

Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong

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Abstract

PM_{2.5} and PM₁₀ samples were collected at two sampling sites in Hong Kong in wintertime from November 2000 to March 2001 and in summertime from June to August 2001. The concentrations of 16 selected polycyclic aromatic hydrocarbons (PAHs) in aerosols were quantified. Spatial and seasonal variations of PAHs were characterized. The dominated PAHs in PM_{2.5} and PM₁₀ included benzo[b]fluoranthene, pyrene, fluoranthene, indeno[1,2,3-cd]pyrene and chrysene, accounting for 50–82% of total PAHs. The sum of 16 PAHs in PM_{2.5} at roadside ranged from 3 to 330 ng/m³, and in PM₁₀ between 5 and 297 ng/m³, whereas at a residential/industrial/commercial site, the total PAHs in PM_{2.5} was from 0.5 to 122 ng/m³, and 2–269 ng/m³ in PM₁₀. Results indicated that most of the PAHs were in the PM_{2.5} fraction. Spatial variations were predominantly due to the difference of source strength. For both PM_{2.5} and PM₁₀, the total PAHs at PU site was higher than that at KT site. The average concentrations of individual PAHs in aerosols at PU site were also higher than that at KT site. Higher winter PAHs concentrations and lower summer concentrations were observed at the two sites. Higher winter PAHs concentrations were mainly caused by local emission sources superimposed by highly polluted air masses from Mainland China. The lower summer PAHs concentrations were likely due to easier dispersion of air pollutants, washout effects and to a lesser extent, photo-degradation and higher percentage in the air in vapor phase. Potential sources of PAHs in aerosols were identified using the diagnostic ratios between PAHs and PCA analysis. At PU site, vehicular emissions were the main contributors of particle-associated PAHs, and stationary combustion sources may also contribute to the particulate PAHs. On the contrary, at the KT site, PAHs in aerosols were predominantly from gasoline and diesel engines.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous constituents of particulate matter and well-known to be carcinogenic and mutagenic (Møller et al., 1982; IARC, 1984). They are products of incomplete combustion and pyrolysis of fossil fuels and other organic

materials from natural and anthropogenic sources. In urban and industrial atmospheres, PAHs are almost entirely anthropogenic (Jones et al., 1989). PAHs exist in the atmosphere in both vapor- and particulate-phase (Bidleman et al., 1986). Low molecular weight PAHs tend to be more concentrated in the vapor-phase while the ones with higher molecular weight are often associated with particulates. Thus, it is important to understand abundance, speciation, distributions and potential sources of PAHs in aerosols so that air pollution caused by particulate matter can be efficiently controlled.

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In Hong Kong, aerosols are one of the most serious air pollution problems according to the Hong Kong government statistics in 1997. Baek et al. (1991a) and Nielsen et al. (1999) stated that vehicle exhaust is the major PAHs contributor in urban area. In Hong Kong, there were 500,000 vehicles registered in 1997 and 526,000 in 2002 (Hong Kong Census and Statistical Department, 2003). Previous studies have demonstrated that PAHs in total suspended particulates (TSP) mainly came from vehicle exhaust in Hong Kong urban areas (Zheng et al., 1997; Panther et al., 1999; Lee et al., 2001; Ho et al., 2002; Ho and Lee, 2002). In addition, the contribution of emission from cooking activities is likely significant due to the characteristic Chinese stir-frying cooking process (Lee et al., 2002). Besides local sources, meteorological conditions may affect the abundance and speciation of PAHs in aerosols significantly. Hong Kong is at the south tip of the Pearl River Delta (PRD) in southern China. The PRD region is a home of several major cities such as Guangzhou, Shenzhen, Macau and Zhuhai. This region has experienced its development with rapid urbanization and industrialization in the past two decades. Major anthropogenic sources of particulate matters in the PRD region are located to the east, north, and southwest, while the South China Sea is to the south. Motor vehicles, industry and power plants in the PRD region are suspected to be the main contributors of regional air pollution (HKEPD, 2002). Since the weather in this sub-tropical coast region is under the effect of the Asian monsoonal circulation, Hong Kong may act as a receptor of the huge anthropogenic emissions from this region by long- and medium-range transport especially in winter.

Although some studies have been done on PAHs in aerosols in Hong Kong, these studies were mainly focused on PAHs in TSP (Zheng et al., 1997; Panther et al., 1999; Lee et al., 2001; Ho et al., 2002; Ho and Lee, 2002). Only one investigation was made by Zheng et al. (2000) on the characterization of PAHs in $PM_{2.5}$ aerosols between 1996 and 1997 with a limited sample size. Hong Kong Environmental Protection Department (HKEPD) reported that 70–80% of respirable suspended particulates are less than $2\mu\text{m}$ in diameter (Air Services Group, HKEPD, 1990), and many studies indicate that fine particles have greater impact on human health than TSP (Schwartz, 1994; Pope et al., 1995). Moreover, the PAHs in aerosols may provide information on source profiles (Simoneit et al., 1991; Khalili et al., 1995; Harrison et al., 1996). However, the characteristics of $PM_{2.5}$ and PM_{10} in Hong Kong have not been fully understood, particularly in roadside environment. The relation of $PM_{2.5}$ with larger particles remains unknown. The PAHs compositions in $PM_{2.5}$ and PM_{10} are not available in Hong Kong. Therefore, the objectives of this study are to investigate PAHs abundance and speciation in $PM_{2.5}$ and PM_{10} ; to

understand seasonal and spatial variability of PAHs in aerosols; and to characterize potential sources of PAHs in aerosols.

