Particle Size Distribution and Gas-Particle Partition of Polycyclic Aromatic Hydrocarbons in Helsinki Urban Area

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Abstract. Ambient concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in Helsinki (Finland). Particle mass size distributions were obtained with a cascade impactor (12 stages) with glass fibre filters as substrates. Simultaneously with the impactor measurements, particulate and gaseous PAHs were collected on a quartz filter and XAD-2 adsorbent, respectively, for evaluation of gas-partition coefficients. Samples were analysed for PAHs by on-line coupled supercritical fluid extraction – liquid chromatography – gas chromatography – mass spectrometry. The impactor results showed that most of the PAHs in Helsinki urban area were concentrated in fine particles (<2.5 μm diameter) with unimode peak at about 1 μm. The results were comparable with the number distribution measured with a differential mobility particle sizer. Total amounts of PAHs (gas + particle) varied from 15 (acenaphthylene) to 1990 (fluorene) pg/m^3. The PAHs lighter than 202 amu (pyrene and fluoranthene) were exclusively in gas phase, whereas those heavier than 202 amu were mostly associated with particles. A plot of the partition coefficients (logKp) versus the temperature dependent sub-cooled vapour pressures (logp$_L^0$) showed a gradient of –0.66, which deviated from equilibrium state (gradient $= –1$).

1. Introduction

Due to the emission of harmful gases and particles, air pollution is a serious environmental problem in many urban areas. Polycyclic aromatic hydrocarbons (PAHs) are classified as pollutants because some of them are carcinogenic and mutagenic. PAHs are formed during incomplete combustion of organic materials, and their sources in cities are exclusively anthropogenic. Because of their many sources, PAHs are present almost everywhere.

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PAHs are categorised as semivolatile compounds, found both in the gas phase and in aerosols. Factors such as their vapour pressures, surface area of particles, organic content of particles and meteorological conditions influence the gas-particle partition of PAHs. It is generally known that when the PAHs are present in particles, they tend to be accumulated in fine particles with diameter smaller than 2.5 μm (Cecinato *et al.*, 1999; Sheu *et al.*, 1997). These small particles can penetrate deep into the respiratory system, where there is no protective mucus layer (Finlayson-Pitts and Pitts, 1999). Direct intake of particulate PAHs by inhalation is thus a serious health risk (Tsai *et al.*, 2001).

The World Health Organisation (WHO) has suggested 8.7×10^{-2} $(\mu g/m^3)^{-1}$ as the unit risk for lifetime benzo(a)pyrene (BaP) exposure. The figure was adopted from an epidemiological study on lung cancer risk of coke oven workers (WHO, 2000). The target ambient BaP concentrations in European Union Member States vary from 0.1 to 1.3 ng/m^3 (EC, 2001). Setting of target values for PAHs is complicated by the uncertainty in the collected data and by the insufficient monitoring of PAHs. Determination of atmospheric PAHs is time consuming and often expensive, so that routine analysis is not attractive. A common procedure includes sampling of particles and/or gases with filters or polyurethane foam, extraction of the analytes from the sample matrix by Soxhlet or ultrasonic extraction, clean-up of the extracts with solid phase or other extraction and final separation by GC-MS or HPLC (U.S. EPA, 1997; Didyk *et al.*, 2000; Kaupp and McLachlan, 1999; Harrison *et al.*, 1996; Lim *et al.*, 1999; Pio *et al.*, 2001).

Unfortunately, the preparation of atmospheric samples is usually manual and may generate errors in the chemical analysis. To minimise such errors, we constructed an on-line supercritical fluid extraction – liquid chromatography – gas chromatography – mass spectrometry (SFE-LC-GS-MS) system (Shimmo *et al.*, 2001). In SFE, the analytes are extracted with supercritical CO_2, an effective extraction fluid that has gas-like mobility and liquid-like dissolving power. One advantage of SFE is that fluid properties and thus the extraction efficiency are easily adjusted through simple change in extraction temperature and pressure. SFE tends to be faster (30–60 min) than conventional Soxhlet or ultrasonic extraction (16–24 h). And it is environmentally friendly since the consumption of organic solvents is low (Hartonen *et al.*, 1997; Chester *et al.*, 1998; Bøwadt and Hawthorne, 1995).

On-line LC-GC is particularly useful for separations of dirty environmental samples. Sample clean-up, fractionation, concentration and final separation are performed automatically in a closed system. In conventional methods, these steps are carried out manually, and they are not only time consuming but may generate errors. Unlike in conventional GC where only few μL of sample is injected, more than 1 mL can be introduced in LC-GC and all reaches the detector, increasing sensitivity and lowering the limits of the determination (Mondello *et al.*, 1999; Hyötyläinen and Riekkola, 2001).

Combination of SFE and LC-GC is still rare despite the evident benefits. The main purpose of our study was to apply to PAHs the on-line SFE-LC-GC-MS

method optimised in our previous study (Shimmo *et al.*, 2002). Atmospheric samples in Helsinki were collected with a cascade impactor, filters and XAD-2 adsorbent. Particle mass size distributions and gas-particle partitions of PAHs were investigated.

