Journal of Environmental Sciences Vol.17, No.3, pp.365—370, 2005

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2005)03-0365-06 **CLC number:** X131.1 **Document code:** A

PAHs pollution from traffic sources in air of Hangzhou, China: Trend and influencing factors

ZHU Li-zhong[1,*], WANG Jing[1,2]

(1. Department of Environmental Science, Zhejiang University, Hangzhou 310028, China. E-mail: lzzhu@mail.hz.zj.cn; 2. Zhejiang Environmental Monitoring Centre, Hangzhou 310012, China. Email: wangj3186@hotmail.com)

Abstract: PAHs pollution in air of arterial roads was investigated from October 1998 to October 2001 in Hangzhou, China. The results showed that Σ10 PAHs was 13—36 μg/m^3, among which, BaP, a strong carcinogenic kind ranged from 0.034 μg/m^3 to 0.12 μg/m^3. PAHs pollutions in four seasons were winter > autumn > spring-summer. The annual averages of ΣPAHs concentration were 25 μg/m^3 for 1999, 28 μg/m^3 for 2000, and 29 μg/m^3 for 2001, respectively. Leaded gasoline was banned in December 1998 in Hangzhou, thus comparative measurements with PAHs in leaded and lead-free gasoline powered motor exhausts made it certain that the use of lead-free gasoline leaded to a heavier PAHs pollution in roadside air from December, 1998, in China, and ΣPAHs in air samples after the lead-banning were more than twice of that in samples before the action. For the large contribution of vehicle discharge to air pollution in roadside, further research was performed to suggest the factors influencing PAHs distribution in vehicle exhaust in order to control air pollution effectively. Compared to gasoline engines, emissions from diesel engines were less toxic, although they might produce more PAHs. Of the same vehicular and oil type, automobiles of longer mileages produced more toxic PAHs. PAHs distributions in the vehicular exhausts were related to the oil type. Large difference was found in the abundance of 3-, 5- and 6-ring PAHs between exhausts from gasoline and diesel oil engines. Diesel oil engines produced relative lighter PAHs such as NAPH, ACEN, FLUOR, while gasoline engines emitted heavier kinds such as BkF, IN and BP. The automobile produced more PAHs with the increase of mileage especially FLUR, PY, BaP, BP. Some significant ratios for traffic source in Hangzhou such as PHEN/AN, FLUR/PY, IN/BP were 0.50—4.3, 0.58—7.4, 0.51—1.5, respectively. A source fingerprint for vehicle exhausts of a mixture of vehicle and oil types in the city district for light-duty vehicle was the abundance of BaA, followed by NAPH, BP, IN. 4-ring PAHs such as FLUR, PY, BaA and CHRY were the most predominant kinds followed by 6-ring PAHs(BP, IN).

Keywords: PAHs; influencing factors; vehicle exhaust; air pollution

Introduction

China is experiencing rapid economic and population growth. The rapid growth and increasing fossil fuel energy consumption have resulted in large amounts of pollutants such as TSP, SO_2, NOx and hydrocarbons to be emitted into ambient atmosphere. Nowadays, national routine monitor has paid much attention to TSP, SO_2 and NOx. High concentrations of SO_2 and NOx can lead to an increase of regional levels of acid deposition and tropospheric ozon, thus impacting human health and crop. According to the National Environmental Quality Report of 1999 (NEQR, 1999; 2000), among the 97 cities covered by the nationally controlled monitoring networks, annual average NOx concentrations in 32 cities exceed the second class standard (50 μg/m^3) of the national average NOx air concentrations. Table 1 shows the annual average concentrations of NOx and SO_2 in some of the large cities in China (NEQR 1999, 2000).

Table 1 Annual average concentration of NOx and SO_2 in large cities(μg/m^3), 1999

City	Province	NOx	SO_2
Beijing	Beijing	140	80
Tianjin	Tianjin	55	68
Shijiazhuang	Hebei	75	129
Taiyuan	Shanxi	101	272
Urumchi	Xinjiang	92	146
Guangzhou	Guangdong	113	54
Shanghai	Shanghai	100	44
Wuhan	Hubei	88	39
Hangzhou	Zhejiang	72	49
Chongqing	Chongqing	62	170

Although organic pollution has received increasing attention in the world, national routine monitor has not covered some toxic hydrocarbons such as polycyclic aromatic hydrocarbon(PAHs) in present China. It is well known that PAHs originate predominantly from authropogenic combustion processes including transportation vehicles, coke oven, steel and iron furnaces, metal smelters, manufactured gas plants, incineration of municipal and domestic heating. Among these sources, traffic and coal related sources have been considered to be the two most important source categories in the 20th century (Rogge, 1993; Lee, 1995; Harrison, 1996). Nowadays, in China, with the increase of vehicle occupation, the urban areas of many metropolitan no longer had a conventional mixture of air pollutants from coal burning and petrol-burning. However, oil burning, such as vehicle discharge was the only predominant contribution to air pollution, the same as cities in other countries (Rogge, 1993; Lee, 1995; Harrison, 1996; Nielsen, 1996; Möller, 1982; Tuominen, 1988; Benner, 1989). PAHs are principal components in exhausts from vehicle, except NO and CO, suggested as tracers of pollution from traffic after the phase-out of lead in petrol(Daisey, 1986). To evaluate the trend of PAHs pollution in road air, data from October 1998 to October 2001 were collected from Hangzhou, a major city in east China.

