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Distribution of particulate- and vapor-phase *n*-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are becoming a major component of atmospheric toxic pollutants (ATPs) in Guangzhou city, China. Studies showed that ATPs may have adverse health effect in urban area. An investigation on particulate- and vapor-phase distribution of *n*-alkanes and PAHs in urban atmosphere has been conducted. In LiWan district, 24 h sampling for three consecutive days was performed in April and July 2001 at ground level. For comparison, samples were also collected on a nine-story building, ca. 25 m above ground level. The ambient concentrations of $\sum n$ -alkanes and \sum PAHs, compositional variations including molecular diagnostic ratios, natural biogenic and anthropogenic sources, as well as phase distributions of *n*-alkanes and PAHs are discussed. In addition, there are discernible differences with height, in terms of concentration and, to a lesser extent, in profiles of the compounds investigated.

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1. Introduction

Atmospheric transport and subsequent wet and dry deposition are important pathway for the movement of contaminants to terrestrial and aquatic systems where bioaccumulation and entry into the human food chain through vegetation, fish, and animal products occur (Lee and Jones, 1999; Nielsen et al., 1996). It was estimated that wet and dry deposition supplied 58–89% of polychlorinated biphenyls (PCBs) and 80–96% of benzo[a]pyrene inputs to Great Waters (US EPA, 1994). The transport, deposition, and chemical transformations

of semi-volatile organic compounds are extensively controlled by their gas/particle-phase partitioning (Bidleman, 1988).

Organic compounds in air are produced from man-made activities and from natural sources (Rogge et al., 1993a, b, 1998). Anthropogenic sources of *n*-alkanes typically include the combustion of fossil fuels, wood and agricultural debris or leaves. Biogenic sources include particles shed from the epicuticular waxes of vascular plants and from direct suspension of pollen, micro-organisms and insects (Simoneit et al., 1977). Concern over their known carcinogenic and mutagenic properties of polycyclic aromatic hydrocarbons (PAHs) has led to efforts to understand their formation and atmospheric chemistry (Bjørseth and Ramdahl, 1985; Fraser et al., 1998; Yassaa et al., 2001a, b). PAHs are widespread harmful compounds generated by different

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sources such as incomplete combustion of fossil fuels and natural combustion such as forest fires and volcanic eruption, but for the most part from emissions of anthropogenic activities such as wood and coal burning, automobile exhaust, heat and power generation. Molecular marker approach and a variety of receptor models have been widely applied to source reconciliation of contaminants in environment (Gogou et al., 1996; Kavouras et al., 1999).

Guangzhou city, with an area of 7434 km² and a population over 6.4 million, is the economic and culture center of Guangdong province (with an area of 178,000 km² and a population of approximately 70.5 million inhabitants). During the past two decades, explosive increases in industrial and agricultural productivity, especially the increase of motor vehicles have led to serious concerns about environment pollution and the utilization of natural resource. In 1991, there were 142,684 motorcycle and 216,237 motor vehicles in Guangzhou. By 1997, the number increased to 222,889 and 362,034 for motorcycle and motor vehicles, respectively (Lin and Lu, 1998). LiWan district is located in the west of Guangzhou city. The location is an old town area and known to have heavy emissions from traffic, industrial activities, and coal utilization for power generation. Dirty fogs are often observed. The inhabitants experience a considerable increase of adverse health effect. Therefore, it is not surprising that the incident of lung carcinogen in the region is the highest in the Guangzhou city. Our preliminary study indicated that the atmosphere in this region contained large amount of carcinogenic and mutagenic PAHs and the concentration of benzo[a]pyrene in particles was considerably high up to 21.7 ng/m³, which was almost 10 times as high as the concentration in Los Angeles atmosphere in 1970s (Cheng et al., 1996). The objective of this work was to compare the concentrations and particle/gas distributions of *n*-alkanes and PAHs from different heights above ground and to identify

the sources of *n*-alkanes and PAHs. Molecular diagnostic ratios, including the carbon preference index (CPI), were used for the reconciliation of compound sources.

2. Experimental section

2.1. Sample collection

The collection site is located in a moderately built-up area of LiWan district with scattered residual houses, schools, heavy traffic, and commercial shops. The samples were collected from the same location within LiWan district with different elevations. One group of samples was collected at ground level from 12 to 18 April and 12 to 14 July 2001 (sample name: LW-G), and another group of samples was collected at 25 m height above ground level from 9 to 11 July 2001 (sample name: LW-H). For LW-G, the samplers were installed at ground level near a road with rushing traffic while for LW-H, the sampling was performed on top of a nine-story building, ca. 25 m above ground level. A total of nine samples were analyzed for this study. Table 1 provides the general view of sampling.