2. Experimental

2.1. SAMPLING SITE

Atmospheric sampling of PAHs was carried out on the roof of the Department of Physical Sciences, University of Helsinki (60°12′ N, 24°58′ E and 50 m above sea level) in a location where the major emission source of PAHs is traffic The sampling site is about 6 km north-east of the city centre, and about 200 m away from a busy road that feeds to a major motorway. Average weekday traffic at the entrance to the motorway for the year 2001 was 53000 vehicles. The corresponding number for heavy traffic at the same site was 5500, of which full and semi-trailers accounted for 1660.

Impactor sampling was carried out three times: 28.09.2001–08.10.2001 (Sample 1), 17.01.2002–25.01.2002 (Sample 2) and 01.02.2002–08.02.2002 (Sample 3). Temperature during sampling was +1 to +15 °C (average +10.2 °C) for Sample 1, −11 to +3 °C (average −0.7 °C) for Sample 2, and −11 to +5 °C (average +0.4 °C) for Sample 3. The air was humid during all sampling periods usually with more than 80% relative humidity and with the occasional shower. The amount of solar radiation was limited during winter owing to the high latitude of Helsinki. During the third sampling period, gases and particles were collected simultaneously onto quartz filter and XAD-2 adsorbent. At the same time, particle number size distribution was measured with a differential mobility particle sizer (DMPS). The instrument included a TSI model 3071 electrostatic classifier (EC) and TSI model 3022 condensation particle counter (CPC). Aerosol was neutralised with TSI 3077 aerosol neutraliser. The measured size range was from 7 to 400 nm with time resolution of 10 min.

2.2. IMPACTOR SAMPLING

Aerosol particles were collected with a Dekati Low Pressure Impactor (model LP1, Dekati, Tampere, Finland). The cascade impactor consisted of 12 stages with 50% cutoff size: 0.27, 0.29, 0.31, 0.42, 0.61, 0.97, 1.5, 2.4, 3.6, 5.8, 9.7, and 14.9 μm (aerodynamic diameter) in 900 mbar vacuum with the air flow rate set at 14 L/min. Uncoated 25-mm glass fibre filters (Whatman, CF/C, Maidstone, U.K.) were applied as impaction substrates (Alves *et al.*, 2000; Sugiyama *et al.*, 1999). The filters were baked at 500 °C for 12 h and kept in a clean dessicator until the sampling. After sampling, each filter was transferred to a glass vial and stored at −20 °C in dark. Two days before chemical analysis, the glass vials containing the filters were transferred to a dessicator at 4 °C in the dark for drying.

2.3. XAD-2 AND FILTER SAMPLING

Parallel to the impactor sampling of aerosols, atmospheric particles and gases were sampled. The air was drawn at 10 L/min first through a 2.5 μm cutoff cyclone, then through two 47-mm quartz filters (Whatman) that collected particles and finally through two XAD-2 resins (polystyrene-divinylbenzene, EGA-Chemie, Steinheim, Germany) for gases (Sanusi *et al.*, 1999; Buehler *et al.*, 2001).

The quartz filters were treated in the same way as the glass fibre filters used in the impactor sampling except that the weights of the filters were measured before and after sampling, after the humidity was removed in a desiccator. As discussed in the literature (U.S. EPA, 1986; Garivait, *et al.*, 1999), the XAD-2 was cleaned by Soxhlet extraction first with dichrolomethane (24 h) and then with methanol (24 h). The extraction procedure was repeated twice. The XAD-2 was then heated at 90 °C to dryness. The cleaned XAD-2 (7.5 g) was packed in a glass resin (6 cm × 1.5 cm i.d.) and kept in a clean dessicator until sampling.

2.4. ANALYTICAL METHODS

The filters and XAD-2 were analysed by on-line SFE-LC-GC-MS. The details of the instrumentation as well as the analytical procedure have been presented in previous papers (Shimmo *et al.*, 2001, 2002) and only a brief description is given here.

The analytes were extracted with supercritical CO_2 (150 °C, 400 bar, 45 min, 1.5 mL/min) and the extracts were collected in a solid-phase trap (8.0 cm × i.d. 2.0 mm) packed with 0.5 g octadecylsilane particles of 60 μm diameter (J & W Scientific, Folsom, CA). The analytes were then eluted from the solid-phase trap and transferred to the liquid chromatograph with pentane/ethyl acetate mixture (98:2, v/v). A 10 cm × 2.1 mm i.d. LUNA silica column with 5 μm particle diameter (Phenomenex, Torrance, CA) was used as LC column. When the fraction containing the analytes arrived at the UV detector, it was transferred to the gas chromatograph (HRGC 5300, Carlo Erba Instrumentation, Milano, Italy) using an on-column interface with partially concurrent solvent evaporation at 43 °C oven temperature and 1.5 bar carrier gas (He) pressure.

Operation and data acquisition of the mass spectrometer (Automass Solo, Thermoquest, Argenteuil Cedex, France) was done with Xcalibur™ software. The MS was operated in total ion current (TIC) mode from 50 to 500 amu.

A PAH mixture (Z-014G-R) containing 17 compounds in CH_2Cl_2/benzene (1:1, v/v) from AccuStandard (New Haven, CT) was used as standard for quantitative analysis. The PAH compounds are summarised in Table I. Detailed information about those compounds, such as their structures and vapour pressures, can be found in literature (Finlayson-Pitts and Pitts, 1999).

