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Spatial distribution and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) using semi-permeable membrane devices (SPMD) and pine needles in the Pearl River Delta, South China

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Abstract

Semi-permeable membrane devices (SPMDs) were deployed at 12 sites in the Pearl River Delta (PRD) during 2001–2002 to elucidate the spatial distribution and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) in the subtropical region. Pine needles from the same sites were also analyzed for PAHs for a comparison with SPMDs. In Guangzhou, high volume active air sampling (HiVol) was carried out weekly through out the year-round sampling campaign. The PAHs sequestered in SPMDs (in $ng\,SPMD^{-1}\,day^{-1}$) were found to be higher in winter than in summer. Using the HiVol data, SPMD sampling rates were calculated seasonally for some dominant gas-phase PAH compounds (Fluorene to Pyrene). These sampling rates ranged from 0.7 to $2.8\,m^3\,day^{-1}$, which were used to determine the atmospheric PAH concentrations at other sites. The calculated PAH concentrations, based on different temperature-dependant SPMD sampling rates, in the air were higher in summer than in winter. The PAH compounds sampled with SPMDs and pine needle were mainly associated with gaseous PAHs, while pine needles accumulated more high molecular weight (HW) PAHs. Good agreements were found in the spatial distribution of atmospheric PAHs measured by SPMDs and pine needles. The potential of using SPMDs for seasonal monitoring of atmospheric organic pollutants at a regional scale was demonstrated.
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Keywords: Semi-permeable membrane device (SPMD); Polycyclic aromatic hydrocarbons (PAHs); Passive air sampling; Seasonal variations; Pearl River Delta

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants in the environment. They originate mainly from anthropogenic sources such as fossil fuel combustion and direct release of

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petroleum and petroleum products. In the atmosphere, PAHs are present both in the vapor and particulate phases, especially aerosols with an aerodynamic diameter less than 2 μm (Venkataraman and Frendlander, 1994). As semi-volatile organic compounds, PAHs may be taken up by human through inhalation or direct intake from diet, which throw health threat to human and wildlife. Some of the PAHs have been described as mutagenic and carcinogenic, being included in the US EPA and the European Community priority pollutant lists. Some of PAHs show similar properties to persistent organic pollutants (POPs).

PAHs in the atmosphere are conventionally monitored by active air sampling techniques (e.g. high volume air sampler (HiVol)). The major drawbacks of active sampling are the high cost of the equipment and requirement of power and training; these restrict its application to widespread locations especially to remote regions. To better understand the regional distribution of POPs in different location, and to elucidate the source and fate of these compounds in environment, more convenient and powerful sampling techniques are needed, which should be cheap, easy to handle, and can be used to sample over periods of time at many locations concurrently. Several interesting studies

have therefore made use of 'environmental media', such as plant leaves (Bacci et al., 1990; Tremolada et al., 1996), tree bark (Simonich and Hites, 1997), to map the spatial distribution of POPs on the assumption that their POPconcentrations broadly reflect the ambient levels. In the past few years, a range of artificial passive air sampling devices have been developed and utilized for the spatial and time-integrated monitoring of POPs, including semi-permeable membrane devices (SPMDs), polyurethane foam (PUF) disks (e.g. Shoeib and Harner, 2002; Jaward et al., 2004) and polymer-coated glass (POG, e.g. Harner et al., 2003).

SPMD were first designed by the US Geological Survey (USGS) for the passive sampling of POPs from water (Huckins et al., 1990, 1993). To date, SPMDs are receiving increasing attention and are accepted as useful samplers for studies into spatial differences in concentrations and profiles of POPs in the atmosphere (Ockenden et al., 1998; Söderström and Bergqvist, 2003; Söderström et al., 2005; Bartkow et al., 2004; Van drooge et al., 2005).

