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Aerosol Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713656376

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First Published on: 01 February 2003

To cite this Article Chiang, Pen-Chi, Chiang, Yu-Chun, Chang, E. -E. and Chang, Sheng-Chi(2003)'Characteristics of Polynuclear Aromatic Hydrocarbons in Ambient Air through a Long-Term Sampling Program at a Metropolitan City in Taiwan',Aerosol Science and Technology,37:2,133 — 144

To link to this Article: DOI: 10.1080/02786820300953

URL: http://dx.doi.org/10.1080/02786820300953

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Aerosol Science and Technology 37: 133–144 (2003)
© 2003 American Association for Aerosol Research
Published by Taylor and Francis
0278-6826/03/$12.00 + .00
DOI: 10.1080/02786820390112579

Characteristics of Polynuclear Aromatic Hydrocarbons in Ambient Air through a Long-Term Sampling Program at a Metropolitan City in Taiwan

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Polynuclear aromatic hydrocarbon (PAH) concentrations in total suspended particulate (TSP) matter as well as gaseous PAH contents are measured at an urban site adjacent to the capital of Taiwan. Several factors, such as seasonal variation, ring number, G/P (gas/particulate) ratio, and C-atom number, are utilized to characterize the pollution features of 14 PAHs. The results show that the total PAH content in TSP has been reduced gradually. The probable carcinogenic PAH compounds exist primarily in the particulate phase. The concentration distributions of each PAH compound are different, and the quantities and ring distributions of PAHs are significantly affected by seasonal fluctuation. The G/P ratio is highly associated with the C-atom number of PAHs. Factor analysis, along with the characteristic ratios of PAHs, is used to qualitatively identify the probable contributors. The results suggest that traffic exhaust and industrial origins are the predominant contributors.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a group of organic compounds composed of 2 or more fused aromatic rings and are generally formed by incomplete combustion of organic materials, as well as through natural and other anthropogenic activities. In the atmosphere, they may adsorb and condense on the surface of aerosols (particulate phase) or exist in the gaseous phase. Distribution of the particulateace or gaseous phase depends on the vapor pressure of the compound and environmental conditions. Some of them are suspected to be mutagenic or carcinogenic to human beings, especially those in the particulate-associated phase (Menzie et al. 1992). As a result, PAHs have been widely studied, including monitoring of ambient PAH concentrations.

Short-term PAH levels, such as diurnal PAH concentration changes, are dominated by recent local/regional source emissions, atmospheric reactions, and deposition processes (Møller et al. 1982; Lee et al. 1998). PAHs collected at sites away from the emission sources tend to partition into larger particles (Allen et al. 1996), and both particulate phase and total PAHs in urban air in winter have higher concentrations than in summer by a factor of about 5 (Smith and Harrison 1996). Although particulate PAH concentrations increase in winter, the PAH partition is affected not only by temperature, but also by particle characteristics (Gustafson and Dickhut 1997), the C-atom number of PAH species (Thrane and Mikalsen 1981), and variations in source emissions and meteorological conditions. Further, other investigators (Yamasaki et al. 1982; Fraser et al. 1998) have reported that an approximately equal amount of PAHs with a molecular weight of 228 is partitioned into gaseous and particulate phases.

Characteristic ratios of PAHs have been considered as an index for source identification. For instance, several studies have used the ratios of some specific PAH species to benzo[a]pyrene to recognize the origin of these PAHs (Fox and Staley 1976; Sexton et al. 1985; Lyall et al. 1988). The benzo[a]pyrene/benzo[ghi]perylene (BaP/BghiPr) ratio could differentiate vehicle pollution from domestic heating sources (NAS 1972; Møller and Alfheim 1980). The pyrene/benzo[a]pyrene (Pyr/BaP) ratio can distinguish pollution from heating and gasoline- or diesel-powered vehicles (Masclet et al. 1986; Lowenthal et al. 1994). Li

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Received 15 August 2001; accepted 7 June 2002.

We are grateful for the support by the ROC EPA grant and ROC NSC (NSC 87-EPA-P-002-012) for a series of research projects and the assistance of the Sanchung Sanitary Bureau.

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and Kamens (1993) found that the ratio of benzo[ghi]perylene to indeno[1,2,3-cd]perylene (BghiPr/IP) from gasoline exhaust is about 3 times that from diesel exhaust. Benzo[ghi]perylene/benzo[e]pyrene (BghiPr/BeP) ratios can distinguish traffic from nontraffic sources (Benner et al. 1989; Nielsen 1996); moreover, the ratio in gasoline exhaust is higher than that in diesel exhaust. Except for vehicle exhaust (Lowenthal et al. 1994), fluoranthene/pyrene (Flu/Pyr) can identify the type of industrial pollution (Masclet et al. 1986).

Stationary sources accounted for about 80–90% of PAH emissions in the 1980s; however, mobile sources have gradually become the predominant contributors for ambient PAHs in urban and suburban areas (Harrison et al. 1996). Several studies have suggested that benzo[ghi]perylene should be a good indicator of automobile exhaust; napthalenes, phenanthrene, fluoranthene, and pyrene would be the tracers for diesel engines (e.g., U.S. EPA 1993; Harrison et al. 1996; Cooper et al. 1996). Nevertheless, pyrene is also found in large quantities in biomass burning (Masclet et al. 1993). Since the concentrations of elemental K, Br, Ca, Pb, and C as well as organic carbons are statistically correlated with PAH levels (Sexton et al. 1985; Currie et al. 1994), PAHs have been suggested as new tracers to replace Pb for gasoline exhaust (Daisey et al. 1986). Harrison et al. (1996) suggested that measurements of both PAHs and inorganic pollutants should provide a better means of source identification.

Although several studies have focused on establishing the source emission profiles of PAHs in the U.S. and Europe (e.g., Li and Kamens 1993; Venkataraman and Friedlander 1994; Khalili et al. 1995), the use of PAH emission profiles is still rather limited because of the collinearity and variability. Consequently, this study was initiated to shed light on the annual and seasonal characteristics of PAHs in ambient air in Taiwan through long-term measurements. Qualitative assessment of the probable sources was determined with the characteristic ratios of PAH species and by performing a factor analysis (FA). The results will aid the authorities in evaluating the performance of their pollution control strategies and proposing alternative actions to improve air quality.