Table I. Names, abbreviations and molecular masses of PAH compounds used in this study

Compounds	Abbreviations	Molecular masses
Naphthalene	N	128
Acenaphthylene	Ay	152
Acenaphthene	Ace	154
Fluorene	Fl	166
Carbazole	Cab	167
Phenanthrene	Phe	178
Anthracene	Ant	178
Fluoranthene	Fla	202
Pyrene	Pyr	202
Benzo(a)anthracene	BaA	228
Chrysene	Chry	228
Benzo(b)fluoranthene	BbF	252
Benzo(k)fluoranthene	BkF	252
Benzo(a)pyrene	BaP	252
Indeno(1,2,3-cd)pyrene	IdP	276
Benzo(g,h,i)perylene	Bghi	276
Dibenzo(a,h)anthracene	DbA	278

3. Results and Discussion

3.1. SAMPLING

Material such as glass fibre or quartz tends to become contaminated during manufacture and storage. It is important therefore to clean the material before sampling. The filters used in this study could be baked at high temperature to remove components causing interferences for GC analysis. High temperature could not be applied in the cleaning of XAD-2, therefore, and solvents were used. No PAHs were observed in the adsorbent after the cleaning procedure. However, it was contaminated with some other compounds, from washing solvents or from the oven atmosphere.

Sampling of semivolatile compounds such as PAHs may be biased in impactor sampling owing to the evaporation of compounds in vacuum. Furthermore, humidity may increase the growth rate of aerosols in the impactor. Estimation of those biases is difficult especially when the sampling time had to be as long as one week. The sampling was, therefore, done under ambient conditions without corrections of those biases.

In ideal impactor sampling, it is assumed that all particles larger than the cutoff size stick when they strike the surface of the impaction substrate. In reality, some particles will bounce off the substrate. The degree of 'bounce off' depends on the

material of the filter used as the impaction substrate (Hinds, 1982). One effective impaction substrate is greased aluminium foil (Hillamo and Kauppinen, 1991). Unfortunately the grease can cause problems in chemical analysis with GC. We therefore decided to apply uncoated glass fibre filters.

Sampling by impactor often also suffers from time resolution, which varies with the number of substrates and the sampling flow rate. Long sampling time was necessary in this study to obtain sufficient particle mass that the amounts of PAHs were above the determination limits for each impaction substrate.

Particle sampling using quartz filters may be biased by the adsorption of gaseous compounds on the front filter or the evaporation of compounds from collected particles (Mader and Pankow, 2001a). A backup filter was therefore installed to allow correction of biases by subtraction of the concentrations of the backup filters from those of the front filters, assuming that the front and backup filters collect the same amount of gases (Turpin *et al.*, 2000; Peters *et al.*, 2000). This assumption may not be correct, however, if the sampling is of long duration or the adsorption capacity of the filters is different (Kirchstetter *et al.*, 2001).

Two XAD-2 resins were employed to estimate the breakthrough of gaseous compounds. Significant breakthrough was not observed for XAD-2 sampling.

3.2. INSTRUMENT PERFORMANCE

The great advantage of on-line SFE-LC-GC-MS is the low limits of detection. In addition, only a small amount of sample is necessary because virtually all analytes reach the detector when the extraction is coupled to LC-GC. Also, filters could be analysed without pretreatment (except drying). The limits of detection for PAHs extracted from impactor substrates varied from 0.01 to 0.02 ng, after the mass spectra with TIC were reconstructed using specific ions of PAHs (i.e., molecular mass). The linear range of the instrument was excellent for 5–200 ng ($R^2 > 0.99$). The relative standard deviations of repeated analysis ($n = 5$), calculated from the average of relative peak area (peak area of the analyte divided by peak area of the standard), ranged from 0.5% (Pyr) to 23% (Ace). Some of the PAHs with identical molecular mass were separated poorly, especially from dirty samples. In those cases, the peaks were calculated as their sum.