2. Experimental

2.1. Sampling sites

Two sampling sites were selected based on their different land-use categories, populations and traffic densities. Two sampling sites including Hung Hom (PU) and Kwun Tong (KT) were selected for particulate matter monitoring. The field descriptions were given in our previous publication (Ho et al., 2003). In brief, the sampling sites are described as follows and locations of the sites are shown in Fig. 1.

Hung Hom (PU): It is situated at about 6 m above ground level, and about 8 m away from the main traffic road. The station is adjacent to Hong Chong Road, which leads to the Cross Harbor Tunnel. The traffic volume of the road is extremely high with more than 170,000 vehicles per day. The site faces the Victoria Harbor with strong wind blowing from the sea which provides good air dispersion. Moreover, the university's restaurants are about 100 m away. Thus, the particulate levels at the site are mainly influenced by vehicle emission, stationary combustion sources and wind direction.

Kwun Tong (KT): Most of the industries in Hong Kong, mainly metal and printing industries, are located in this area. They are close to the residential buildings and most of the vehicles are light and heavy duty ones. KT is one of the HKEPD air quality monitoring stations, which was chosen for data comparison representing as mixed residential/commercial/industrial area. The samples were collected on the rooftop which was 25 m above the ground level.

2.2. Meteorological conditions

The climate of Hong Kong is humid sub-tropical. The weather is under the influence of the Asian monsoon system which is characterized by a marked change of wind direction, temperature, humidity and rainfall between summer and winter. In winter, when north-easterly winds are prevailing, emissions from the Asian continent are brought to Hong Kong. The stability of the weather conditions and the ability to disperse are factors that profoundly influence the air quality of urban areas of Hong Kong. Besides the winds, the mass concentration is also affected by rainfall and relative humidity. Meteorological data were obtained from the Hong Kong Observatory. It was found that the relative humidity in Hong Kong is rather high (80% on daily

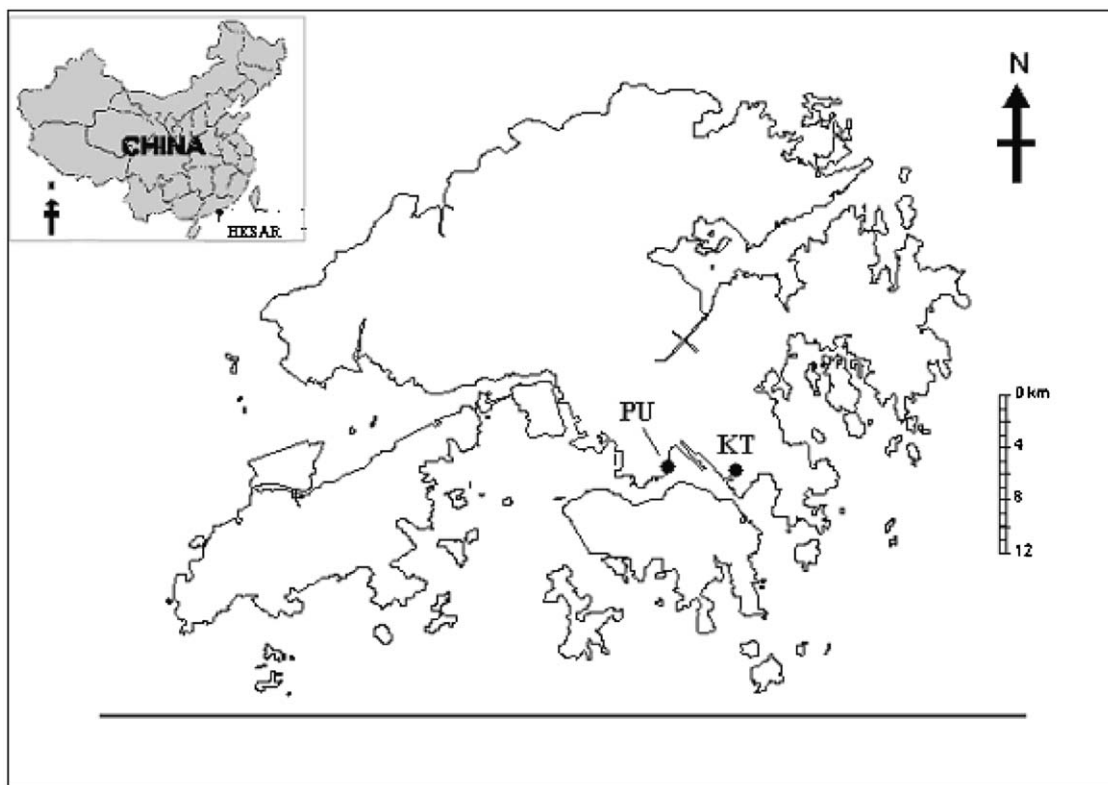


Fig. 1. Location of monitoring stations.

average), while the variations occur predominantly between 70% and 90%.