A high-volume air sampler equipped with collecting samples at the flow rates 0.4–0.6 m³/min (Tianhong Intelligent Instrument Plant of Wuhan, China). Particulate-associated and gaseous contaminants were isolated from the atmosphere by drawing air through a Whatman glass fiber filter (GFF, 20.3 cm × 25.4 cm) and one-and-a-half polyurethane foam plug (PUF, 5 cm × 6.25 cm), connected in series, for about 24 h. The back half foam plug served as an indicator of breakthrough of vapor-phase compounds through the front plug. The GFFs were combusted at 450°C for 12 h and stored in aluminum foil packages until used. The PUFs were pre-extracted in dichloromethane (DCM) for 72 h, dried under vacuum

Table 1
Sampling and meteorological condition

Sample name	Sampling date	Elevation (m)	Ambient temperature (°C)	Predominant wind direction	Weather and traffic
LW-G	4/12	1.5	11–23	North	Fair, adjacent to major road, heavy traffic
LW-G	4/16	1.5	20–27	Not available	Poor, haze, adjacent to major road, heavy traffic
LW-G	4/18	1.5	22–27	Not available	Poor, haze, adjacent to major road, heavy traffic
LW-H	7/09	25	26–34	Southeast	Cloudy, natural vegetation, vehicular traffic
LW-H	7/10	25	26–35	Southeast	Cloudy, natural vegetation, vehicular traffic
LW-H	7/11	25	27–36	Southeast	Cloudy, natural vegetation, vehicular traffic
LW-G	7/12	1.5	28–35	Southeast	Poor, haze, adjacent to major road, heavy traffic
LW-G	7/13	1.5	24–29	Southeast	Poor, haze, adjacent to major road, heavy traffic
LW-G	7/14	1.5	26–32	Southeast	Poor, haze, adjacent to major road, heavy traffic

condition, placed in glass jars, and stored in plastic bags in a freezer.

After collection, foam plugs were stored in glass jars with aluminum foil-lined lids in a freezer. Filters were wrapped in baked aluminum foil. The concentrations of total suspended particulate (TSP) were determined by weighing the filters before and after exposure.

2.2. Analytical procedure

Sixteen PAHs (16 compounds specified on US EPA 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. (North Kingston, RI, USA). 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. All PUF samples were extracted for 72 h with DCM in a Soxhlet apparatus. Filters were extracted ultrasonically 3 times with 150 ml DCM. Each extraction lasted 30 min. The organic extract was combined, 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 with mass selective detection (GC-MS) using a Hewlett-Packard (HP)-6890 equipped with a 50 m HP-5 capillary column coupled to a HP-5972 mass spectrometer 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 $3^\circ\text{C}/\text{min}$, 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 and m/z 85 were used for quantification of PAHs and *n*-alkanes, respectively.

2.3. 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. The major contaminants observed were primarily residual phthalate esters, trace of *n*-alkanes ranging from C₁₈ to C₂₆, with no carbon number predominance. 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. Because the recovery of naphthalene was very low, the result of naphthalene was not concluded in this study. Compound sampling breakthrough is not a problem at this study. Typically, the backup PUF contained $<25\%$ of the total vapor phase component, with greater penetration to the second plug observed for the lighter compounds, as expected.

3. Results and discussion

3.1. *n*-Alkanes

The concentrations for *n*-alkanes ranging from C₁₂ to C₃₅ are listed in Table 2. The content of $\sum n$ -alkanes varied between 150.7 and 1457.7 ng/m³ with the lighter congeners (e.g. C₁₉–C₂₄) making major contributions to the total. Broad seasonal variations in *n*-alkane concentrations including the vapor and particulate phase were noted during the study, corresponding to seasonal temperature changes, with April concentrations tending to be higher than July ones. Particulate-phase *n*-alkanes accounted for 39.3–50.3% of the total (Table 2). This ratio increased during April. In addition, the variation of alkanes concentrations in different sampling heights is significant. The level in the samples taken near ground level (LW-G) was twice as high as the level in the samples taken at 25 m height (LW-H).