Plants play an important role in the regional and global distribution of POPs, and many studies have found that POPs accumulate in plants (Jones et al., 1992; Tremolada et al., 1996; Simonich and Hites, 1994). The epicuticular waxy layer in pine needles
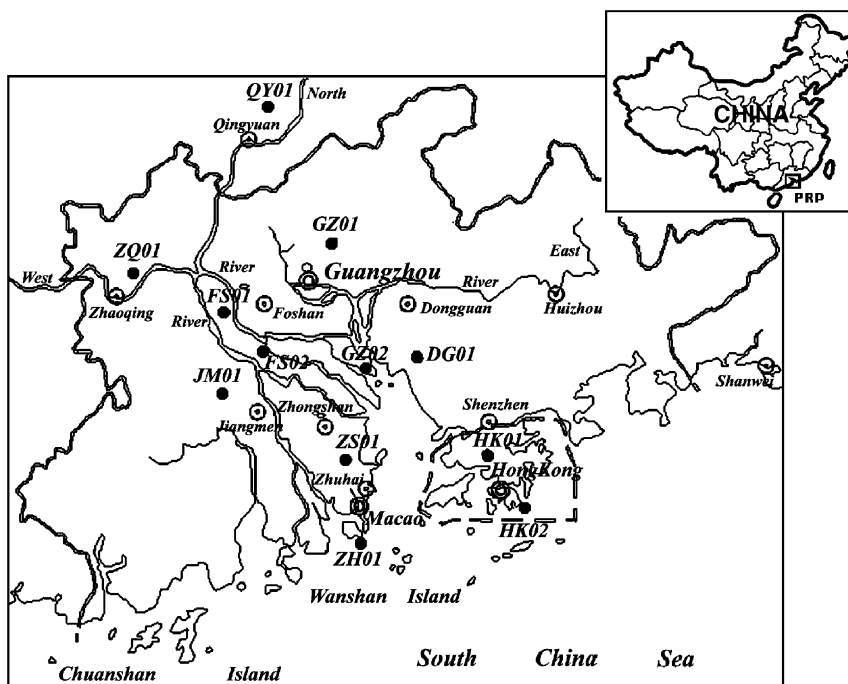

Fig. 1. Map of the sampling stations in the PRD.

can accumulate organic compounds from surrounding air. Studies indicated that gaseous deposition from the air to the waxy layer in plant is a major uptake process for lipophilic organic contaminants (McLachlan et al., 1995, 1999), and hence the concentrations of target compounds measured in pine needles may represent the integrated concentrations of those chemicals in surrounding air over time. Pine needles are widespread distributed, can be easily collected and the age is easy to determine. They may serve as good bio-monitors for atmospheric POPs pollution (Eriksson et al., 1989; Tremolada et al., 1996; Hwang et al., 2003; Hellström et al., 2004).

Located in the subtropical region, the Pearl River Delta (PRD) (Fig. 1) in the Guangdong Province has undergone fast economic development, urbanization and industrialization in the last two decades. It has become one of the leading economic regions and a massive manufacturing centre in China. Between 1980 and 2000, the population in the PRD has nearly doubled (from 21.4 million to 40.8 million). Regional Gross Domestic Product (GDP) grew from just over US$8 billion in 1980 to more than US$89 billion in the year 2000 (Guangdong Yearbook, 1981, 2001). However, the rapid urbanization and industrialization may have posed negative effect on the environment. Recent studies have shown that organic contaminants, including PAHs, polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are presented in various environmental media in the PRD (Fu et al., 2003; Zhang et al., 2002; Liu et al., 2005a; Mai et al., 2005).

In the Delta, few studies are available on atmospheric PAHs pollution, and most studies are defined to urban areas with single sampling sites using active sampling technique (Qi et al., 2001; Bi et al., 2003; Guo et al., 2003; Li et al., 2006). An over-all PAH spatial distribution study across the region is still lacking. In this study, the concentrations of atmospheric PAHs in the PRD were investigated using SPMDs and pine needles, aiming to evaluate the seasonal and spatial distribution of atmospheric PAHs in this area.

2. Experiment section

2.1. Study region

Located in the subtropical monsoon zone, the PRD is formed by alluvium delivered from the West, North, and East Rivers. The PRD includes Hong Kong, Macao and eight municipalities

in Guangdong provinces (namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Huizhou and Jiangmen). The region has an annual average temperature of 22 °C, annual precipitation of 1714 mm, and annual sunshine of 1990–2300 h.

