Estimation of the annual scavenged amount of polycyclic aromatic hydrocarbons by forests in the Pearl River Delta of Southern China

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Our results suggest that forests perform an important step for the fate of PAHs in the atmosphere.

Abstract

Leaves of six main tree species from the Pearl River Delta (PRD) in Southern China were collected to identify the interspecific variability, the spatial variability and the seasonal variations of polycyclic aromatic hydrocarbons' (PAHs) concentrations, and to calculate the amount of PAHs removed by leaves. PAHs concentrations in pine needles were much higher than in broad-leaves and leaves from urban/industrial areas (Baiyunshan and Heshan) exhibited two times greater concentrations than leaves from the rural area (Dinghushan). Seasonal variations of PAHs in leaves occurred with lesser concentrations in September. Leaves in PRD scavenged 3.7 ± 0.9 t PAHs y^{-1}, accounting for about 10% of the total amount emitted in this region. This result suggests that forests play an important role in the fate of PAHs.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one class of persistent organic pollutants, ubiquitous in the environment. They mainly are byproducts of the incomplete combustion of coal/petroleum and pyrolysis of organic materials. Some PAHs are carcinogenic and/or mutagenic (Menziec et al., 1992) and represent considerable public health hazards, therefore, they are being widely studied to assess their toxicity and distribution (Alves et al., 2001; Chang et al., 2006; Hwang et al., 2003; Lee et al., 1981; Lehndorff and Schwark, 2004). Most PAHs are originally generated as gases and their fate depends on their size. In general, high volatile compounds (2- and 3-ring) remain as gases in the atmosphere and low volatile compounds (5- and 6-ring) agglomerate into or are adsorbed onto particles subsequently and are distributed randomly (Mader and Pankow, 2002). Compounds of intermediate volatility (4-ring) exist in both gaseous and particle-bound forms and the percentage of partition depending on temperature (Bidleman, 1988; Cortes and Hites, 2000; Pankow, 1987).

Gaseous PAHs can deposit onto tree leaves, crops or aquatic environments via dry/wet deposition and diffusion, thereby reducing the concentration of free pollutants in the atmosphere and accordingly decreasing the risks of human exposure (Bacci et al., 1990; Franzaring and Eerden, 2000; Horstmann and McLachlan, 1998; Wania and McLachlan, 2001). The accumulation of PAHs on the vegetation depends on various parameters: the chemical and physical properties of the molecules such as molecular weight, lipophilicity and aqueous solubility, the environmental conditions such as air temperature, rainfall, and pollutant concentration in the atmosphere, and the plant species which determine the physical properties of leaves and their ability to adsorb PAHs (Barber et al., 2002, 2004; Böhme et al., 1999; McLachlan, 1999). Therefore, PAHs concentrations deposited on vegetation vary

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greatly across environments and plant species. Values were reported to range from negligible concentrations to several orders of magnitude (Hwang et al., 2003; Lehndorff and Schwark, 2004; Liu et al., 2006; Nadal et al., 2004; Simonich and Hites, 1994a; Smith et al., 2001; Wagrowski and Hites, 1997). In a study led over the northeastern region of USA, Simonich and Hites (1994a) estimated that the vegetation removed about 40% of the PAHs emitted into the atmosphere. This percentage was later revised downward to 4% by Wagrowski and Hites (1997) using a broader sampling, however, the role of vegetation in sequestering gaseous PAHs should not be neglected.

Forests cover almost 50% of the Pearl River Delta (PRD) (Editorial Committee of Forests of Guangdong, 1990). This region has become a growing concern for air pollution over the last two decades following a rapid urbanization and industrialization, especially PAHs emission (Fu et al., 2003). Past studies in the region mostly took interest in the distribution of PAHs in the atmosphere, soil and water, and no investigation was led to assess their presence on plants (Fu et al., 2003; Li et al., 2006; Liu et al., 2005a, 2006; Luo et al., 2004; Mai et al., 2002; Wang et al., 2007). However, forests may be important in sequestering gaseous PAHs. In this study, we aimed at determining the PAHs accumulation capacity of different plant species from PRD and the spatial and temporal variability of PAHs deposition on plants. Using these information, we evaluated the amount of PAHs sequestered annually on plant leaves in PRD and how much this accounted to total PAHs emission. We were interested in studying the accumulation of gaseous PAHs, therefore, our study ignored PAHs accumulation by wet and dry particle-bound depositions.

2. Materials and methods

2.1. Site description

PRD includes nine districts that cover an area of about $4.2 \times 10^4 \, \text{km}^2$ (Fig. 1) close to the Tropic of Cancer. Annual average temperature is 21–23 °C and ranges from 13–15 °C in January to 28–29 °C in July. The annual precipitation fluctuates between 1500 and 1800 mm with about 80% falling during the wet season from April to September (Editorial Committee of Forests of Guangdong, 2005).