2.3. Sampling

PM_{2.5} and PM₁₀ samples were collected by high-volume (hi-vol.) samplers manufactured by Graseby–Andersen during two sampling campaigns. The periods were from 23 November 2000 to 1 March 2001 in winter and from 27 June 2001 to 20 August 2001 in summer, respectively. All filters were maintained in a condition of 50% RH and 25°C for over 48 h and weighted before sampling. The hi-vol. samplers were operated at flow rates of 1.13–1.41 m³/min. Both PM₁₀ and PM_{2.5} were collected on 20.3 cm × 25.4 cm Whatman quartz microfibre filters. Partisol 2000 low-volume sampler with 10 or 2.5 μm inlet was used to collect PM₁₀ and PM_{2.5} samples, respectively, for data comparison. The flow rate of Partisol 2000 is, 16.7 l/min and samples were collected by a 47 mm quartz filter. All quartz filters were pre-heated at 900°C for 24 h before being used. PM₁₀ and PM_{2.5} samples were collected for 24 h simultaneously at two sites. Background contamination was monitored by using operational blanks (unexposed filters) which were processed simultaneously with field samples.

It is worth mentioning the selection of the PAHs to be analyzed and the adopted sampling conditions while the hi-vol. samplers were used in the sampling campaigns. Hi-vol. sampling on fiber filters, the most widely used particle sampling method, is prone to sampling losses due to “blow-off” effect on volatile species and filter-catalyzed oxidation (Van Vaeck et al., 1984; Ligocki and Pankow, 1989). The evaporation stage of the analytical procedure may also cause loss of some PAHs in particulate phase (Caricchia et al., 1995). To minimize the loss, the sampling conditions should be constant such as 24-h sampling duration, same sampling stations, narrow range of the ambient temperature, etc.

2.4. PAHs analysis

Analysis of PAHs in aerosols was conducted in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Detailed description of analytical procedure is in publications by Bi et al. (2003). Briefly, the PAHs analysis is described as follows.

Sixteen PAHs specified on USEPA Method 610 in a mixture and surrogate, consisting of naphthalene-D₈, acenaphthene-D₁₀, phenanthrene-D₁₀, chrysene-D₁₂ and perylene-D₁₂ standards, were obtained from Ultra Scientific Inc. Coronene and internal standard

(hexamethylbenzene) were acquired initially as a solid of 99% purity (Aldrich Chemical, Gillingham, Dorset, USA). All reagents utilized were redistilled in all-glass distilling appliance.

Surrogate PAHs were added prior to extraction. Filters were extracted ultrasonically 3 times with 150 ml dichloromethane (DCM). Each extraction lasted 30 min. The organic extract was filtered and concentrated on a Büchi Rotary evaporator (bath temperature $\leq 30^{\circ}\text{C}$). Interfering compounds were removed by liquid–solid chromatography using 2:1 silica-alumina column. Two fractions were eluted. Fraction I (50 ml of hexane) contained the aliphatic hydrocarbons, while fraction II (50 ml of DCM-hexane (1:1)) contained the PAHs. This was followed by rotary evaporation. Then the samples were reduced to dryness under a gentle stream of nitrogen and then redissolved with n-hexane to approximately 0.4 ml. Internal standard hexamethylbenzene was added at this point.

All samples were analyzed using gas chromatography (HP 6890) with mass selective detection (HP 5972) equipped with a 50 m HP-5 capillary column operated in the electron impact mode (70 eV). The chromatographic conditions were as follows: injector temperature, 280°C ; ion source temperature, 180°C ; temperature program: 65°C (5 min), 65 – 290°C at a rate of $3^{\circ}\text{C}/\text{min}$, 290°C (30 min). The carrier gas was helium at a constant flow rate of 1.5 ml/min. Sample of 1 μl was injected with splitless model. Mass range m/z 50 and 500 was used for quantitative determinations. Data acquisition and processing were controlled by a HP Chemstation data system.

Chromatographic peaks of samples were identified by GC-MS analysis and coinjection with authentic standard compounds. If no authentic standards were available, compounds were identified by the retention indices and the library mass spectrum. Molecular ion was used for quantification of PAHs.

2.5. Quality control

Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were analyzed. PAHs were not detectable. These contaminants did not interfere with the recognition or quantification of the compounds of interest. In addition, surrogate standards were added to all the samples (including QA samples) to monitor procedural performance and matrix effects. The mean recoveries (%) for surrogates in field samples were 30–128%. The average recoveries of 16 PAHs in six matrix spikes varied from 39% (naphthalene) to 101% (benzo[ghi]perylene). PAH concentrations were corrected for recovery efficiency during extraction.