2.2. Sample collection

SPMDs, of the USGS Standard designed (97 × 2.5 cm membrane containing 1 mL triolein), were deployed at 12 sites concurrently (within 3 days among sites) in the PRD, South China. SPMDs were exposed and collected every 3 months during 2001–2002 (April–June 2001; July–Sepember 2001; October–December 2001; January–March 2002). The sampling sites, on top of hills, were carefully chosen to avoid influences from air pollution point sources. The South China coastal sites HK02 and ZH01 were selected as the background of this area and characteristic to South China Sea. SPMDs were spread and secured in Stevenson screen boxes to minimize the influences from direct sunlight, rain, wind, and particulate deposition. Before and after sample collection, SPMDs were stored in sealed cans at −20 °C until analysis. Pine needles (*Pinus massoniana Lamb*) were collected at the same locations as SPMD deployments. Samples were collected from at least five trees, and only 1-year-old needles (according to their position on branches) were sorted and collected. The samples were packed into glass jars and stored at −20 °C until analysis.

Concurrent with the SPMD sampling, active air sampling was carried out weekly in Guangzhou (GZ01) each for a full day (24 h) using an HiVol. Approximately 335 m³ of air was sampled each time. The particulate phase was nominally described as what was retained by a Whatman 10 cm glass microfiber filter (GFF; grade GF/A) and the vapor phase by a PUF plug (length 8 cm, diameter 6.25 cm, density 0.035 g cm⁻³). Prior to sampling, GFFs were baked at 450 °C for 4 h, the PUF plugs were Soxhlet extracted (4–6 cycles/h) in dichloromethane for 24 h before use and dried under vacuum in a desiccators. After sample collection, PUF plugs and GFFs were stored frozen (−20 °C) in solvent-cleaned glass jars.

2.3. Exaction and clean-up

The analytical method used for the extraction and clean-up of PAHs in GFF and PUF was detailed in previous studies (Li et al., 2006). Briefly, Deuterated

PAH standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, pyrene-d12, chrysene-d12, and perylene-d12) were added as recovery surrogates, and GFF and PUF were Soxhlet extracted (4–6 cycles/h) with dichloromethane (DCM) for 48 h, the extracts were then fractioned and cleaned up using a mixed silica gel/alumina column.

The procedures of SPMD extraction and clean-up largely followed those described by Lohmann (2001). The particular matters on the exterior of the SPMDs were cleaned prior to extraction (this part did not analyze for PAHs). Surrogates were injected into and sealed with the SPMDs to monitor recoveries. SPMDs were then dialyzed for 2×24 h in hexane. The extracts were cleaned up through a mixed silica gel/alumina column, and further by a gel-permeation chromatography (GPC) column.

Pine needles were rinsed three times with deionized water, and air dried at 16 °C in a dark clean room with an air conditioner. The dried needle were minced and about 5–8 g samples were spiked with PAH surrogates and extracted by an accelerated solvent extractor (Dionex ASE 300) using a mixture of acetone and hexane (1:1) at 1500 psi and 100 °C for 2 cycles, each last for 20 min. Extracts were cleaned by silica/alumina column chromatography and further purified by GPC column (details were described in Liu et al., 2005b).

2.4. Instrument analysis

SPMDs, pine needles, GFFs and PUFs were analyzed for PAHs by GC-MSD (HP-5890 series II GC, HP-5972 MSD, equipped with a $30 \, \text{m} \times 0.25 \, \text{mm}$ HP5-MS column), GC temperature program was as follows: 60 °C for 2 min, 3 °C min^{-1} to 290 °C, and 290 °C for 30 min. The following 16 EPA PAHs were analyzed: naphthelene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DiA), and benzo[g,h,i]perylene (BghiP). Total PAHs ($\sum$PAH) was defined as the sum of the above compounds excluding Nap.

2.5. QA/QC

SPMD field blanks (SPMDs which were taken to the field in sealed containers but not exposed) and solvent/laboratory blanks each constituted 1 sample in 6. All data were blank corrected. Detection limits were calculated as mean plus three times the standard deviation of the blank and data below the limit of detection were rejected. Concentrations of all analytes were calculated relative to the GC internal injection standards. For HiVol samples, one field blank was collected every month, and a National Institute of Standards and Technology standard reference material (SRM 1941) sample were routinely analyzed with field samples. The recoveries of the surrogates ranged between 95–120% for the HiVol samples, 72–112% for SPMDs and 80–110% for pine needle samples. Presented results (SPMDs, pine needles, HiVol samples) were corrected for recoveries.