Three sampling sites were selected to represent the various regional conditions according to previous studies (Liu et al., 2006). In order to estimate PAHs pollution over the whole region, we selected three moderately polluted sites rather than extreme sites. Study sites included Baiyunshan (23°11′N, 113°19′E), an urban area spot in the north of Guangzhou city, Heshan (22°41′N, 112°54′E), an industrial area spot set up in the Open Experimental Station for Comprehensive Exploitation of Hilly Lands of the Chinese Academy of Sciences (CAS) and Dinghushan (23°10′N, 112°31′E), a rural area spot set up in the northwest of PRD at Dinghushan Forest Ecosystem Research Station of CAS. In order to avoid the influence of point source pollution, sampling spots were chosen away from roads and other emission sources. Samples were collected in March, June, September and December 2006 so as to capture the seasonal variations of PAHs deposition.

2.2. Sampling method

We selected the following six tree species for our study since they are major species in PRD (Editorial Committee of Forests of Guangdong,

1990): *Pinus massoniana* Lamb. (*Pm*), *Cunninghamia lanceolata* (Lamb.) Hook. (*Cl*), *Eucalyptus citriodora* Hook. (*Ec*), *Acacia auriculaeformis* A. Cunn. ex Benth. (*Aa*), *Acacia mangium* Willd. (*Am*) and *Schima superba* Gardn. et Champ. (*Ss*). All six species were sampled in Heshan while only *Pm* and *Ss* were sampled in the other two sites. Each sample was made of a mixture of many healthy and mature leaves picked with scissors at different heights and orientations from the canopy of at least five trees per species per site. Harvested leaves were immediately stored in polyethylene bags and carried to the laboratory.

2.3. PAHs extraction and analysis

Leaves were washed with deionized water until no particles adhered to their surfaces (Liu et al., 2005b) and then cut into 1 cm squares. Leaf squares were freeze-dried and kept frozen at −20 °C for analysis.

Sample (5 g) mixed with 5 g anhydrous sodium sulfate was added with a mixture (200 ppb, 5 μl) of naphthalene-d_8, acenaphthane-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} as surrogate standards, and Soxhlet-extracted with dichloromethane for 48 h. In order to eliminate the disturbance of elemental sulfur, activated copper granules were added to the collection flasks.

Extracts were rotary evaporated to 10 mL, then the solvent was exchanged two times with 20 mL hexane, and they were rotary evaporated to 5 mL. Extracts were further concentrated to 1 mL under a gentle stream of nitrogen, then purified on an 10 mm i.d. aluminum/silica/florisil column filled from bottom to top with neutral silica gel (10 cm, 3% deactivated), neutral aluminum (6 cm, 3% deactivated), neutral florisil (5 cm) and anhydrous sodium sulfate (2 cm). The column was eluted with 70 mL of dichloromethane/hexane (1:1). The collected fraction was concentrated to 0.5 mL under a gentle nitrogen steam. After that, extracts were purified on a gel permeation chromatography (GPC) column (10 mm i.d., filled with 10 g of S-X3 Bio-beads) to eliminate lipids. The GPC column was eluted with 80 mL dichloromethane/hexane (1:1). The first 35 mL eluent was discarded, and the following 45 mL that contained PAHs were collected and concentrated to 0.2 mL (Liu et al., 2005b). A known amount of hexamethylbenzene was added as an internal standard prior to GC–MS analysis.

GC–MS analysis was carried out using a GC 8000 Top and Voyager (Finnigan-MAT) in selected ion monitoring (SIM) mode. Samples (1 μL) were injected with a 15 min solvent delay time. The oven temperature started down at 50 °C for 5 min and increased up to 290 °C (10 min hold time) at a rate of 3 °C min^{-1}. The following 15 PAHs were analyzed: acenaphthene (Ace), acenaphthylene (DiH), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[123-*cd*]pyrene (Ind), dibenzo[*ah*]anthracene (DiB), and benzo[*ghi*]perylene (BghiP).

Quality assurance and quality control were ensured using laboratory blanks and recovery standards (Lin et al., 1999). The laboratory blanks did not show any detectable PAHs. The mean percent recoveries were as follows: naphthalene-d_8: 30.3%, acenaphthane-d_{10}: 80.6%, phenanthrene-d_{10}: 98.8%, chrysene-d_{12}: 112.4%, perylene-d_{12}: 106.2%. Final PAHs concentrations in extracts were corrected to take into account the recoveries. Each sample was analyzed three times and results presented below are the average values.

2.4. Measurement of lipid content and specific leaf area (SLA)

Lipids were extracted from 3 g of sample using Soxhlet-extraction with dichloromethane/hexane (1:1) for 48 h. Extracts were concentrated, dried, and weighed to calculate lipid contents.

