



Occurrence and carcinogenic potential of airborne polycyclic aromatic hydrocarbons in some large-scale enclosed/semi-enclosed vehicle parking areas



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HIGHLIGHTS

- Atmospheric PAH levels in enclosed/semi-enclosed parking lots were much higher than urban areas.
- BaPeq values of these parks far exceed the air quality standards of China and WHO.
- Monte Carlo simulation results suggest the lifetime PAH inhalation cancer risks were acceptable.
- Vehicle exhaust, oil and/or coal combustion are dominant PAH contributors in these parks.
- Absorption into organic matter dominate PAH partition process over adsorption onto black carbon.

ARTICLE INFO

Article history:

Received 3 December 2013

Received in revised form 20 March 2014

Accepted 12 April 2014

Available online 21 April 2014

Keywords:

Vehicle exhaust

Cancer risk

Monte Carlo simulation

Source analysis

Principal component analysis-multiple

linear regression (PCA-MLR)

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) originating from vehicle exhaust have aroused much attention due to their potential healthy effect. In this study, air samples were collected from three representative parking lots in a metropolitan area, analyzed for PAHs and evaluated for inhalation risk. Atmospheric PAH levels of these parking areas ranged between 1178–4793 ng m⁻³, one order of magnitude higher than general urban areas. Their benzo[a]pyrene equivalent (BaPeq) values varied in 11.0–98.0 ng m⁻³, far exceeding the air quality standard of WHO (1.0 ng m⁻³). Monte Carlo simulation (100,000 trials) results suggest that the potential lifetime inhalation cancer risks of PAHs were 0.27 × 10⁻⁵ to 7.11 × 10⁻⁵ for park employees, which are in the acceptable range acknowledged by US EPA (1.0 × 10⁻⁶ to 1.0 × 10⁻⁴). Several source diagnostic methods proved that vehicle exhaust was the dominant PAH contributor of these parks with the contribution percentages being >53%; oil combustion and/or coal combustion were other important sources. Logarithms of gas-particle distribution coefficients (K_{ps}) of PAHs in all studied parks were linearly correlated with those of both their sub-cooled vapor pressures (p_{ls}) and octanol-air partition coefficients (K_{OAS}). The correlation coefficients indicated that both adsorption onto black carbon and absorption into organic matter were involved in the partition process, but the latter was dominant.

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1. Introduction

According to the *third national death reason survey* of China in 2008 (<http://www.moh.gov.cn/>), cancer is now the primary cause of death in Chinese cities, accounting for ~25% of all deaths; and lung cancer has replaced liver cancer in causing the largest

number of cancer deaths each year, at approximately 23% of all cancer deaths [1]. Besides smoking, ambient air pollution is known as a major cause of lung cancer [1,2]. Among various airborne carcinogens, polycyclic aromatic hydrocarbons (PAHs) were reported as a dominant contributor to lung cancer [3]. Generally, PAHs have petrogenic origins (e.g. crude oil, oil refined products and coals) and pyrogenic sources (e.g. incomplete combustion of fossil fuels and biomass) [4,5]. Vehicle exhaust has been proved as one of the largest contributors of airborne PAHs in urban areas [6,7].

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Typically, highly carcinogenic PAHs in exhaust are mainly associated with the particulate matters emitted from motor vehicles [8,9]. These contain fine particles with the peak diameter between 0.1 and 0.2 μm [10,11], which can be inhaled deeply into lung. Therefore, PAHs from vehicle exhaust and their related adverse health effects have become an issue of concern [7]. PAH emission factors from tailpipe reportedly change from 0.7 to 1600 $\mu\text{g km}^{-1}$ and relate to fuel type (leaded/unleaded gasoline, diesel) and quality, engine type, load and age, driving mode, etc. [5]. Diesel, cold start and congested traffic conditions promote PAH emission [5,12,13]. Traffic areas, e.g. highway tunnel [9], road intersection [14], traffic roadside [15], distribution center and bus terminal [16], etc., all showed significantly higher airborne PAH levels than common urban areas. Data also indicate that traffic-related workers, e.g. traffic policemen, tollbooth attendants, taxi/bus drivers, etc., are exposed to comparatively higher PAH inhalation risks [14,17,18]. Concentrations of 1-hydroxypyrene, a metabolite of pyrene (Pyr), in urine of non-smoking traffic policemen are statistically higher than those of nonsmoking control cohort [17]. PAH inhalation exposure levels of 44 traffic policemen in Bangkok, Thailand are about 20-fold higher than those of 45 office policemen from the same city [19].

Guangzhou is the third largest city of China (area: 7434 km^2 , population: ~16 million in 2012). As an important area of Chinese reform and open-up policy, Guangzhou has undergone rapid economic development, accelerated urbanization progress and also a sharp vehicle increase in recent years. Total vehicles of Guangzhou in 2006 were 1.83 million, including 22,430 liquefied petroleum gas (LPG)-powered buses/taxis. The number increased to 2.15 million by the end of 2010, and then to 2.40 million by May, 2012. Similar to many other mega-cities, Guangzhou is also troubled with severe traffic congestion and insufficient parking space. To make full use of limited and expensive urban land, many parking lots in mega-cities were constructed underground or in buildings [20], so did Guangzhou. However, this enclosed/semi-enclosed mode hinders exhaust diffusion and therefore concentrates vehicle-related pollutants [16,20]. So far, very little is known about airborne PAHs and their associated cancer risks in such parking areas. Herein, we conducted air-sampling schemes in three representative parking lots in Guangzhou, and analyzed for 16 US EPA priority PAHs both in gaseous and particulate phases with the aim to investigate their levels, inhalation cancer risks, source apportionments and gas-particle distributions.