EXPERIMENTAL METHODS

Sampling

Taipei city is the capital of Taiwan. In addition to heavy traffic, a variety of industrial activities (e.g., steel mill, metal smelter, foundry, and solvent factory) have significantly deteriorated the air quality. The sampling location is on the roof of the Sanchung Sanitary Bureau Building near the Tan-Shui River. The height of the building is approximately 10 m above ground, located about 10 m from the main road, in front of a playground, on the right side of the city hospital. The building is in the neighborhood of a road circle and an overpass, with a nearby gas station and a bus station.

Ambient PAH samples were collected using a high-volume sampler (Andersen) from 1990 to 1998 and a PS1-PUF sampler (General Metal Works) from 1994 to 1998. The high-volume sampler was equipped with a preconditioned glass fiber filter (Whatman EPM 2000) with a flow rate of 1400 lpm. A 24 h particulate sample was collected at 7:00 am once per month, occasionally twice per month. A total of 125 total suspended particulate (TSP) samples were collected. The PS1-PUF sampler employed a preconditioned glass fiber filter (10 cm diameter) to collect particulate matter and 2 polyurethane foam (PUF) plugs in series (with a flow rate of 280 lpm) to adsorb gaseous PAHs. The rear PUF plug was used to prevent the breakthrough of gaseous PAHs. In this study, the amounts of gaseous PAHs adsorbed onto the PS1 filter preceding the PUFs and particulate PAHs off-gassing and blown off to the PUFs are negligible. Sampling dates for PAHs were the same as those for TSP samples, although the sampling frequency was twice per day (from 7:00 am to 7:00 pm and from 7:00 pm to 7:00 am). A total of 84 particulate and gaseous samples were obtained. PUF cartridges are preferable because they are inexpensive and easy to use and they produce a low blank value and a low pressure drop (Hart et al. 1992). Filters were weighted before and after sampling, and the TSP concentrations were determined from the weight difference.

Extraction and Analysis

All filter and PUF samples were stored in darkness inside a refrigerator to prevent PAH loss. The samples were extracted with dichloromethane, using a Soxhlet extraction apparatus at 45°C for 16 h, in the dark to avoid photodegradation. The extracts were concentrated in a rotary evaporator under low pressure. The concentrated extracts were then dissolved in dichloromethane and cleaned by thin-layer chromatography on silica gel in a solvent mixture of cyclohexane to benzene of 2 to 1 (volume). Prior to extraction, internal standards were spiked in the extracts to account for losses of compounds due to differences in extraction efficiency, wall loss to glassware, volatilization during evaporation, and injection irregularities. The dichloromethane, cyclohexane, benzene, and silica gel were purchased from Merck.

PAHs were analyzed by the GC-MS (HP 5971A), with an Ultra 2 capillary column (25 m × 0.2 mm i.d.). The carrier gas used was helium, and the temperature program started from 70°C for 4 min to 300°C with a rate of 6°C/min. Fourteen PAH species, including phenanthrene (PhA), fluoranthene (Flu), pyrene (Pyr), 2,3-benzofluorene (Ben), benzo[a]anthracene (BaA), triphenylene (Tph), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo-[e]pyrene (BeP), benzo[a]pyrene (BaP), Perylene (Pr), indeno-[1,2,3-cd]perylene (IP), dibenzo[a, h]anthracene (DbA), and benzo[ghi]perylene (BghiPr), were determined. The PAH standards were obtained from Aldrich (Flu, Pyr, BaA, Chr, BbF, BaP, BeP, BghiPr, and DbA), Tokyo Co., Tokyo (PhA, Pr, and IP), and Wako Pure Chemical Industries, Osaka (Ben and Tph). The recovery rate of each compound ranged from 47 to 90%. The PAHs in the filter blanks and PUF plug were analyzed and subtracted from the sample concentrations.

Factor Analysis

The data set of gaseous and particulate PAH compounds proceeded with the source identification using FA. The computations were performed by SAS software. The FA technique is a multivariate method for qualitatively determining the probable pollution source type. Multivariate methods extract information about a source contribution on the basis of the variability of pollutants measured at the receptor sites. The objective in FA is to reduce the number of dimensions in a multivariate data set while retaining most of the variance of the system (Gordon 1988). The original variables are replaced by new factors, where the first factor accounts for most of the variance in the data. Each new factor represents a probable source type, which is recognized by major variables with a larger factor loading. The factor loadings indicate the correlation of each pollutant with the factor and are related to the source emission composition. Henry et al. (1984) have suggested that to conduct a FA, the degree of freedom should be at least 30 and preferably 50–100. In this study, the FA was performed using the orthogonal transformation method with Varimax rotation and retained the factors that explained variances greater than unity (Roscoe et al. 1982). When the absolute value of the factor loading of a variable is >0.7, it is regarded as the major element of this factor. If it is between 0.5 and 0.7, it is considered the secondary element. The major and secondary elements in a factor are the primary indicators for source identification. Comparing these elements to the markers for specific sources, the implied probable source type can be recognized for each factor.

RESULTS AND DISCUSSION

Characteristics of Particulate PAH Levels

The annual arithmetic averages of 14 PAH species for ambient TSP samples measured from 1990 to 1998 are shown in Table 1. The standard deviations are also listed in the parentheses under the mean values, which implicitly explain the fluctuant

Table 1

Summary of annual arithmetic average values of PAHs measured on total suspended particulate matters