3.3. PARTICLE MASS DISTRIBUTION OF PAHs

Particle mass distributions of PAHs are shown in Figures 1–3. In general, concentrations of light PAHs such as Fl and the sum of Phe and Ant are small owing to the high vapour pressure. These compounds also are distributed more or less evenly in all size ranges. There is a small peak at about 1 μm and a second peak in the coarse particle size, >10 μm. As the PAHs increase in mass and their vapour pressures decrease, they become concentrated in narrower size range (Fla, Pyr and the sum of
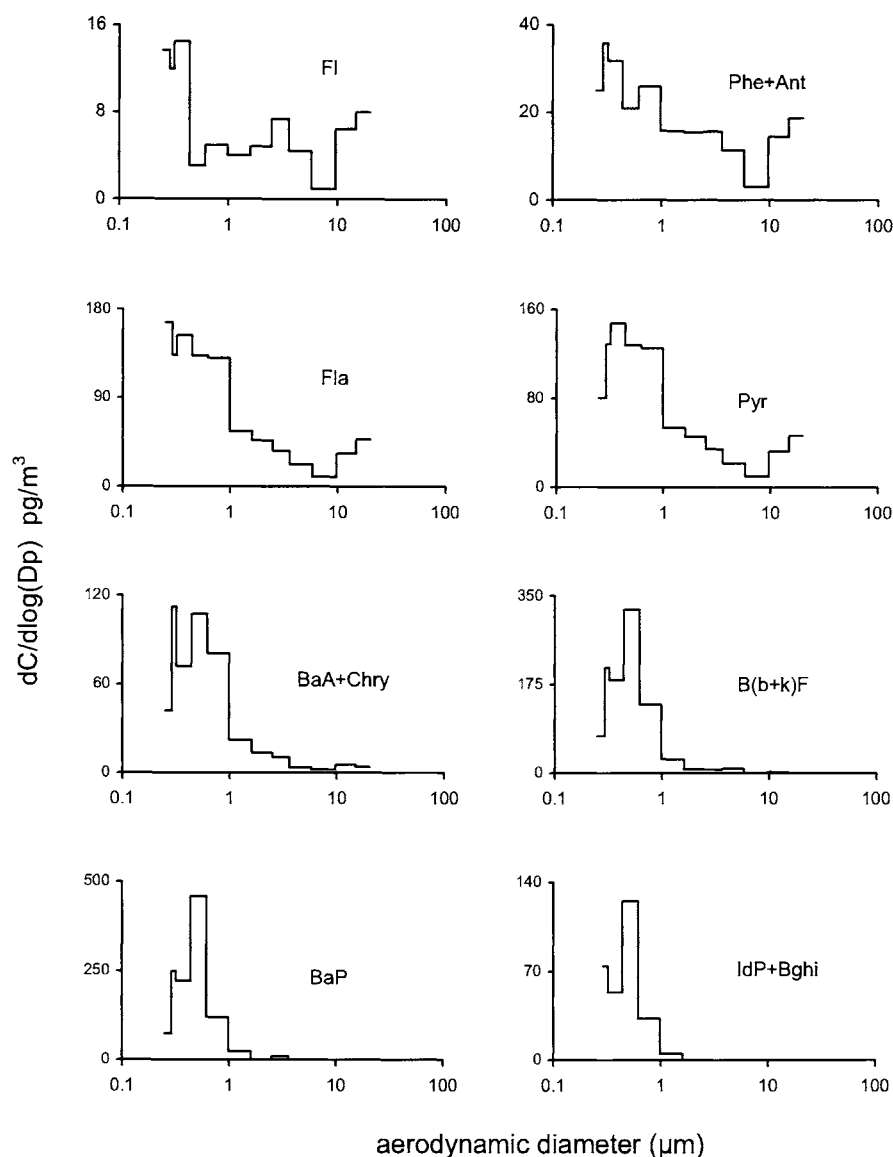
Figure 1. Mass distribution of PAH compounds for Sample 1 (28.09.2001–08.10.2001).

BaA and Chry). When the masses of PAHs exceed 252 amu, a sharp peak appears at about 1 μm.

Table II summarises the total particulate PAH concentrations and their relative amounts in particles smaller than 440 nm and 2.5 μm. For every PAH the total concentration was smaller for Sample 1 than Sample 2 and 3. This finding agrees with our previous study, which showed that PAH levels in particles are highest in winter due to the low temperature (Shimmo *et al.*, 2002). In all cases, significant

Table II. Total particulate PAHs collected by a cascade impactor (pg/m³) and the proportions of submicron (<440 nm) and fine particles (<2.5 μm)

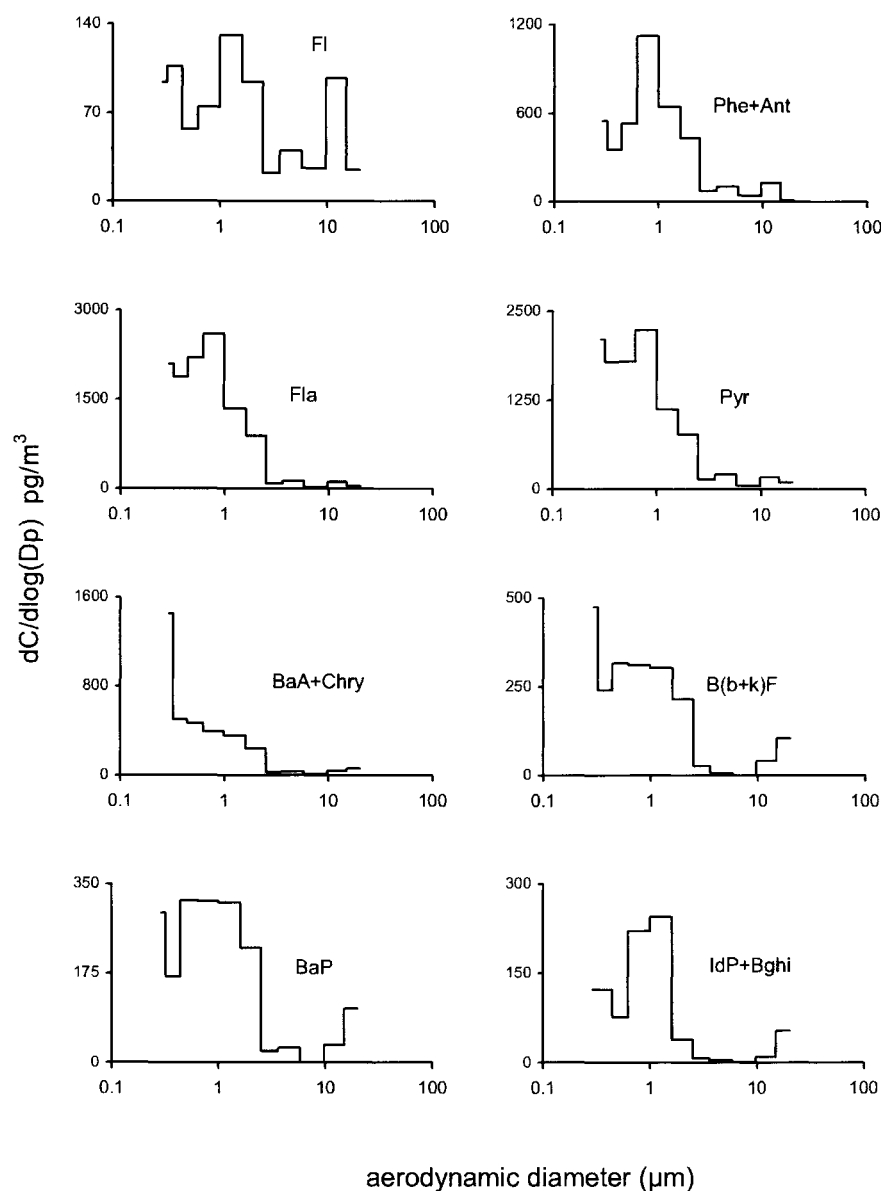|	Sample 1			Sample 2			Sample 3		
	Σ(pg/m³)	<440 nm	<2.5 μm	Σ(pg/m³)	<440 nm	<2.5 μm	Σ(pg/m³)	<440 nm	<2.5 μm
Fl	12	47%	71%	127	21%	72%	142	26%	80%
Phe + Ant	34	36%	76%	665	23%	91%	444	25%	91%
Fla	135	47%	86%	1729	39%	96%	1145	23%	85%
Pyr	129	47%	86%	1557	38%	93%	1125	26%	84%
BaA + Chry	62	52%	95%	431	46%	95%	372	24%	85%
B(b + k)F	125	70%	98%	295	34%	92%	415	22%	89%
BaP	145	79%	100%	286	29%	91%	397	21%	92%
IdP + Bghi	37	80%	100%	148	22%	93%	99	26%	94%

