# Size distribution of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhou, China

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## Abstract

*n*-Alkanes and polycyclic aromatic hydrocarbons (PAHs) were identified in particle-sized aerosols of the urban and rural atmospheres of Guangzhou, China. Most of the organic compounds were mainly associated with fine particles with aerodynamic diameters less than 1.5 μm in the urban and rural atmospheres. In the urban aerosol close to the road, about 57% of *n*-alkanes and 62% of PAHs were found in the particle fraction with diameters of $<0.49$ μm. Size distributions of particulate mass and low molecular weight organic compounds exhibited bimodal patterns, while high molecular weight organic compounds exhibited unimodal distribution. Mass mean diameter (MMD) of total *n*-alkanes calculated over the whole size range was 0.43 μm in urban and 0.83 μm in rural. A similar trend was observed for PAHs. MMD for total PAHs in the urban and rural aerosol was 0.40 and 0.69 μm, respectively.
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## 1. Introduction

During the past decades much attention has been paid to the study of organic aerosol because (1) atmospheric particle deposition is recognized as the major transfer pathway of organic compounds from the atmosphere (Halsall et al., 1997; Stern et al., 1997); (2) organic aerosol is associated with a range of adverse effects on human health (e.g., asthma) when particles bounded with toxic compounds enter the respiratory tract (Seaton et al., 1995; Oanh et al., 2002). Organic aerosols are widespread in the environment, of which the sources typically include natural combustion such as forest fires and volcanic eruption, the anthropogenic combustion of fossil fuels, wood, agricultural and industrial product debris or leaves, and from direct suspension of pollen, micro-organisms and insects (Simoneit et al., 1977, 1991; Rogge et al., 1991, 1993a, b, 1998). Generally, organic material contributes 20–50% of the total fine particulate mass (Saxena and Hildemann, 1996; Venkataraman et al., 2002). In tropical forested areas, this contribution can be up to 90% (Talbot et al., 1988, 1990; Andreae and Crutzen, 1997). Since organic aerosols have been a concern of scientists, an intense research interest has been underway for the chemical composition and source apportionment of organic aerosol (Gogou et al., 1996; Harrison et al., 1996; Azevedo et al., 1999; Kavouras et al., 1999).

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The potential for organic aerosols to remove the aerosol-bound contaminants (Van Vaeck and Van Cauwenberghe, 1985) and enter into the respiratory tract of humans (Viras et al., 1990; Pagano et al., 1996; Hannigan et al., 1998) is partly governed by the particle size, chemical composition and surface characteristics (such as hydrophobicity, surface tension, etc.). Since particles with diameters $<0.1\,\mu m$ coagulate relatively fast and the lifetimes are less than 1 h (Pui and Chen, 1997), different size distributions of particle and particle-bound compounds versus the distance of the sampling site are expected (Schnelle-Kreis et al., 2001). It is well known that small particles tend to diffuse deeper into the respiratory system, thus they can pose a direct mutagenic threat to humans (Pagano et al., 1996). Particle size distributions of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) have been mostly studied in Europe and America (Van Vaeck and Van Cauwenberghe, 1985; Sicre et al., 1987; Aceves and Grimalt, 1993; Poster et al., 1995; Kavouras et al., 1998). Geographical location and the meteorological conditions can result in significant differences in aerosol size distribution (Aceves and Grimalt, 1993; Brunnemann et al., 1996; Schnelle-Kreis et al., 1999). China is unique in many aspects because the basic emission control technologies have not been intensively used yet, although the eastern part of China including the Pearl River Delta region has been developed economically very fast in recent two decades. In this paper, a preliminary study was conducted to investigate the particle size distribution of n-alkanes and PAHs sampled from urban and rural areas of Guangzhou, one of the largest cities within the Pearl River Delta region.

In previous papers, we reported the detailed studies on the organic compound distribution in the atmosphere of LiWan district (Bi et al., 2002, 2003). The purpose of this study is (1) to present a discussion on the distribution of n-alkanes and PAHs associated with size

segregated atmospheric aerosols collected in urban and rural areas of Guangzhou city and (2) to determine if the rural areas will show measurable differences in particle size distributions in comparison with the urban environment.

## 2. Experiment

### 2.1. Sampling

Sample acquisition was carried out from January 1 to 16, 2002. The collection sites were located in LiWan district with scattered schools, residential houses, heavy traffic, and commercial shops (urban) and HeShun country (rural). At LiWan district, the samples were taken at the same site with different elevation. One group of samples were taken at ground level near a road with rushing traffic (sample name: LW-G). The height of the inlet is 1.5 m above ground level. Another group of samples were taken at the top of a nine-story building, ca. 25 m above ground level (sample name: LW-H). At HeShun country, the samplers were placed at Meijing dam near a village and fish pool (sample name: HS). The sampling height was about 5 m. The nearest main road was around 100 m away. The emission sources of anthropogenic pollution included some vehicle emission by truck for transporting the fish and agricultural material, wood burning and other anthropogenic activities. HeShun country is located 40 km northwest upwind from LiWan district. Table 1 provides the general view of sampling.