2. Materials and methods

2.1. Sample collection

Details about the three studied 24 h open parks were: (1) Park SY lies beneath a large shopping mall of Guangzhou and consists of two underground levels, >1500 parking spaces. It is equipped with a ventilation system (running time: 9:00–23:00) and >90% of the vehicles parked are operated with unleaded gasoline. The traffic rate per hour is ~1000 cars on average and peaks at night-fall. Considering the employees' dominant working area and power access reason, samples were only collected at the middle of its first level and 1 m high above the floor; (2) Park GJ is an important bus terminal (1-level, area: 17,000 m^2) located beneath the square of the second largest railway station in Guangzhou. The ventilation system equipped for GJ operates daily from 6:00 to 23:00. During the sampling period, 26 bus lines connected and about 5000 buses per day entered and departed from it. Among them, >90% were LPG-propelled and the others worked with diesel. Samples were collected in the middle of this park and 1 m high from the ground; (3) Park HY was built for a centralized freight transport

market, in which >1000 transport routes connect and daily goods trading volume is >6000 tons. Unlike SY and GJ, HY is an outdoor but semi-enclosed area (60,000 m^2 , >300 parking spaces) surrounded by storehouses (10–15 m high) with only two entrances being left. Vehicles parked here are mainly heavy-duty diesel trucks and the daily average traffic volume exceeds 10,000. Samples were collected at 2 m inside away from one entrance tollgate and 1 m high above the ground.

Short consecutive sampling schemes of ~2 weeks were carried out individually in SY, GJ and HY between August 23 and November 11, 2006, using high-volume air samplers operating at 1.05 $\text{m}^3 \text{min}^{-1}$. Flow rate calibration was conducted at each air sampling interval, which ranged in 2–4 h. Glass fiber filter (GFF, 20.3 cm \times 25.4 cm, Whatman) and polyurethane foam (PUF, 90 mm \times 65 mm i.d.) plug were used to collect total suspended particulate (TSP) and gaseous organic compounds, respectively. A total of 8, 10 and 9 samples were obtained for SY, GJ and HY, respectively. After sampling, the filters and PUFs were separately stored at $<-20^\circ\text{C}$ until analyzed. Each time before and after sampling, the filters were equilibrated in a constant condition (25 $^\circ\text{C}$, 50% RH) for 24 h and weighed to calculate TSP concentrations. Sampling details are provided in Table S1 of the supporting information.

2.2. Analysis

2.2.1. Chemicals

Standard solutions of 16 native PAHs (naphthalene – Nap, acenaphthylene – Acy, acenaphthene – Ace, fluorine – Flu, anthracene – Ant, phenanthrene – Phe, fluoranthene – Flua, Pyr, benz[a]anthracene – BaA, chrysene – Chry, benzo[b]fluoranthene – BbF, benzo[k]fluoranthene – BkF, benzo[a]pyrene – BaP, indeno[1,2,3-cd]pyrene – IncdP, dibenz[a,h]anthracene – DiB, and benzo[g,h,i]perylene – BghiP), 5 deuterated PAHs (d_8 -Nap, d_{10} -Ace, d_{10} -Phe, d_{12} -Chry and d_{12} -Perylene) and hexamethylbenzene (HMB) were all purchased from AccuStandard (New Haven, CT, USA). The solvents and reagents used were HPLC or pesticide grade from Merck (Darmstadt, Germany) or J.T. Baker (Phillipsburg, NJ, USA). Prior to use, silica gel (70–230 mesh, Aldrich, USA) and alumina (60–100 mesh, Merck, Germany) were activated at 180 $^\circ\text{C}$ and 250 $^\circ\text{C}$ for 24 h, respectively, then were deactivated with 5% (w/w) distilled water, equilibrated for 12 h, added *n*-hexane and stored in desiccators.

2.2.2. Clean-up procedure

The cleanup procedure for PAH analysis was described in detail previously [21,22] and thus is only briefly covered here. After added *d*-PAHs, air samples were Soxhlet-extracted with *n*-hexane:acetone (1:1, v:v) for 48 h, together with activated copper to remove sulfur. The extract was cleaned through a complex silica-alumina column, which was flushed with *n*-hexane and 7:3 (v:v) *n*-hexane:dichloromethane. The second fraction was concentrated to 200 μl under a gentle high-purity nitrogen stream and spiked with HMB for instrumental analysis.

2.2.3. Instrumental analysis

PAH analysis was performed with a QP2010 GC-MS (Shimadzu, Japan) running in EI (70 eV) and selected ion monitoring mode. A DB-5 MS fused silica capillary column (J&W Scientific, CA, 30 m \times 0.25 mm i.d., 0.25 μm) was used. The GC temperature gradient was 80 $^\circ\text{C}$ to 280 $^\circ\text{C}$ at 3 $^\circ\text{C min}^{-1}$, then to 300 $^\circ\text{C}$ at 10 $^\circ\text{C min}^{-1}$ (kept for 10 min). A 1 μL of sample was injected in splitless mode with helium as the carrier gas (2.0 ml min^{-1}). Temperatures of injection port, ion source and transfer line were 290 $^\circ\text{C}$, 230 $^\circ\text{C}$ and 300 $^\circ\text{C}$, respectively. Ions monitored for individual PAHs were listed in detail in Zhang et al. [22] and Table S2 of the supporting information.