2.6. Performance test

Performance tests on hi-vol. samplers had been conducted before the field study by gravimetric analysis. Twenty samples of $\text{PM}_{2.5}$ and 20 samples of PM_{10} were collected by using hi-vol. sampler and Partisol 2000 simultaneously for instrumental comparison in order to determine the deviations among these samplers. The deviations of mass concentration of hi-vol. samplers and Partisol samplers were within 13% for PM_{10} and within 15% for $\text{PM}_{2.5}$.

3. Results and discussion

3.1. Size distributions of PAHs in aerosols

Mean and median values of individual PAHs concentrations in $\text{PM}_{2.5}$ and PM_{10} in summer and winter at the two sites are presented in Tables 1 and 2, respectively. It was found that the sum of 16 PAHs in PM_{10} was higher than that in $\text{PM}_{2.5}$ at the two sites in the same season. For instance, at PU site, in summer, the total PAH concentration in $\text{PM}_{2.5}$ was $4.87 \text{ ng}/\text{m}^3$ while in PM_{10} the summation of PAHs was $5.82 \text{ ng}/\text{m}^3$ (Table 1). At KT site in winter, the sum of PAHs in $\text{PM}_{2.5}$ was $27.93 \text{ ng}/\text{m}^3$ and the total PAHs in PM_{10} was $38.63 \text{ ng}/\text{m}^3$ (Table 2). For individual PAHs, most of them at these two sites had similar patterns to $\text{PM}_{2.5}$ and PM_{10} except for BAP and BKF. The dominant PAHs in $\text{PM}_{2.5}$ and PM_{10} were very similar at both sites. At PU site, BBF, PYR, FLT and INP were predominant in $\text{PM}_{2.5}$ and PM_{10} . On the other hand, the most significant PAHs were BBF, PYR, FLT and CHR at KT site. The ratio of individual PAHs in $\text{PM}_{2.5}$ to that in PM_{10} at PU site was between 0.55 and 1.32, and the ratio of total PAHs in $\text{PM}_{2.5}$ to total PAHs in PM_{10} ranged from 0.76 to 0.84. At KT site, the ratio of individual PAHs in $\text{PM}_{2.5}$ to that in PM_{10} ranged from 0.48 to 1.13, and $\sum \text{PAHs}$ in $\text{PM}_{2.5}/\sum \text{PAHs}$ in PM_{10} was between 0.72 and 0.79. The results indicate that most of the PAHs are in the $\text{PM}_{2.5}$ fraction. This is consistent with other studies (Baek et al., 1991a, b; Venkataraman et al., 1994; Schnelle-Kreis et al., 2001). Schnelle-Kreis et al. (2001) found that in most cases the amount of PAHs associated with coarse mode particles is $< 10\%$ of the total. Baek et al. (1991a, b) reported that 95% of particulate PAHs sampled in London were $< 3.3 \mu\text{m}$ in diameter. Venkataraman et al. (1994) measured size distribution of PAHs in a tunnel and found that over 85% of the mass was in particles $< 0.12 \mu\text{m}$ aerodynamic diameter.

The $\text{PM}_{2.5}/\text{PM}_{10}$ ratio for BAP and BKF was > 1 at the two sites. The reason for this could be complicated. One explanation is the strong affinity of BAP and BKF on $\text{PM}_{2.5}$ and the possibility that the pressure drop on the filters may eventually cause blow-on of BAP and

Table 1
Mean particulate PAH concentrations at PU sampling site (ng/m³) (*n* = sample size)

	PM _{2.5}				PM ₁₀			
	Mean (range)		Median		Mean (range)		Median	
	Summer (<i>n</i> = 16)	Winter (<i>n</i> = 14)	Summer	Winter	Summer (<i>n</i> = 4)	Winter (<i>n</i> = 7)	Summer	Winter
NAP	ND (ND–ND)	ND (ND–ND)	ND	ND	ND (ND–ND)	ND (ND–ND)	ND	ND
ACEY	0.01 (ND–0.02)	ND (ND–ND)	0.01	ND	0.01 (ND–0.01)	ND (ND–ND)	0.01	ND
ACE	0.01 (ND–0.01)	ND (ND–ND)	0.01	ND	ND (ND–ND)	ND (ND–ND)	ND	ND
FLU	0.03 (0.01–0.05)	0.28 (0.01–1.09)	0.03	0.11	0.03 (0.03–0.03)	0.31 (0.01–0.95)	0.03	0.30
PHE	0.36 (0.13–0.85)	0.55 (0.08–2.22)	0.32	0.42	0.39 (0.30–0.46)	0.65 (0.09–2.35)	0.40	0.33
ANT	0.29 (0.06–0.92)	0.01 (0.01–0.09)	0.29	0.01	0.22 (0.08–0.41)	0.01 (0.01–0.01)	0.19	0.01
PYR	0.30 (0.14–0.74)	6.43 (0.77–31.52)	0.26	3.94	0.33 (0.28–0.43)	7.86 (1.04–30.84)	0.31	3.17
FLT	0.53 (0.14–0.82)	5.94 (0.81–30.79)	0.48	3.58	0.82 (0.60–1.06)	7.02 (1.08–28.83)	0.82	3.20
BAA	0.36 (0.14–0.66)	1.10 (0.07–8.84)	0.35	0.42	0.33 (0.27–0.39)	1.48 (0.08–7.92)	0.32	0.52
CHR	0.55 (0.13–0.87)	3.47 (0.30–26.34)	0.53	1.66	0.62 (0.58–0.67)	4.50 (0.01–23.72)	0.61	1.42
BAP	0.67 (0.24–1.12)	3.24 (0.20–18.66)	0.65	1.85	1.22 (0.82–2.11)	2.65 (0.07–15.49)	0.97	0.65
BBF	0.53 (0.16–0.87)	12.12 (0.58–108.34)	0.53	2.85	0.63 (0.42–1.08)	16.85 (0.62–97.73)	0.51	4.44
BKF	0.53 (0.18–0.93)	0.36 (0.01–2.93)	0.53	0.14	0.43 (0.26–0.64)	0.39 (0.01–2.28)	0.40	0.11
BGP	0.10 (0.02–0.42)	2.88 (0.01–34.11)	0.05	0.27	0.14 (0.01–0.36)	4.47 (0.01–29.53)	0.10	0.43
INP	0.58 (0.13–1.79)	4.70 (0.01–56.47)	0.49	0.44	0.64 (0.10–1.42)	7.38 (0.01–48.94)	0.52	0.71
DBA	0.07 (ND–0.29)	4.71 (ND–8.98)	0.01	4.71	ND (ND–ND)	7.99 (ND–7.99)	ND	7.99
∑PAH	4.87 (3.21–6.93)	41.75 (3.10–330.30)	4.72	16.71	5.82 (4.95–8.15)	54.72 (3.81–296.56)	5.09	15.90