Hangzhou has an average temperature of 16.2℃ (28.6℃ in summer and 3.6℃ in winter) and 1453 mm rainfall. Many hills lie around the city, thus making air pollutants difficult to diffuse. A large population of 1.75 million and 20% annual growth of automobile occupation led to an ignorable air pollution in the city where lead-free gasoline has been put into use instead of leaded gasoline from December 1998. However it was still uncertain in China whether the use of lead-free gasoline would result into changes of PAHs pollution in air. At the same time traffic emissions were playing more and more important role in PAHs pollution in urban air, so research on PAHs in traffic

* Corresponding author

emissions was one of interesting fields in the world (Marklund, 1987; Mi, 2000; Bingham, 1989; Oehme, 1991). It was sure that PAHs discharged from vehicles were affected by oil types, vehicle types and mileage, which differed much from country to country. For instance, SANTANA, SANTANA 2000 and PASSAT vehicles were the popular vehicles in China, while things might be quite different in USA. Thus PAHs fingerprint from vehicle discharge was of special regional characteristics. Consequently, the paper taking Hangzhou as a case was designed to have a comprehensive understanding of pattern and trend of PAHs pollution in air of arterial roads. Occurrence of PAHs in exhausts from vehicles fueled with leaded and lead-free gasolines were also presented to explain the difference of PAHs concentrations fore- and after the lead banning action. However, factors affecting PAHs discharges in traffic exhausts, for example, oil type and mileage were further investigated in order to obtain a detailed PAHs fingerprint for traffic source. This study includes three parts of experiments: (1) to survey PAHs pollution in air of arterial roads (Experiment 1); (2) to comparatively study PAHs from vehicle powered with leaded and lead-free gasoline (Experiment 2); (3) to investigate the factors affecting PAHs production in vehicle discharges (Experiment 3).

1 Experimental design

1.1 Experiment 1

Three monitoring sites were located near arterial roads in Hangzhou, and the most important source of PAHs was vehicles emission: Site 1, a crossroad in the cultural and educational area, situated in the west of the city; Site 2, a crossroad in the commercial area. These two sites were in relatively narrow roads with high buildings on the two sides; Site 3, a crossroad in the east.

The samplers were located at a height of 1.5 m, 1 m away from the road. The air-sampling program was carried out on January, April, July, and October from 1998 to 2001, which were representative months of winter, spring, summer and autumn, respectively. Each sampling activities were conducted in duplicate. The weather conditions in detail were given in Table 2.

Table 2 The conditions during the sampling activities

Date	Weather condition
1998 - 10	Sunny to cloudy, average temperature of 20℃
1999 - 01	Sunny to cloudy, average temperature of 10℃
1999 - 04	Sunny to cloudy, average temperature of 22℃
1999 - 07	Sunny to cloudy, average temperature of 28℃
1999 - 10	Sunny to cloudy, average temperature of 17℃
2000 - 01	Sunny to cloudy, average temperature of 8℃
2000 - 04	Sunny to cloudy, average temperature of 20℃
2000 - 07	Sunny, average temperature of 30℃
2000 - 10	Sunny, average temperature of 18℃
2001 - 01	Sunny to cloudy, average temperature of 7℃
2001 - 04	Sunny, average temperature of 19℃
2001 - 07	Sunny, average temperature of 33℃
2001 - 10	Sunny, average temperature of 19℃

Notes: Sampling time: 7:00—10:00, 11:00—14:00, 15:00—18:00

1.2 Experiment 2

This experiment carried out in a park far away from any arterial roads, with no other PAHs sources nearby was aimed to supply sufficient proof for the change of PAHs in arterial roads air of Hangzhou, and the effect of lead-free gasoline on PAHs emissions. A truck, driven for about 100000 km, with carburetor spark ignition engine was used for the research. The experiment simulated the truck meeting red lights, and the engine was idle. The leaded gasoline (70 #) and lead-free gasoline (90 #) were separately used. For each oil type used, the engine was washed with 2 L of toluene and idles for 10 min. Each test lasted for 30 min, and was performed in duplicate. The sampler was located 1 m away from tail tube and 0.5 m above the ground. Because the sampler was only 1 m to the tail tube, the transported PAHs of long-distance transportation were neglected.