	Annual arithmetic average, ng/m^3 (Standard deviation)								
Year PAH	1990 (20)$^{\xi}$	1991 (22)	1992 (23)	1993 (14)	1994 (11)	1995 (10)	1996 (13)	1997 (10)	1998 (8)
PhA	0.67	0.17	0.30	0.39	0.77	1.43	0.15	0.06	0.09
	(0.68)	(0.13)	(0.35)	(0.28)	(0.48)	(1.40)	(0.15)	(0.05)	(0.12)
Flu	1.18	0.16	0.17	0.41	1.06	0.34	0.33	0.16	0.21
	(1.26)	(0.16)	(0.14)	(0.46)	(0.97)	(0.39)	(0.25)	(0.09)	(0.32)
Pyr	1.29	0.39	0.92	0.42	0.94	0.35	0.68	0.22	0.25
	(1.07)	(0.40)	(1.65)	(0.43)	(0.81)	(0.41)	(0.49)	(0.17)	(0.37)
Ben	1.00	0.02	0.002	0.01	0.06	0.03	0.03	0.02	0.01
	(1.12)	(0.02)	(0.01)	(0.03)	(0.05)	(0.05)	(0.03)	(0.01)	(0.01)
BaA	0.45	0.07	0.11	0.12	0.28	0.12	0.11	0.16	0.42
	(0.61)	(0.11)	(0.13)	(0.10)	(0.66)	(0.16)	(0.10)	(0.12)	(1.06)
Tph/Chr	0.34	0.04	0.06	0.11	0.20	0.25	0.12	0.11	0.18
	(0.37)	(0.04)	(0.06)	(0.09)	(0.35)	(0.50)	(0.10)	(0.08)	(0.41)
BbF	1.38	0.55	0.59	0.53	0.93	0.31	0.60	0.43	0.32
	(1.54)	(1.01)	(0.61)	(0.54)	(1.58)	(0.33)	(0.53)	(0.40)	(0.37)
BeP	0.63	0.42	0.54	0.51	0.82	0.37	0.63	0.39	0.23
	(0.71)	(0.96)	(0.59)	(0.50)	(1.38)	(0.36)	(0.60)	(0.32)	(0.22)
BaP	0.28	0.37	0.30	0.14	0.45	0.22	0.26	0.24	0.11
	(0.36)	(1.58)	(0.61)	(0.20)	(0.98)	(0.28)	(0.49)	(0.20)	(0.13)
Pr	0.33	0.05	0.04	0.02	0.10	0.04	0.03	0.04	0.02
	(0.66)	(0.20)	(0.12)	(0.04)	(0.22)	(0.08)	(0.07)	(0.03)	(0.02)
DbA	ND*	0.02	0.08	0.10	0.10	0.01	0.08	0.20	0.02
		(0.08)	(0.14)	(0.13)	(0.26)	(0.02)	(0.12)	(0.53)	(0.02)
IP	0.05	0.21	0.65	0.67	0.83	0.46	0.84	0.95	0.17
	(0.15)	(0.50)	(0.74)	(0.69)	(1.19)	(0.36)	(0.80)	(2.11)	(0.15)
BghiPr	0.90	0.65	1.50	1.34	1.57	1.14	1.72	2.03	0.38
	(0.72)	(1.15)	(1.73)	(1.19)	(2.25)	(0.93)	(1.53)	(4.48)	(0.24)

$^{\xi}$Sample size.

*ND: not detected.

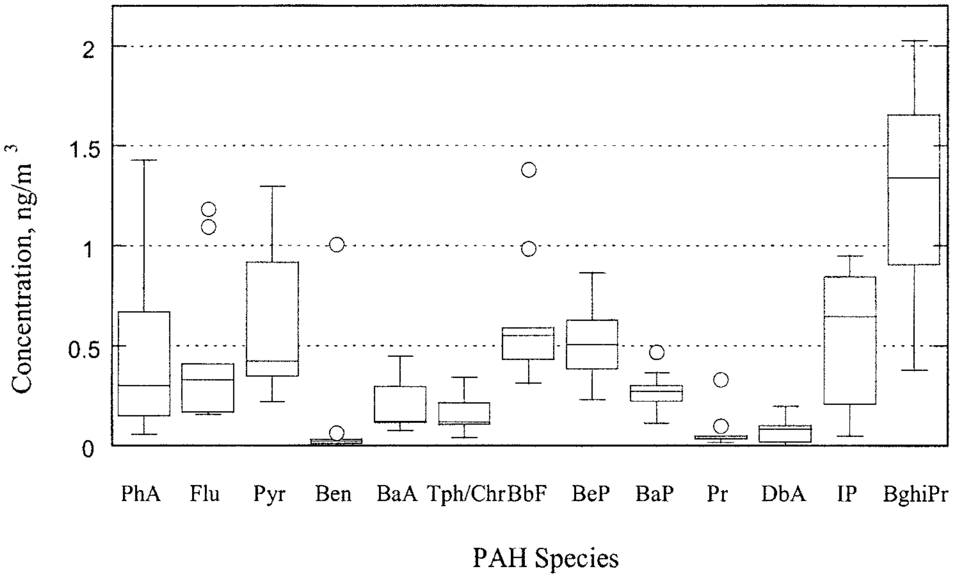

Figure 1. Distribution of particulate PAH concentrations averaged over several years from 1990 to 1998.

PAH levels. In general, except for a few years and some PAHs, the mean values of each individual PAH compound in the particulate phase are below 1 ng/m^3 during the sampling period, and the results are comparable to the study in Denver (Foreman and Bidleman 1990) and lower than those in Copenhagen (Nielsen 1996). The arithmetic average concentration of total PAHs in the particulate phase over several years was 5.2 ng/m^3 (0.5–36.0 ng/m^3). It is noted that BghiPr concentration is predominant among all PAH species; this reveals that the contribution from gasoline-powered vehicles may be significant (e.g., Nikolaou et al. 1984).

Figure 1 represents the distribution of PAH measurements from 1990 to 1998 in box plots in which the median value of each PAH species is displayed as a line inside the box. The top