2.3. Quality assurance and quality control (QA/QC)

Prior to use, the filters were heated at 450 °C for 4 h to remove possible organic background contaminants and sealed with aluminum foil; the foam plugs were Soxhlet-extracted with methanol, dichloromethane, toluene and acetone for 24 h respectively, then were vacuum-dried and sealed in pre-cleaned amber glass jars. Compounds were considered identified and quantified when the GC retention time deviations from those of the standards were within ± 0.1 min and the signal-to-noise ratios (S/N) were ≥ 10 . All samples were spiked with *d*-PAHs to evaluate the extraction and clean-up procedure, and their recoveries ranged in 41–110%. One field GFF/PUF blank, laboratory blank, standard spiked blank/matrix samples were included with every twelve samples. Recoveries of spiked PAHs in eight standard-spiked samples ranged from 31% to 113%. Concentrations of air samples were recovery- and blank-corrected. The significance for data statistical analysis is defined as $p < 0.05$.

3. Results and discussion

3.1. Concentrations of airborne PAHs in the parking areas

The minimum, maximum, median, arithmetic mean concentrations and standard deviations (SD) of \sum_{16} PAHs in gaseous and particulate samples are listed in Table 1, together with the corresponding TSP values. The mean \pm SDs of \sum_{16} PAHs were 2891 ± 716 , 1910 ± 783 and 2713 ± 856 ng m^{-3} for SY, GJ and HY, respectively. Atmospheric \sum_{16} PAHs of a typical urban area in Guangzhou was reported to vary from 74.0 to 142 ng m^{-3} (mean: 117 ng m^{-3}) [21]. The annual average concentration of airborne PAHs in a city park of Guangzhou, ~ 5 km away from our sampling sites, was 337 ng m^{-3} [23]. By contrast, our values (1178–4793 ng m^{-3}) are one order of magnitude higher. In addition, the particulate PAH levels in our study (84.6–291 ng m^{-3}) are also significantly higher than the corresponding data of Guangzhou in 1988 (15.6 ng m^{-3}), 2004 (50.6 ng m^{-3}) [24] and 2008 (55.6 ng m^{-3}) [25]. All these indicate local PAH sources in these parks.

Data of airborne PAHs in some traffic-related areas, e.g. intersection, tunnel, road and highway, etc. were summarized in Table S3 of the supporting information. Han and Naeher [26] reviewed atmospheric PAHs in traffic areas of developing countries, and the concentrations were 0.05–929 ng m^{-3} for PAHs and 16–910 ng m^{-3} for particulate PAHs, respectively. Comparatively, total PAHs (1178–4793 ng m^{-3}) and particulate PAHs (50.5–644 ng m^{-3}) in our study were at higher levels, which might impose a higher inhalation risk on the park workers.

3.2. Carcinogenic potential assessment of PAHs

Generally, the carcinogenic potency of PAHs is expressed as BaP equivalent (BaPeq), which is calculated by multiplying concentrations with their toxicity equivalency factors proposed by Nisbet and Lagoy [27]. In our study, the atmospheric BaPeq concentrations were 18.0 ± 6.3 , 19.5 ± 6.1 and 40.4 ± 22.4 ng m^{-3} for Park SY, GJ and HY, respectively (Table 1). Obviously, all these values exceed Chinese national upper limits for both indoor air (1 ng m^{-3} , Chinese National Standard GB/T 18883-2002) and ambient air (10 ng m^{-3} , Chinese National Standard GB3095-1996), and WHO's guideline for BaPeq (1.0 ng m^{-3}) in ambient air [5,28]. Among 16 PAH isomers, BaP was the most important BaPeq contributor, with percentages of 40.5–52.8%. The following isomers (average percentage) were DiB (9.4%), BbF (9.0%), Ant (7.9%), BaA (6.6%), IncdP (5.6%) and Phe (5.4%), respectively. These seven PAHs accounted for >90% of

the total BaPeqs. Therefore, combining BaP together with other high molecular PAHs to evaluate the risk would be more reasonable than BaP alone. This point is also supported by Kameda et al. [29].

The potential inhalation cancer risk of PAHs is quantified based on whole life inhalation doses, multiplied by the cancer potency factor (3.9 kg day mg^{-1} for BaP) [30]. The inhalation dose was calculated according to *Exposure Factors Handbook* of US EPA [31].