Particulate matter smaller than 10 μm was sampled over glass fiber filter with an Andersen model SA235 equipped with a size-selective inlet, high-volume cascade impactor (Andersen Instruments Inc.). Aerosol particles were separated into six fractions (five stages and a backup filter), resulting in size ranges of 10–7.2; 7.2–3.0;

Table 1
Sampling and meteorological condition

| Sample name | Sampling date | Elevation (m) | Ambient temperature (°C) | Weather and traffic |
| --- | --- | --- | --- | --- |
| LW-H | 1/1/2002 | 25 | 8–25 | Cloudy, natural vegetation, vehicular traffic |
| LW-H | 2/1 | 25 | 12–24 | Cloudy, natural vegetation, vehicular traffic |
| LW-H | 3/1 | 25 | 11–23 | Fair, natural vegetation, vehicular traffic |
| LW-H | 4/1 | 25 | 8–22 | Fair, natural vegetation, vehicular traffic |
| LW-G | 8/1 | 1.5 | 13–26 | Cloudy, adjacent to major road, heavy traffic |
| LW-G | 9/1 | 1.5 | 12–24 | Cloudy, adjacent to major road, heavy traffic |
| LW-G | 10/1 | 1.5 | 11–24 | Cloudy, adjacent to major road, heavy traffic |
| LW-G | 11/1 | 1.5 | 10–26 | Cloudy, adjacent to major road, heavy traffic |
| HS | 13/1 | 5 | 13–27 | Cloudy, natural vegetation, traffic |
| HS | 14/1 | 5 | 16–28 | Cloudy, natural vegetation, traffic |
| HS | 15/1 | 5 | 18–24 | Poor, haze, natural vegetation, traffic |
| HS | 16/1 | 5 | 19–26 | Poor, haze, natural vegetation, traffic |

3.0–1.5; 1.5–0.95; 0.95–0.49 and $<0.49\,\mu m$. Meanwhile, an Andersen model GUV-16HBL $PM_{10}$ sampler was deployed in order to inter-compare and evaluate the performance of the cascade impactor. Particulate samples were obtained with an air flow of $1.13\,m^3\,min^{-1}$. To reduce artifacts that may alter contaminant size distribution, filters were exchanged every 24 h during sampling (Alves et al., 2000). Other special devices such as diffusion denuders and foam plugs were not used due to the difficulties in applying these devices. Consequently, volatilization losses or adsorption artifacts may occur on the filter for semi-volatile organic compounds especially for the low molecular weight compounds because these compounds exhibit high volatility (Kavouras et al., 1999; Poster et al., 1995). At each site, the samples were collected for 4 days.

Glass fiber filters were baked out at 450 °C for 12 h and stored in aluminum foil packages until used. The total concentrations of particulate matter were determined by weighing the filters under controlled temperature and moisture conditions (25 °C, 50%RH) before and after exposure.

## 2.2. Analytical procedure

A detailed description of the analytical procedure has been published elsewhere (Bi et al., 2002, 2003). Briefly, five PAHs surrogate consisting of naphthalene-$D_8$; acenaphthene-$D_{10}$; phenanthrene-$D_{10}$; chrysene-$D_{12}$ and perylene-$D_{12}$ standards were added prior to extraction. Sample filters were extracted with dichloromethane (DCM) using ultrasonic agitation and filtered. This procedure was repeated three times. The extracts were analyzed using gas chromatography with mass selective detection (GC/MS). Prior to instrumental analysis, known quantities of internal standard hexamethylbenzene were added to the samples. The GC/MS system consisted of a Hewlett-Packard (HP) 5890 and HP 5972 MS operated in electron impact mode (70 eV). A $50\,m \times 0.32\,mm$ i.d. HP-5 (film thickness $0.25\,\mu m$) capillary column was used. The chromatographic conditions were as follows: injector temperature was 280 °C and detector temperature was 180 °C. The temperature ramp was: an initial oven temperature of 65 °C maintained for 5 min, and increased at $3\,°C\,min^{-1}$ to a maximum of 290 °C for 30 min. Helium was the carrier gas. $1\,\mu l$ sample was injected with splitless mode. The mass scanning ranged between $m/z$ 50 and 500. Data acquisition and processing were controlled by a HP Chem-Station data system.

Chromatographic peaks of samples were identified by comparison of mass spectra with those obtained from NBS 75 mass spectra library of the GC/MS instrument, and by matching of retention times and fragmentation profiles against corresponding standards. Sixteen PAHs (16 compounds specified on US EPA Method 610) in a

mixture and six $n$-alkanes ($C_{16}$, $C_{19}$, $C_{24}$, $C_{28}$, $C_{30}$, $C_{32}$) were used for quantification. If no authentic standards were available, compounds were identified by the retention indices and the library mass spectrum. Molecular ion and $m/z$ 85 were used for quantification of individual PAHs and $n$-alkanes, respectively. $n$-Alkanes and PAHs were quantified relative to internal standard hexamethylbenzene. For compounds without standard available, the rough quantifications were made relative to the compounds with the closest molecular weight.

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. The major contaminants observed were primarily residual phthalate esters, trace of $n$-alkanes ranging from $C_{18}$ to $C_{26}$, with no carbon number predominance. PAHs were not detectable. 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) with the higher losses for the lighter compounds. All samples were corrected for surrogate recoveries. Because the recovery of naphthalene was very low, the result of naphthalene was not included in this study.

# 3. Results and discussion

## 3.1. Size distribution of particulate matter

The sum of all size fraction concentrations of particulate matter ranged from 129.9 to $362.7\,\mu g\,m^{-3}$ in the urban atmosphere and from 175.9 to $201.1\,\mu g\,m^{-3}$ in the rural atmosphere (mean concentration: LW-G: $288.8\,\mu g\,m^{-3}$; LW-H: $235.8\,\mu g\,m^{-3}$; HS: $192.1\,\mu g\,m^{-3}$). The particle matter levels in the urban area were higher than those in rural area. In addition, the sum of six size fractions represented $94\% \pm 10\%$ (average $\pm$ SD) of the aerosol mass measured by the high volume $PM_{10}$ sampler. Furthermore, the discrepancies between the particle mass collected by the impactor and $PM_{10}$ sampler were not significant with regard to the concentrations of $n$-alkanes and PAHs as described below, which suggests that the impactor and $PM_{10}$ sampler collected approximately the same particles. The $PM_{10}$ level in Guangzhou city was close to those in Santiago (Chile) and Baghdad (Iraq) (Didyk et al., 2000; Kanbour et al., 1990), but significantly higher than those in Hong Kong, Japan, Australia, Europe and North America ($13–119\,\mu g\,m^{-3}$) (Panther et al., 1999; Chan and Kwok, 2000; Chan et al., 2000; Wal and Janssen, 2000; Houthuijs et al., 2001; Röösli et al., 2001).