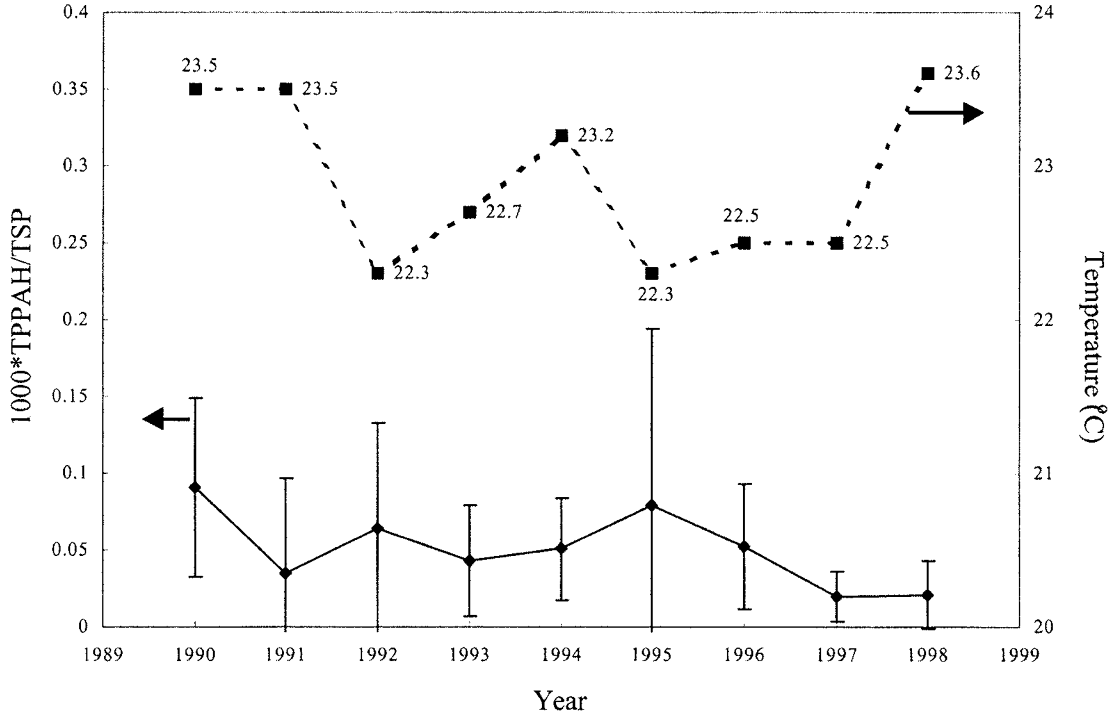

Figure 2. Annual distribution of the ratios of TPPAH analyzed to the TSP level and the corresponding annual average temperature. The picture plots the mean with one standard deviation of the ratio.

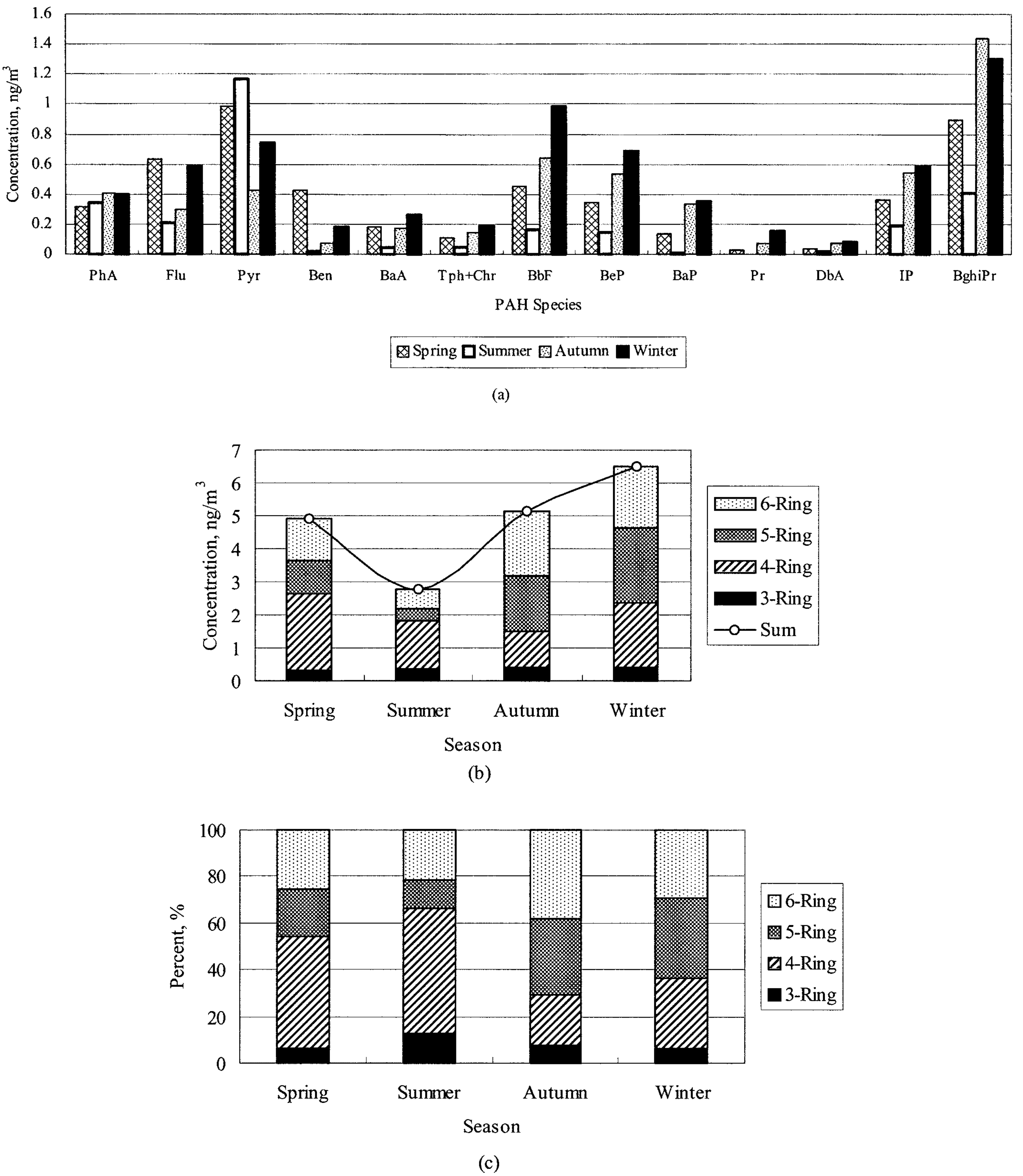

Figure 3. Season effect of particulate PAH concentrations averaged over several years on individual species and the groups by ring number.

and bottom of the box mark the limit of 25% (LQ) and 75% (UQ) of the distribution. The lines extending from the top and bottom of each box represent the minimum and maximum values that fall within an acceptable range [UQ + 1.5 × (UQ − LQ) to LQ − 1.5 × (UQ − LQ)]. The value outside this range, called an *outlier*, is displayed as an individual circular point. These plots illustrate that the levels of individual PAH compounds vary significantly and the distribution patterns are quite distinctive. Some PAH species are right skewed (i.e., the mode is larger than the median value), while others are left skewed. The ratios of total particulate PAH (TPPAH) content to the TSP level are shown in Figure 2. Generally, the ratios show a decreasing trend from the year 1990 to 1998, with the annual mean ratio below 10^{-4}. The temperature profiles are also included in Figure 2 for reference.