Potential cancer risk

$$= \text{Inhalation dose} (\text{mg kg}^{-1} \text{day}^{-1}) \times 3.9 \text{ kg day mg}^{-1} \quad (1)$$

$$\text{Inhalation dose} (\text{mg kg}^{-1} \text{day}^{-1}) = \frac{(C_i \times IR \times A \times EF \times ED)}{(BW \times AT)} \quad (2)$$

where C_i is pollutant concentration in air ($\mu\text{g m}^{-3}$); IR is inhalation rate ($\text{m}^3 \text{day}^{-1}$); A is inhalation absorption factor; EF is exposure frequency (day per year); ED is exposure duration (years); BW is body weight; and AT is average time period over which exposure is averaged (day). In our study, A is conservatively assumed as 1 due to the shortage of inhalable particulate data; park related works are regarded as light activities with the inhalation rate of $1.3 \text{ m}^3 \text{h}^{-1}$; park employees' occupational time is presumed as 40 years (8 h/day and 250 days/year) and their average life span is 70 years (365 days/year); an average BW of 65 kg is used; BaPeq values of our studied parks are used as $C_{\text{on-duty}}$; the average airborne BaPeq of Guangzhou is calculated as 8.53 ng m^{-3} according to Bi et al. [21] and adopted as $C_{\text{off-duty}}$. The detailed calculation is presented in Eq. (S1) of the supporting information.

As shown in Table 2, PAH inhalation cancer risks of park workers (1.66×10^{-5} to 3.78×10^{-5}) are all significantly higher than that of general residents in Guangzhou (1.60×10^{-5} , *t*-test, $p < 0.05$). Moreover, they are also statistically higher than PCDD/F risks of these park workers (1.08×10^{-5} to 2.07×10^{-5} , *t*-test, $p < 0.05$, [32]). This suggests that PAH pollution caused by vehicle exhaust in Guangzhou is a more significant health concern than PCDD/Fs.

However, use of averages of abovementioned parameters, e.g. BaPeq, BW, ED, etc., to estimate exposure risk will result in a degree of uncertainty. Monte Carlo simulation is based on repeated random sampling of the probability distributions, which are defined for the principal factors of variation and uncertainty of each parameter. It has been successfully used in many risk assessments [33]. Based on this, we conducted Monte Carlo simulation (100,000 trials, Oracle Crystal Ball software, Version 7.3.1) to evaluate the risk calculation uncertainty in our study. In the simulation, BaPeq and occupational time are assumed as uniformly distributed; BW has normal distribution. Therein, on-duty BaPeq data are within our minimum and maximum values (11.0–98.0 ng m^{-3}); off-duty levels vary in 2.43–18.7 ng m^{-3} according to Bi et al. [21]; occupational time range in 0–40 years; and BW is in the range of 40–90 kg with an average of 65 kg.

As shown in Table 2, the possible risks ranged in 0.27×10^{-5} to 7.11×10^{-5} with a mean value of 1.94×10^{-5} . Correspondingly, the cancer risks per million were 3–71 people with a mean value of 19 people. All these values are in range of 1.0×10^{-6} to 1.0×10^{-4} , which is acknowledged as acceptable by US EPA [30]. But most of them are higher than the target criteria of Japan (1×10^{-5} , [29]). Therefore, necessary personal protective equipment should be used to lower the park-workers' inhalation cancer risk. In addition, sensitivity analysis of abovementioned principal variables was also performed in the simulation to evaluate their influences on the total inhalation cancer risk. The result (Fig. S2, supporting information) suggests that off-duty BaPeq was the most dominant variance and

Table 1
Data of PAH and BaPeq concentrations (ng m^{-3}), TSP concentrations and some PAH source diagnostic isomer ratios in the three studied parks (SY, GJ and HY).

Parameters		Sampling sites					
		SY		GJ		HY	
		$\sum_{16}\text{PAHs}$	BaPeq	$\sum_{16}\text{PAHs}$	BaPeq	$\sum_{16}\text{PAHs}$	BaPeq
Gaseous	Min	1932	4.00	1082	2.15	1566	4.01
	Max	4381	9.94	3677	6.43	4149	13.8
	Median	2693	5.45	1562	3.14	2504	5.99
	Mean	2807	5.99	1751	3.46	2422	6.46
	SD	694	1.80	696	1.16	740	2.79
Particulate	Min	50.5	6.75	94.7	8.58	179	16.1
	Max	136	20.0	276	27.7	644	84.2
	Median	75.1	10.3	154	16.0	260	28.7
	Mean	84.6	12.0	159	16.0	291	33.9
	SD	27.7	4.6	52	5.5	135	19.7
Total	Min	1997	11.6	1178	11.0	1759	22.1
	Max	4518	30.0	3953	32.2	4793	98.0
	Median	2748	15.1	1732	20.0	2754	33.6
	Mean	2891	18.0	1910	19.5	2713	40.4
	SD	716	6.3	783	6.1	856	22.4
TSP ($\mu\text{g m}^{-3}$)	Range	102–289		309–544		689–1517	
	Median	166		424		998	
	Mean \pm SD	180 \pm 56		427 \pm 69		1026 \pm 222	
Ant/(Ant + Phe)	Mean \pm SD	0.14 \pm 0.01		0.12 \pm 0.01		0.11 \pm 0.02	
BaA/(BaA + Chry)	Mean \pm SD	0.39 \pm 0.02		0.35 \pm 0.02		0.31 \pm 0.04	
Flua/(Flua + Pyr)	Mean \pm SD	0.59 \pm 0.02		0.59 \pm 0.01		0.43 \pm 0.03	
IncdP/(IncdP + BghiP)	Mean \pm SD	0.44 \pm 0.02		0.45 \pm 0.01		0.44 \pm 0.02	

contributed 76.1% to the total risk, followed by occupational time (9.1%) and on-duty BaPeq (9.1%). BW contributed 5.8% of the total variance.