3. Result and discussion

3.1. PAHs in SPMDs and pine needles

In both SPMD and pine needle samples, the major PAHs were fluorene, phenanthrene, fluoranthene, pyrene and chrysene with phenanthrene dominating (accounted for 32–64% of the total PAHs); only small amount of high molecular weight (HMW) PAHs were detected in SPMDs, including BbF, BkF, BaP and Ind (Fig. 2). However, some differences in the PAH profiles were observed between the SPMD and pine needle samples. In Fig 2, HiVol-PUF/-GFF showed the nominally ascribed "vapor phase" and "particle phase" PAHs, respectively. Although SPMDs sample mainly of vapor-phase compounds, it is possible that there may have been uptake of PAHs from particle deposition to the oily surface of the SPMDs. By comparison, pine needles accumulated more of the HMW PAHs than SPMD did. As for plant/leaf passive air sampling, gaseous deposition has been shown to be the key process for many semi-volatile organic compounds (SOCs) (McLachlan et al., 1995; Tremolada et al., 1996). The difference of PAH profiles between SPMD and pine needles may suggest that pine needles had taken up more of particle deposition PAHs compared to SPMDs, or/ and some of the lighter PAHs in the pine needles may have reached equilibrium during their much longer exposure in the air. Moreover, SPMDs were deployed in Stevensons screens housing to protect from particulate deposition, and the exterior of SPMDs were cleaned prior to dialysis, these
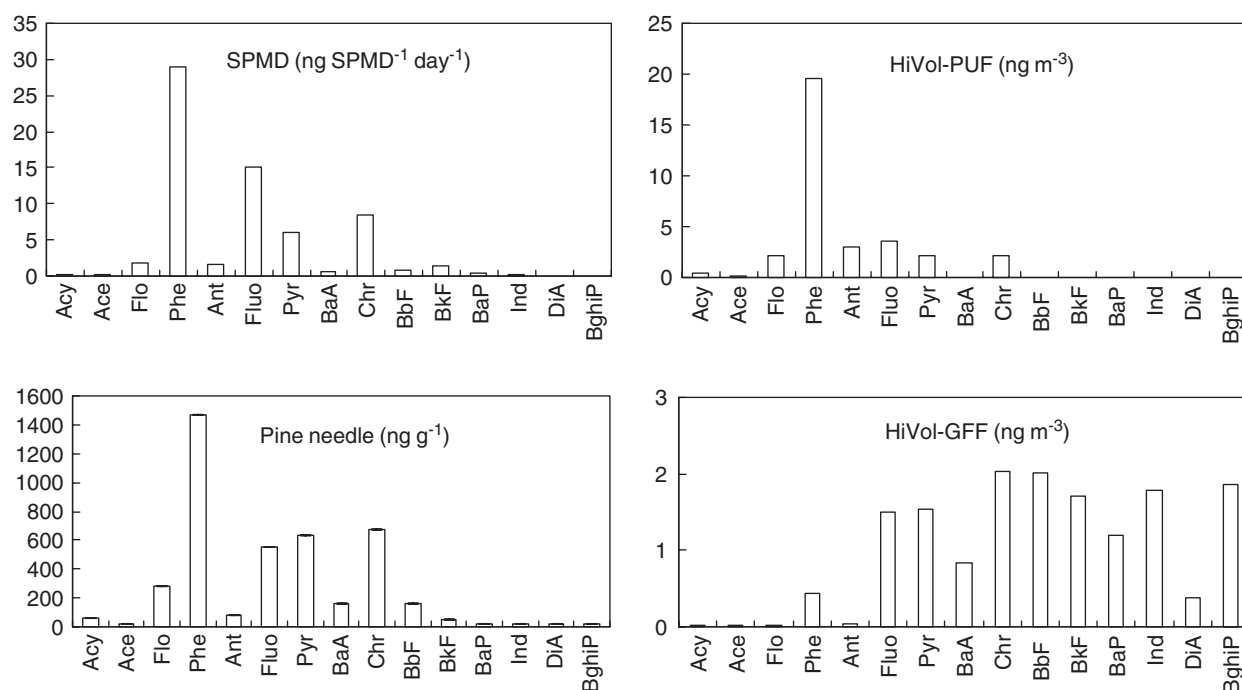
Fig. 2. Comparison of the PAH distribution patterns in SPMDs, pine needle and HiVol samples.

approaches would certainly had addition effect on the pollutant profiles.