Figure 2. Mass distribution of PAH compounds for Sample 2 (17.01.2002–25.01.2002).

fractions (20–80%) of PAHs were associated with particles smaller than 440 nm. The fine particles (<2.5 μm) accounted for 70–100% of the particle associated PAHs. Total concentrations of particle bound PAHs first increased with mass due to decreasing vapour pressure. The highest level of PAHs was at amu 202 (Fla and Pyr). Concentrations then decreased for the heavier PAHs. Similar observations have been made in other studies (Kiss *et al.*, 2001; Allen *et al.*, 1996). This decrease
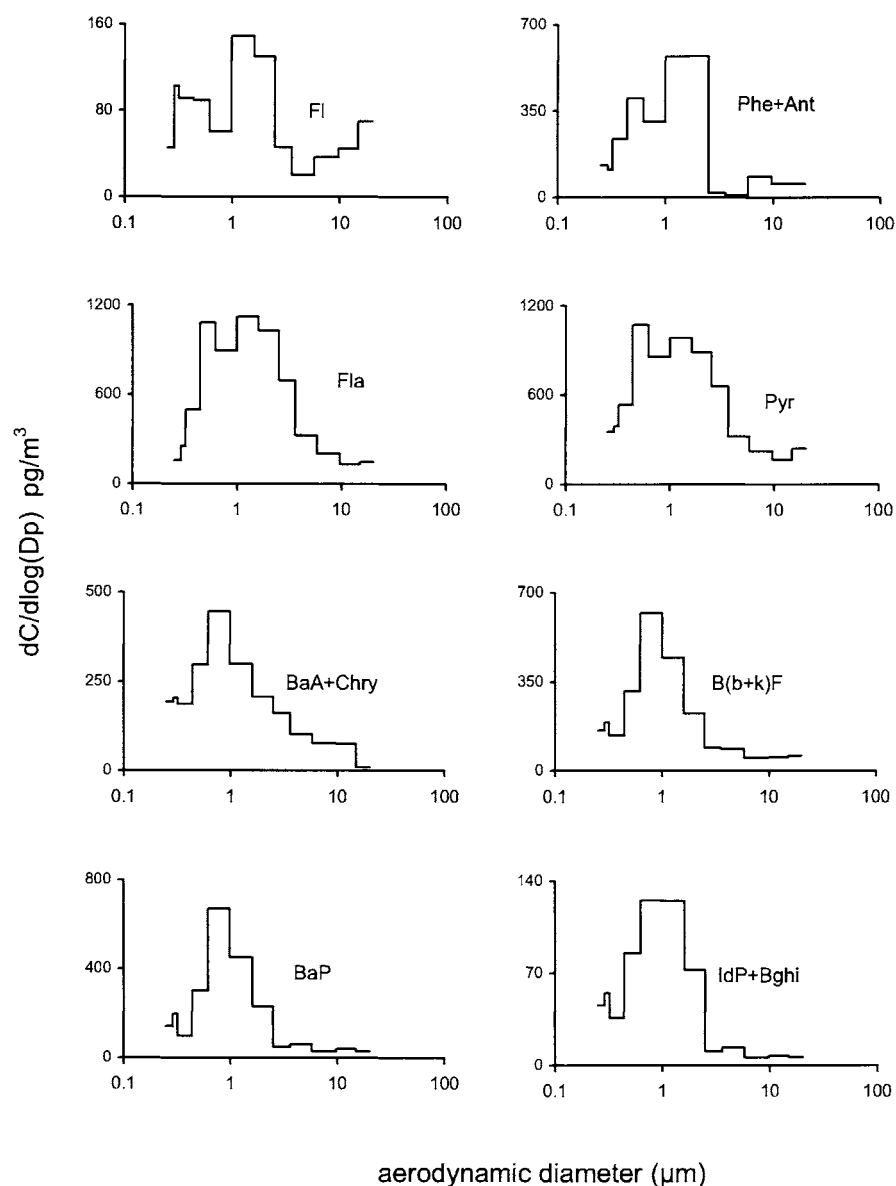
Figure 3. Mass distribution of PAH compounds for Sample 3 (01.02.2002–08.02.2002).