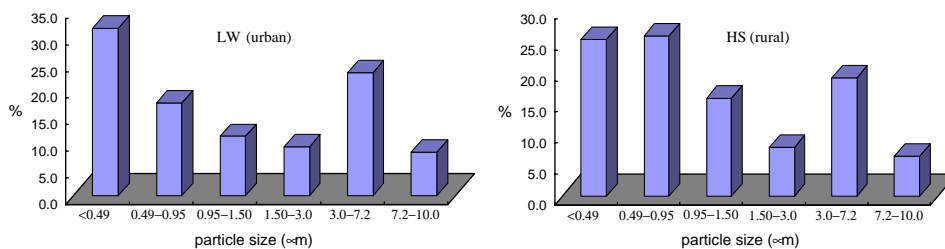Fig. 1 indicates that the particle size distributions showed bimodal with a fine mode mass median diameter

Fig. 1. Particle size distribution of air expressed as % of the total particle mass.

of $< 0.49\,\mu m$ and a coarse mode mass median of $3.0$–$7.2\,\mu m$. On average 29% and 62% of the mass of $PM_{10}$ particles were found to be $< 0.49$ and $< 1.5\,\mu m$, respectively. Generally, fine particles include ultrafine particles (aerodynamic diameter $(D_p)$ less than $0.1\,\mu m$) and accumulation particles $(0.1 < D_p < 2.0\,\mu m)$ are probably caused by primary emission from combustion sources and coagulation and/or gas to particle condensation on the surface of preexisting particles, whereas resuspension of urban dust and soils, plant tissue, pollen, and waxen flakes are likely sources of the large aerosols (Allen et al., 1996; Offenberg and Baker, 1999; Schönbuchner et al., 2001). The differences in samples taken at different height were minor. However compared with urban aerosol, aging of rural aerosol during transport resulted in a shift of particle size from $< 0.49\,\mu m$ towards $0.49$–$0.95\,\mu m$ by growth processes (Schönbuchner et al., 2001).

Mass mean diameter (MMD), which splits the diameters from the smallest to the largest into two equal halves (Yang et al., 1999), was calculated using an equation provided by Kavouras and Stephanou (2002). For the total particle mass, the MMD was 0.98, 1.05 and $0.93\,\mu m$ for LW-G, LW-H, and HS, respectively. There were no significant differences between the sampling elevation and sampling location. The literature reported values for MMD were 0.572, 0.385 and $62.5\,\mu m$, for gasoline-powered cars, motorcycles, and resuspendable road dust, respectively (Yang et al., 1999). The values in this study were significantly higher than the fresh combustion emissions, resulting from the occurrence of accumulation of aerosols or different aerosol sources.

### 3.2. Distribution of n-alkanes between the particle size fractions

Total n-alkanes (sum of all size fractions) varied in the range of $233.2$–$1037.0\,ng\,m^{-3}$, which was 96% of n-alkanes measured by $PM_{10}$ sampler. n-Alkane traces were dominated by $C_{15}$–$C_{35}$ with no odd–even carbon number predominance in the $C_{15}$–$C_{27}$ range and a slight odd carbon number preference in the $C_{28}$–$C_{33}$ range which are characteristic of higher plant wax resources. 27–57% of the total n-alkanes contents were found on the backup filter $(< 0.49\,\mu m)$ and 78–85% on particles $< 1.5\,\mu m$ (Table 2). The total n-alkanes concentration in the smallest size fraction was generally more than 10 times higher than that in the largest size fraction. The absolute concentrations of n-alkanes including the vascular plant n-alkanes were higher in the smaller aerosol sizes and exhibit the highest values in the smallest fraction in the urban aerosol $(< 0.49\,\mu m)$. At rural area, a larger fraction of n-alkanes were found in the size range of $0.49$–$0.95\,\mu m$. The maximum of the distribution shift toward larger particle size within the accumulation mode may reflect long-term aging (Van Vaeck and Van Cauwenberghe, 1985).

Table 2 provides information on diagnostic ratios between n-alkanes, which shows no variation to be dependent on particle size. The low carbon preference index (CPI) values over the whole particle size range were consistent with their anthropogenic origin. In general, CPI values greater than three, indicate that the n-alkanes are from predominantly biological materials. In rural areas, the CPI values were not observed to be high, which suggest that the rural atmosphere was polluted by anthropogenic activities during the study period. The slight decrease of $CPI_3$ (the split range of higher plant waxes $C_{25}$–$C_{35}$) with particle size suggests that biogenic n-alkanes accumulate in the fine particles, which is not in agreement with the other studies which reported that natural n-alkanes were preferentially associated with the coarse particles and the anthropogenic compounds in the smaller particles (Sicre et al., 1987; Alves et al., 2000; Kavouras and Stephanou, 2002). However, the decrease of CPI with particle size was found in the indoor samples collected in smoking areas (Kavouras et al., 1998). Organic compounds emitted from cooking also showed a high CPI values and the compounds were generally associated with the fine particles (Rogge et al., 1991). Therefore, biomass burning such as environmental tobacco smoke and restaurant cooking emissions may be the major source of these compounds in the areas.