1.3 Experiment 3

Currently, in the city district, there were mostly light-duty vehicles including SANTANA 2000, SANTANA, SUZUKI, PASSAT and IVECO. And heavy-duty vehicles were forbidden to enter the downtown. Diesel oil (0 #), gasoline (90 #, 93 # raking by their octane levels) were the three types of oil presently used, and are the five popular vehicle types in the city district. In order to evaluate the effect of oil type, mileage, and vehicle type on PAHs discharge, so as to control PAHs pollution in road air and obtain a comprehensive PAHs fingerprint of vehicle emission in the city zone, 10 automobiles were selected and driven to the park, the same as that in Experiment 2. Table 3 gave the detailed information about the vehicle. All automobiles were kept idle one by one for 30 min to simulate automobile meeting red lights. Each experiment was performed in duplicate. Between every two experiments, 30 min was left to minimize the effect of former run on the latter one. The sampler was located 1 m away from tail tube and 0.5 m above the ground.

Table 3 Detailed information about automobiles selected

Vehicle No.	Mileage, km	Oil type
1	42758	90 #
2	10573	90 #
3	17802	90 #
4	536229	90 #
5	37098	90 #
6	216686	90 #
7	21586	93 #
8	123969	0 # (diesel oil)
9	120353	90 #
10	295590	90 #

Notes: Vehicle 1—3 were of the same type; vehicle 4—6 were of the same type; Vehicle 9—10 were of the same type and vehicle 7, 8 belonged to the different type

1.4 Sampling and analysis

All air samples were taken with low noise small samplers (MP-15CF mini pump, Shibita, Japan) operated at 1.0 L/min equipped with a Whatman glass fiber filter (GFF, 25 mm, Whatman, England) collecting particle-bound PAHs and XAD-2 (2.5 g) retaining PAHs in gaseous phase, respectively. GFFs were combusted overnight and sealed in the aluminum foil prior to use. XAD-2 was pre-extracted in dichloromethane (DCM) and methanol for 48 h, vacuum-dried in desiccators and stored in solvent-rinsed glass jars prior to use. Sample flow was measured before and after sampling using calibrated rotameters with an accuracy of ± 1%. For the study on PAHs pollution in arterial roads, three samples were taken for each site every day (7:00—10:00, 11:00—14:00, 15:00—18:00). However, tests designed to investigate the factors affecting PAHs emissions, such as

oil type, car type and mileage lasted for half an hour. And all samples were taken to the laboratory in a black plastic bag, and kept in a −68℃ refrigerator until analysis.

All samples were analyzed within 24 h and the analysis of PAHs in air samples were described elsewhere (Liu, 2001). In general, PAHs samples were extracted by sonication for 30 min with a 20 ml mixture of DCM and acetonitrile(V:V = 3:2). During sonication, the temperature of water bath was kept under 30℃. Then 10 ml of extraction raffinate with 30 μl dimethyl sulfoxide (DMSO) was evaporated under a gentle flow of nitrogen gas at room temperature and then was added to 1 ml with methanol. After sample preparation, 100 μl extraction was injected with autosampler to be analyzed by HPLC system(Hitachi, L-7000 series, Japan) consisted of a precolumn(Supelco, 5C-18, Φ4.6 mm × 50 mm, U.S.A.) for PAHs condensation and cleanup, a main column(Wakosoil, 5C-18, Φ4.6 mm × 250 mm, Japan) for PAHs separation, a fluorescence detector (Hitachi, L-7480, Japan), a data processor, and a system controller. The detection limits of this method for 12 PAHs ranged from 0.53 pg to 29.13 pg and recoveries of each PAHs from XAD-2 and the filter were all over 90% and the relative standard deviations of the recoveries of each PAHs(n = 5) were less than 2.64%.

Because of the absence of PAHs standard, in experiment 1 and 2, 10 PAHs including fluorine(FLUOR), phenanthrene (PHEN), anthracene (AN), fluoranthene (FLUR), pyrene (PY), benzo [a] anthracene (BaA), chrysene (CHRY), benzo [e] pyrene (BeP), benzo [k] fluoranthrene (BkF) and benzo [a] pyrene (BaP) were accounted, while 4 PAHs like naphthalene (NAPH), acenaphthene (ACEN), benzo [ghi] perylene (BP), indeno [1, 2, 3-cd] pyrene (IN) except for the ten PAHs in Experiment 3.

2 Results and discussion

2.1 PAHs pollution in air of arterial roads

The ΣPAHs concentrations in air of arterial roads for four years (October 1998—October 2001), are presented in Table 4 ranged from 13 to 36 μg/m^3 among which, BaP is a strong carcinogenic kind ranged from 0.034 μg/m^3 to 0.12 μg/m^3, being much higher than that in air of central Copenhagen (Nielsen, 1996), with the heaviest PAHs pollution found in January of each year followed by October. And in 1999—2000, PAHs concentrations in April were higher than those in July, which were different in 2001. In winter, pollutant was difficult to diffuse because of the strengthened atmospheric stability. At the same time, heating in winter resulted in an increase of energy consumption, all of which led to a heaviest PAHs pollution in January. However, in April and July with a relative high temperature and frequent air convection it was easy for pollutants to diffuse once produced. Furthermore large quantity of rainfall in spring and summer might lead to strengthen cleaning effect by rain on PAHs pollution in air.