SLA, the ratio of leaf surface area to dry weight, was obtained by two different procedures depending on tree species. For broadleaved species (including *Cl*), leaf area of 50 intact random leaves per species was determined with a light box equipped with an area meter (LI-3000A). Total area was obtained by adding individual areas. For needle-leaf species, a representative cluster was selected. The length and diameter were recorded and we calculated the total surface area of the cluster as $d\pi l$, where d is the needle diameter and l
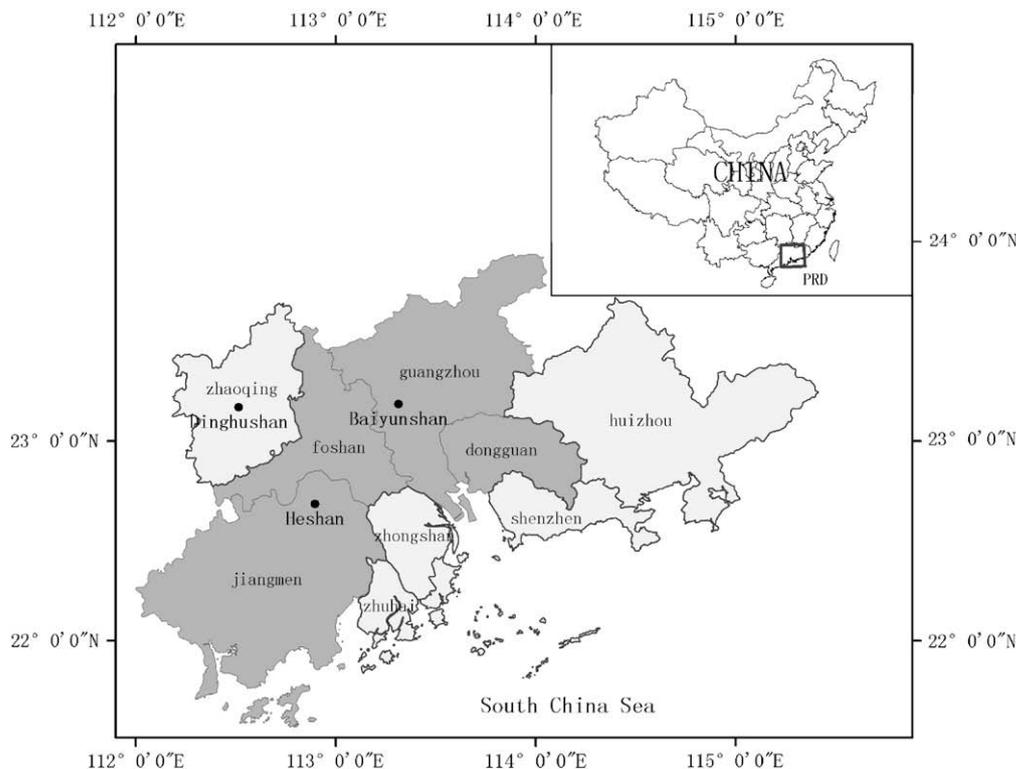
Fig. 1. Sampling locations: (●) sample locations, (▨) urban/industrial areas, (▢) rural areas.

is the length of the needle (Wagrowski and Hites, 1997). Leaves were dried at 95 °C for 24 h prior to weighing.

2.5. Data analysis

All analyses were conducted using the SPSS 11.5 software with $\alpha = 0.05$.

Correlations between $\sum$PAHs and the individual components of PAHs were analyzed using bivariate correlations with Spearman correlation coefficients. Differences among species, seasons and sites were analyzed using ANOVA. When significant differences existed, they were further analyzed with the Tukey multiple comparison test. Analysis was performed either directly on PAHs concentrations when their variances were tested as homogeneous or on log transformed concentrations in the other case.

Annual amounts of scavenged PAHs by forests were calculated as follows:

$$\text{Scavenged PAHs} = \frac{1}{\text{LLS}} \sum_{i=1}^{3} (\text{FA}_i \text{LAI}_i C_i) \quad (1)$$

where LLS is the leaf life-span, i is one of three different forest types, FA is the forest area, LAI is the corresponding leaf area index and C is the concentration of PAHs. A detailed classification of forest types and regions is given in Section 3.

Annual PAHs emissions in PRD were calculated using formulas that are as follows:

$$\text{Emitted PAHs} = P \sum_{k=1}^{6} \sum_{j=1}^{15} (\text{Source}_k \text{EF}_{kj}) \quad (2)$$

where k is one of six types of PAHs emission sources (consumptions of: coal by power plant and industry, coal by cocking plants, domestic coal, petroleum by transports, petroleum by non-transports, natural gas), j is one of the 15 compounds of PAHs, Source is the PAH amount annually emitted by each fossil energy consumption in Guangdong province (Editorial Committee of China Energy Statistical Yearbook, 2007), EF is the corresponding emission factors of PAHs (Xu et al., 2005), P is the percentage of gross domestic product (GDP)

that PRD accounted for the whole province (80%) (Editorial Committee of Forests of Guangdong, 2005).

3. Results and discussion

3.1. Leaf PAHs concentrations

3.1.1. Interspecific variability

Flu, Phe, Fluo, Pyr and Chr were the major compounds in the samples, accounting for about 80% of total PAHs concentrations, similar to atmospheric gaseous PAHs composition (Li et al., 2004). Fig. 2 shows that the same trends occurred for both conifers and broadleaved species. The concentrations of Ace, DiH, Ant, BaA, BaP, Ind, BghiP, and DiB were all very low. Ace, DiH, Ant, and BaA are susceptible to photolysis (Wang et al., 2005) while BAP, Ind, BghiP and DiB mainly exist as particles, therefore, they are little adsorbed by leaves (Simonich and Hites, 1994b, 1995). Correlation analysis showed that most of PAH concentration positively correlated with one another and $\sum$PAHs except BghiP and DiB (Table 1). This is consistent with results from Wagrowski and Hites (1997) and we can conclude that kinetics for PAHs removal, volatilization and degradation were similar for the different tree species we studied here. No specific accumulation or metabolic transformation occurred.