The sequestered PAHs in SPMD and pine needles in the air of PRD ranged between 15–120 ng $SPMD^{-1} day^{-1}$ and 280–3000 ng g^{-1} dw, respectively. The SPMD PAH values are similar to those found in the northwest England (53–320 ng $SPMD^{-1} day^{-1}$, Lohmann et al., 2001) and Thailand (17–130 ng $SPMD^{-1} day^{-1}$, Söderström and Bergqvist, 2003), but in a narrow range than those (5.0–1.2×10^3 ng $SPMD^{-1} day^{-1}$) reported by Söderström et al. (2005) who deployed SPMDs at 40 sites in five European countries. PAH concentrations in the pine needles are in the same range as those reported in the UK (27–3090 ng g^{-1} dw, Tremolada et al., 1996), but higher than those found in Germany (50–410 ng g^{-1} dw, Lehndorff and Schwark, 2004).

3.2. Seasonal variations of PAHs sequestered by SPMD

Fig. 3 presents the sequestered PAHs in SPMDs during the four deployments. PAH concentrations (geometric mean, $n = 12$) in the SPMDs were 35 ng $SPMD^{-1} day^{-1}$ (April–June 2001), 30 ng $SPMD^{-1} day^{-1}$ (July–September 2001),

61 ng $SPMD^{-1} day^{-1}$ (October–December 2001), and 63 ng $SPMD^{-1} day^{-1}$ (January–March 2002), respectively. The ambient temperatures (3 months' average) during the sampling stages were 25.1 °C, 28.4 °C, 20 °C and 17.6 °C, respectively. The sequestered PAHs amounts tended to be higher in winter than in summer and generally increased with decreasing temperature. However, the active sampling (at station GZ01) results showed a positive relationship between air temperature and gaseous PAHs concentrations (Li et al., 2006), indicating a higher PAH concentration in the ambient air in summer than in winter, which may largely be due to the enhanced evaporation of PAHs from the ground surface, and/or a shift of gas-particulate equilibrium favoring more PAHs in the gaseous phase (Li et al., 2006; Lee and Jones, 1999).

It is interesting to note the contrary results in the seasonal variations of PAHs derived from SPMD and HiVol analysis. The amount sequestered in SPMD depends on the chemical's sampling rate, SPMD capacity for the analyte, air concentration, exposure conditions and duration. The SPMD sampling rate (RS) is affected by the physicochemical properties of the target compounds, and ambient environmental conditions (Ocenken et al., 1998, 2001). Söderström and Bergqvist (2004) reported that an increase in wind-speed will increase
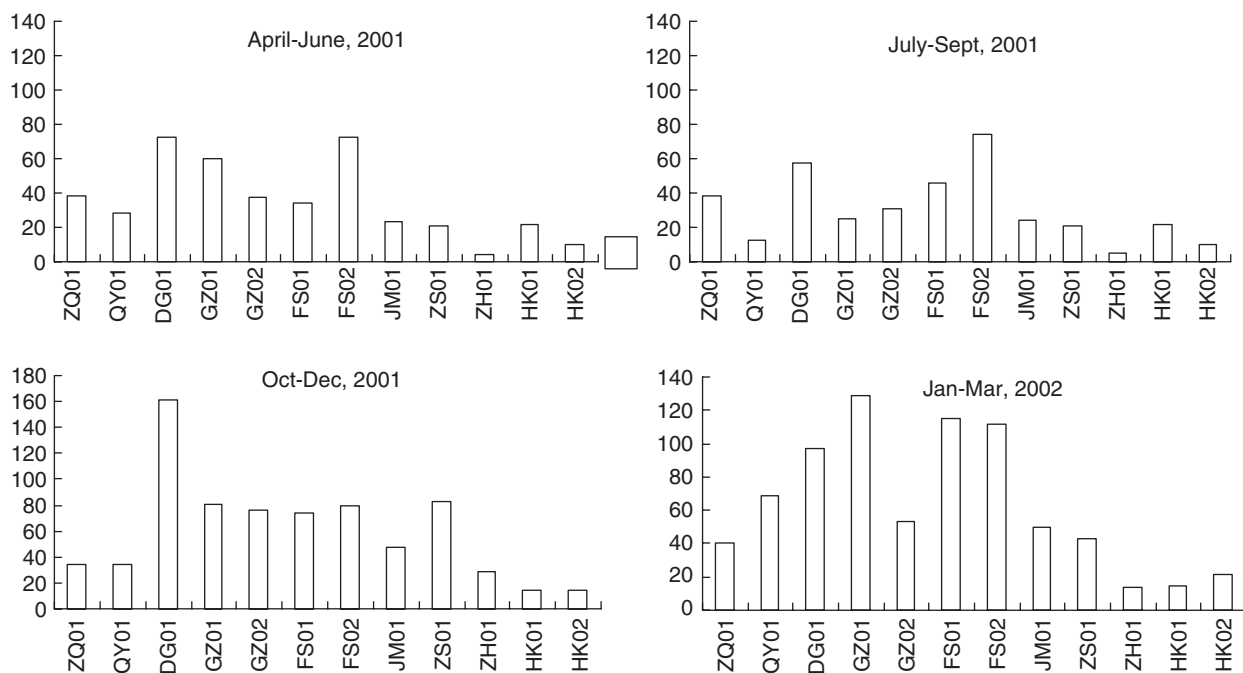
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Fig. 3. Seasonal variations of PAHs sequestered by SPMDs.