Table 4 PAHs concentrations(μg/m^3) in air of arterial roads in October 1998—October 2001

		FLUOR	PHEN	AN	FLUR	PY	BaA	CHRY	BeP	BkF	BaP	ΣPAHs
1998	Oct.	1.9	5.7	0.71	2.8	0.49	0.53	1.1	0.19	0.026	0.034	13
1999	Jan.	4.5	12	0.89	5.8	2.8	3.7	3.8	0.22	0.048	0.051	34
	Apr.	1.4	7.9	0.53	3.2	2.4	2.1	1.5	0.092	0.047	0.040	19
	Jul.	3.2	9.0	0.94	1.8	1.1	0.62	0.53	0.58	0.027	0.088	18
	Oct.	5.7	8.6	2.0	5.4	2.2	1.8	2.0	0.97	0.049	0.095	29
	Annual average concentration											25
2000	Jan.	7.1	12	1.1	6.0	3.1	2.2	2.5	1.6	0.070	0.12	36
	Apr.	4.8	9.4	0.94	3.6	3.1	2.0	1.8	0.12	0.052	0.068	26
	Jul.	3.4	11	1.1	2.2	1.3	0.85	0.62	0.72	0.030	0.059	21
	Oct.	6.1	11	1.5	4.0	2.7	1.6	1.9	0.16	0.050	0.095	31
	Annual average concentration											28
2001	Jan.	5.6	12	1.1	6.6	2.9	2.0	2.1	1.4	0.062	0.11	34
	Apr.	4.1	10	0.64	3.8	3.2	1.9	1.5	0.21	0.062	0.072	26
	Jul.	3.4	11	1.5	4.0	2.8	1.6	1.9	0.19	0.059	0.10	26
	Oct.	3.6	11	1.1	4.5	2.7	1.8	2.2	1.1	0.073	0.093	28
	Annual average concentration											29

Fig. 1 shows that PAHs pollution in road air of Hangzhou presented a heavier trend from 1999(25 μg/m^3) to 2000(28 μg/m^3) however was stable after 2000(29 μg/m^3). Lead-free gasoline had been widely used since Dec. 1998. ΣPAHs concentrations of air samples collected in October from 1998 to 2001 were compared with the same weather condition during sampling activities to show the change of PAHs pollution in air after leaded gasoline banning action and the result presented an uprise in October 1999(from 13 to 29 μg/m^3), and little difference in those of the following three years. Certainly, PAHs pollution in air was influenced by many factors such as sources discharges and weather conditions. In this study, weather condition was ignored for the similarity of that in the sampling days. Sources were affected by oil consumption for transportation and oil type. Traffic intensity for sampling sites was not measured for each sampling, however, it was reported that, there had been a 20% increase in vehicle occupation in the whole city since 1998(Liu, 2001). It was believed, that, PAHs in sampled air zone mainly came from traffic emissions. In this way, the trend of PAHs pollution(a sudden uprise then almost little change in ΣPAHs of samples in October) in these years could not attribute to the increase vehicle occupation and other sources. In China, rapid economic growth led to a boom in type and quantity of vehicle, and cars have entered into many family. Whereas, quality of many Chinese vehicle had greatly improved, and vehicle exhausts of some types could meet European Ⅱ or Ⅲ standard. At the same time, family cars have only been quickly developed in recently years, and the short driving mileages accounted for less pollutants discharges

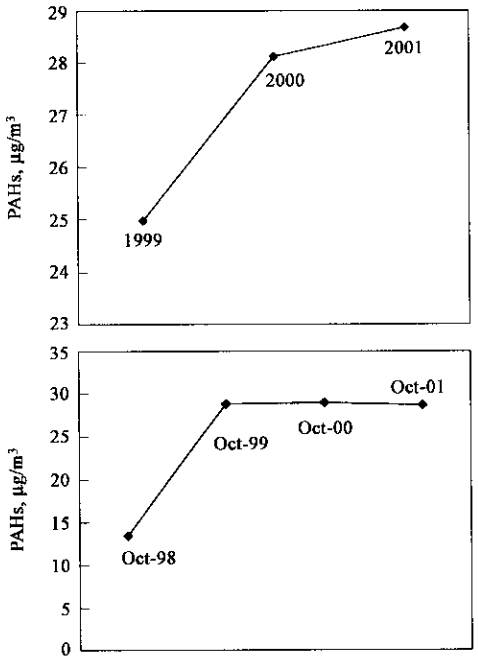

Fig.1 Variation of PAHs concentrations

compared with cars of longer mileages. As a result, PAHs in air did not show a continuous increase, but a sudden uprise. Banning leaded gasoline was the great action affecting the oil type from 1990s. In this way, the influence accounting for the heavier PAHs pollution resulted from lead-free oil was further concerned below.