3.3. Isomer/homologue profiles and source diagnostics

Homologue and isomer profiles of PAHs are presented in Fig. 1. Obviously, airborne PAHs in the three parking areas were dominated by lighter isomers. Phe was the most abundant isomer and contributed 43–55% of total PAHs, followed by Nap, Flua, Flu and Pyr. As for homologue, 3-ring PAHs were the most important contributor with the mean relative percentages of 59–72%, followed by 2-ring (19–24%) and 4-ring (7–14%) compounds. 5- and 6-ring ones only contribute 1.0–2.8% to total PAHs.

Source marker, diagnostic ratio and principal component analysis (PCA) were generally used to identify PAH sources [5]. According to previous literatures, significantly higher level of Phe was proposed for motor vehicle emission [5,7]; higher percentages of 2- or 3-ring PAHs (65–92%) were also found in airborne PAHs from diesel engine, petrol engine and highway tunnels [5,34]. All these confirm the petroleum and vehicle-related sources of PAHs in our studied parking areas.

Values of Ant/(Ant + Phe), Flua/(Flua + Pyr), BaA/(BaA + Chry) and IncdP/(IncdP + BghiP) below 0.10, 0.40, 0.50 and 0.20, respectively have been reported indicate petrogenic sources, and otherwise suggest pyrogenic origins [4]. As shown in Table 1, all our values suggest pyrogenic sources in these parks except those of BaA/(BaA + Chry), which indicate the existence of petroleum sources. We plotted Ant/(Ant + Phe) versus BaA/(BaA + Chry) and Flua/(Flua + Pyr) versus IncdP/(IncdP + BghiP) of the three parks and other PAH sources (Fig. S3 in Supporting information). Congested cluster of the former two ratios suggests that our plots are very close to those of gasoline and diesel exhausts [4]. However, the latter two ratio plots of Parks SY and GJ show obviously deviation from vehicle exhaust ones. This indicates some coal combustion or incineration sources involved. The three parking areas are not completely enclosed and therefore are unavoidably influenced by outside air. Seen from previous annual data of urban air in Guangzhou [23], average Flua/(Flua + Pyr) and IncdP/(IncdP + BghiP) ratios were 0.62 and 0.47, respectively. Both SY and GJ are equipped with ventilation systems, which helped to facilitate air exchange with outside. Therefore, they showed comparatively higher Flua/(Flua + Pyr) and IncdP/(IncdP + BghiP) ratios. As for HY, passive insufficient natural air-exchange inside together with busy surrounding roads outside

Table 2
Lifetime PAH inhalation carcinogenic potentials for park workers of the three parks (SY, GJ and HY).

Sampling areas	BaPeq (ng m^{-3})			Cancer risk			Cancer risk per million		
	max	mean	min	max	mean	min	max	mean	min
SY	30.0	18.0	11.6	2.12×10^{-5}	1.83×10^{-5}	1.67×10^{-5}	21	18	17
GJ	32.2	19.5	11.0	2.17×10^{-5}	1.86×10^{-5}	1.66×10^{-5}	22	19	17
HY	98.0	40.4	22.1	3.78×10^{-5}	2.37×10^{-5}	1.93×10^{-5}	38	24	19
General		8.53			1.60×10^{-5}			16	

Monte Carlo simulation results for park workers (100,000 trials, all data together)

	Min	10%Percentile	Mean	Median	90%Percentile	Max
Cancer risk	0.27×10^{-5}	0.91×10^{-5}	1.94×10^{-5}	1.89×10^{-5}	2.99×10^{-5}	7.11×10^{-5}
Cancer risk per million	3	9	19	19	30	71