In order to investigate the distribution pattern of n-alkanes within different size ranges, the normalized individual species concentrations for different size fractions were calculated for each sample. An increase

Table 2
Concentration and diagnostic parameters for size-distributed particles and organic compounds[a]

| | <0.49 μm | 0.49–0.95 μm | 0.95–1.5 μm | 1.5–3 μm | 3–7.2 μm | 7.2–10 μm |
|---|---|---|---|---|---|---|
| PM ($\mu g\, m^{-3}$) | 21.1–34.8 | 11.2–35.9 | 5.6–24.6 | 4.8–10.0 | 8.0–34.8 | 2.4–13.1 |
| $n$-alkanes ($ng\, m^{-3}$) | 63.7–588.8 | 72.5–244.2 | 52.1–137.7 | 22.8–88.9 | 18.6–76.6 | 3.6–30.1 |
| PAHs ($ng\, m^{-3}$) | 17.2–86.1 | 16.5–48.0 | 10.2–25.2 | 2.7–11.3 | 1.4–7.5 | 0.3–2.2 |
| $CPI_1$ ($C_{15}$–$C_{35}$) | 1.28–1.41 | 1.24–1.38 | 1.22–1.36 | 1.18–1.31 | 1.24–1.28 | 1.18–1.25 |
| $CPI_2$ ($C_{15}$–$C_{24}$) | 0.76–0.88 | 0.69–0.83 | 0.71–0.90 | 0.78–0.93 | 0.87–1.02 | 0.89–1.01 |
| $CPI_3$ ($C_{25}$–$C_{35}$) | 1.26–1.70 | 1.39–1.69 | 1.33–1.67 | 1.32–1.52 | 1.32–1.52 | 1.30–1.35 |
| Phe/(Phe + An) | 0.80–0.87 | 0.82–0.88 | 0.82–0.89 | 0.85–0.89 | 0.90–0.97 | 0.88–0.91 |
| BaA/(BaA + CT) | 0.28–0.33 | 0.30–0.33 | 0.28–0.31 | 0.24–0.28 | 0.11–0.28 | 0.22–0.25 |
| Flu/(Flu + Pyr) | 0.47–0.49 | 0.46–0.48 | 0.48–0.49 | 0.48–0.50 | 0.47–0.68 | 0.48–0.56 |
| BeP/(BeP + BaP) | 0.51–0.52 | 0.46–0.47 | 0.49–0.50 | 0.56–0.61 | 0.59–0.95 | 0.63–0.74 |
| IcdP/(IcdP + BghiP) | 0.47–0.50 | 0.50–0.52 | 0.44–0.48 | 0.40–0.48 | 0.39–0.58 | 0.38–0.44 |
| BghiP/BeP | 1.45–1.67 | 1.21–1.38 | 1.42–1.99 | 1.43–1.62 | 0.47–1.36 | 1.29–1.75 |
| BaPE | 2.25–10.58 | 2.33–5.82 | 1.29–2.43 | 0.28–0.87 | 0.03–0.32 | 0.02–0.11 |
| CPAH/ΣPAH | 0.71–0.72 | 0.67–0.72 | 0.63–0.71 | 0.64–0.69 | 0.55–0.62 | 0.57–0.71 |

Phe: phenanthrene; Ant: anthracene; BaA: benzo[a]anthracene; CT: chrysene + triphenylene; Flu: fluoranthene; Pyr: pyrene; BeP: benzo[e]pyrene; BaP: benzo[a]pyrene; IcdP: indeno[1,2,3-cd]pyrene; BghiP: benzo[ghi]perylene; $BaPE = BaA \times 0.06 + BF \times 0.07 + BaP + DBahA \times 0.6 + IcdP \times 0.08$ (Yassaa et al., 2001); CPAH: total concentration of nine combustion PAH (including fluoranthene, pyrene, benzo[a]anthracen, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[cd]pyrene and benzo[ghi]perylene); ΣPAH : the sum of parent and alkyl PAHs.

[a]Abbreviations are as follows: CPI: carbon preference index; $CPI_1 = (\sum C_{15}-C_{33} + C_{17}-C_{35})/2\sum C_{16}-C_{34}$; $CPI_2 = \sum C_{15}-C_{23}/\sum C_{16}-C_{24}$; $CPI_3 = (\sum C_{25}-C_{33} + C_{27}-C_{35})/2\sum C_{26}-C_{34}$.

in the relative concentration of low molecular weight compounds such as $n$-alkanes of $<C_{24}$ with increasing particle size was observed. On the other hand, some high molecular weight compounds such as $C_{25}$–$C_{28}$ exhibited decreasing relative concentrations with increasing particle size. The other compounds such as $>C_{28}$ $n$-alkanes showed no dependence on the particle size. In addition, the shift of carbon number maximum ($C_{max}$) toward long-chain $n$-alkanes with decreasing particle size was also observed. $C_{max}$ were reached by $C_{25}$ for the smallest particle fraction and by $C_{21}$ for the largest particle fraction, which could be explained that lower molecular weight $n$-alkanes readily shift toward larger particle size.