2.2 PAHs emissions from burning of leaded and lead-free gasoline

This section of experiment aimed to ensure that the lead-free gasoline result into PAHs increase in air. Notable changes are shown in Table 5. Except BaA, larger amount of PAHs were produced from lead-free gasoline(90 #) powered engine, among which BaP, AN, FLUR, PY, FLUOR showed larger increase comparing to PHEN, CHRY. Certainly, PAHs pollution levels in air were affected by many factors such as weather conditions, PAHs input from all sources. It was an obvious fact that, automobile fueled with lead-free gasoline discharged more PAHs and have an ignorable responsibility for heavier PAHs pollution in roadside air.

2.3 Effect of oil, vehicle type and mileage on PAHs emissions

Since December 1998, lead - free gasoline including 90 # and 93 # has taken place of leaded gasoline named 70 # in Hangzhou. Besides gasoline, diesel oil is another important fuel for engine-powering in the city. In order to have a comprehensive understanding of PAHs emissions affected by oil type, vehicle type and mileage, 10 automobiles selected in this study were described in Table 3. 14 selected PAHs in emissions were determined, and results are presented in Table 6. The total PAHs concentration in ambient air were 42—121 $\mu g/m^3$, with an average concentration of 61 $\mu g/m^3$, and BaP ranged from 0.37 $\mu g/m^3$ to 3.1 $\mu g/m^3$, BP and IN were 3.8—32 $\mu g/m^3$ and 4.3—16 $\mu g/m^3$, respectively. The carcinogenic potential can be expressed as toxic equivalency factors (TEF) that were proposed for 17 PAHs as for BaP by Nisbet and LaGoy (Nisbet, 1992). The TEF adjusted concentrations of total PAHs (Total*) were also presented in Table 6 with ratios of Total/Total* . It was obvious that Total and Total* did not share the same trend and the Total was vehicle 10 > 8 > 9 > 1 > 4 > 6 > 7 > 3 > 2 > 5, while the Total* was vehicle 10 > 1 > 9 > 7 > 6 > 5 > 8 > 3 > 4 > 2. The ratios of Total/Total* could indicate relative toxicity of vehicle discharges, the larger the ratio was, the more toxic the vehicle exhausts was. As shown in Table 6, the ratios were 19.3—56.2, and the highest one was for vehicle 8, the only diesel oil automobile, which showed that compared to gasoline engines, emissions diesel engines were less toxic, although they might produce more PAHs. The two lowest ratios were found in emissions from vehicle 5 and 10. Comparing the same type of vehicle 1, 2 and 3, the ratios decreased with the increase of mileage. The same results could also be reached in comparison of No. 9 and 10, which improved that, the longer automobiles were driven, and the more toxic PAHs were produced. At the same time, of the same type, automobiles of longer mileage produced more total PAHs, 121 $\mu g/m^3$ for vehicle 10(295590 km) > 79 $\mu g/m^3$ for vehicle 9 (120353 km), 77 $\mu g/m^3$ for vehicle 1 (42758 km) > 52 $\mu g/m^3$ for vehicle 3 (17802 km) > 48 $\mu g/m^3$ for vehicle 2(10573 km).

Table 5 PAHs emissions from vehicle powered by leaded and lead-free gasoline($\mu g/m^3$)

PAHs	FLUOR	PHEN	AN	FLUR	PY	BaA	CHRY	BeP	BkF	BaP
Lead-free gasoline(90 #)	9.1	11	2.5	4.9	4.2	5.0	7.7	0.31	0.041	0.032
Leaded gasoline(70 #)	2.1	7.3	0.58	2.6	0.64	7.7	5.4	0.28	0.022	0.011

PAHs distributions in the exhaust of vehicle were related to the oil type. PAHs fingerprints of gasoline were obtained by averaging the relative concentrations of each PAHs in emissions of 9 gasoline automobiles in this study, and the same was done to the only diesel oil automobile with the results presented in Fig.2. It was obvious that BaA was the most predominant kind for emissions from both gasoline and diesel oil automobiles. Diesel oil engines produced relative more light PAHs such as NAPH, ACEN, FLUOR, while gasoline engines emitted more heavy kinds such as BkF, IN and BP. Distributions of PAHs with different rings were also