Typical distributions for *n*-alkanes in LiWan atmosphere are shown in Fig. 1(a). It can be seen that the vapor–particulate partitioning differs between individual congener. The lower molecular weight compounds generally had a greater vapor-phase component, while the higher molecular weight and less volatile compounds exhibited greater association with the particulate phase. Concentrations of $<C_{23}$ *n*-alkanes in PUF samples were higher than in the TSP samples. The opposite was true

Table 2
Average concentrations of *n*-alkanes identified and molecular diagnostic ratios

<i>n</i> -Alkanes	Diagnostic ion (<i>m/z</i>)	April (LW-G) (ng/m ³)	July (LW-G) (ng/m ³)	July (LW-H) (ng/m ³)
C ₁₂	85/170	0.40	2.75	3.24
C ₁₃	85/184	0.51	2.19	3.26
C ₁₄	85/198	1.44	2.55	3.03
C ₁₅	85/212	2.14	3.43	2.53
C ₁₆	85/226	8.25	5.52	3.31
C ₁₇	85/240	23.73	6.19	2.91
C ₁₈	85/254	62.00	10.04	4.07
C ₁₉	85/268	149.28	18.23	5.67
C ₂₀	85/282	226.10	32.57	7.98
C ₂₁	85/296	216.23	50.67	13.16
C ₂₂	85/310	168.07	52.92	16.73
C ₂₃	85/324	117.97	44.13	15.78
C ₂₄	85/338	90.41	30.51	11.03
C ₂₅	85/352	78.03	24.93	10.69
C ₂₆	85/366	54.43	17.05	8.92
C ₂₇	85/380	42.97	12.06	8.63
C ₂₈	85/394	32.26	7.87	6.38
C ₂₉	85/408	38.37	8.01	8.11
C ₃₀	85/422	25.55	4.11	4.03
C ₃₁	85/436	44.05	5.28	5.66
C ₃₂	85/450	15.89	1.39	1.72
C ₃₃	85/464	23.79	1.41	2.25
C ₃₄	85	19.36	0.91	0.92
C ₃₅	85	16.45	0.71	0.68
∑alkanes		1457.7	345.4	150.7
C _p /∑alkanes ^a		50.3	39.3	44.3
Molecular diagnostic ratios		Range (mean)		
CPI ₁ (C ₁₂ –C ₃₅) ^b		1.03–1.16 (1.08)		
CPI ₂ (C ₁₂ –C ₂₅)		1.03–1.13 (1.08)		
CPI ₃ (C ₂₅ –C ₃₅)		0.77–1.18 (0.98)		
U:R ^c	(PUF)	3.10–7.30 (5.29)		
	(TSP)	7.35–14.47 (10.65)		
%Wax ^d	(LW-G)	1.05–4.63 (2.59)		
	(LW-H)	2.35–7.54 (5.09)		

^a C_p, the concentration of *n*-alkanes in particulate phase (TSP).

^b Whole range for *n*-alkanes: CPI₁ = ∑C₁₃–C₃₅/∑C₁₂–C₃₄; petrogenic *n*-alkanes: CPI₂ = ∑C₁₁–C₂₅/∑C₁₀–C₂₄; biogenic *n*-alkanes: CPI₃ = ∑C₂₅–C₃₅/∑C₂₄–C₃₄.

^c U:R are determined from the gas chromatogram by the area of unresolved material above the background divided by the sum of the GC area of resolved *n*-alkanes and other major components.

^d %Wax C_n = ∑(C_n – 0.5(C_{n-1} + C_{n+1}))/∑alkanes × 100%, negative values of C_n were taken as zero.

for higher molecular weight compounds. The compositional differences in various vapor-phase samples were only minor, which were characterized by strong peaks of C₁₈–C₂₅. Small compositional differences were found in the particulate samples taken from different height. The strongest peaks in the chromatograms of particulate *n*-alkanes were C₂₃–C₂₇ for LW-G and C₂₇–C₃₁ for LW-H (Fig. 2). The relative distribution of *n*-alkanes between homologues of differing molecular weight provides some insight into the likely sources that contribute to an ambient sample. This seems to indicate

that fossil fuel sources are responsible for the presence of hydrocarbons into the atmosphere near the ground level, while a big contribution of high plants should lead to predominance of *n*-C₂₅–*n*-C₃₃ congeners with odd–even predominance. The different patterns indicate an enhanced input of vascular plant to the particulate *n*-alkanes in the samples taken at 25 m height (Fig. 2).

Unresolved complex mixture (UCM) can be used as an approximated measure of the level of contamination by petroleum residues. Vapor- and particulate-phase samples in LiWan exhibit a UCM with a maximum at