Aerosol composition and size distribution differs significantly between the anthropogenic aerosol and the natural aerosol. In this study, a systematic description of the size distribution of these hydrocarbons is provided by means of the Lundgren plots (Poster et al., 1995; Kavouras and Stephanou, 2002). The lower limit of particle size collected on the backup, $D_p = 0.01\, \mu m$, has been arbitrarily selected. The concentrations of the wax $n$-alkanes were calculated by subtraction of the average of the next higher and lower even carbon numbered homologs:

$$Wax\, C_n = C_n - 0.5(C_{n-1} + C_{n+1}),$$

negative values of $C_n$ were taken as zero (Simoneit et al., 1991). From Fig. 2, a similar particle size distribution pattern between the total $n$-alkanes and wax $n$-alkanes was observed for urban and rural aerosols. Both total
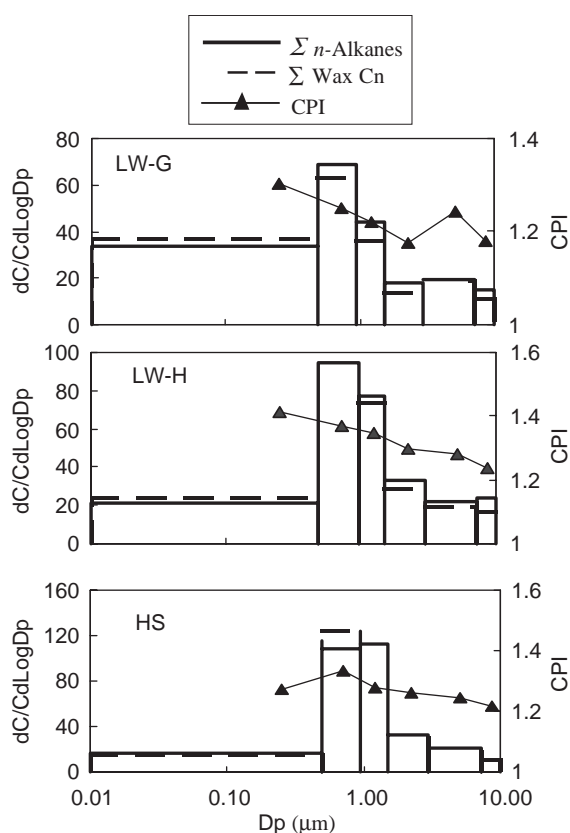


Fig. 2. Lundgren diagrams for $\Sigma n$-alkanes, $\Sigma$Wax $C_n$ concentration and carbon preference index (CPI).

*n*-alkanes and wax *n*-alkanes exhibited a predominant occurrence in the particle size fraction <1.5 μm. Preferential occurrence of anthropogenic organic compounds in the fine particles has been extensively reported (Van Vaeck and Van Cauwenberghe, 1985; Sicre et al., 1987; Alves et al., 2000). Our results were in contrast with the studies on long-range transport of aerosol in the atmosphere, which generally report biogenic organic compounds such as *n*-alkanes to accumulate in the coarse particles (Alves et al., 2000; Kavouras and Stephanou, 2002). However, the wax *n*-alkanes enrichment in the finer particle fraction was also observed in other investigations (Van Vaeck and Van Cauwenberghe, 1985; Aceves and Grimalt, 1993; Kavouras et al., 1998). This perhaps shows the difference of distance between source and sampling site or suggests that fossil fuel combustion and/or biomass burning are probably major contributors to long-chain alkanes in the sampling sites as described earlier.

Particle size distribution of organic compounds is influenced by the compound vapor pressure, the variation of compound adsorption and absorption affinity, atmospheric processes, as well as the emission source (Venkataraman and Friedlander, 1994; Allen et al., 1996; Venkataraman et al., 1999). Some typical examples of size distribution are shown in Fig. 3. Similar profiles were observed for the other two aerosol samples. The diagram indicates the existence of a bimodal distribution, in which lower molecular weight species were associated with fine and coarse particles. This can be explained that lower molecular weight compound have a higher concentration in the gas phase than in particulate phase (Bi et al., 2003). After emission, volatilization from fine particles and condensation on the surface of pre-existing aerosols may lead to the

changes in particle-size distribution in an effort to establish the equilibrium between the different particle size fractions during atmospheric transport. Higher molecular weight species exhibited unimodal distribution predominant in the fine mode aerosol. The size distribution in the small particle is possibly associated with gas-to-particle transformation after hydrocarbon emission to the atmosphere and cooling (Aceves and Grimalt, 1993; Kavouras and Stephanou, 2002). No preference exists between odd and even homologues.