in concentration may in part be due to the lower capacity of SFE to extract heavier PAHs caused by the limited solubility of those compounds in supercritical CO_2. It has been shown that the extraction efficiency of Bghi and DbA collected on glass fibre filters is lower for SFE by 10–30% compared with that of Soxhlet extraction (Shimmo *et al.*, 2002). Application of those values to correct the extraction efficiency of SFE must be, however, carried out with caution because Soxhlet is not

free of errors either because of a number of manual sample pre-treatment steps required before GC-MS analysis.

The results presented in Figures 1–3 and Table II agree reasonably well with the results reported from other locations (Garivait *et al.*, 2001; Sheu *et al.*, 1997; Alves *et al.*, 2000; Kaupp and McLachlan, 1999, 2000; Offenberg and Baker, 1999; Mészáros *et al.*, 1997), though direct comparison may be misleading because the levels of PAHs as well as the mass size distribution may vary significantly with the sampling location (e.g., meteorological conditions, local sources of PAHs, sampling devices).

The difference in distribution patterns between light and heavier PAHs has been explained by gas-solid partitioning (Venkatarman *et al.*, 1999; Allen *et al.*, 1996). PAHs are emitted by sources (in this study mainly by vehicles) either as gases or in fine particles. The lighter PAHs with high vapour pressures repeat the process of condensation to particles and evaporation from particles. The degree of partition depends on the meteorological conditions (e.g., temperature, humidity), the amount of available surface of particles as well as contents of the particles (e.g., amount of hydrophobic surface). As a result, the lighter PAHs are present in a wide range of particle sizes. The heavier PAHs, on the other hand, do not undergo the evaporation and condensation process owing to their lower vapour pressure. They stay in the particles that are originally emitted, and they were observed in the accumulation mode as the particles grow.

3.4. COMPARISON OF IMPACTOR AND DMPS DATA

The mass distributions of PAHs were further evaluated with the particle number distribution obtained by the DMPS. In Figure 4(a), the solid line represents the measured average of the number distributions for Sample 3. The number distribution was then assumed to contain two log-normally distributed modes. The results of the curve fitting suggest the concentration median diameter (CMD) of 21 nm with the geometrical standard deviation (GSD) of 1.71 for the first mode and CMD of 55 nm and GSD of 2.42 for the second mode. The patterns of these log-normal distributions appear as dashed lines in Figure 4(a).

The volume median diameters (VMD) can be calculated from the log-normal number distributions using the equation (Seinfeld and Pandis, 1998)

$$\ln(VMD) = \ln(CMD) + 3\ln^2(GSD). \tag{1}$$

Solving of the equation gave VMDs of 49 nm and 570 nm. The log-normal volume distributions were further converted to the log-normal mass distributions by multiplying by density. In this procedure, it was assumed that all the particles are spherical with uniform density of 1.0 g/cm^3. The log-normal mass distributions are plotted as dashed lines in Figure 4(b). Despite the smaller number of particles in the second mode, the mass occupied in that mode (peak at 570 nm) completely dominates the mass of the first mode (peak at 49 nm), as the volume increases
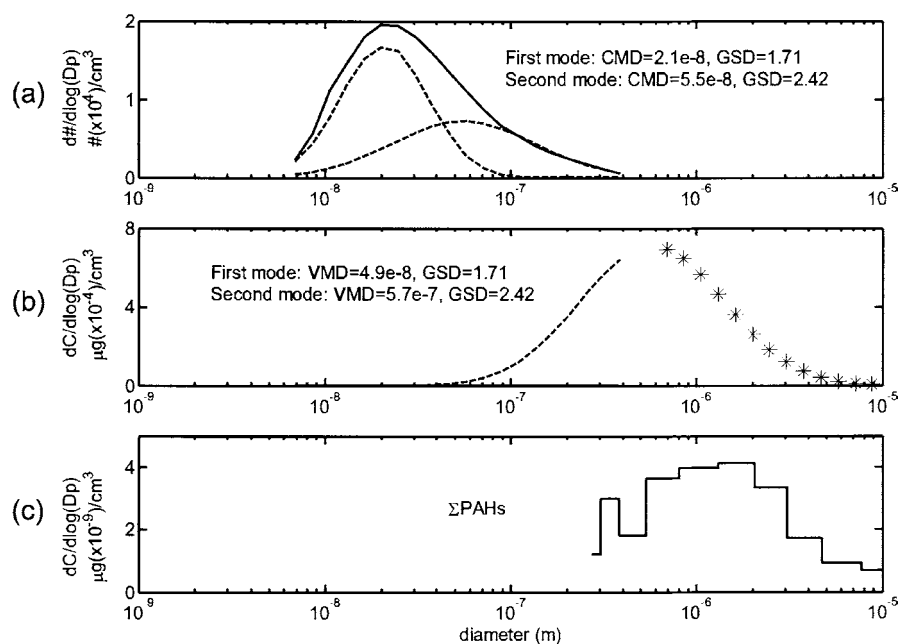
Figure 4. (a) Average particle number distribution for Sample 3 measured by differential mobility particle sizer (solid line). Log-normal fittings with two modes (dashed line). The fitted curves show the concentration median diameters (CMD) of 21 and 55 nm with geometrical standard deviations of 1.71 and 2.42, respectively. (b) Mass distribution calculated from the log-normal fittings (dashed line). Density was assumed to be 1.0 g/cm^3. Volume median diameters (VMD) for the curves were 49 and 570 nm. The second mode was extrapolated for larger diameters (dots). (c) Mass distribution of the total PAHs measured with a cascade impactor.