Fig. 3 shows $\sum$PAHs concentrations for the various tree species and sites. For all sites and periods, different tree species showed different levels of accumulation of PAHs and PAHs concentrations in pine needles were much greater than
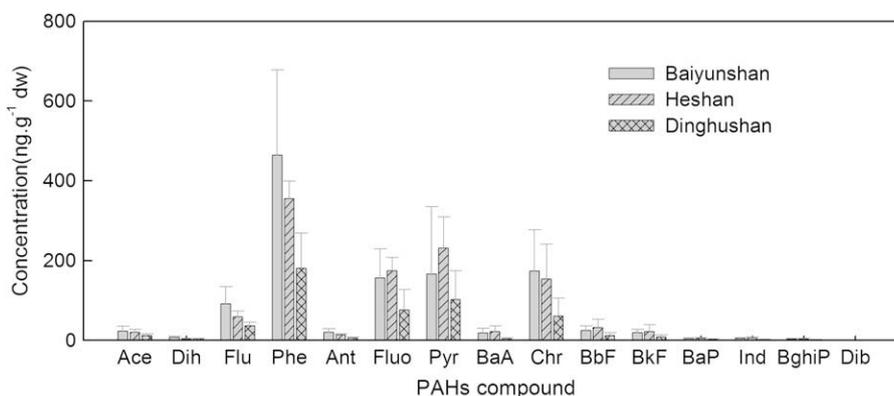
Fig. 2. PAHs concentrations in pine needles of the three sites. Vertical bars are the standard deviation.

in broad-leaves ($P < 0.01$ except Ec). Plant parameters, which are often considered as affecting PAHs concentration in leaves, are specific leaf area (SLA), lipid content and leaf surface roughness (Franzaring and Eerden, 2000; Howsam et al., 2000; Simonich and Hites, 1995). Leaves with greater lipid content or roughness tend to adsorb more strongly gaseous PAHs while a greater SLA implies a larger adsorption surface for a same leaf weight (Simonich and Hites, 1994b).

The leaf lipid contents of our six species are given in Table 2. The highest values were found in pine needles (152.4 mg g^{-1}), followed by Cl and Ec while the values for other broad-leaves were close to each other. This result corroborates observations from Simonich and Hites (1994b) that greater lipid content cause greater PAHs adsorption. However, no correlation existed between PAHs and lipid content for species with moderate lipid content, and even a negative correlation existed for Aa. The PAHs concentration based on lipid content was 4.2 ± 2.5 ng mg^{-1}, with its variation to be much smaller than that based on dry weight (610.2 ± 408.9 ng g^{-1}) (Fig. 4). This suggests that concentration based on lipid content can reduce the difference of inter-species greatly and lipids play a significant role in limiting the accumulation of PAHs in leaves although it is not the only cause of variation.

The $\sum$PAHs concentration based on leaf area enlarged the difference of inter-species in accumulating PAHs. The value (6.7 ± 6.4 ng cm^{-2}) dispersed much more than based on dry weight (Fig. 4), giving prominence to the influence of surface character of leaves in adsorbing PAHs. Further investigation indicated that rough (for example, Aa) or pinnate (for example, Cl) leaves had higher PAHs concentrations than flat and smooth leaves for those species with comparable lipid contents. This result is consistent with other study (Howsam et al., 2000).

3.1.2. Intersite variability

PAHs concentrations observed in Baiyunshan and Heshan were higher than in Dinghushan (Fig. 3). The average values in pine needles were 1172.6 ng g^{-1} dw, 1095.1 ng g^{-1} dw, and 505.3 ng g^{-1} dw, respectively. Concentrations in urban/industrial areas were twice as great as in the rural area of Dinghushan while no difference existed

between Baiyunshan and Heshan, which suggests that the forests near pollution sources play a more important role in adsorbing PAHs from atmosphere. This result is consistent with studies which showed that PAHs emission sources are mainly located in urban or industrial areas (Li et al., 2006; Simonich and Hites, 1995; Wagrowski and Hites, 1997; Yunker et al., 2002). Although PAHs concentrations in leaves from the rural area were lower than from urban/industrial areas in PRD, differences were much smaller than in USA. There the ratio between urban and rural areas was almost 10-fold (Cotham and Bidleman, 1995; Wagrowski and Hites, 1997). This may be related to the large diffusion of small factories over the whole region, resulting in a concerning regional contamination.