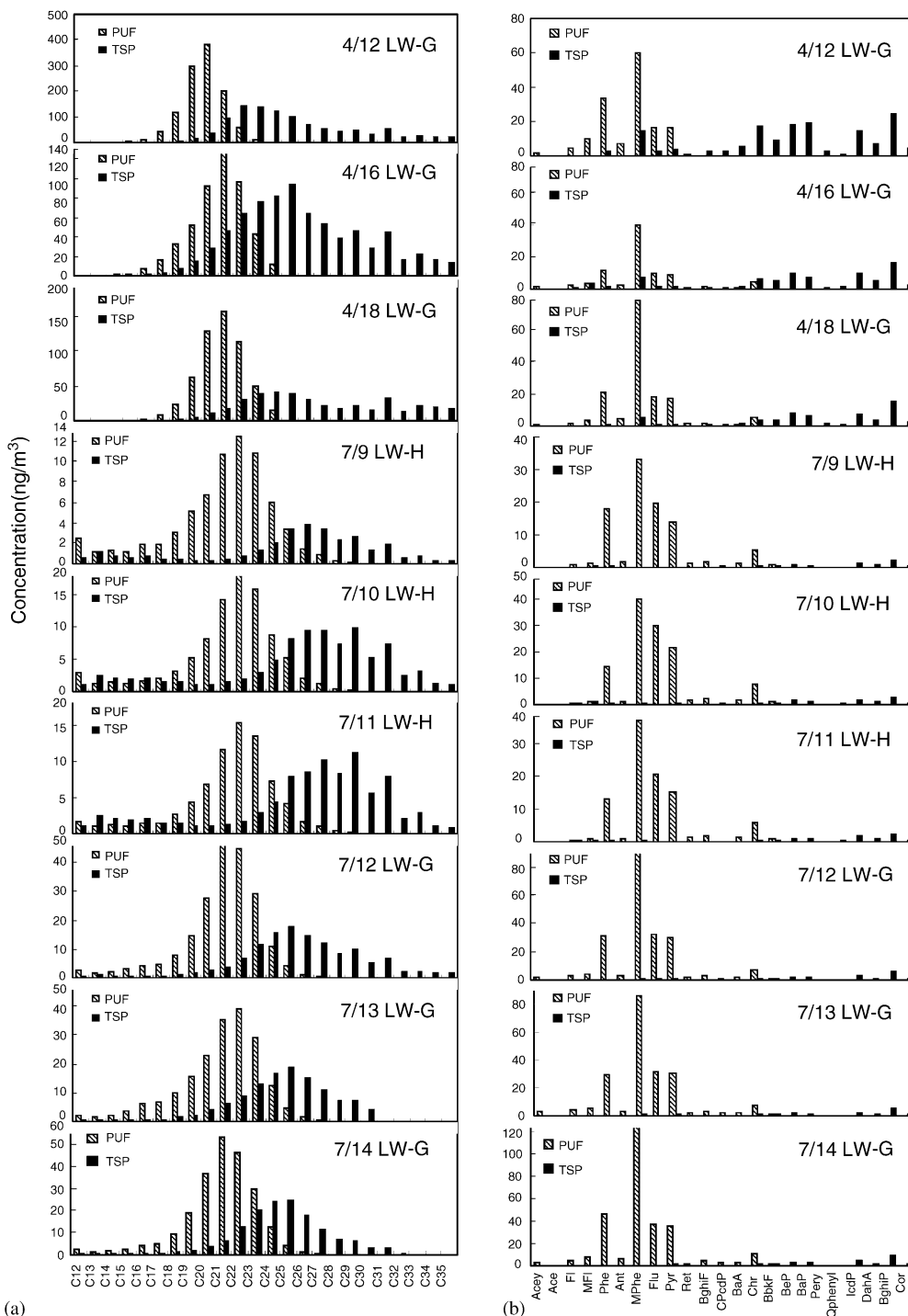


Fig. 1. Distribution of *n*-alkanes (a) and selected PAHs (b) in the vapor (PUF) and particulate phase (TSP) (for the abbreviation see Table 3).

C₂₂–C₂₃ and C₂₈–C₃₀, respectively (Fig. 2). The samples taken at ground level in this study have a broad UCM, which is interpreted to be derived from engine emissions,

lubricants and fuels (Simoneit et al., 1991). A less-abundant UCM is observed for the samples taken from 25m above ground level, indicating a minor