the uptake by SPMDs in air. In urban Guangzhou (station GZ01), the wind speed ranged from 0.4 to $3.3\,\mathrm{m\,s^{-1}}$ (daily mean) during the year-round experiment. As we deployed SPMDs in Stevenson screens boxes during sampling, the wind speed differences inside would be small and not significantly affect the uptake rates (Ocenken et al., 2001; Söderström and Bergqvist, 2004). We suggested that the differences in uptake rates may mainly be due to temperature variances (see discussion below).

3.3. Spatial variations

SPMDs and pine needles, as a source of environmental information, have allowed for demonstrating differences in atmospheric PAH concentrations and profiles among sites (Tremolada et al., 1996; Ockenden et al., 1998; Lohmann et al., 2001; Söderström and Bergqvist, 2003; Hwang et al., 2003). Fig. 4 shows the spatial variation of PAHs sequestered in SPMDs (annual average) and pine needles in the PRD. Significant differences in atmospheric PAHs concentrations between sites were found. These were higher in the center of the PRD (Guangzhou, Fushan, Dongguan) and lower in the North and South. It is interesting to note that good agreements were found in the spatial trends of atmospheric PAHs sequestered in the SPMDs and
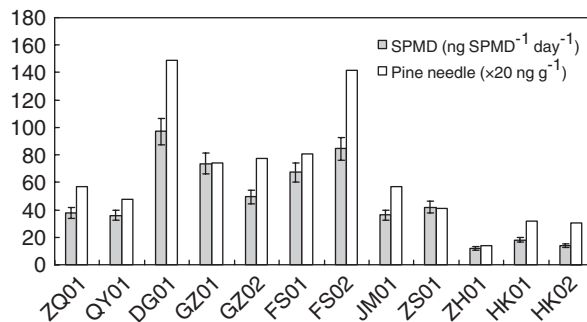

Fig. 4. Spatial variations of atmospheric PAHs sequestered by SPMDs and pine needles.

pine needles. SPMD passive sampling is achieved by physical absorption in the membrane, or diffusion through the membrane, and absorption into triolein (Söderström and Bergqvist, 2004). Pathways to plants include vapor exchange from the air into the waxy layer, atmospheric deposition of contaminated particulates, and root uptake from soil solution (Bacci et al., 1990). Despite the mechanism differences between SPMD and leaf sampling, they both effectively sample vapor phase PAH compounds, and kinetic gaseous deposition has been shown to be the key process for the uptake of PAHs (MW < 228) (Muller et al., 2001; Bartkow et al., 2004). The mechanistic similarities exhibited by

SPMDs and pine needles for sequestering atmospheric organic compounds contribute to the potential of using SPMDs and pine needles for time integrated air monitoring of organic pollutants at a regional scale. Small differences may explain the differences in exposure conditions, as the two matrices are differently exposed to sunlight and wind, undergoing different exposure time which will affect the net-flux into leaves/samplers.