This shift in the maximum between the sampling height and sampling sites was also reflected in the overall MMD. The MMD of individual *n*-alkane had a broad range from 0.31 μm to 1.24 μm (Table 3). The MMD of total *n*-alkanes were 0.43, 0.73, and 0.83 μm for LW-G, LW-H, and HS, respectively. The low MMD values reflect condensation mechanisms since the gas–particle condensation always enriches the aerosol fraction in the accumulation size range (Van Vaeck and Van Cauwenberghe, 1985; Sicre et al., 1987; Aceves and Grimalt, 1993). The above data indicate a clear differentiation between the urban and rural aerosols and between the different sampling heights. This difference between the sampling heights may be due to the longer residence time permitting gas-to-particle condensation and the different emission sources. A greater percentage of biogenic hydrocarbons was observed at 25 m height than at 1.5 m above ground level (Bi et al., 2003). Higher MMD values for rural area can be explained by physical aging during long-range transport which usually tends to shift toward larger particle sizes (Van Vaeck and Van Cauwenberghe, 1985; Kavouras and Stephanou, 2002). Of course, the different source, perhaps some local emission, may be an additional explanation for the higher MMD values found for the rural samples.
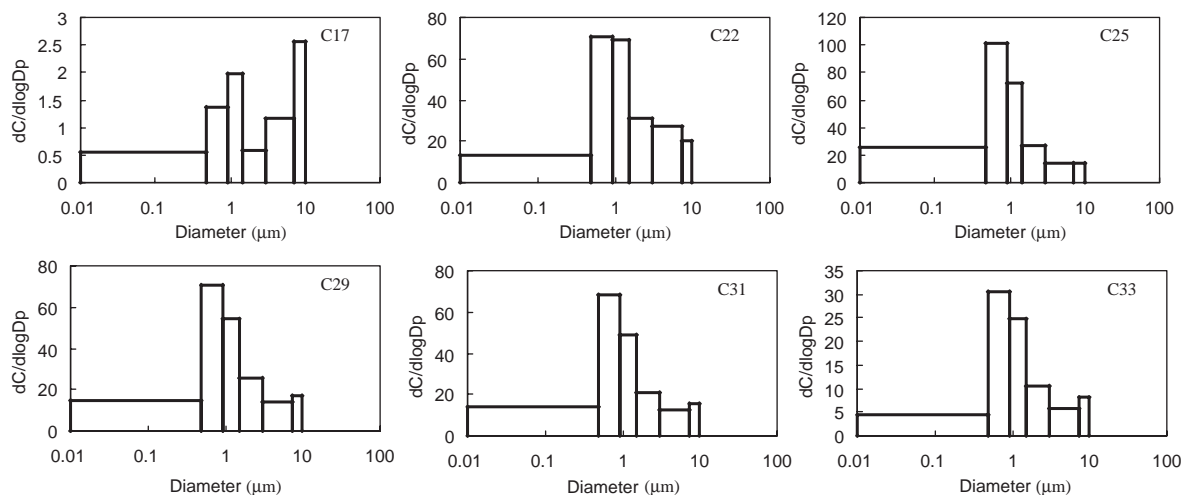


Fig. 3. Particle size distribution of six *n*-alkanes in LW-H samples.

Table 3
MMD of *n*-alkanes for urban and rural areas of guangzhou (unit: µm)

| *n*-alkanes | LW-G (urban) | LW-H (urban) | HS (rural) |
|---|---|---|---|
| $C_{15}$ | 0.53 | 1.07 | 0.86 |
| $C_{16}$ | 0.56 | 0.98 | 1.13 |
| $C_{17}$ | 0.56 | 0.99 | 0.94 |
| $C_{18}$ | 0.71 | 1.03 | 0.91 |
| $C_{19}$ | 0.72 | 1.19 | 0.80 |
| $C_{20}$ | 0.72 | 1.24 | 0.68 |
| $C_{21}$ | 0.68 | 0.92 | 0.77 |
| $C_{22}$ | 0.58 | 0.88 | 0.83 |
| $C_{23}$ | 0.47 | 0.73 | 0.87 |
| $C_{24}$ | 0.40 | 0.63 | 0.86 |
| $C_{25}$ | 0.37 | 0.61 | 0.81 |
| $C_{26}$ | 0.38 | 0.63 | 0.80 |
| $C_{27}$ | 0.39 | 0.66 | 0.80 |
| $C_{28}$ | 0.42 | 0.75 | 0.81 |
| $C_{29}$ | 0.40 | 0.74 | 0.82 |
| $C_{30}$ | 0.37 | 0.80 | 0.80 |
| $C_{31}$ | 0.34 | 0.71 | 0.83 |
| $C_{32}$ | 0.37 | 0.87 | 0.90 |
| $C_{33}$ | 0.34 | 0.82 | 0.89 |
| $C_{34}$ | 0.31 | 0.66 | 0.96 |
| $C_{35}$ | 0.32 | 0.70 | 1.04 |
| Total *n*-alkanes | 0.43 | 0.73 | 0.83 |

### 3.3. Distribution of PAHs between the particle size classes

Total PAH concentrations measured with the impactor, which ranged from 48.3 to 148.6 ng m$^{-3}$, agree well with those collected with PM$_{10}$ sampler. An average of 87% of total PAHs was measured using the impactor. The particle matter levels in the urban area were higher than those in rural area. In addition, more than 36% of the total PAH contents were found on the backup filter ($<0.49 \mu$m) and more than 86% on particles $<1.5 \mu$m (Table 2). There was a general trend that resulted from the strong decrease in concentration of PAHs, particularly the higher molecular weight compounds, with increasing size. Similar results have been reported by others (Sicre et al., 1987; Schnelle-Kreis et al., 2001; Kavouras and Stephanou, 2002). Diagnostic PAHs ratios, such as BaA/BaA + CT, BeP/BeP + BaP, Flu/Flu + Pyr, and IcdP/BghiP + IcdP, which are used to investigate their origin or as an indication of the aging of air samples (Cotham and Bidleman, 1995; Lohmann et al., 2000), are listed in Table 2. No significant discrepancy was observed between different particle size ranges except for the second stage (3.0–7.2 µm). The reason is still unknown. Apart from the exception, the parameter values were compared with those reported in the literature. In particular, the values for BaA/BaA + CT was 0.22–0.33, which can be comparable to