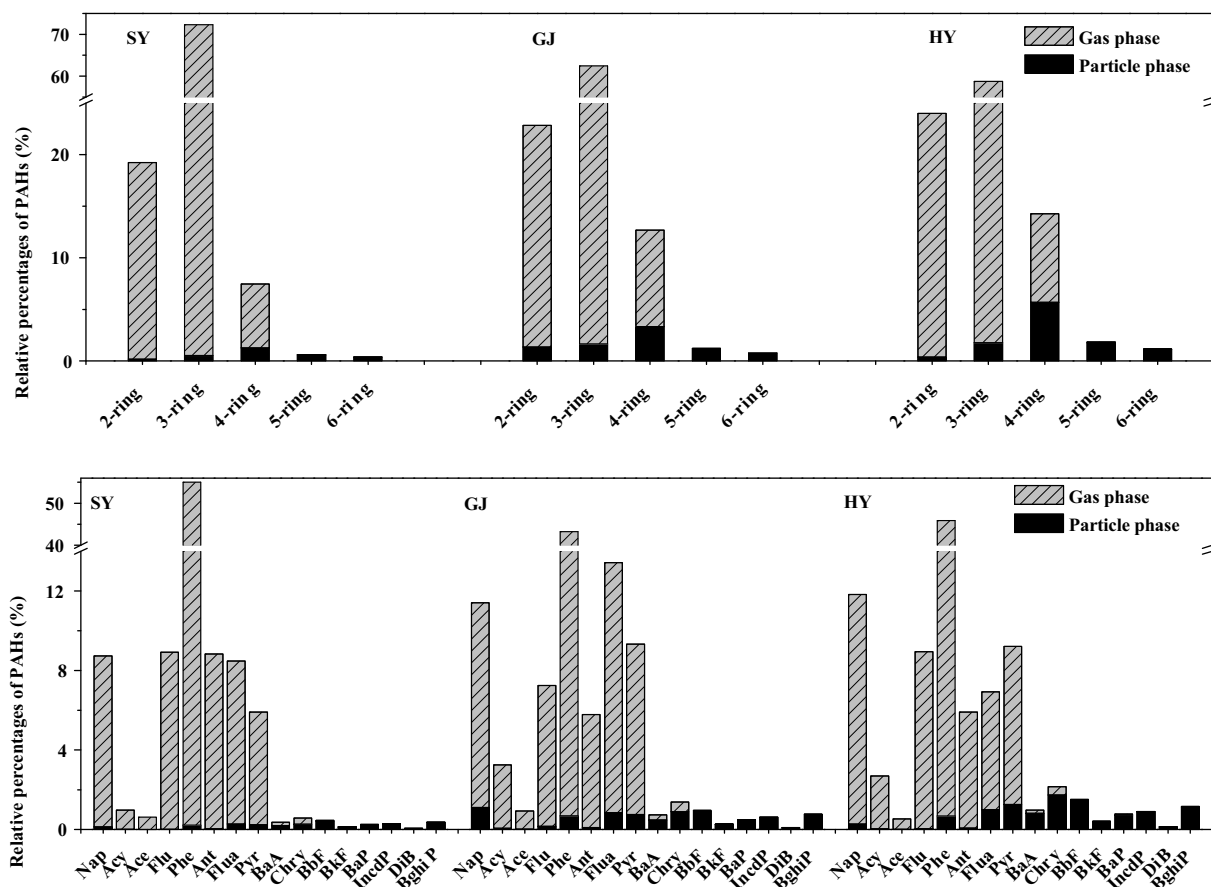


Fig. 1. Relative percentages of PAHs isomers and homologues in ambient air around the three studied parking areas (SY, GJ and HY).

keep its ratios staying close to those of vehicle exhaust (Table 1, Fig. S3).

PCA in conjunction with multiple linear regression (MLR) has been performed to identify and apportion PAH sources in air around many cities [35–37]. In our study, a total of three, two and two factors responsible for 96.3%, 91.9% and 91.3% of total variances were obtained for Park HY, GJ and SY, respectively (Table 3). The first factors of HY, GJ and SY respectively account for 58.9%, 49.7% and 57.9% of their total variances, and are all heavily weighted in 4, 5, and 6-ring PAHs, including BaA, Chry, BbF, BkF, BaP, IncdP, BghiP and DiB. Among them, BbF, BkF, BaP, IncdP and BghiP are typically reported as tracers of auto exhaust [4,23,35,36]. In considering our sampling areas, these factors are assigned to vehicle emission. The second factor of HY, responsible for 25.0% of its total variance, is highly weighted with NaP, Ace and moderately weighted with Phe and Flua. NaP was reported as a characteristic marker of volatilization from creosote/coal tar or oil combustion [5,36]. The contribution of this factor did not relate to our sampling temperatures in HY. In addition, Flua and Phe show reasonably high levels in combustion emission [5]. Therefore, the volatilization source was excluded and this factor is regarded as oil combustion. The third factor of HY and the second factors of SY and GJ are all predominately composed of Flu and Ace. Flu was reported as dominant PAH in coke oven emission [34], and also was used as a tracer of coal combustion in PCA [37]. A study of coal combustion under different conditions by Masclat et al. [38] showed that Flu was the major PAH product. Therefore, these factors should be related to urban coal combustion. The concentration contribution results of different factors are presented in Table 3 and Fig. S4 in our supporting information. Contribution

by vehicular source dominates all parking areas (>53.0%). Compared with SY and HY, vehicular source contribution in GJ is lower. This might be related to the main fuel used in GJ, LPG, which is reported cleaner than gasoline and diesel oil. Coal combustion contributions to PAHs of HY (7–23%) are comparatively lower than those of SY (26–54%) and GJ (34–60%). This is in accordance with the above discussion of the diagnostic ratios: ventilation systems in Parks SY and GJ help their air exchange with outside. Moreover, the PCA-MLR predicted values show good linear accordance with our measured data ($R^2 = 0.7575$, Fig. S5, Supporting information).

3.4. Gas-particle distribution of PAHs

In our study, 94–99% of light molecular PAH isomers (≤ 3 ring) were partitioned into gas phase and almost all heavier PAHs (≥ 5 ring, 95–100%) were associated with particulate matter. 4-ring PAHs, however, were abundant both in gaseous (17–40%) and particulate (60–83%) phases. Due to the dominance of light PAH homologues in our air samples, 86–98% of total PAHs were partitioned in gas phase while only 1.8–14% were particle-bound. However, particulate PAHs contributed 57–87% of total BaP_{eq} concentrations due to their high toxicity equivalency factors.

Gas-particle partitioning coefficient K_p ($\text{m}^3 \mu\text{g}^{-1}$) of semivolatile organic compounds (SOCs) can be calculated with their particulate concentration (C_{GFF}) being divided by TSP ($\mu\text{g m}^{-3}$) and their gaseous concentration (C_{PUF}). Their $\log K_p$ s correlate with the logarithms of their subcooled liquid–vapor pressures (p_L° s) both in adsorptive and absorptive partitions (Eq.