Figure 3 depicts the seasonal effect on ambient particulate PAH concentrations averaged over several years. Except for PhA and Pyr, the particulate PAH concentrations are the lowest in summer and exhibit maximum levels in winter (most) or spring (Figure 3a). In contrast, Pyr exhibits a maximum value in summer, while the PhA level is quite stable during all 4 seasons. The total mean particulate PAH concentration in winter is the highest, and the order in turn is autumn, spring, and summer (Figure 3b). Classifying by ring number of PAH molecular structures, the PAH compounds can be categorized into 4 groups, i.e., from 3- to 6-ring. Specifically, the amount distribution of particulate PAHs by ring number corresponds to the fact that the effect of their chemical reactivity on PAH species levels is more important than that of volatilization. Figure 3c provides the relative percentages of 4 groups of PAHs in each season, which indicates that the contents of 5- and 6-ring PAHs are >60% in winter and autumn. Although the total particulate PAH levels are similar in spring and in autumn (Figure 3b), their ring distributions are substantially different (Figure 3c). Since the suspected mutagenic or more active PAHs are 5- or 6-ring chemicals, this finding suggests that these PAHs present in the TSP may possess a greater human health risk in autumn and winter.

Features of Gaseous to Particulate (G/P) Ratio

PAH species belong to the semivolatile organic compounds, and their distributions in particulate and gaseous phases are controlled by their chemical properties and environmental conditions. Figure 4 shows the ratios of gaseous to particulate PAH levels (G/P ratio) for individual compounds in daytime and nighttime, as well as diurnal means from 1994 to 1998. The G/P ratios for more volatile compounds (such as PhA, Flu, Pyr, Ben, BaA, and Tph+Chr) are higher than those of the other species with higher molecular weights. This could be attributed to the effects of both vapor pressure and reaction activity of PAH species. For PhA, Flu, and Pyr, the G/P ratios in nighttime are slightly higher than those in daytime, which implies that the radical reactions of those gaseous PAHs under sunlight may be significant, providing that the PAH source emissions in this

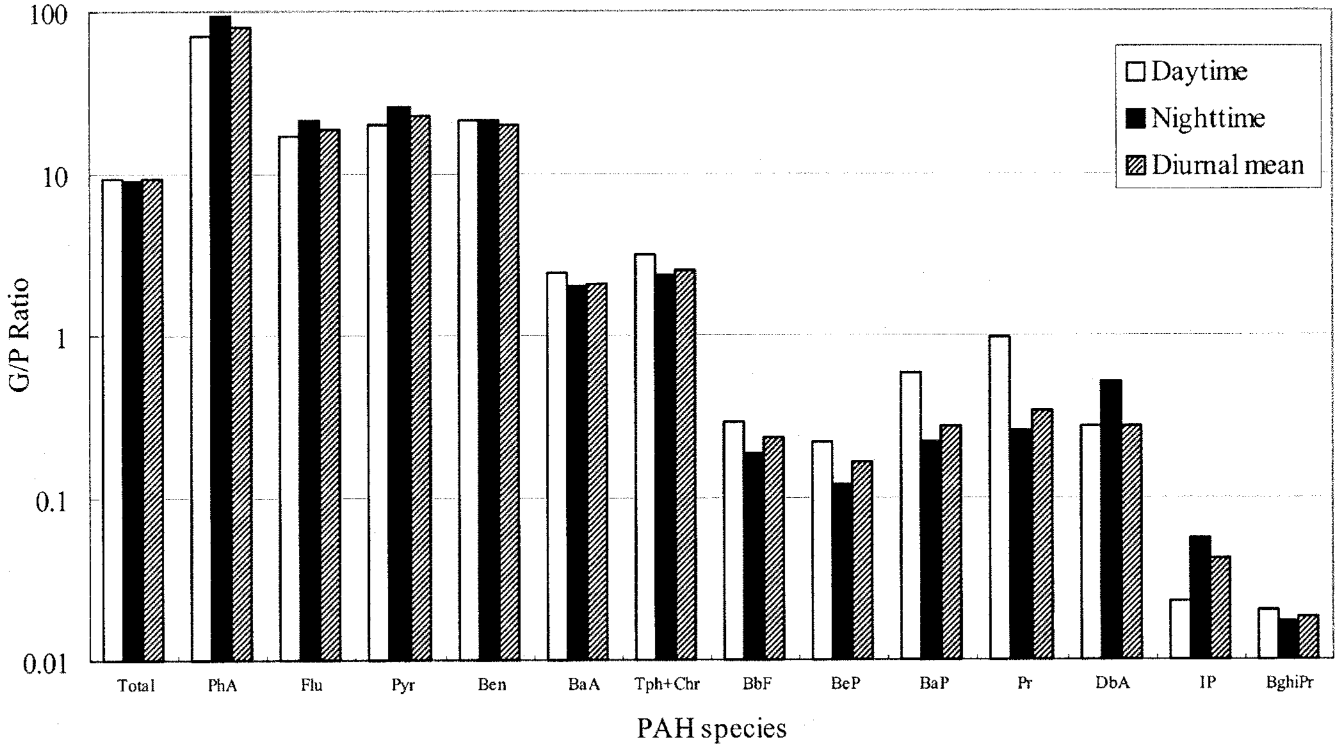

Figure 4. Ratios of gaseous to particulate PAH levels (G/P ratio) in daytime and nighttime (averaged over several years) and annual means.