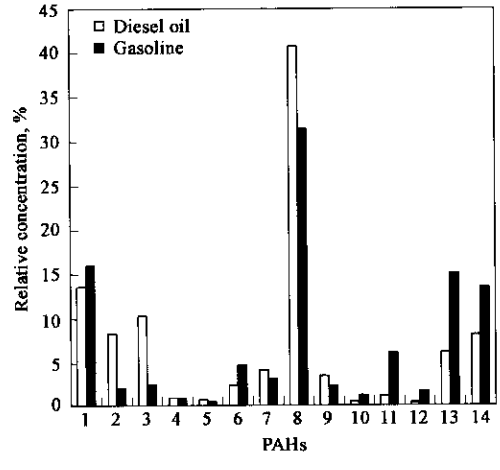

Fig.2 PAHs distribution in emissions from diesel oil and gasoline automobiles
1—14: NAPH, ACEN, FLUOR, PHEN, AN, FLUR, PY, BaA, CHRY, BeP, BkF, BaP, BP, IN

presented in Table 7 for exhausts from gasoline and diesel oil powered engine, respectively. Large difference was found in the contributions of 3-, 5-, and 6-ring PAHs to the total concentrations and the relative concentrations of 3-, 5-, and 6-ring PAHs in exhausts from gasoline powered engines were about three times, five times and twice as those from diesel oil powered engine.

As given in Table 3, vehicle 9 and 10 were of the same type, powered with 90 # gasoline and of different mileages (120353 km and 295590 km). PAHs in exhausts from the two vehicle described in Fig. 3 made it certain that the automobile produced more PAHs with the increase of mileage, especially, FLUR, PY, BaP, BP, with the total concentration rising from 79 $\mu g/m^3$ to 121 $\mu g/m^3$.

Table 6 Concentrations of 14 PAHs in vehicle discharges($\mu g/m^3$)

Vehicle no.	1	2	3	4	5	6	7	8	9	10
Mileage, km	42758	10573	17802	536229	37098	216686	21586	123969	120353	295590
Oil type	90 #	90 #	90 #	90 #	90 #	90 #	93 #	90 #	90 #	90 #
NAPH	9.2	13	9.4	11	9.1	6.2	6.8	16	6.5	7.5
ACEN	0.46	2.1	2.2	1.7	0.92	0.92	0.18	9.5	3.6	3.0
FLUOR	1.6	0.38	1.6	2.3	0.57	2.0	1.8	12	2.6	5.0
PHEN	0.061	0.68	0.55	1.1	0.34	0.28	0.57	1.1	0.50	0.69
AN	0.12	0.38	0.13	0.79	0.17	0.12	0.35	0.82	0.36	0.50
FLUR	2.3	1.8	2.0	4.6	0.76	1.8	5.5	2.7	2.4	7.8
PY	2.7	3.0	2.2	1.6	0.94	1.5	0.75	4.6	2.2	6.1
BaA	20	14	17	32	14	17	13	46	26	26
CHRY	2.3	1.2	1.2	0.89	0.30	0.74	2.5	3.9	0.33	3.0
BeP	0.46	0.52	0.53	0.71	0.62	0.41	1.4	0.52	1.1	1.6
BkF	4.2	1.3	2.4	1.2	3.8	6.1	5.2	1.2	5.4	7.1
BaP	1.7	1.0	0.98	0.65	1.1	0.37	0.82	0.37	1.3	3.1
BP	20	3.8	6.1	5.1	4.3	13	8.9	6.8	12	32
IN	12	4.3	5.3	7.7	4.7	11	8.9	9.1	14	16
Total	77	48	52	72	42	62	57	114	79	121
Total *	3.8	1.8	2.0	2.0	2.1	2.4	2.5	2.0	3.6	6.1
Total/Total *	20.4	26.2	25.6	36.9	19.3	25.5	22.9	56.2	21.8	19.8

Table 7 Distribution of PAHs with different rings

Rings	2	3	4	5	6
Gasoline engine, %	15	6.5	41	9.2	29
Diesel engine, %	14	20	50	1.9	14
Traffic emission, %	15	7.9	41	8.4	28

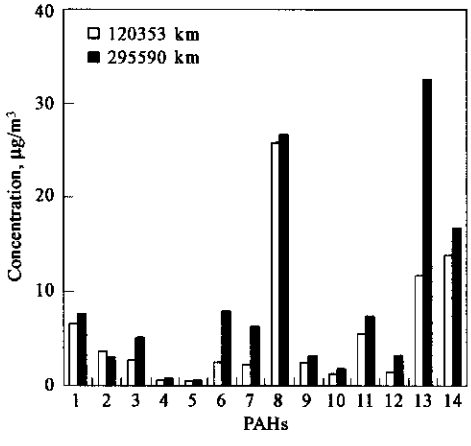

Fig. 3 PAHs in exhausts from vehicle of different mileages
1—14 is the same as Fig. 2

For the identification of PAHs sources, a lot of significant molecular ratios of specific hydrocarbons had been developed including FLUR/PY, PHEN/AN, IN/BP, and so on (Baumard, 1998; Yunker, 1996; Benlahcen, 1997; Maher, 1992), which were also calculated in this study in Table 8, with results showing that, PHEN/AN, FLUR/PY, IN/BP were 0.50—4.3, 0.58—7.4, 0.51—1.5, respectively. Because these ratios were influenced by vehicle and oil, the results of this study may be helpful for Chinese