3.1.3. Seasonal variability

Fig. 3 shows that PAHs concentration in pine needles varied with the season. We did not detect any significant changes for broadleaved species which may be related to their lower lipid contents that restrict PAHs adsorption. However, significant season differences in pine needles only occurred in Dinghushan. Concentrations were greater in March and June and lower in September and December while no significant difference occurred within each season. The lack of significant seasonal variation in Baiyunshan and Heshan may be linked to the difference of pollution sources amongst the sites. In the rural area, point source pollutions are relatively few, and PAHs volatilization from the polluted ground (road, contaminated soil, etc.) depending on temperature mainly might play an important role. In urban or industrial areas, emission of vehicles and industry may cover up the effect of temperature change to some degree (Alves et al., 2001; Li et al., 2006).

In addition, the seasonal variation of PAHs concentrations in leaves did not coincide with that in the atmosphere. Higher PAHs concentrations were in summer in the atmosphere (Li et al., 2006). As seeking for the reasons of the contradiction, considering PAHs in leaves are the result of air–vegetation partition during a period of time (several weeks or several months) (Simonich and Hites, 1994b), we retrospected to an early period. The annual variations of temperature, relative humidity and sunlight time in this region were shown in Table 3.

Table 1
Cross correlations of PAHs concentrations between 15 compounds and ∑PAHs for our samples

		Ace	Dih	Flu	Phe	Ant	Fluo	Pyr	BaA	Chr	BbF	BkF	BaP	Ind	BghiP	Dib	∑PAHs
Ace	Correlation coefficient	1.000															
	P value	0.000															
Dih	Correlation coefficient	0.624**	1.000														
	P value	0.000	0.000														
Flu	Correlation coefficient	0.783**	0.729**	1.000													
	P value	0.000	0.000	0.000													
Phe	Correlation coefficient	0.732**	0.684**	0.920**	1.000												
	P value	0.000	0.000	0.000	0.000												
Ant	Correlation coefficient	0.555**	0.633**	0.701**	0.706**	1.000											
	P value	0.000	0.000	0.000	0.000	0.000											
Fluo	Correlation coefficient	0.732**	0.521**	0.639**	0.761**	0.621**	1.000										
	P value	0.000	0.001	0.000	0.000	0.000	0.000										
Pyr	Correlation coefficient	0.801**	0.527**	0.677**	0.773**	0.496**	0.925**	1.000									
	P value	0.000	0.000	0.000	0.000	0.001	0.000	0.000									
BaA	Correlation coefficient	0.602**	0.405**	0.505**	0.658**	0.555**	0.887**	0.825**	1.000								
	P value	0.000	0.010	0.001	0.000	0.000	0.000	0.000	0.000								
Chr	Correlation coefficient	0.640**	0.453**	0.511**	0.677**	0.582**	0.920**	0.832**	0.954**	1.000							
	P value	0.000	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.000							
BbF	Correlation coefficient	0.381*	0.305	0.199	0.361*	0.461**	0.755**	0.624**	0.843**	0.835**	1.000						
	P value	0.015	0.056	0.217	0.022	0.008	0.000	0.000	0.000	0.000	0.000						
BkF	Correlation coefficient	0.382*	0.307	0.208	0.361*	0.446**	0.752**	0.607**	0.834**	0.855**	0.965**	1.000					
	P value	0.015	0.054	0.197	0.022	0.004	0.000	0.000	0.000	0.000	0.000	0.000					
BaP	Correlation coefficient	0.341*	0.341*	0.128	0.248	0.481**	0.616**	0.505**	0.718**	0.733**	0.876**	0.906**	1.000				
	P value	0.031	0.031	0.431	0.123	0.002	0.000	0.001	0.000	0.000	0.000	0.000	0.000				
Ind	Correlation coefficient	0.269	0.281	0.118	0.206	0.372*	0.566**	0.438**	0.666**	0.630**	0.895**	0.867**	0.877**	1.000			
	P value	0.093	0.079	0.469	0.203	0.018	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000			
BghiP	Correlation coefficient	0.124	0.199	0.002	0.114	0.269	0.403**	0.297	0.529**	0.485**	0.784**	0.753**	0.794**	0.931**	1.000		
	P value	0.444	0.219	0.992	0.486	0.093	0.010	0.070	0.000	0.002	0.000	0.000	0.000	0.000	0.000		
Dib	Correlation coefficient	0.282	0.237	0.128	0.188	0.303	0.335*	0.338*	0.456**	0.355*	0.499**	0.373*	0.520**	0.555**	0.545**	1.000	
	P value	0.078	0.140	0.430	0.245	0.057	0.035	0.033	0.003	0.025	0.001	0.018	0.001	0.000	0.000	0.000	
∑PAHs	Correlation coefficient	0.806**	0.611**	0.751**	0.863**	0.642**	0.956**	0.941**	0.882**	0.904**	0.676**	0.688**	0.557**	0.487**	0.338*	0.308	1.000
	P value	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.033	0.053	0.000