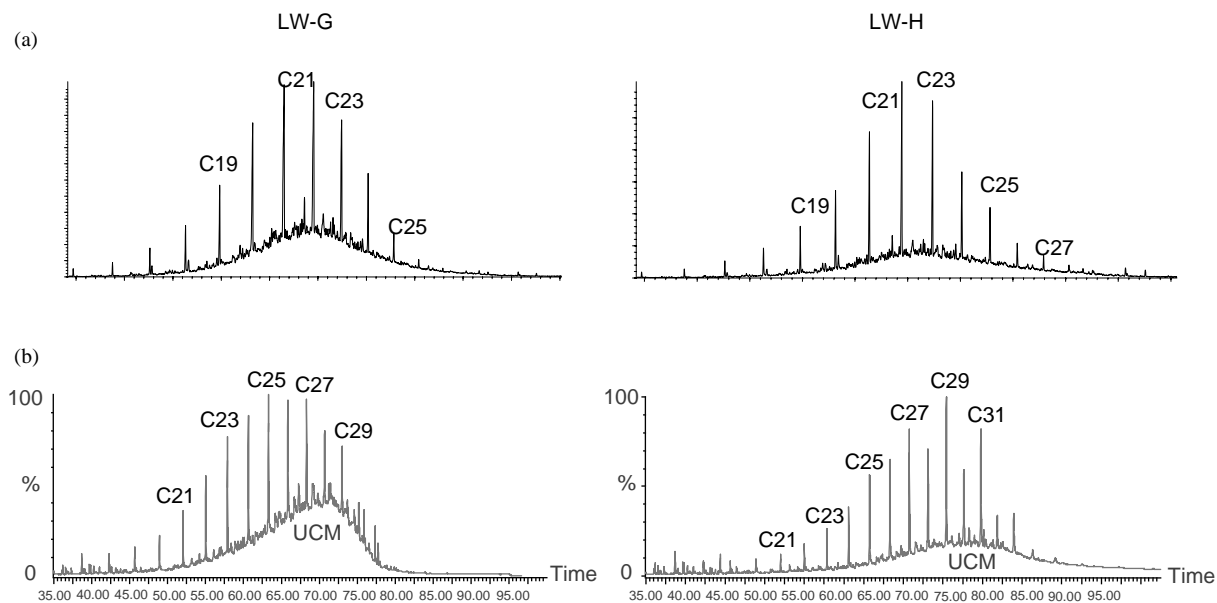


Fig. 2. TIC chromatogram of the aliphatic fraction for LW-G (left) and LW-H (right): (a) PUF and (b) TSP.

contamination from vehicular emissions and industrial sources. Another diagnostic parameter that can be used to assess the magnitude of fossil fuel contributions to atmospheric aerosols is the ratio of the unresolved to resolved hydrocarbon compounds ($U:R$). Wood and coal combustion exhibit UCM/n -alkanes ratio values from 2.3 to 3.9, whereas vehicular emissions result values higher than 4.0 (Kavouras et al., 2001). $U:R$ values for rural, mixed and urban western United States samples are 0.2–4, 1.4–3.4 and 0.9–25, respectively (Azevedo et al., 1999). $U:R$ observed from LiWan vapor and particulate phase were in the range of 3.10–7.30 and 7.35–14.47, respectively (Table 2), which imply that the major sources of n -alkanes can be attributed to fossil fuel combustion in this typical urban region.

CPI of n -alkanes fractions is usually calculated with the objective of discriminating between biogenic and fossil fuel contributions (Rogge et al., 1993b; Fang et al., 1999). The aerosol samples CPI₁ values for the whole range of n -alkanes (C_{12} – C_{35}), CPI₂ values for petrogenic n -alkanes (C_{12} – C_{24}) for petrogenic hydrocarbons and CPI₃ values for biogenic- n -alkanes, as shown in Table 2, were close to those observed for other urban areas (Kavouras et al., 1998, 1999). The CPI values near unity signify the importance of petroleum and diesel residues and gasoline emissions and the minor contribution of n -alkanes emitted directly from epicuticular waxes. The characteristics can also be verified by the wax values.

To determine the relative importance of biogenic and petrogenic sources, the contribution of wax terrestrial

n -alkanes (wax) was estimated. The contribution of biogenic wax n -alkanes to the total n -alkane concentrations in the LiWan district was 1.05–7.54%, indicating that the emissions from epicuticular waxes of terrestrial plants had a low input to ambient organic aerosol concentration (Kavouras et al., 1999). The comparison of values in Table 2 shows the %wax C_n of LW-H samples to be 5.09% higher than those of LW-G (2.59%), in other words, a greater percentage of biogenic hydrocarbons was observed at 25 m height than at 1.5 m above ground level.

3.2. Polycyclic aromatic hydrocarbons

Total non-alkylated PAHs and methyl-alkylated PAHs were determined in the samples (Table 3). A characteristic chromatogram of PAHs collected on PUF and TSP is presented in Fig. 3. Average \sum PAH concentrations were in the range from 134.4 to 298.5 ng/m³. Comparing the investigation result with other data, the total concentration of PAHs at Manchester has been found to be in the general range 20–164 ng/m³ (Coleman et al., 1997). The average \sum PAH concentrations in London, Esthwaite Water and Castleshwa were 165, 40, 22 ng/m³, respectively (Gardner et al., 1995). Simcik et al. (1997) reported that the total concentration ranged from 48.3 to 538 ng/m³ in Chicago. At remote sites the levels are 1–2 orders of magnitude lower within the range of 0.1–10 ng/m³ (Halsall et al., 1997).