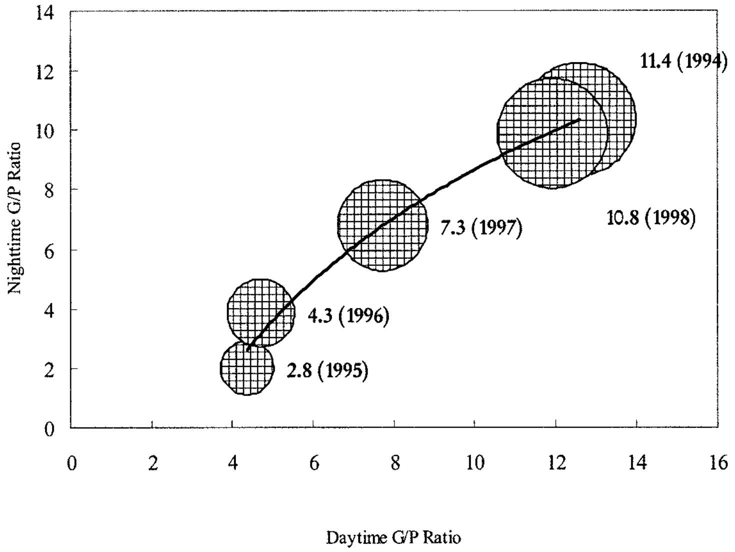

Figure 5. Bubble plot of the ratios of gaseous to particulate PAH levels in daytime, nighttime, and annual means. Circle size signifies the annual daily mean G/P ratio.

urban city are consistent. The truck fleet, where lighter PAHs are known as the markers of their exhaust, is usually operated in nighttime, which might also account for this phenomenon. On the other hand, for other compounds, except for DbA and IP, the G/P ratios in daytime are higher.

Figure 5 plots the annual nighttime G/P ratios against the annual daytime ratios, where the size of the circle indicates the annual daily mean. It is noted that from 1995 to 1998, the G/P ratios, regardless of the sampling time, always increased with year. This tendency is consistent with the decrease of mean particulate PAHs (Figure 1) and annual mean temperature (Figure 2).

Seasonal effect on the G/P ratios for each PAH compound averaged over several years is shown in Figures 6a and b. The G/P ratios of PAHs exhibit maximum levels in summer only in Ben, BaA, BeP, and BaP, and the ratios in spring and summer are practically the same for Pr, DbA, and IP. The G/P ratios reached the maximum in spring for PhA and Tph+Chr. In general, the G/P ratios of 5- and 6-ring PAHs are much lower than the lighter species (Figure 6b). Figure 6b further indicates that the G/P ratios in 4-ring PAHs are relatively independent of the season; but the 3-ring PAH exhibits the maximum in spring. This finding suggests that chemical reaction mechanisms of the PhA in the atmosphere may be significantly distinct from the other PAHs.

The mean values of ring distribution of PAHs averaged over several years are summarized in Table 2. The data in the particulate phase were obtained from TSP samples from 1990 to 1998, while the gaseous and G/P results are from 1994 to 1998. In summary, in the particulate phase, 6-ring PAHs account for 38% of total PAHs, and 5- and 4-ring PAHs are both close to 30%. In contrast, 3-ring PAHs constitute more than 50% of total PAHs in the gaseous phase. The sum of gaseous and particulate PAHs shows that the masses of 5- and 6-ring PAHs are about 10% of the measured PAHs. Table 2 also indicates that the mean G/P ratios in 4 groups of PAHs are in different orders. The amounts of carcinogenic PAH species, i.e., BaA, Tph, Chr, BbF, BaP, DbA, IP, and BghiPr (Menzie et al. 1992), and active ones,

Table 2
The average ring distribution of PAHs in ambient air over several years

	Classification					
	3-Ring	4-Ring	5-Ring	6-Ring	Carcinogenic$^{\Phi}$	Active$^{\Gamma}$
Particulate (P, ng/m^3)	0.03–0.77	0.46–2.54	0.34–2.39	0.39–4.38	0.72–5.68	0.54–3.40
Gaseous (G, ng/m^3)	3.91–47.04	3.53–45.16	0.08–0.45	0.01–0.09	0.31–1.88	0.18–0.85
P+G (ng/m^3)	3.94–47.81	4.33–47.70	0.42–2.84	0.41–4.39	1.02–6.25	0.78–4.25
G/P	24–152	4–18	0.1–0.3	0.002–0.05	0.1–0.4	0.1–0.4

$^{\Phi}$The sum of BaA, Tph, Chr, BbF, BaP, DbA, IP, and BghiPr.
$^{\Gamma}$The sum of BaA, BbF, BeP, BaP, DbA, and IP.