** Correlation is significant at 0.01 1evel (two-tailed).
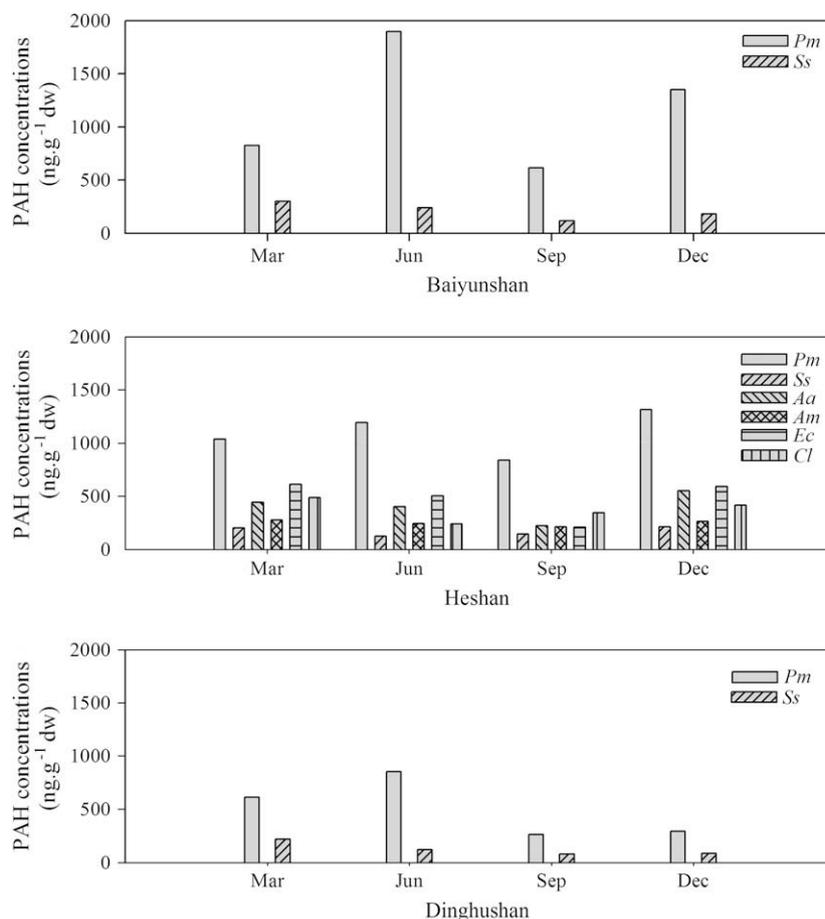* Correlation is significant at 0.05 1evel (two-tailed).

Fig. 3. PAHs concentrations in leaves of the urban, industrial and rural areas of the Pearl River Delta, China, for the various species studied. Baiyunshan: urban site; Heshan: industrial site; Dinghushan: rural site.

Obviously, the highest temperature appears in the third season, almost 30 °C, which could lead to more PAHs partition to the atmosphere (Simonich and Hites, 1994b; Yamasaki et al., 1982). At the same time, the lower relative humidity and longer sunlight hours also happened in this quarter, and all of these factors can increase the photolysis of PAHs greatly (Wang et al., 2005). Hence, in hot season, although PAHs may be volatilized from contaminated ground surface (road, water, soil, etc.), the continuous maintenance of a relative high concentrations in the atmosphere (Li et al., 2006) for a good time was needed to partition to the plant from the atmosphere.

Regarding the fact that the PAHs concentration in leaves was not in the trough in December when the PAHs content in the atmosphere was the lowest. This was because the vegetation–air partition coefficient increases in winter (Simonich and Hites, 1994b), namely, PAHs susceptible to accumulating to plants in the cold weather. When we monitored the atmospheric quality with plants, it should be fully considered whether the climatic conditions might induce inconsistent PAHs concentrations between plants and atmosphere before drawing the conclusion.

3.2. PAHs scavenging by forests

In order to properly calculate the amount of PAHs scavenged by forests in PRD, we had to perform the following operations: (1) classifying forest types according to PAHs concentrations in leaves; (2) dividing the region into subregions depending on the contamination level; and (3) calculating the values of two important parameters: leaf area index and leaf life-span.

Table 2
Leaf areas and lipid contents of the six species

Species	Pm	Cl	Ec	Aa	Am	Ss
Lipid content (mg g^{-1})	152.39	115.72	103.62	70.85	87.62	74.86
Leaf area (cm^2 leaf^{-1})	2.36	0.60	33.51	22.95	75.61	20.88

Pm, *Pinus massoniana*; *Cl*, *Cunninghamia lanceolata*; *Ec*, *Eucalyptus citriodora*; *Aa*, *Acacia auriculaeformis*; *Am*, *Acacia mangium* Willd.; *Ss*, *Schima superba*.
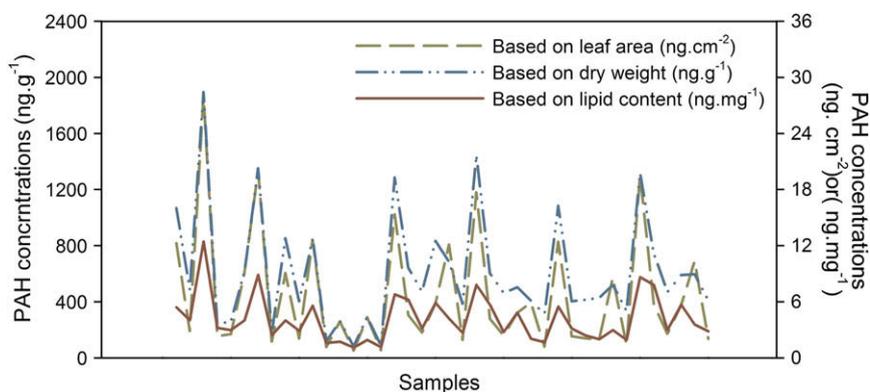
Fig. 4. PAHs concentrations in leaves based on dry weight, leaf areas and lipid contents.