Table 8 Significant ratios in traffic exhausts

Vehicle No.	Mileage, km	Oil type	PHEN/AN	FLUR/PY	IN/BP
1	42758	90 #	0.50	0.86	0.62
2	10573	90 #	1.4	2.9	1.5
3	17802	90 #	1.6	7.4	1.0
4	536229	90 #	1.8	0.62	1.1
5	37098	90 #	1.3	0.58	1.3
6	216686	90 #	2.0	0.81	1.1
7	21586	93 #	4.3	0.91	0.88
8	123969	0 # (diesel oil)	2.3	1.2	0.87
9	120353	90 #	1.4	1.1	1.2
10	295590	90 #	1.4	1.3	0.51

scientists to identify PAHs sources. In this way, if the ratios in environmental samples were in the range, certainly, the chief PAHs source was vehicle exhausts.

Because vehicle types in this study were typical in the city, thus were selected to have deep insight of PAHs in vehicle exhausts in order to determine a PAHs fingerprint for vehicle source in the downtown of Hangzhou. Firstly, each PAHs in emission samples of the 10 automobiles were normalized with the total PAHs and relative concentrations of each PAHs were thus obtained, which were then averaged to have a comprehensive PAHs sourceprint for traffic source in Hangzhou (Fig. 4). BaA had the largest contribution (33.3%), the followed were NAPH, BP, IN which could be regarded as mark kinds of this source, a little different from Khalili's report (Khalili, 1995). It was believed that, vehicle type was a significant factor to PAHs distribution in emission. Only the light-duty vehicle can be driven in the city zone, which 10 automobiles in this study belong to. Reports were different from Khalili's tunnel study, where heavy-duty vehicle may have relative larger contributions. It

was obviously found in Table 7, 4-ring PAHs such as FLUR, PY, BaA, CHRY were the most predominant kinds in traffic discharges followed by 6-ring PAHs (BP, IN).

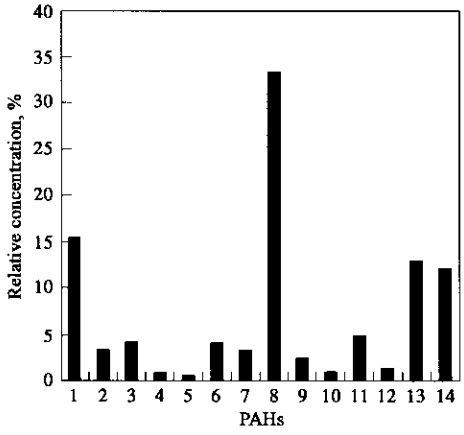

Fig.4 PAHs fingerprint of vehicle emission
1—14 is the same as Fig. 2

3 Conclusions

PAHs pollution in air of Hangzhou was serious with ΣPAHs being 13—36 $\mu g/m^3$, and the highest one was found in samples of January, 2000 (36 $\mu g/m^3$), compared the lowest in autumn, 1998(13 $\mu g/m^3$), among which, BaP was a strong carcinogenic kind ranged from 0.034 $\mu g/m^3$ to 0.12 $\mu g/m^3$. PAHs pollutions in four seasons were winter > autumn > spring-summer. The annual average PAHs concentrations showed that, PAHs pollution in 2000 and 2001 were comparable with almost similar concentrations of 28 and 29 $\mu g/m^3$, respectively, more serious than that in 1999(25 $\mu g/m^3$). As for four sampling activities with the same weather condition in October, a sudden uprise of ΣPAHs concentration was found in air samples in 1999, then almost little change was presented after October, 1999. Comparative research carried out on the exhausts from leaded and lead-free gasoline powered engines made it certain that the trend of PAHs pollution in recent years could not attribute to the increase vehicle occupation but the use of lead-free gasoline.

To prove the effect of lead on the change of PAHs pollution in air, PAHs in discharges from a truck powered with leaded and lead-free gasoline, was separately studied. Except BaA, larger amount of PAHs were produced from lead-free gasoline (90 #) powered engine, among which BaP, AN, FLUR, PY, FLUOR showed larger increase comparing to PHEN, CHRY. In a word, it was sure that, the use of gasoline led to heavier PAHs pollution in air of the downtown except the increases in coal consumption, oil consumption and vehicle quantity.