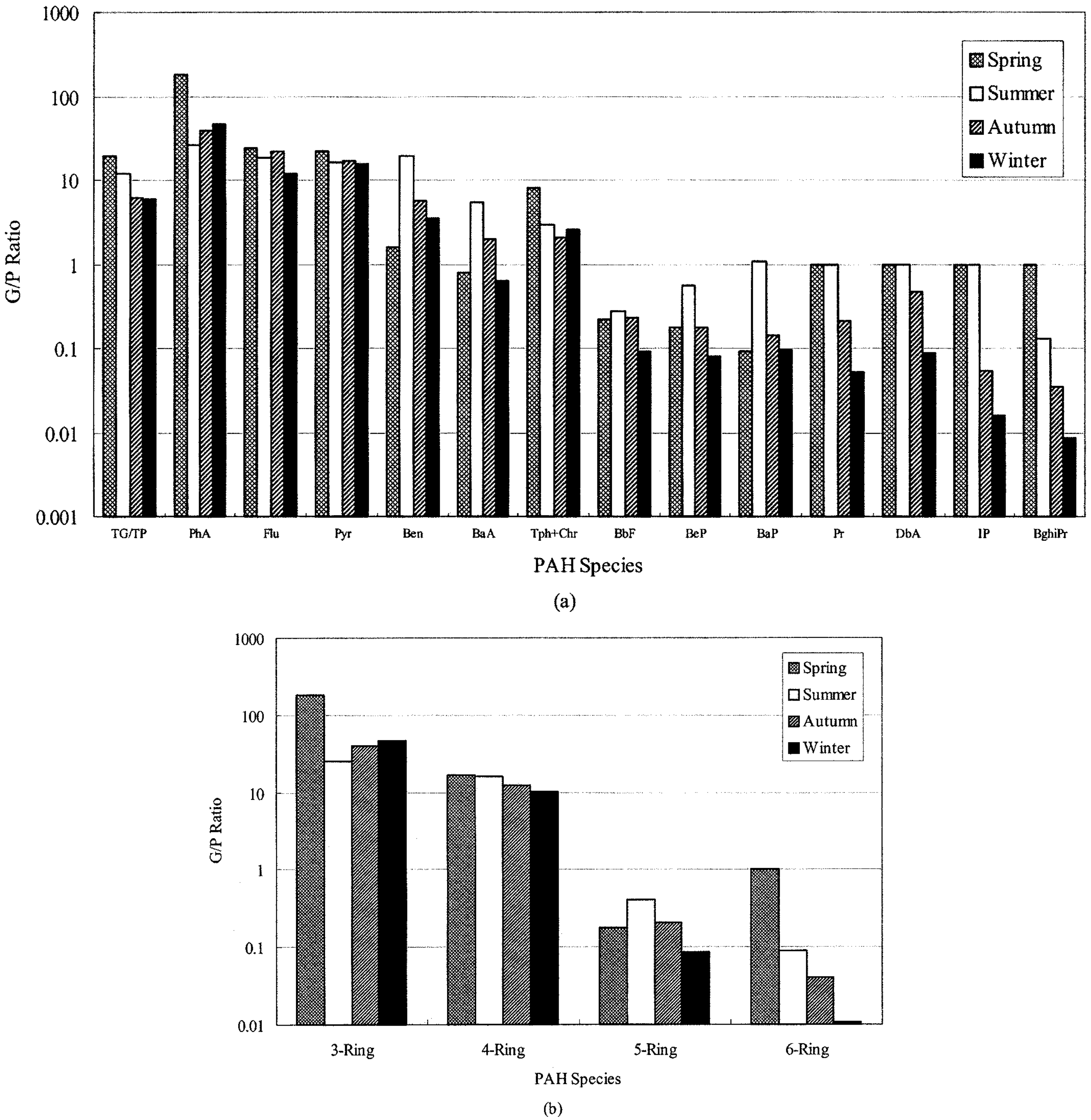

Figure 6. Ratios of gaseous to particulate PAH levels (G/P ratio) averaged over several years observed in this study: (a) for each PAH compound; (b) for 3-ring to 6-ring PAHs.

i.e., BaA, BbF, BeP, BaP, DbA, and IP (Futoma et al. 1981), are also shown in Table 2. It should be noted that the percentage of particulate carcinogenic PAHs is more than 50% of the PAHs measured. The G/P ratios further demonstrate that 5- and 6-ring PAHs, carcinogenic and active PAHs, are primarily present in the particulate phase. As a result, although the total concentration of gaseous 3- and 4-ring PAHs is higher, the threat of health risks from 5- and 6-ring PAHs comes mostly from the particulate phase.

The G/P ratio is highly correlated with the C-atom number of PAHs, as shown in Figure 7. For 16- and 17-C PAHs, G/P ratios are about 20, and the ratios are approximately 2 for 18-C PAHs; the G/P ratios are further reduced to below 0.5 for the PAHs with a C-atom number larger than 20.

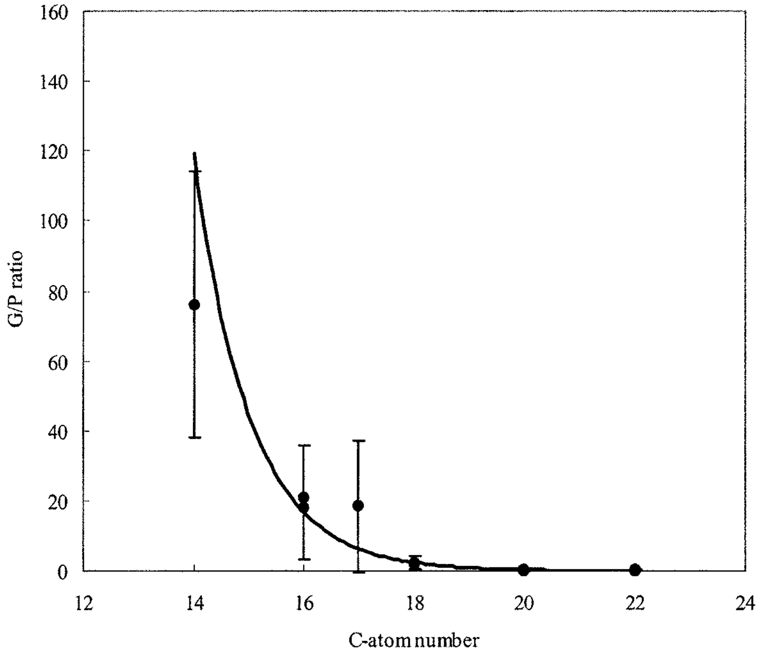

Figure 7. Relationship between C-atom number and G/P ratio averaged over several years observed in this study. The distribution represents the mean with one standard deviation. The solid line represents the best fit.

Characteristic Ratio of PAHs

The ratios of PAH species are used to feature the characteristics of source emissions. Table 3 summarizes some characteristic ratios of PAHs measured in the TSP samples. The mean ratio of BghiPr/BeP (2.6) is indicative of a gasoline exhaust contribution (Benner et al. 1989; Nielsen 1996). The ratio of BghiPr/IP (2.3 with the exclusion of one data point) represents a combination of gasoline (3.5–3.8) and diesel (1.1–1.2) pollution (Li and Kamens 1993). The average BghiPr/BbF ratio (2.3) reveals that there may be a contribution from traffic emission rather than wood heating

Table 3
Characteristic ratios of PAH species for TSP samples in ambient air

Year	Characteristic ratio							
	BghiPr/BeP	BghiPr/IP	BghiPr/BbF	Bap/BghiPr	Pyr/BaP	Flu/Pyr	BaA/BaP	Tph+Chr/BeP
1990	1.4	19.3	0.7	0.3	4.6	0.9	1.6	0.5
1991	1.5	3.1	1.2	0.6	1.1	0.4	0.2	0.1
1992	2.8	2.3	2.5	0.2	3.0	0.2	0.4	0.1
1993	2.6	2.0	2.5	0.1	3.0	1.0	0.9	0.2
1994	1.9	1.9	1.7	0.3	2.1	1.1	0.6	0.3
1995	3.1	2.5	3.6	0.2	1.6	1.0	0.5	0.7
1996	2.7	2.1	2.9	0.2	2.6	0.5	0.4	0.2
1997	5.2	2.1	4.7	0.1	0.9	0.7	0.7	0.3
1998	1.6	2.2	1.2	0.3	2.2	0.9	3.8	0.8
Mean	2.6	4.2 (2.3)[ξ]	2.3	0.3	2.3	0.7	1.0	0.4
Max.	5.2	19.3 (3.1)[ξ]	4.7	0.6	4.6	1.1	3.8	0.8
Min.	1.4	1.9	0.7	0.1	0.9	0.2	0.2	0.1

[ξ] Excluding the 1990 data.