3.2.1. Classifying forest types

PAHs concentrations were greater in pine needles than in broad-leaves while little differences occurred amongst the later. Therefore, we classified forest types into three classes: coniferous forests, broadleaved forests and mixed forests. These three types constitute about 75.6% of the total forested land in PRD (Peng, 2003).

3.2.2. Classifying areas

Seasonal differences, whether they were significant or not, exhibited the same pattern in all areas. Since the whole PRD is subjected to the same climatic conditions, we assumed that this pattern is consistent and could be extended to the whole region. PAHs concentrations were not different between Baiyunshan and Heshan where they were double of Dinghushan concentrations. Therefore, we divided the whole region into two classes: urban/industrial areas and rural areas.

According to the results about PAHs concentrations in the atmosphere in PRD (Liu et al., 2006; Wang et al., 2007), we attributed each of PRD areas to one of the two classes defined above as shown in Fig. 1. The urban/industrial areas were marked dark grey, and the rural areas grayish. There may be some pieces of clean areas in the urban/industrial areas, or contaminated pieces in the rural areas, however, we assumed that their overall effect was very limited and we did not consider them. We did not classify the region according to the real urban and rural areas, because an urban area may be not a contaminated one, such as Shenzhen, pollution is affected not only by the industrial structure but also by the investment in protecting environment and geographical location (Hwang et al., 2003; Liu et al., 2006; Wang et al., 2007).

PAHs concentrations for urban/industrial areas were taken as in Heshan with 4.4 ± 3.1 ng cm^{-2} and 16.2 ± 3.1 ng cm^{-2}

for broadleaved and coniferous forests, respectively. The mean (10.3 ± 2.7 ng cm^{-2}) of the two values was taken as PAHs concentration for mixed forests (Table 4). Similarly, rural areas' concentrations were taken as in Dinghushan with 7.5 ± 4.1 ng cm^{-2} for coniferous forests. Given that only two species were measured in Dinghushan, PAHs concentration for broadleaved forests was calculated as half the value of Heshan broadleaved forests considering the concentration ratio in pine needles for the two sites. Accordingly, 4.9 ± 1.7 ng. cm^{-2} was calculated as the concentration for mixed rural forests.

3.2.3. Calculating leaf area index (LAI) and leaf life-span (LLS)

Leaf area index (LAI), the total area of leaves per unit of land area covered by the vegetation, is an important factor that influences regional loads of PAHs in leaves. It can be calculated from SLA by multiplying this value by the estimated leaf biomass per land surface unit. LAI values of all forest types from the literature often differed from one region to another (Ren et al., 1994; Shen et al., 2003; Zhang et al., 2004b; Zhao et al., 2002). For example, in Dinghushan, the LAI of broadleaved forest, pine forest and mixed forest were 17.6, 8.8 and 12.3, respectively (Ren et al., 1994), while in Heshan the values declined to 2–4, 2.2–3.92 and 2 (Ren et al., 1994; Zhao et al., 2002). In order to minimize errors, we took the medians of all LAI values available in the region, which were 3.68, 3.92 and 4 for broadleaved forest, pine forest and mixed forest, respectively.

Leaf life-span (LLS) ranges from 8–9 months to 4–5 years in PRD, but mainly 1–2 years for those main species we considered (Wang, 1988). The LLS of pine trees is about 1.5 years, *Ss* and *Ec* 1.5 years, *Aa* about 1–1.5 years, *Am* 1 year and other broadleaved trees also 1–1.5 years. Only the LLS of *Cl* is longer and can reach 4–5 years (Wang, 1988; Zhang and Luo, 2004a). So we retained an LLS of 1.5 year for all species. The amount of litter-fall varies with different species and seasons, but the fluctuations are small (Guan et al., 2004), hence we regarded the average of PAHs concentrations in March, June, September and December as the annual averages.

Table 3
Meteorologic parameters in the Pearl River Delta region during 2006

Month	Temperature (°C)	Relative humidity (%)	Sunlight hour (h)
1–3	17.2	73.0	205.7
4–6	25.8	80.0	259.1
7–9	28.4	75.0	471.5
10–12	21.8	67.0	455.6

Table 4
Total amount of PAHs cleared by forests (with standard deviation) in the Pearl River Delta, China

	Forest areas (km^2)	PAHs concentrations (ng cm^{-2})	Annual removal PAHs (kg)	% of PAHs emitted
Urban/industrial areas				
Broadleaf	2657	4.4 ± 3.1	288 ± 198	0.8 ± 0.5
Needle-leaf	3117	16.2 ± 3.1	1323 ± 249	3.6 ± 0.7
Needle−broadleaf	461	10.3 ± 2.7	127 ± 33	0.3 ± 0.1
Rural areas				
Rural broadleaf	5737	2.2 ± 1.5	311 ± 218	0.9 ± 0.6
Rural needle-leaf	7450	7.5 ± 4.1	1458 ± 808	4.0 ± 2.2
Rural needle−broadleaf	1631	4.9 ± 1.7	211 ± 73	0.6 ± 0.2
$\sum$	21,052		3718 ± 899	10.2 ± 2.5