Table 3
Average concentrations of PAHs identified and molecular diagnostic ratios

PAH compounds	Diagnostic ion (<i>m/z</i>)	April LW-G (ng/m ³)	July LW-G (ng/m ³)	July LW-H (ng/m ³)
Acenaphthylene (Acey) ^a	152	1.74	2.73	0.18
Acenaphthene (Ace)	154	0.25	0.23	0.05
Fluorene (Fl)	166	3.34	3.67	1.10
Methylfluorene (MFl)	180	6.95	5.97	1.60
Dimethylfluorene	194	13.59	12.46	3.71
Phenanthrene (Phe)	178	23.92	35.92	15.33
Anthracene (Ant)	178	5.08	4.50	1.31
Methylphenanthrene (Mphe)	192	30.03	47.03	15.80
Dimethylphenanthrene	206	24.94	39.14	13.99
Trimethylphenanthrene	220	13.07	17.21	7.32
Fluoranthene (Flu)	202	16.49	34.02	23.36
Pyrene(Pyr)	202	16.53	32.97	17.02
Methylpyrene	216	6.08	11.06	6.00
Dimethylpyrene	230	1.72	4.44	1.97
Terphenyl	230	0.45	0.51	0.50
Retene (Ret)	219/234	1.60	1.68	1.40
Benzo[ghi]fluoranthene (BghiF)	226	2.84	3.92	1.98
Cyclopenta[cd]pyrene (CPcdP)	226	1.72	2.19	0.27
Benzo[c]phenanthrene	228	0.44	0.69	0.45
Benzo[a]anthracene (BaA)	228	3.91	2.50	1.54
Chrysene/ triphenylene (Chr)	228	12.41	9.73	6.76
Methylchrysene	242	2.06	2.23	1.34
Benzo[b+k]fluoranthene (BbkF)	252	6.01	2.35	1.59
Benzo[a]fluoranthene	252	0.54	0.08	0.03
Benzo[e]pyrene (BeP)	252	12.13	2.98	1.49
Benzo[a]pyrene (BaP)	252	10.71	1.81	0.79
Perylene (Pery)	252	1.90	0.32	0.16
Quaterphenyl (Qphenyl)	306	1.13	0.36	0.26
Indeno[7,1,2,3-cdef]chrysene	276	3.93	1.15	0.60
Indeno[1,2,3-cd]pyrene(IcdP)	276	10.70	3.28	1.66
Dibenzo[ah]anthracene (DahA)	278	5.52	1.50	1.00
Picene	278	0.90	1.05	0.53
Benzo[b]chrysene	278	0.66	0.19	0.21
Benzo[ghi]perylene (BghiP)	276	18.71	6.52	2.32
Anthanthrene	276	1.52	0.40	0.17
Coronene (Cor)	300	3.46	1.24	0.30
Dibenzopyrene	302	1.45	0.50	0.30
∑PAHs		268.4	298.5	134.4
Diagnostic ratios	Range (mean)	Diagnostic ratios	Range (mean)	
Phe/Phe + Ant	0.82–0.93 (0.88)	IcdP/IcdP + BghiP	0.32–0.42 (0.37)	
BaA/BaA + Chr	0.17–0.25 (0.21)	BghiP/BeP	1.35–2.30 (1.80)	
Flu/Flu + Pyr	0.48–0.59 (0.53)	CPAH ^b /∑PAHs	0.31–0.46 (0.38)	
BeP/BeP + BaP	0.49–0.69 (0.61)	BaPE ^c	1.38–25.44(6.86)	

^a Abbreviations are given in bracket.

^b CPAH: total concentration of nine CPAHs (including fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[ghi]perylene, benzo[e]pyrene, benzo[a]pyrene, indeno[cd]pyrene and benzo[ghi]perylene).

^c BaPE = BaA × 0.06 + BF × 0.07 + BaP + DahA × 0.6 + IcdP × 0.08 (Yassaa et al., 2001b).

The mass distribution in air (including vapor and particulate phase) was dominated by phenanthrene, methylphenanthrene, fluoranthene, pyrene, chrysene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene which accounted for 69% of the total at LW-G and 77% at LW-H. Little change was observed in the total PAH

concentrations between April and July (Table 3). From Fig. 1(b), however, it can be seen that the higher concentration of low molecular weight compounds such as phenanthrene, fluoranthene and pyrene occurred in July PUF samples, exhibiting a positive correlation with air temperature, while higher molecular weight such as