ND—non-detectable; NAP—naphthalene; ACEY—acenaphthylene; ACE—acenaphthene; FLU—fluorene; PHE—phenanthrene; ANT—anthracene; PYR—pyrene; FL—Fluoranthene; BAA—benz[a]anthracene; CHR—chrysene; BAP—benzo[a]pyrene; BBF—benzo[b]fluoranthene; BKF—benzo[k]fluoranthene; BGP—benzo[ghi]perylene; INP—indeno[1,2,3-cd]pyrene; DBA—dibenzo[a,h]anthracene.

Table 2
Mean particulate PAH concentrations at KT sampling site (ng/m³) (*n* = sample size)

	PM _{2.5}				PM ₁₀			
	Mean (range)		Median		Mean (range)		Median	
	Summer (<i>n</i> = 15)	Winter (<i>n</i> = 12)	Summer	Winter	Summer (<i>n</i> = 16)	Winter (<i>n</i> = 15)	Summer	Winter
NAP	ND (ND–ND)	ND (ND–ND)	ND	ND	ND (ND–ND)	ND (ND–ND)	ND	ND
ACEY	0.01 (ND–0.02)	ND (ND–ND)	ND	ND	0.01 (ND–0.02)	ND (ND–ND)	0.01	ND
ACE	0.02 (ND–0.04)	ND (ND–ND)	ND	ND	0.01 (ND–0.04)	ND (ND–ND)	0.01	ND
FLU	0.02 (0.01–0.08)	0.25 (0.01–0.71)	0.02	0.24	0.02 (ND–0.04)	0.33 (0.01–1.00)	0.02	0.26
PHE	0.22 (0.03–0.70)	0.55 (0.13–1.43)	0.22	0.52	0.26 (0.05–0.75)	0.80 (0.12–2.08)	0.19	0.62
ANT	0.17 (0.04–0.27)	0.01 (0.01–0.01)	0.13	0.01	0.15 (0.05–0.28)	0.01 (0.01–0.04)	0.18	0.01
PYR	0.19 (0.03–0.54)	6.35 (1.09–17.72)	0.21	5.42	0.24 (0.11–0.59)	7.78 (0.98–32.10)	0.19	5.32
FLT	0.35 (0.05–0.92)	5.47 (1.09–13.91)	0.39	4.35	0.47 (0.19–1.10)	6.97 (0.97–30.30)	0.31	4.51
BAA	0.16 (0.02–0.54)	0.65 (0.09–3.07)	0.20	0.38	0.21 (0.07–0.53)	1.08 (0.08–7.02)	0.14	0.71
CHR	0.34 (0.07–0.93)	2.63 (0.32–12.06)	0.36	1.85	0.41 (0.18–0.87)	3.54 (0.01–24.67)	0.33	2.06
BAP	0.73 (0.11–1.64)	2.06 (0.38–8.23)	0.68	1.38	0.94 (0.26–2.30)	1.91 (0.15–16.11)	0.67	0.71
BBF	0.41 (0.06–1.20)	6.64 (0.64–39.08)	0.36	3.11	0.50 (0.14–1.17)	10.31 (1.08–86.31)	0.35	5.24
BKF	0.27 (0.02–0.86)	0.19 (0.01–1.26)	0.60	0.08	0.56 (0.23–0.92)	0.27 (0.01–2.20)	0.21	0.15
BGP	0.15 (ND–0.41)	1.20 (0.01–10.91)	0.10	0.25	0.17 (0.01–0.46)	2.07 (0.01–24.50)	0.11	0.43
INP	0.64 (0.01–1.83)	1.66 (0.01–14.75)	0.46	0.36	0.71 (0.09–2.93)	3.14 (0.01–37.26)	0.49	0.70
DBA	0.07 (ND–0.23)	3.16 (ND–3.16)	0.08	3.16	0.10 (ND–0.25)	6.35 (ND–6.35)	0.03	6.35
∑PAH	3.71 (0.48–9.87)	27.93 (4.66–121.90)	3.74	17.61	4.67 (1.92–10.20)	38.63 (4.61–268.64)	3.18	23.56

ND—non-detectable.