3.2.4. Amount of PAHs scavenged by forests

We calculated that about 1.7 ± 0.3 t PAHs y^{-1} and 2.0 ± 0.8 t PAHs y^{-1} were removed from the atmosphere by the forests from urban/industrial and rural areas, respectively, for a total of 3.7 ± 0.9 t PAHs y^{-1}. As mentioned before, the main PAHs compounds in leaves were Flu, Phe, Fluo, Pyr and Chr. Given the percentage they accounted in $\sum$PAHs, we calculated their individual amounts removed by forests as: 200 ± 50 kg Flu y^{-1}, 1200 ± 300 kg Phe y^{-1}, 600 ± 150 kg Fluo y^{-1}, 700 ± 200 kg Pyr y^{-1} and 550 ± 150 kg Chr y^{-1}, respectively.

We calculated that the annually emitted PAH amount was 36.6 t y^{-1} in PRD. Phe, Fluo and Flu were the top three, accounting for 53% of the total emission (Fig. 5).

Comparing the amount of PAHs removed by forests with that emitted by sources, we found that the removal ratio of Chr was the highest (41%), followed by Pyr and Flu (about 20%). The emission of high ring PAHs compounds is moderate, whereas their removal amounts are only little for the limitation of accumulation in leaves. However, high ring PAHs compounds mainly take part in particles and vegetation reduce wind speed efficiently, which is propitious to the deposition of particles. Therefore, forests might play an important role in the deposition of high ring PAHs (McLachlan and Horstmann, 1998; Smith and Jones, 2000; Wania and McLachlan, 2001).

PRD forests in our simulation absorbed about 10% of total yearly PAHs emissions in 2006. Although our study ignored other forms of vegetation such as grasses and crops, the ratio of absorbed PAHs emission by the vegetation in PRD is still larger than in the northeastern USA (Wagrowski and Hites, 1997). This difference is probably due to the difference of the vegetation, PAHs concentrations in the atmosphere and regional climate. From our results, we can conclude that greater forest coverage near pollution sources, greater percentage of coniferous forests and lower regional temperatures are factors that increase PAHs sequestration by forests.

The PAHs removed by plants are degraded by biotic and abiotic process in forest soil and only a small part re-volatilizes into the atmosphere. Most of the compounds in forest soils are adsorbed by the soil organic matter which reduces human exposure (Simonich and Hites, 1994b; Wang et al., 2005). Forests perform an important process, concentrating gaseous PAHs into the soil and, therefore, probably accelerating their degradation (Simonich and Hites, 1995; Smith et al., 2001; Wania and McLachlan, 2001).

Given the limited number of sampling sites and samples we used, the simplification of residence time in leaves and leaf area index and the uncertainty of emission factors, the present evaluation is only a rough estimate. Precise calculation needs more detailed information.

4. Conclusion

PAHs concentrations were greater in pine needles than in broad-leaves. Flu, Phe, Fluo, Pyr, and Chr were the five dominant PAHs compounds. Tree species showed variable abilities to sequester PAHs and their ability could be explained by the differences in leaf cuticle lipid contents and leaf surface areas.
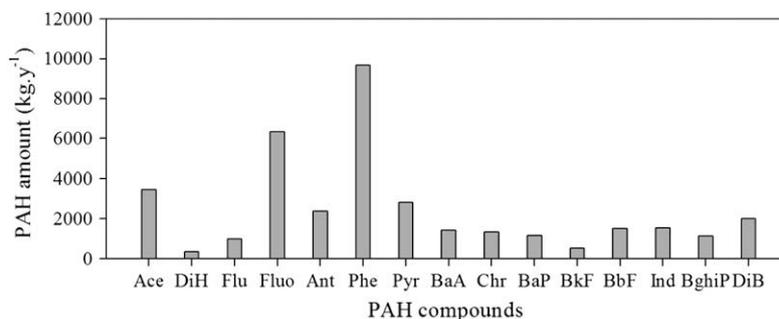

Fig. 5. Yearly amount of PAHs emitted in Pearl River Delta. Abbreviations: acenaphthene (Ace), acenaphthylene (DiH), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene(Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (Ind), dibenzo[ah]anthracene (DiB), and benzo[ghi]perylene (BghiP).

Trees from urban/industrial areas concentrated in their leaves twice as more PAHs than trees growing in rural areas. The PAHs concentration in leaves varied with seasons but these variations were not consistent with PAHs variations in the atmosphere. The lowest leaf concentrations were observed in September and these were probably related to higher temperatures and longer days at this time, which led to high photolysis. We estimated that forests scavenged around 3.7 ± 0.9 t PAHs y^{-1}. About 10% of PAHs emitted in PRD were absorbed from the atmosphere by forests.

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