by an order of three with diameter. As a result, the mass distribution for the first mode cannot even be seen in the figure. The mass distribution of the second mode continued beyond the maximum particle size that was measured by the DMPS (400 nm). The dots in Figure 4(b) represent the curve of the second mode fitted as a log-normal function.

The mass size distribution of the sum of PAHs in Sample 3 is depicted in Figure 4(c). Good agreement can be seen for the data obtained by the impactor and the DMPS. These results support the general concept, as discussed above, that the heavier PAHs are generated by combustion sources that emit fine particles. As particles in accumulation mode tend to contain organic layers, and also because of their low vapour pressure, heavier PAHs are exclusively found in particles in accumulation mode.

The results visualised in Figure 4 may be criticised on at least five counts. (1) The average density of particles is assumed to be 1.0 g/cm^3, but it can be higher. We note, however, that higher density does not change the values of VMDs. (2) Particles are assumed to be uniform in density and shape, but are not. (3) The

Table III. Gaseous and particulate concentrations of PAHs (pg/m^3) and the proportion (%) of the gas concentrations for Sample 3

	Gas (pg/m^3)	Particle (pg/m^3)	Gas %
Ay	15	–	100
Ace	192	3	98
Fl	1862	21	99
Phe + Ant	1223	150	89
Fla	170	328	34
Pyr	399	587	40
BaA + Chry	74	530	12
B(b + k)F	37	498	7
BaP	13	565	2
IdP	8	212	4
Bghi	13	276	5
DbA	–	195	0

DMPS did not measure particles larger than 400 nm, and it is possible that there is another mode at the larger size. As a consequence, the curve fitting in Figure 4(b) may not be appropriate. (4) The mass of the total PAHs is only a fraction of the total mass of particles, and thus the mass distribution may appear different when other compounds are taken into account. (5) Different definitions of diameters are used for the impactor (classical aerodynamic diameter) and DMPS measurements (electrical mobility equivalent diameter). If the average density of ambient particles is greater than 1.0 g/cm^3, as is often the case, the classical aerodynamic diameter becomes smaller by a square root of the corresponding Stokes diameter that is similar to the electrical mobility equivalent diameter (Seinfeld and Pandis, 1998).

3.5. GAS-PARTICLE PARTITION

XAD-2 and the quartz filter for Sample 3 were analysed to study the gas-particle partition. The concentrations of gaseous and particulate PAHs as well as the proportions of gaseous PAHs are summarised in Table III. The total concentration of individual PAH varied from 15 to 1900 pg/m^3. These concentrations are similar to or slightly lower than those found at other suburb locations with similar gas-particle distribution patterns, i.e., more gaseous phase for the lighter and more particulate phase for the heavier PAHs (Dachs and Eisenreich, 2000; Gigliotti *et al.*, 2000; Harrison *et al.*, 1996; Lim *et al.*, 1999; Didyk *et al.*, 2000; Garivait *et al.*, 2001).

The concentrations of particulate PAHs presented in Table III differ from those obtained with the impactor (Table II). For smaller PAHs up to Pyr, the concen-

trations obtained by the impactor sampling were higher than those obtained by
the filter sampling. However, the concentrations of large PAHs were lower in the
impactor sampling than the filter sampling. The difference was most pronounced
for Fl, whose concentrations were 114 (142 × 80% pg/m^3 for <2.5 μm) and
21 pg/m^3 in the impactor and filter sampling, respectively. This result is not con-
sistent with the generally accepted theory that more volatile compounds should
be underestimated in impactor sampling because of enhanced vapour pressure in
vacuum.

One reason for the lower than expected concentrations of smaller PAHs in filter
sampling than impactor sampling could be the use of a back filter for error correc-
tion. Possiblly the back filter collected more gases than predicted, which caused the
corrected particle concentration (particle concentration = front filter – back filter)
to be underestimated (Kirchstetter *et al.*, 2001; Turpin *et al.*, 2000). Although arte-
facts caused by filter sampling have been investigated in laboratory scale and their
importance has been pointed out (Mader and Pankow, 2000, 2001b), application
of the results is not straightforward in field measurement. At the moment it is not
known which sampling method is more reliable.