that for crude oil emission (0.16 ± 0.12) (Sicre et al., 1987). The Flu/Flu + Pyr ratio was 0.46–0.56, which is similar to that for vehicular emissions and especially emissions from catalytic converter equipped automobiles (0.44) (Rogge et al., 1993a). The literature reported values for IcdP/BghiP + IcdP are 0.18, 0.37 and 0.56, for cars, diesel, and coal, respectively (Grimmer et al., 1983). The mean ratio in this study was 0.40–0.52, which is comparable to that for diesel and/or coal emissions. The ratio of BghiP/BeP in this study ranged from 1.21 to 1.99, which was comparable to those reported in the literature (0.62 for heavy duty diesel vehicle and 2.35 for catalyst-equipped autos) (Rogge et al., 1993a). Overall, our results suggest that the major source of organic compounds in the urban and rural aerosol was fossil fuel combustion from automobiles, with a substantial contribution from unburned petroleum (Kavouras et al., 1999). In fact, LW-G and LW-H samples were collected close to a busy city street; therefore, the samples have been strongly influenced by the nearby vehicle emissions, as expected. It is worthy to note that BeP/BeP + BaP ratio is regarded as an index of the aging of the particles (Cotham and Bidleman, 1995). The BeP/BeP + BaP ratio increase with particle size suggests the long-term aging of large particle. In addition, benao(a)pyrene-equivalent carcinogenic power (BaPE) is an index to parameterize aerosol carcinogenicity, which has been introduced instead of the sole benzo(a)pyrene since the latter is easily decomposed in "reactive" air (Yassaa et al., 2001). In BaPE calculating formula, five carcinogens (BaA, BF, BaP, DBahA and IcdP) are taken into consideration. BaPE mainly concentrated on the smallest particle, which suggest that small particles may significantly contribute to the genotoxicity of aerosol samples, which has been verified by Pagano et al. (1996).

Similar to *n*-alkanes, at LW-G, PAHs were found to be predominant in the smallest size and the loading decreased steadily with increasing particle size. LW-G and LW-H were at the same location, and the visible differences of PAHs distribution between them seemed to be correlated with the sampling height that is the distance to emission source. In fact, the shorter the distance to the source, the higher was the portion of PAH associated with small particles (Schnelle-Kreis et al., 2001). Of course, other aged particles may influence LW-H by atmospheric transport since the particles were collected at high altitude. The different distribution between LW-G and HS could result from physical changes and/or differences in emission size distributions of these species.

Fig. 4 shows the size distributions of five different molecular weights PAHs and total PAHs with particle size at LW-H. Similar Lundgren diagrams were obtained for the other samples studied. These distributions showed that PAHs were distributed among aerosol size fractions based on molecular weight. Nearly unimodal distribution predominant in the fine mode aerosol was
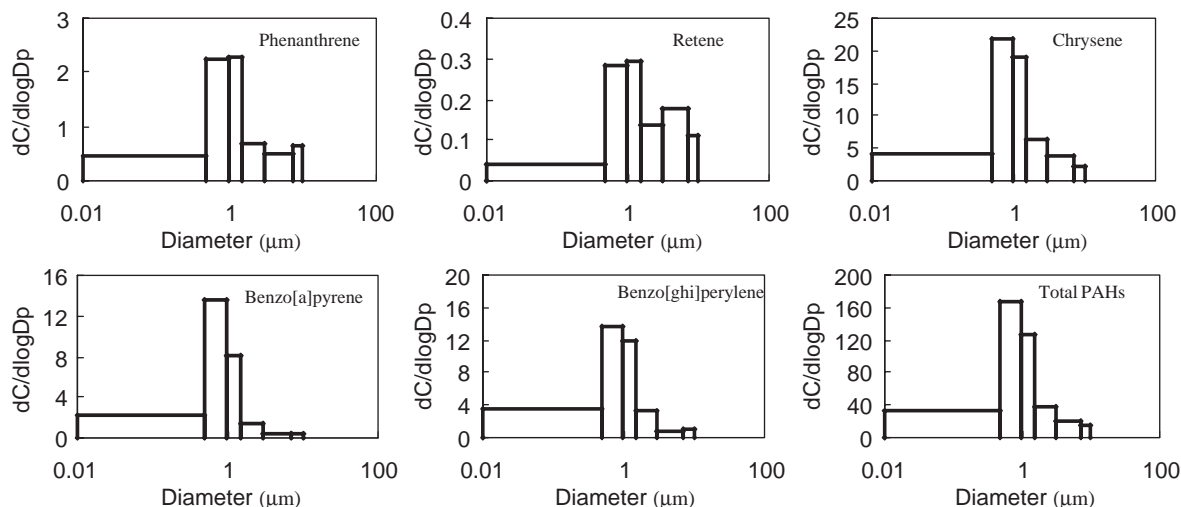
Fig. 4. Particle size distribution of five PAHs and total particle mass measured PAHs in LW-H samples.

found for the four-ring and more ring PAHs, while three-ring phenanthrene and retene showed bimodal pattern predominant in the fine and coarse aerosol. These results indicate that non-volatile PAHs size distribution basically reflects the gas-to-particle transformation after their emission, whereas semi-volatile PAH species could result from their volatilization and adsorption to pre-existing particles (Venkataraman and Friedlander, 1994; Kavouras and Stephanou, 2002). Freshly emitted PAHs are adsorbed mainly to fine aerosol and they can become associated with coarse particles by volatilization from fine particles followed by condensation onto coarse particles. Lower molecular weight PAHs have higher vapor pressures, higher concentrations in the gas phase and higher diffusivities and, therefore, readily shift toward larger particle size. The high molecular weight PAHs generally have much lower vapor pressures, and the characteristic time for this repartitioning process is much greater (Allen et al., 1998; Offenberg and Baker, 1999). In addition to the different gas–particle partitioning behavior, the preferential accumulation of lower molecular weight PAHs in larger particles could result from differences in emissions size distributions of these species (Venkataraman and Friedlander, 1994). It has been suggested that the observed partitioning of PAHs as a function of molecular weight might be due to lower molecular weight PAHs being co-emitted with larger particles, for example, in diesel-power vehicle and meat cooking emissions (Allen et al., 1996; Miguel et al., 1998). Moreover, the differences in chemical affinities between PAHs and different size particles can result in the observed PAHs patterns. If coarse mode aerosols contain larger fraction of water, thus more hydrophobic high molecular weight PAHs would tend to partition to

the smaller particles. Similarly, if high molecular weight PAHs have stronger adsorption behavior than lower molecular weight PAHs, then high molecular weight PAH would tend to associate with the fine aerosol fraction which has a much higher total surface area than the coarse fraction (Allen et al., 1996).