Traffic exhaust was an important source to air pollution in present in China, the research performed to understand the effects of oil type, mileage on PAHs discharge showed that the total PAHs concentrations in discharges were 42—121 $\mu g/m^3$, with an average concentration of 61 $\mu g/m^3$, among which BaP ranged from 0.37 $\mu g/m^3$ to 3.1 $\mu g/m^3$, BP and IN were 3.8—32 $\mu g/m^3$ and 4.3—16 $\mu g/m^3$, respectively. Compared to gasoline engines, emissions from diesel engines were less toxic, although they might produce more PAHs. Of the same type, the longer automobiles were driven, the more toxic PAHs and more total PAHs were produced. PAHs distributions in the exhaust of vehicle were related to the oil type. BaA was the most predominant kind for emissions from both gasoline and diesel oil automobiles. Large difference was found in the distributions of 3-, 5- and 6-ring PAHs of emissions from gasoline (6.5%, 9.2% and 29.1%) and diesel oil engines (20.2%, 1.9% and 13.9%). Diesel oil engines produced relative more light PAHs such as NAPH, ACEN, FLUOR, while gasoline engines emitted more heavy kinds such as BkF, IN and BP. The automobile produced more PAHs with the increase of mileage, especially, FLUR, PY, BaP, BP. For the identification of PAHs sources, significant molecular ratios of specific hydrocarbons including FLUR/PY, PHEN/AN, IN/BP, calculated for traffic source were 0.50—4.3, 0.58—7.4, 0.51—1.5, respectively. A source fingerprint in the city zone for light-duty vehicle was the abundance of BaA, followed by NAPH, BP, IN. 4-ring PAHs(FLUR, PY, BaA, CHRY) was the most predominant kinds followed by 6-ring PAHs(BP, IN).

References:

Baumard P, Budzinski H, Garrigues P, 1998. Determination of polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of western Mediterranean Sea[J]. Environ Toxicol Chem, 17: 765—776.

Benlahcen K T, Chaoui A, Budzinski H *et al*., 1997. Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments [J]. Marine Pollution Bulletin, 34: 298—305.

Benner B A, Gordon G E, Wise S A, 1989. Mobile sources of atmospheric PAHs: a roadway tunnel study[J]. Environmental Science and Technology, 23: 1269—1277.

Bingham A G, Edmunds C J, Graham B W L *et al*., 1989. Determination of PCDDs and PCDFs in car exhaust[J]. Chemosphere, 19: 669—673.

Daisey J M, Cheney J L, Lioy P J, 1986. Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling[J]. J Air Pollut Control Ass, 36: 17—33.

Harrison R M, Smith D J T, Luhana L, 1996. Sources apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham UK[J]. Environmental Science and Technology, 30: 825—832.

Khalili N R, Scheff P A, Holsen T M, 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions[J]. Atmospheric Environment, 29: 533—542.

Lee W J, Wang Y F, Lin T C *et al*., 1995. PAH characteristics in the ambient air of traffic source[J]. The Science of Total Environment, 159: 185—200.

Liu Y J, Zhu L Z, Shen X Y, 2000. Polycyclic aromatic hydrocarbons(PAHs) in indoor and outdoor air of Hangzhou, China[J]. Environmental Science and Technology, 35: 840—844.

Liu Y J, 2001. Polycyclic aromatic hydrocarbons(PAHs) in indoor and outdoor air of Hangzhou[D]. Zhejiang University Master Thesis.

Maher W A, Aislabie J, 1992. Polycyclic aromatic hydrocarbons in nearshore marine sediments of Australia[J]. The Science of the Total Environment, 112: 143—164.

Marklund S, Rappe C H, Tysklind M, 1987. Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars on leaded gasoline[J]. Chemosphere, 16: 29—36.

Mi H H, Lee W J, Chen C B *et al*., 2000. Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine[J]. Chemosphere, 41: 1783—1790.

Möller M, Alfheim I, Larssen S *et al*., 1982. Mutagenicity of airborne particles in relation to traffic and air pollution parameters[J]. Environmental Science and Technology, 16: 221—225.

NEQR 1999, 2000. National Environmental Quality Report of 1999[S]. State Environmental Protection Administration(SEPA) of China.

Nielsen T, 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a larger city[J]. Atmospheric Environment, 30: 3481—3490.

Nisbet I C T, LaGoy P K, 1992. Toxic equivalency factors(TEFs) for polycyclic aromatic hydrocarbons (PAHs) [J]. Regulatory Toxicology and Pharmacology, 16: 290—300.

Oehme M, Larssen S, Brevik E M, 1991. Emission factors of PCDD and PCDF for road vehicles obtained by tunnel experiment[J]. Chemosphere, 23: 1699—1708.

Rogge W F, Hildemann L M, Mazurek M A *et al*., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel truck[J]. Environmental Science and Technology, 27: 636—651.

Tuominen J, Salomaa S, Pyysalo H *et al*., 1988. Polynuclear aromatic compounds and genotoxicity in particulate and vapor phase of ambient air: effect of traffic, season, and meteorological conditions[J]. Environmental Science and Technology, 22: 1228—1234.

Yunker M B, Snowdon L R, MacDonald R W *et al*., 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas[J]. Environmental Science and Technology, 30: 1310—1320.

(Received for review August 19, 2004. Accepted September 23, 2004)