The gas percentages of Fla and Pyr in this study (34 and 40%, respectively) were
lower than those obtained in other studies: 83–85% Pyr in New Jersey (Gigliotti
et al., 2000), 83–94% Pyr and 83–91% Fl in Birmingham (Harrison *et al.*, 1996)
and 70–90% Pyr in Bangkok (Garivati *et al.*, 2001). The partition balance is more
sensitive for Fla and Pyr than for lighter (exclusively in gas phase) and heavier
PAHs (exclusively in particle phase). The probable reason for the smaller gaseous
partition in our case is the relatively low temperature during sampling (average
+0.4 °C with min. –10 °C and max. +6 °C) which forced those compounds to
associate more strongly with particles.

To obtain a better understanding of the temperature dependence of gas-particle
partition, we compared partition coefficients (*Kp*) with the sub-cooled liquid
vapour pressures of PAHs (Offenberg and Baker, 2002; Simcik *et al.*, 1998;
Garivait *et al.*, 2001):

$$Kp = \frac{(F/TSP)}{A}, \tag{2}$$

where *Kp* (m^3/μg) is the partition coefficient, *F* and *A* are the particulate and
gaseous concentrations of the analytes (ng/m^3) and *TSP* (μg/m^3) is the weight of
the total suspended particulate matter on the filter. The measured partition coef-
ficients were further correlated with the sub-cooled liquid vapour pressures, p_L^0
(mmHg), of the analytes:

$$\log(Kp) = m \log(p_L^0) + b, \tag{3}$$

where *m* and *b* are constants. The sub-cooled liquid vapour pressure is tempera-
ture dependent. The values for several PAHs at the sampling temperature in this
study (0.4 °C) were calculated using the Clausius-Clapeyron equation and the data
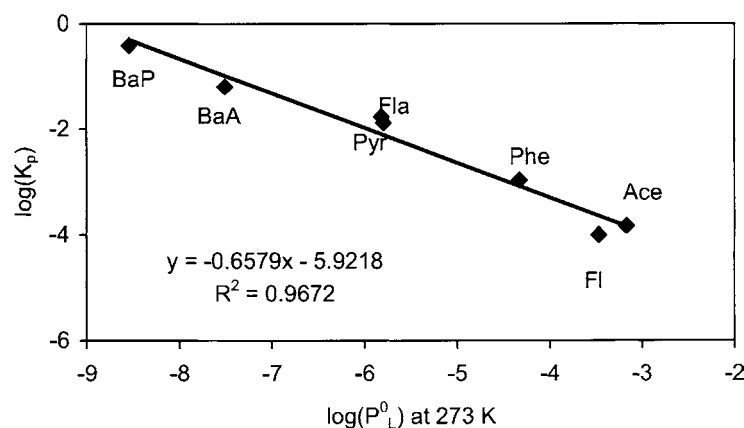
Figure 5. Relationship between partition coefficients (*Kp*) and temperature correlated subcooled vapour pressures (p_L^0) for Sample 3.

obtained by Yamasaki *et al.* (1984), assuming that the enthalpy of vaporisation is constant over small changes of temperature.

Figure 5 shows a linear relationship between log(Kp) and log(P_L^0). The regression was excellent ($R^2 > 0.96$) with gradient of –0.66 and interception of –5.92. In ideal equilibrium, the gradient is expected to be –1. Wide varieties have been observed in the values of the gradient –(0.43–0.89), the interception –(2.26–6.66) and R^2 (0.60–0.97) (Garivait *et al.*, 2001; Lohmann *et al.*, 2000; Simcik *et al.*, 1998). The gradient depends on the nature of the sorption process and on the composition and chemical activity coefficients of particles, which in turn are dependent on ambient temperature and humidity, and on changes in PAH concentrations during sampling (Goss and Schwarzenbach, 1998). The non-exchangeability of PAHs, and especially light PAHs, may be important if they are irreversibly trapped inside the soot particles during the emission process (Fernández *et al.*, 2002). Volatilisation of particle phase PAHs from filter is relevant to underestimation of light particulate PAHs (Turpin *et al.*, 2000). Thus, the nonequilibrium state is not necessarily the case when the gradient deviates from –1 (Simcik *et al.*, 1998).

Besides the biases associated with sampling and the nonequilibrium state in the atmosphere, we should also note the errors caused by the analytical procedure itself. The extraction efficiency of a given method tends to be matrix dependent, so a difference in recoveries may be expected from filter and XAD-2. Furthermore, PAHs are bound to the same matrix in different strengths depending on their mass. It is known that the extraction by SFE may be less efficient for heavier PAHs than for light PAHs.

4. Conclusions

The levels of PAHs measured in this study are comparable with those reported from other urban areas (level of ng/m^3). The mass distributions showed that most of the PAHs were associated with fine particles ($<$2.5 μm in diameter). The distribution showed that the accumulation mode accounts for the highest concentrations of PAHs, which is important information for inhalation toxicology. The gradient for partition coefficient (logKp) expressed as a function of temperature correlated sub-cooled vapour pressure (logp$_L^0$) was –0.66. The value varied from the expected value of –1 for equilibrium partition. However, still shallower gradients have been reported in other studies. The particulate PAHs collected by impactor and filter differed significantly. The error estimation for atmospheric sampling has been an important topic for decades, and requires further investigation.

Besides the attention needed to the non-equilibrium of gas-particle partitioning and sampling artefacts, errors during chemical analysis need to be minimised. The on-line SFE-LC-GC-MS provided an alternative to conventional methods. Though the instrument is fairly complicated, the whole analysis could be carried out semi-automatically in a closed system, providing more accurate results and low limits of detection.

Acknowledgements

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