The MMD of individual PAH mass was between 0.33 and 0.84 μm for LW-G, 0.53 and 1.09 μm for LW-H, and 0.57 and 0.89 μm for HS, respectively (Table 4). The total PAH mass was 0.40, 0.68, and 0.69 μm for LW-G, LW-H, and HS, respectively. The MMDs of total-PAH mass were 0.45 μm for the engine exhaust of the gasoline-powered cars and 0.35 μm for the engine exhaust of the motorcycles (Yang et al., 1999). Site LW-G is close to a busy road (a distance of 5 m), so freshly emitted aerosol was sampled at this site. The low MMDs imply that LW-G was mainly contributed by vehicle emission. The MMDs of organic compounds were generally larger in HS than in LW-G, but the MMDs of cyclopentapyrene and retene in rural aerosol were the smallest, which reflects the shortest distance to the source. It suggests that the rural sites have local PAHs sources in addition to long-term transport. In addition, the compound-to-compound differences in the MMD (higher values for low molecular weight) suggest that higher molecular weight PAHs were mainly associated with the finer particle. This result shows good agreement with those published by Kiss et al. (1998) and is consistent with the above discussion.

## 4. Conclusion

n-Alkanes and PAHs were primarily associated with small particles. Generally, more than 80% of the total

Table 4
MMD of PAHs for urban and rural areas of Guangzhou
(unit: μm)

| PAHs compound | LW-G (urban) | LW-H (urban) | HS (rural) |
|---|---|---|---|
| Acenaphthylene | 0.47 | 0.71 | 0.66 |
| Fluorene | 0.54 | 0.93 | 0.81 |
| Phenanthrene | 0.52 | 0.78 | 0.77 |
| Anthracene | 0.46 | 0.67 | 0.60 |
| Methylphenanthrene | 0.47 | 0.79 | 0.68 |
| Fluoranthene | 0.63 | 0.82 | 0.66 |
| Acephenanthrylene | 0.67 | 0.71 | 0.57 |
| Pyrene | 0.62 | 0.81 | 0.65 |
| benzo(a)fluorene | 0.64 | 0.78 | 0.61 |
| Retene | 0.84 | 1.09 | 0.77 |
| benzo(b)fluorene | 0.58 | 0.83 | 0.65 |
| Benzo[ghi]fluoranthene | 0.52 | 0.78 | 0.70 |
| Cyclopenta(cd)pyrene | 0.69 | 0.74 | 0.61 |
| benzo(c)phenanthrene | 0.62 | 0.81 | 0.79 |
| Benzo[a]anthracene | 0.43 | 0.71 | 0.70 |
| Chrysene + triphenylene | 0.46 | 0.73 | 0.75 |
| Benzo[b + k]fluoranthene | 0.35 | 0.59 | 0.68 |
| Benzo[a]fluoranthene | 0.38 | 0.64 | 0.69 |
| Benzo[e]pyrene | 0.35 | 0.63 | 0.69 |
| Benzo[a]pyrene | 0.35 | 0.63 | 0.67 |
| Perylene | 0.35 | 0.64 | 0.67 |
| Quaterphenyl | 0.43 | 0.79 | 0.89 |
| Indeno[7,1,2,3-cdef]chrysene | 0.33 | 0.53 | 0.76 |
| Indeno[1,2,3-cd]pyrene | 0.35 | 0.59 | 0.64 |
| Dibenzo[ah]anthracene | 0.42 | 0.68 | 0.57 |
| Benzo[ghi]perylene | 0.35 | 0.59 | 0.66 |
| Total PAHs | 0.40 | 0.68 | 0.69 |

concentrations of *n*-alkanes and PAHs were accumulated in particles $< 1.5 \, \mu m$. The size distribution diagram of *n*-alkanes indicates the existence of a bimodal distribution, which can be explained by non-equilibrium. Unimodal distribution of high molecular weight PAHs basically reflects the gas-to-particle conversion after their emission, whereas the low molecular weight PAHs were distributed in bimodal distributions, which can be interpreted by partitioning to larger particles by vaporization and sorption processes. The MMDs of the total *n*-alkanes and PAHs were between 0.43 and $0.83 \, \mu m$, and between 0.40 and $0.69 \, \mu m$, respectively. The variation of MMD could be due to the particle size change during transport. Taking into account the small sampling number, the available data did not allow us to explain the variability of the size distributions in terms of different distances to emission sources. Different meteorological conditions, different sources and different transporting distances may affect the size distribution of organic compounds. Long sampling periods and more elaborate data analyses are scheduled to achieve a

better understanding of the evolution of particle size distribution of organic compounds in the atmosphere.

The major peaks of PAHs particle size distribution located at the fine particle not only indicate the gas-to-particle condensation, but also reveal some important information related to health hazards. First, BaPE was mainly concentrated on the smallest particle, which suggest that small particles may significantly contribute to the genotoxicity of aerosol samples compared to the total particulate matter. Second, the high molecular weight PAHs such as benzo[a]pyrene were primarily associated with the fine particles. Thus, these compounds are not readily removed by atmospheric deposition. The long-period exposure of these compounds for humans living and working in the urban area studied is expected. That is, these fine aerosols will enhance the adverse effect on human health.

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