BKF on fine particles due to freeing of sorption sites occupied by water vapor at normal pressure (McDow and Huntzicker, 1990). On the other hand, the reduced pressure on the filters could result in desorption of coarse particle-adsorbed BAP and BKF (Zhang and McMurry, 1991).

ANOVA analysis was conducted on the ratios of individual PAHs in $PM_{2.5}$ to that in PM_{10} in summer and winter at PU and KT sites, respectively. The results showed that there was no statistical difference in ratios for individual PAHs in either season at the two sites. This reflects that the ratios of individual PAHs in $PM_{2.5}$ to that in PM_{10} in Hong Kong have the common patterns regardless of speciation, season and sampling locations.

3.2. Spatial variations of PAHs in aerosols

Significantly spatial variations were found at the two sampling sites (Tables 1 and 2). The mean concentrations of individual PAHs in the aerosols at PU site were much higher than that at KT site, especially in winter. The total PAH concentrations in $PM_{2.5}$ and in PM_{10} at PU site were about 1.25 and 1.45 times that at KT site, respectively. The major cause was the characteristics of sampling sites. The PU site is adjacent to a road with very high traffic volume. It is well known that PAHs are major components of vehicle exhausts especially gasoline- and diesel-powered vehicles (Miguel et al., 1998). On the other hand, the KT site was a mixture of residential/industrial/commercial area. The major sources of PAHs were household cooking activities, industrial sources and vehicle emissions at this site. However, the source strength of PAHs at this site was much lower than that at PU site, because the traffic volume was much lower and the sampling site was far away from the ground level. It is known that all of the compounds, whether released by anthropogenic or biogenic processes, have their primary sources near the surface and are lost as they are transported from the surface to the boundary layer (Goldan et al., 2000).

The PAH concentrations measured in this study are compared with the published data (Venkataraman et al., 1994; Caricchia et al., 1999; Menichini et al., 1999; Fraser et al., 2002) (Table 3). Although the conditions of these studies are different, they provide an overall picture of particle-associated PAHs in different countries. The results showed that most PAHs concentrations in Hong Kong are generally higher than that in the USA and European countries suggesting varied source strength and different meteorological conditions. For instance, the sum of PAHs in $PM_{2.5}$ at roadside (33.96 ng/m^3 , PU site) was 1.4 times that in Los Angeles tunnel while at the KT site it was over 13 times that in Houston urban air. For the PAHs in PM_{10} , the total PAHs in Naples was similar to that at KT site, but both

cities had much higher total PAHs in PM_{10} than in Rome.

3.3. Seasonal variations of PAHs in aerosols

The seasonal distribution of particle-associated PAHs is controlled by a combination of emission factors, dispersion conditions and chemical mechanisms (Caricchia et al., 1999; Menichini et al., 1999). This balance will depend on the relative importance of degradation processes and emission sources.

In Hong Kong, winter includes the 4 months of November through February while summer is from May to August. Strong monsoon wind and dry weather characterize winter seasons, whereas hot and humid climate with occasional showers and thunderstorms represent summer seasons. The seasonal variations of PAHs in $PM_{2.5}$ and PM_{10} in Hong Kong are presented in Tables 1 and 2. Higher PAHs concentrations in winter and lower concentrations in summer were observed at the two sites. The ratio of winter to summer total PAHs was 8.6 at PU site and 7.5 at KT site, respectively. At PU site, the winter to summer ratio of individual PAHs ranged from 1 to 48, while at KT site, the ratio was between 1 and 27, indicating significant seasonal variations of individual PAHs. The ratios at PU and KT sites were in accordance with results reported by other studies in Europe and in the USA: PAHs in winter were generally higher by a factor of 1.5–10 than that in summer (Baek et al., 1991a; Harrison et al., 1996; Caricchia et al., 1999; Menichini et al., 1999). In Hong Kong, there is little seasonal variation in emissions from stationary sources as space heating is unnecessary. Thus, the higher PAHs in winter were probably due to the contribution of outside sources. It is known that in winter the prevailing wind in Hong Kong is northeasterly which brings in highly polluted air masses from the mainland to the sampling sites. On contrary, in summer, the Asian monsoon brings in clean oceanic air from the Tropics and unstable rainy weather. Thus, lower PAHs levels were likely attributed to the combination of easier atmospheric dispersion of pollutants, wash-out effects, and to a lesser extent, photodegradation and higher percentage in the air in vapor phase. Correlation analysis between PAHs levels and relevant meteorological parameters was not presented here.