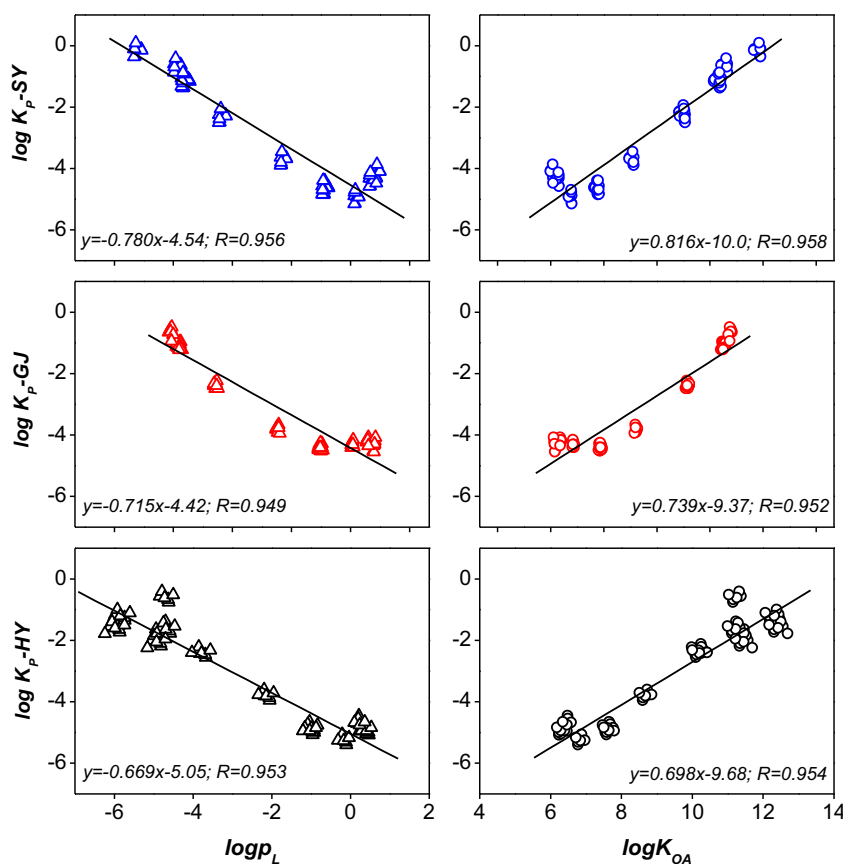


Fig. 2. Relationships of $\log K_p$ – $\log p_L$ and $\log K_p$ – $\log K_{OA}$, p_L and K_{OA} were calculated based on our sampling temperatures and the equations established by Odabasi et al. [40].

(3)), with m_r and b_r being constants [39]. In our study, p_L 's of PAH isomers were calculated based on our sampling temperatures and the equation established by Odabasi et al. [40], then the dependence of $\log K_p$ on $\log p_L$ was investigated. As shown in

Fig. 2, the dependence is well demonstrated in all three parks ($p < 0.0001$, $R^2 > 0.900$). The linear-fitted m_r s for $\log K_p$ – $\log p_L$ varied from -0.669 to -0.780 and b_r s changed from -4.42 to -5.05 . These values are in accordance with many previous field

Table 3
Rotated component matrix of principle factors of total atmospheric PAHs (gas- combined with particle-phase) in the three studied parks (SY, GJ and HY) and their concentration contribution percentages.

Component	HY			GJ		SY	
	F1	F2	F3	F1	F2	F1	F2
Nap	0.213	0.927	0.100	-0.087	0.958	-0.724	-0.193
Acy	0.353	0.872	0.196	0.567	0.725	0.708	0.607
Ace	-0.229	0.306	0.879	0.547	0.588	0.278	0.860
Flu	0.342	0.099	0.912	0.334	0.850	0.233	0.955
Phe	0.442	0.707	0.401	0.125	0.960	0.607	0.780
Ant	0.815	0.472	0.242	0.193	0.974	0.666	0.725
Flua	0.675	0.707	0.175	0.015	0.957	0.749	0.626
Pyr	0.788	0.560	0.194	0.185	0.918	0.738	0.638
BaA	0.906	0.375	0.136	0.781	0.542	0.835	0.515
Chry	0.876	0.469	0.085	0.835	0.481	0.873	0.430
BbF	0.958	0.271	0.042	0.983	0.144	0.919	0.374
BkF	0.947	0.306	0.054	0.979	0.145	0.921	0.376
BaP	0.950	0.291	0.098	0.975	0.184	0.894	0.434
IncdP	0.977	0.192	0.029	0.993	0.058	0.868	0.323
BghiP	0.975	0.192	0.025	0.987	0.064	0.885	0.314
DiB	0.967	0.229	0.045	0.994	0.032	0.837	0.471
Estimated source	Vehicle emission	Oil combustion	Coal combustion	Vehicle emission	Coal combustion	Vehicle emission	Coal combustion
Variance (%)	58.9	25.0	12.4	49.7	42.2	57.9	33.3
Total	96.3			91.9		91.3	
Concentration contribution (% average)	60.4	26.4	13.2	53.5	46.5	63.0	37.0

studies, in which m_r s and b_r s were -0.61 to -1.04 and -4.26 to -5.95 , respectively [41].