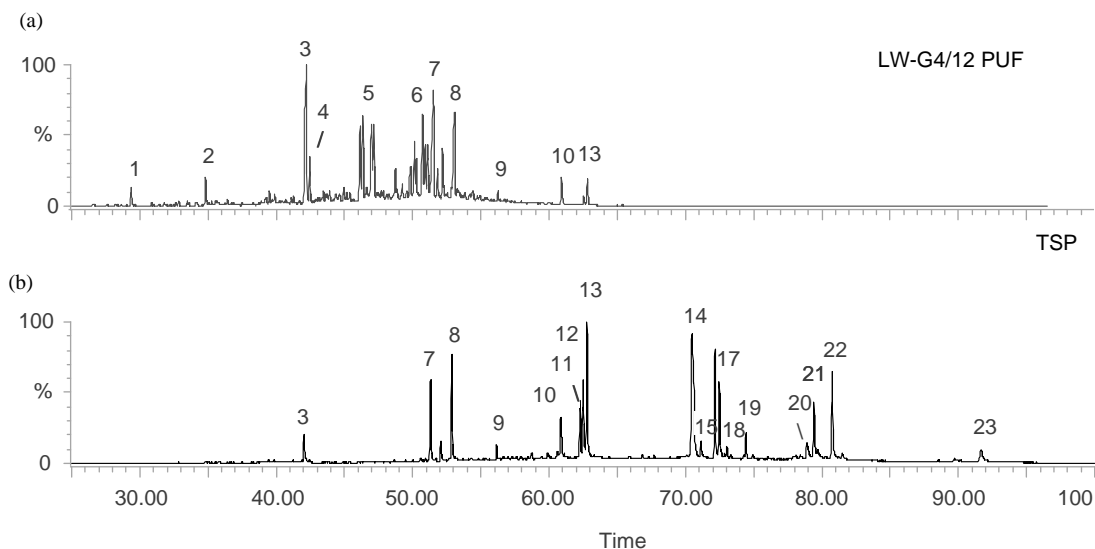


Fig. 3. Example of summed mass fragmentograms for selected PAH in LiWan air: (a) PUF: $\sum m/z$: 152, 154, 166, 178, 192, 206, 202, 226, 228, and 234; (b) TSP: $\sum m/z$: 152, 154, 166, 178, 202, 226, 228, 234, 252, 276, 278, 300, and 306. Peak number: 1, acenaphthylene; 2, fluorene; 3, phenanthrene; 4, anthracene; 5, methylphenanthrene; 6, dimethylphenanthrene; 7, fluoranthene; 8, pyrene; 9, retene; 10, benzo[ghi]fluoranthene; 11, cyclopentapyrene; 12, benzo[a]anthracene; 13, chrysene/triphenylene; 14, benzo[b+k]fluoranthene; 15, benzo[a]fluoranthene; 16, benzo[e]pyrene; 17, benzo[a]pyrene; 18, perylene; 19, quaterphenyl; 20, indeno[7,1,2,3-cdef]chrysene; 21, indeno[1,2,3-cd]pyrene; 22, benzo[ghi]perylene; and 23, coronene.

benzofluoranthene and benzopyrene were negatively correlated. Higher concentration in particulate phase was present in April. This is consistent with other results (Lee and Jones, 1999). The particle phase contribution ranged from 9.4% of the total PAHs in July to 44.8% in April. Furthermore, comparing the PAH concentrations with height, it was found that PAHs measured at 25 m (LW-H) decreased to 30–50% of the PAHs measured at ground level (LW-G) which is consistent with the results of Lohmann et al. (2000).

PAHs belong to the semi-volatile organic contaminant class and occur in both gaseous and particulate phases in the atmosphere. The vapor–particle partition exhibits a strong dependence on molecular weight. Low molecular weight PAHs tend to have a higher concentration in the vapor phase while high molecular weight ones are often associated with the particulates. PAH profiles in gas and particle phases are shown in Fig. 1(b). The vapor-phase PAH chromatograms are characterized by strong peaks of congeners with 3–4 rings, of which fluorene, phenanthrene and their methylated derivatives, fluoranthene and pyrene are the dominant PAH species in the gas phase, while higher molecular weight (> 252) PAHs species were not detected in the vapor phase due to their low volatility. Higher molecular weight PAHs, from chrysene to coronene except perylene, dominated PAHs in the particulate phase with benzo(ghi)perylene as the maxima.

It has been suggested that it would be possible to use PAHs to assist in distinguishing emissions (Harrison

et al., 1996; Yassaa et al., 2001a). Cyclopentapyrene (usually regarded as marker compound for gasoline-fuelled cars) and retene (1-methyl-7-isopropylphenanthrene, thought to be the low-temperature product from the combustion of coniferous wood) were also present in the vapor and particulate phase (Simoneit et al., 1991; Yassaa et al., 2001b). Their higher concentrations in PUF samples suggest that the emissions from gasoline-fuelled cars and wood combustion focus on the vapor phase. Benzo[ghi]perylene and coronene could potentially be used as vehicular emission tracers for petrol-powered vehicles. Their abundant amounts in the aerosols show that vehicle emission may be the major sources. Quaterphenyl is detected in minor amount in the aerosol samples, which is also present in the combustion product of waste and polymer (Hawley-Fedder et al., 1984; Karasek and Tong, 1985). This compound is not found in aerosols from petroleum source (Rogge et al., 1993a), indicating that other sources may have existed in the LiWan district. Direct sampling and analysis of waste and polymer smoke in this area is needed to further quantify this source component.