3.4. Potential sources of PAHs

It is suggested that it be possible to use PAHs in distinguishing emissions (Venkataraman et al., 1994; Cotham and Bidleman, 1995; Harrison et al., 1996; Alves et al., 2001). The concentrations of some marker compounds and their ratios can give some indication about the impact of different sources of airborne

Table 3
Comparison of average PAH concentrations in PM_{2.5} and PM₁₀ (ng/m³)

Location	PM _{2.5}				PM ₁₀			
	Hong Kong (this study)		Houston (Fraser et al., 2002)	Los Angeles (Venkataraman et al., 1994) ^a	Naples (Caricchia et al., 1999)	Rome (Menichini et al., 1999)	Hong Kong (this study)	
	PU	KT	Industrial/suburban areas	Tunnel	Urban areas	Urban areas	PU	KT
NAP	ND	ND	N/A	N/A	N/A	N/A	ND	ND
ACEY	ND	ND	0.04	N/A	N/A	N/A	ND	ND
ACE	ND	ND	0.02	N/A	N/A	N/A	ND	ND
FLU	0.16	0.15	0.04	N/A	N/A	N/A	0.21	0.17
PHE	0.47	0.39	0.14	N/A	0.93	N/A	0.55	0.50
ANT	0.15	0.15	0.08	N/A	0.17	N/A	0.11	0.16
PYR	3.84	2.95	0.17	2.00	2.18	N/A	5.13	3.86
FLT	3.79	2.69	0.14	2.06	1.44	N/A	4.77	3.55
BAA	0.98	0.40	0.21	0.93	1.57	0.82	1.06	0.60
CHR	2.60	1.40	0.25	1.08	2.47	N/A	3.40	1.95
BAP	2.54	1.44	0.18	2.01	2.21	1.38	2.13	1.30
BBF	9.10	3.23	0.22	2.04	5.68 ^b	2.95 ^b	10.96	5.20
BKF	0.58	0.44	0.24	0.98	—	—	0.40	0.29
BGP	2.73	0.68	0.31	5.78	7.11	—	2.90	1.15
INP	4.63	1.18	0.28	2.93	3.73	1.51	4.93	1.91
DBA	2.39	1.62	0.18	4.21	0.32	0.22	7.99	3.22
∑PAH	33.96	16.72	2.50	24.02	27.81	6.88	44.54	23.86

N/A: not available. ND: non-detectable.

^aPM diameter <1.0 μm.

^bSum of BBF, BKF and BKP.

Table 4
Diagnostic ratios between PAHs in PM_{2.5}

Sampling site	INP/BGP+INP		BAP/BAP+CHR		PHE/PHE+ANT	
	Summer	Winter	Summer	Winter	Summer	Winter
PU	0.85±0.07	0.62±0.04	0.55±0.14	0.49±0.08	0.56±0.17	0.98±0.12
KT	0.81±0.09	0.58±0.04	0.69±0.10	0.44±0.09	0.64±0.17	0.98±0.02

compounds. Studies indicated that particulate organic samples collected in tunnels were enriched in benzo[ghi]perylene and coronene, which are characteristic of gasoline engines (Miguel et al., 1998). Masclet et al. (1986) found that diesel exhaust was enriched in FLT, CHR and PYR. Khalili et al. (1995) identified that ANT, PHE, FLT, and PYR were source fingerprints of wood combustion while ANT, PHE, FLT, PYR, BAA and CHR were markers of coal combustion.

Table 4 lists the diagnostic ratios between PAHs in PM_{2.5}, e.g. INP/BGP+INP, BAP/BAP+CHR and PHE/PHE+ANT, which are used to investigate their origin. The values were compared with those reported in the literature. The ratio INP/BGP+INP was found to be 0.18 for gasoline emissions and >0.3 for emissions from diesel engines (Kavouras et al., 1999). The ratio INP/BGP+INP ranges from 0.58 to 0.62 in winter and between 0.81 and 0.85 in summer in Table 4, indicating diesel emissions are main sources. The ratio BAP/BAP+CHR is also used to evaluate the contribution of vehicular emissions. Gogou et al. (1996) reported a value of 0.33 for an urban environment where the circulation of catalyst equipped automobiles was predominant. Furthermore, the ratio BAP/BAP+CHR was 0.49 for gasoline emissions and 0.73 for diesel engines, respectively (Khalili et al., 1995). In this study, the ratio was 0.55 in summer and 0.49 in winter at PU site, respectively. It implies that gasoline emissions may be the major source of PAHs at PU site. At the KT site, the ratio BAP/BAP+CHR was 0.69 in summer and 0.44 in winter, respectively, suggesting that diesel and gasoline emissions existed simultaneously. To further understand the contribution of potential PAHs sources at the two sites, the ratio PHE/PHE+ANT was used for source identification, representing the importance of petrogenic hydrocarbons. Sicre et al. (1987) stated that value higher than 0.70 was typically associated with crude oil, while Khalili et al. (1995) found that the ratio PHE/PHE+ANT was 0.65 for diesel emissions, 0.50 for gasoline and 0.76 for coal combustion, respectively. In this study, the ratio in summer was 0.56 and 0.64 at PU and KT sites, respectively. The results indicate that gasoline emissions were dominant at PU site and emissions from diesel engines may be the main source of PAHs at KT site. In winter season, the ratios PHE/PHE+ANT were over 0.70 at the two sampling sites,