(Cretney et al. 1985), and the ratio of BaP/BghiPr (0.3) implies vehicle exhaust contributions (NAS 1972; Møller and Alfheim 1980).

Because BghiPr is regarded as an evident indicator of gasoline exhaust, the following discussion will focus on the characteristic ratios of the individual PAH related to BghiPr. The BghiPr/BeP ratio in this study is close to that measured in the roadway tunnel in our previous study in the roadway tunnel (Chiang et al. 1996). This finding suggests that BeP should have additional sources to compensate for its reaction loss because BeP is supposed to be more active than BghiPr. The ratios of BghiPr/IP, BghiPr/BbF, and BaP/BghiPr are lower than those in the tunnel. Because the BghiPr is considered less active in the ambient air, the results indicate that in addition to traffic volumes, there may be other sources for IP and BbF. BaP has been reported as a very active compound in the air, so a lower BaP/BghiPr ratio is expected.

The ratio of Pyr/BaP (about 2.3) is fairly comparable to the finding reported by Masclet et al. (1986). The Flu/Pyr ratio is observed to be about 0.7, which indicates the pollution of petroleum or vehicles (Masclet et al. 1986; Lowenthal et al. 1994). These 2 ratios are higher than those measured in the roadway tunnel, especially for Pyr/BaP, due to the high reactivity of BaP and nontraffic sources of Pyr and Flu. Therefore petroleum refinery could be a probable source. While the BaA/BaP ratio (about 1.0) indicates the wood or diesel soot sources, gasoline pollution might also be predominant (Li and Kamens 1993). The ratio of (Tph+Chr)/BeP (0.4) is within the range measured in the roadway tunnel; thus traffic would be a probable source (Benner et al. 1989).

Qualitative Source Resolution of PAHs

Qualitative identification of probable sources of PAHs over several years was performed by FA, and the results are summarized in Table 4. Four factors in particulate PAHs are retained, and the total explained variance is 72%. Factor 1 is significantly related to BaP, Pr, BeP, and BbF, which is indicative of the industrial origins. High factor loadings of DbA, IP, and BghiPr are associated with Factor 2, which suggests contributions from gasoline exhaust and oil combustion. Higher loadings of BaA and Tph+Chr are obtained in Factor 3, indicating a potential pollution of coal combustion. Factor 4 is moderately correlated with Ben and contains average loadings of PhA and Flu. This could be attributed to petroleum refinery, diesel exhaust, or biomass burning.

The resolution of probable contributors of gaseous PAHs determined by FA is also shown in Table 4. There are 3 factors retained, accounting for 77% of variance in the system. Factor 1 is highly associated with Pyr, Flu, Ben, PhA, and Tph+Chr, which is primarily due to incineration and diesel exhaust. Heavy factor loadings of BbF, Pr, BaA, and BaP and moderate loadings of

Table 4

Results of factor analysis for particulate and gaseous PAH species measured in TSP samples over several years

	Particulate				Gaseous		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3
PhA	0.17	0.10	0.20	0.50	**0.85**	0.30	−0.08
Flu	0.16	0.15	0.21	0.45	**0.98**	0.15	−0.04
Pyr	0.03	0.06	0.07	0.12	**0.99**	0.09	−0.02
Ben	0.21	0.14	0.21	*0.62*	**0.92**	0.23	−0.03
BaA	0.26	0.15	**0.87**	0.13	0.32	**0.82**	−0.003
Tph+Chr	0.21	0.16	**0.78**	0.38	**0.72**	0.43	−0.07
BbF	**0.77**	0.33	0.31	0.27	0.45	**0.84**	−0.0001
BeP	**0.81**	0.38	0.24	0.23	*0.51*	*0.68*	0.07
BaP	**0.94**	0.23	0.09	0.08	0.32	**0.79**	0.06
Pr	**0.89**	0.27	0.20	0.18	0.03	**0.83**	0.19
DbA	0.21	**0.92**	0.13	0.09	−0.06	0.04	**0.81**
IP	0.31	**0.91**	0.13	0.15	−0.04	*0.61*	0.28
BghiPr	0.34	**0.91**	0.10	0.12	−0.03	0.15	**0.79**
Explained variance	26.1%	22.9%	13.5%	9.4%	36.1%	30.2%	10.8%
Total	**72%**				**77%**		
Probable sources	• Industrial origins	• Gasoline exhuast • Oil combustion	• Coal combustion	• Petroleum refinery • Diesel exhaust • Biomass combustion	• Incineration • Diesel exhaust	• Oil burning • Coal combustion	• Gasoline exhaust

BeP and IP are related to Factor 2, which suggests a combination of oil burning and coal combustion. Factor 3 is correlated with DbA and BghiPr, possibly from gasoline exhaust.

The qualitative source resolution by FA shows that the contributors of particulate PAHs are much more complicated than the gaseous PAHs. Lower molecular weight species of particulate PAHs behave quite uncertainly in the atmosphere; thus it should be with caution that they be considered as tracers for the source identification of particulate PAHs.

CONCLUSIONS

The features of PAH species are characterized by a long-term measurement program. Results show that the PAH concentrations measured in a metropolitan area are lower than those in several countries. The concentration distributions of PAH compounds are not consistent, which implies complicated contributors and distinct reaction mechanisms. The ratios of total particulate PAH to TSP represent a decreasing trend. The particulate PAH level in winter is about 2.5 times higher than that in summer. The contents of 5- and 6-ring particulate PAHs associated with high health risks are higher in cold weather, and their percentages in autumn and winter are more than 60% of the total particulate PAHs. The results derived from G/P ratios of PAHs suggest that different reaction mechanisms occur among PAH compounds. The G/P ratio is obviously related to the C-atom number of PAHs. The findings from different characteristic ratios of PAHs are consistent with the results of the FA. In short, traffic exhaust should be the primary contributor in conjunction with the emission from industrial origins. The suspected carcinogenic compounds yield much higher levels in autumn and winter.

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