHs in the tunnel, and the y-intercept value is forced to zero

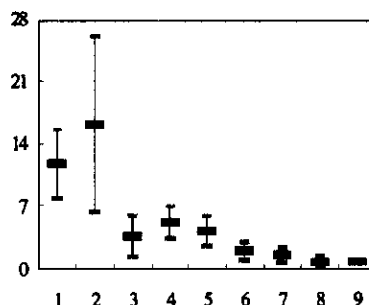


Fig.5 The atmospheric PAH composition (relative to benzo(a)pyrene) from traffic sources in the tunnel

In the investigation the street to campus ratio of NO_x (NO and NO₂) which was regarded as traffic gas was 2.45. In the street air, the content of phenanthrene was mean to 5.53 $\mu\text{g}/\text{m}^3$ and 2.33 $\mu\text{g}/\text{m}^3$ in the campus area and those of benzo(a)pyrene were 0.322 and 0.108 $\mu\text{g}/\text{m}^3$ respectively. The street to campus ratio of NO_x (2.45) was similar to that of phenanthrene (2.37) suggesting phenanthrene are coming from traffic gases almost exclusively. For the ratio of PHEN to BaP originating from tunnel traffic exhaust gases was determined to be 23.0. If one assumes all PHEN comes from traffic exhaust emissions, 75% (0.263 $\mu\text{g}/\text{m}^3$) of BaP in the arterial street air would come from traffic and remaining 25% (0.059 $\mu\text{g}/\text{m}^3$) from non-traffic sources. In the campus area, 92% (0.100 $\mu\text{g}/\text{m}^3$) of BaP would come from traffic, and the remaining 8% (0.008 $\mu\text{g}/\text{m}^3$) would come from non-traffic sources. During the sampling time, in 7:00—10:00 a.m. 89% of BaP, in 11:00—14:00 71% of BaP and in 15:00—18:00 68.5% of BaP would

come from traffic source. For the other influence factors to the content of BaP in the arterial street air, the correlation between $\Delta\Sigma\text{PAHs}$ and ΔBaP ($r=0.1$) was less than that of the tunnel.

3 Conclusion

This paper has focused on the concentration, variation and influential factor, distribution between vapor and particulate phases of the nine PAHs, and traffic contribution of BaP in the arterial street air of Hangzhou. The total concentrations of the nine PAHs were mean to $11.7 \mu\text{g}/\text{m}^3$ in the street air, and benzo(a)pyrene was up to $0.108 \mu\text{g}/\text{m}^3$ in the street air. The PAHs contents in air had relevance to the traffic intensity of the sampling sites. However, the terrain and meteorological conditions would affect it, too. Under the similar pollution conditions, the PAHs concentration was lower than others when the terrain and meteorological conditions were helpful to dilution. The distribution of PAHs between vapor and particulate phases was mainly affected by their physical, chemical characters and surrounding temperature. In the ambient air, the PAHs ($\text{MW} \leq 228$) were mainly in vapor phase, the PAHs ($\text{MW} > 228$) were predominantly in particulate phase. The fraction of vapor phase PAHs was prevail in the total nine PAHs. Among the nine PAHs measured in this investigation, phenanthrene was the most abundant PAHs. It is over 30% in the total sum. In the arterial street air of Hangzhou, the concentrations of PAHs in the morning and evening were higher than that on the noon during the collections. And the variation was closed to the traffic gas NO_x , but contrary to SO_2 . It could be assumed that the major PAHs source in the arterial street air was the traffic. And 75% of BaP would come from traffic source and remaining 25% of BaP would come from non-traffic source.

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