Table 3 provides information on diagnostic ratios for PAHs, such as BaA/BaA + Chr, BeP/BeP + BaP, Flu/Flu + Pyr, and IcdP/BghiP + IcdP, which can be used to investigate their origin or as an indication of the aging of air samples (Cotham and Bidleman, 1995; Lohmann et al., 2000). Because only TSP may result in a significant underestimation of the contribution of anthropogenic emissions, these ratios were determined by the total

concentration including the vapor and particulate phase. In particular, the BaA/BaA + Chr values were determined to be 0.17–0.25, which are comparable to the values reported for crude oil emission (0.16 ± 0.08) (Sicre et al., 1987). BeP/BeP + BaP ratio may be affected by the strong reactivity in the atmosphere since BaP is easily decomposed by light and oxidants. Most of the fresh exhausts have similar contents of benzo(e)pyrene and benzo(a)pyrene (Grimmer et al., 1983), thus the above ratio can be regarded as an index of the aging of particles. The mean values measured in this study reached 0.49–0.69, which means that new emission of PAHs was concurrent. The mean Flu/Flu + Pyr ratio was 0.53, which is similar to that for vehicular emissions and especially catalytic automobiles emissions (Rogge et al., 1993a). The literature reported values for IcdP/BghiP + IcdP are 0.18, 0.37 and 0.56, for cars, diesel vehicles, and coal combustion, respectively (Grimmer et al., 1983). The mean ratio in this study was 0.37, which is comparable to that for diesel emissions. The BghiP/BeP ratio was used as an indicator for traffic, with higher ratios indicating a higher traffic contribution (Nielsen et al., 1996). The parameter values were compared with those reported in the literature (Rogge et al., 1993a). Overall, our results suggest that the major source of organic compound in the air of LiWan during the study period was fossil fuel combustion from automobiles, with a substantial contribution from unburned petroleum residues (Kavouras et al., 1999). The ratios of total concentration of nine combustion PAHs (CPAHs) (fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) to the total concentration of PAH (\sum PAHs) were determined by Rogge et al. (1993a) for non-catalyst (0.41), and catalyst-equipped (0.51) automobiles and for heavy-duty diesel trucks (0.3). The ratio was calculated to be 0.31–0.46 in this study, which is close to the value for non-catalyst-equipped automobiles. In Guangzhou city, most of the old automobiles produced before 2000 were not equipped with the catalyst converter, but new automobiles are equipped with the converters.

Benzo(a)pyrene-equivalent carcinogenic power (BaPE) is index that has been introduced instead of the sole benzo(a)pyrene since the latter can be decomposed in “reactive” air (Yassaa et al., 2001b). The BaPE values in this study ranged from 1.38 to 25.44, which was higher than the sole benzo(a)pyrene concentration. The values were higher than those in downtown Algiers (Yassaa et al., 2001b).

4. Conclusions

\sum n-alkanes concentration had a wide range from 150.7 to 1457.7 ng/m³. Total non-alkylated PAHs and

methyl-alkylated PAHs were determined in the samples. Average concentrations of \sum PAHs including 37 PAH compounds identified both in particulate- and vapor-phase samples were in the range from 134.4 to 298.5 ng/m³ in the LiWan district. The aerosol samples from 25 m above ground level had significant overall lower concentrations of n-alkanes and PAHs, compared to the samples near ground level. The contributions of biogenic wax n-alkanes to the total n-alkanes were measured to be 1.05–7.54%, showing significant difference between samples taken at near ground (2.59%) and at 25 m height (5.09%). The variations may be due to dilution of aerosols generated near ground level and due to slight increase of biogenic input as height increases. Variation of particulate- and vapor-phase distribution of n-alkanes and PAHs were evidenced and found to be in accordance with similar investigations reported in the literature. The lower molecular weight compounds such as n-alkanes of <C₂₃ and two-ring and three-ring PAHs generally had a greater vapor-phase component, while the higher molecular weight exhibited greater association with the particulate phase. Because of the limited samples, the source of organic compounds in this area still need more evidence. In addition, the temperature and wind directions have an effect on the distribution of organic compounds in different phase. All of them are needed to be done in the near future.

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