$$\log K_p = m_r \cdot \log p_L^\circ + b_r \quad (3)$$

According to Pankow [39], theoretically, m_r should be near or equal to -1 . However, slopes in field studies always deviated from -1 , which were attributed either to deviation from true equilibrium or to experimental problems [39,42]. Due to high temperature in combustion chamber, PAHs from vehicles were reportedly primarily emitted as gas phase, and then as the exhaust mixed with ambient air and cooled down; PAHs were incorporated onto particles via condensation and sorption processes [43]. Kamens et al. [44] reported that times to this equilibrium are very short for ultra-fine aerosols. Particulate matters emitted from automobile are fine respirable particles with a peak diameter of $0.1\text{--}0.2\ \mu\text{m}$ [11]. After added to combustion particles from a diesel car, volatilized deuterated pyrene equilibrated rapidly between gas and particle phase in a Teflon film chamber with warm temperature ($22\text{--}25\ ^\circ\text{C}$) [43,44]. Spezzano et al. [43] reported that exhaust collected from all mopeds attained gas-particle equilibrium of PAHs, even though the equilibrating time with diluting air was 8 s. Therefore, we believe that all our measurements in this study were under or close to equilibrium conditions. Goss and Schwarzenbach [42] found that such slope deviations do not necessarily indicate nonequilibrium effects, and if true equilibrium partitioning data are available, the slope is a characteristic parameter for specific sorption process. A slope steeper than -1 suggests adsorption governance, while a slope shallower than -0.6 indicates absorption dominance [42]. Our data are lightly steeper than -0.6 and might suggest that both adsorption and absorption processes were involved in, but the latter dominated in partitioning of PAHs in these three parks.

As for absorptive partitioning of SOCs into organic matter, their $\log K_p$ s show linear correlation with the logarithms of their octanol-air partition coefficients (K_{OAS}) [41], which is depicted in Eq. (4) with m and b being constants. After reviewing many field studies, Finizio et al. [41] suggested that K_{OA} may be a valuable direct descriptor of SOC volatility due to the experimental inaccessibility of their p_L° s. In our study, K_{OAS} of PAH isomers were calculated based on our sampling temperatures and the equation established by Odabasi et al. [40]. As shown in Fig. 3, $\log K_{OAS}$ of PAHs also showed significantly linear correlation with their $\log K_p$ s. Our linear-fitted m s ($0.698\text{--}0.816$) and b s (-9.37 to -10.0) are very close to the empirical values for PAHs raised by Finizio et al. [41], i.e. 0.79 and -10.01 , respectively. This result confirms that absorption dominated the gas-particle distribution of PAHs in these three parks.

$$\log K_p = m \cdot \log K_{OA} + b \quad (4)$$

Spezzano et al. [43] found that the gas-particle partitioning of PAHs in freshly emitted vehicle exhaust was predominant absorption process into organic matter, with m_r and b_r for $\log K_p\text{--}\log p_L^\circ$ being -0.19 and -4.10 and m and b for $\log K_p\text{--}\log K_{OA}$ being 1.10 and -12.75 , respectively. Similar results were also found for PAHs freshly emitted from wood combustion [45] and indoor crop residue burning [46]. Some reports showed that adsorption on diesel soot (mainly elemental carbon) also plays an important role in partitioning of PAHs in urban atmosphere influenced by vehicular emission [47,48]. As abovementioned, our data suggest that both absorption into organic matter and adsorption onto black carbon governed the partitioning of PAHs in these three parks, and the former was more important. This confirms the existence of freshly emitted exhaust in these three parks, in accordance with our source apportionment results. It also indicates that PAHs in our study were promptly redistributed between gas and particle once they were emitted from vehicles and mixed with ambient air. But further tailpipe samples are needed to prove this.

4. Conclusion

Among the three parking areas, GJ showed the lowest total PAH levels, which are significantly lower than those of SY ($p=0.006$, t -test). Source analysis results also indicate that vehicle exhaust contribution to PAHs in GJ was lower than those in HY and SY. This suggests that the use of LPG might help to reduce PAH emission to a certain degree. However, this does not mean it can reduce the emission's negative health effect, because BaPeq levels of GJ were even higher than those of SY.

Monte Carlo simulation results suggest that the estimated lifetime cancer risks of park workers fall in the acceptable range of the US EPA, and that off-duty concentration was the dominant variance. However, all BaPeq concentrations in these three parks exceeded the air standards of China and WHO. Besides, other important PAHs in vehicle emission, e.g. dibenzo(a,e)pyrene, cyclopenta(c,d)pyrene, coronene and perylene with the toxic equivalent factor of 1, 0.1, 0.001 and 0.01, respectively [18], were not included in our study. This might underestimate the lifetime cancer risk of park workers. Altogether, attention should be given to such parks during their design and construction. Since particle phase contributed 57–87% of total BaPeq concentrations, use of personal protective equipment will greatly decrease the inhalation cancer risk.

Acknowledgements

We would like to thank Dr. Thomas M. Mainor for his generous help with the English grammar and phraseology. The research was financially supported by National Natural Science Foundations of China (Nos. 41273002, 41130752, 40903043), the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (No. SKLOG2011A01). This is a contribution No. IS-1870 from GIGCAS.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2014.04.016>.

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