suggesting that vehicular emissions were the dominated sources of PAHs and that other fossil fuels such as liquefied petroleum gas, natural gas and coal may also contribute to ambient PAHs. HKEPD reported that two dominant emission sources for respirable suspended particles in Hong Kong are vehicle emission (44%) and power generation (30%) (HKEPD, 2002). Furthermore, in Hong Kong, approximately 30% of the vehicles are powered by diesel, of which, 48% are diesel light vehicles and 27% for medium/heavy trucks and lorries (Hong Kong Transport Department, 2003). Overall, at PU and KT sites, emissions from gasoline and diesel engines were the main sources of PAHs in aerosols.

3.5. Principal component analysis (PCA)

In addition to the diagnostic ratios between PAHs, PCA is often used as an exploratory tool to identify the major sources of air pollutant emissions and to select statistically independent source tracers (Harrison et al., 1996; Guo et al., 2003). The results from application of PCA to the data at PU and KT sites are presented in Tables 5 and 6. Two components were identified at the two sites, which probably represented the source categories of vehicular emissions and stationary combustion sources. At PU site, the sampling location was close to a main road. Vehicular emission is assumed to be a major source of PAHs. The high loading factors of source markers of vehicular emissions for Factor 1 such as FLU, PHE, PYR, BAP and BGP in Table 5 confirmed that vehicle emission was one of the major sources of PAHs. Factor 1 explained 67.4% of the variance. For Factor 2 in Table 5, only ANT had the loading factor >0.50, indicating ANT was from other sources than vehicle emissions. ANT had been identified in coal combustion, coke production and wood combustion by many studies (Duval and Friedlander, 1981; Khalili et al., 1995). Further exploration is needed to identify this source at PU site. Factor 2 explained 20.1% of the variance.

At the KT site, PAHs with high loading factor for Factor 1 were BAA, BAP, BBF, BGP and INP (Table 6). Factor 1 explained 84.6% of the variance. These are all indicators of gasoline emissions, suggesting that gasoline-powered vehicular emissions were the main sources of PAHs at KT site. Factor 2 explained 8.7% of

Table 5
PCA analysis of PAHs in PM_{2.5} at PU site in winter and summer

PAHs	Factor 1	Factor 2
FLU	0.810	
PHE	0.916	
ANT		0.983
PYR	0.945	
FLT	0.967	
BAA	0.987	
CHR	0.987	
BAP	0.974	
BBF	0.984	
BKF	0.929	
BGP	0.977	
INP	0.977	
Initial eigenvalue	8.09	2.41
% Of variance	67.45	20.08
Cumulative %	67.45	87.53
Source	Vehicular emission	Stationary combustion source

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Eigenvalue > 1.00.
Factor loading ≥ 0.5 listed.

Table 6
PCA analysis of PAHs in PM_{2.5} at KT site in winter and summer

PAHs	Factor 1	Factor 2
FLU		0.863
PHE		0.778
ANT		0.713
PYR	0.516	0.824
FLT	0.601	0.781
BAA	0.915	
CHR	0.877	
BAP	0.906	
BBF	0.918	
BKF	0.688	0.522
BGP	0.959	
INP	0.974	
Initial eigenvalue	10.15	1.05
% Of variance	84.60	8.72
Cumulative %	84.60	93.32
Source	Gasoline exhaust	Diesel exhaust

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Eigenvalue > 1.00.
Factor loading ≥ 0.5 listed.

the variance. The PAHs with high loading factors for Factor 2 in Table 6 included FLU, PHE, ANT, FLT and PYR, which are the tracers of diesel vehicles (Miguel et al., 1998; Ho et al., 2002). Our site observation demonstrated that both gasoline vehicles and diesel vehicles were at KT site. Therefore, another major source of PAHs at the KT site was a diesel vehicle origin. The PCA results are consistent with that obtained by diagnostic ratios.

4. Conclusions

In this study, PAHs in different sizes of particles were characterized. It was found that most of the PAHs are in the PM_{2.5} fraction. Obviously, the PAHs levels in aerosols were closely associated with source strength and meteorological conditions. The spatial variations were predominantly due to the stronger vehicle source emissions at PU site, whereas the seasonal variations were caused by local sources superimposed by polluted air masses from Asian continent in winter, and easier dispersion, wash-out effects, higher temperature and photo-degradation of pollutants in summer.

Based on the diagnostic ratios and PCA analysis, it is concluded that vehicular emissions were the predominant source of airborne PAHs in Hong Kong. Other sources might come from stationary combustion sources such as cooking activities and industrial emissions. However, due to the similarity of PAH profiles from different source types, it suggests that individual PAH species can be used as source markers only when combined with other air pollutants such as inorganic pollutant data.

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