3.4. SPMD-derived air concentrations

SPMDs are a potential tool to identify sources of pollutants and measure time-integrated atmospheric organic pollutants. However, this technology, without sampling rates, is limited to giving qualitative results and does not provide actual air concentrations. In integrative SPMD sampling, the sequestered amount of each analyte in SPMDs, C_{SPMD}, can be used to calculate the concentrations in the air (C_{air}) from

$$C_{air} = C_{SPMD}/(R_s t), \tag{1}$$

where t is the exposure time in days, and R_s ($m^3 day^{-1}$) is the precalibrated sampling rate. To our knowledge, the field-calibrated R_s data of SPMDs in air were limited to two studies by Ockenden et al. (1998) and Shoeib and Harner (2002). In a more recent study, R_s values were measured for 12 US EPA priority PAHs using HiVol air concentration data, and excellent agreement was found between air concentrations derived from SPMDs and HiVol analysis (Bartkow et al., 2004).

In this study, SPMD sampling rates were calculated for some dominant atmospheric PAHs using the HiVol-PUFs data (3-months' average) from site GZ01. Vapor phase PAHs in PUFs (3-months' average) were used to calculate the sampling rates. As shown in Table 1, the calculated SPMD sampling rates in this study were 0.7–1.8, 1.1–2.5, 1.2–2.4, 1.4–2.5 and 1.4–2.8 $m^3 day^{-1}$ for Flo, Phe, Anth, Fluo and Pyr, respectively. The SPMD sampling rates tend to be higher in winter than in summer and generally increased with decreasing temperature. In integrative SPMD sampling, the uptake rate is largely controlled by the boundary layer at the membrane–air interface (Bartkow et al., 2004; Söderström and Bergqvist, 2004). In air, a decrease in temperature will cause the lipid–air partition coefficient to favor accumulation in the lipid, while the diffusivity in the membrane is reduced (Ockenden et al., 1998). Wind speed is another aspect to consider when air-side resistance dominates uptake rates. Ockenden et al. (2001) demonstrated that when deployed in Stevenson screens housing, wind speed did not significantly affect uptake rates. Based on this, we suggested that the differences in summer/winter uptake rates are mainly due to temperature affecting compound permeability through the membrane. This correlation has also been noted in previous studies by Ockenden et al. (1998, 2001) who found that PCBs sampling rates were higher in winter than in summer.

SPMD sampling rates ranged from 0.7 and 2.8 $m^3 day^{-1}$ for the calculated PAH compounds (fluorene to pyrene). These sampling rates were relatively lower than those reported by Bartkow et al. (2004). Although Stevenson screen boxes may minimize the influences from direct sunlight, rain, and wind, the Stevenson screen boxes are not entirely light proof and photo-degradation of sequestered PAHs may still occur. Bartkow et al. (2004) showed that photo-degradation was the major loss process for deuterated pyrene which

Table 1
The mean concentrations of PAHs (conc., $ng m^{-3}$) and sampling rates (R_s, $m^3 day^{-1}$) in GZ01

Compounds	This study								Reference
	Apr–Jun 2001 25 °C		Jul–Sep 2001 28 °C		Oct–Dec 2001 20 °C		Jan–Mar 2002 18 °C		Bartkow et al. (2004) 22 °C
	Conc	R_s	Conc	R_s	Conc	R_s	Conc	R_s	R_s
Flo	3.1	0.7	1.7	1.0	1.8	1.4	2.1	1.7	1.8
Phe	24.4	1.2	25.4	1.1	18.2	2.0	17.2	2.5	4.4
Anth	3.9	1.2	3.9	1.1	2.0	2.4	2.0	2.2	4.1
Fluo	3.8	1.8	5.2	1.4	3.6	2.3	3.5	2.5	4.5
Pyr	2.2	1.8	3.1	1.4	1.6	2.6	1.6	2.8	2.0

was used as a performance reference compounds (PRCs) in their study. Loss of PAHs due to photo-degradation in the SPMDs, if not included, may lower the apparent SPMD uptake rates. In this study, PAHs in the SPMDs depleted of photo-reactive components (e.g. anthracene). The phenan-threne/anthracene ratios obtained by the SPMDs (20–50) were much higher than those measured by HiVol (6–8), indicating a "photolysis" or "weath-ering" of PAHs after the 3-month exposure. As we did not use PRCs, the sampling rates were not corrected for the effects of photo-degradation; the calculated sampling rates may thus be under-estimated.

The sampling rates we obtained also displayed a tendency to increase with increasing MW. The lower sampling rates for Flo may indicate that it has reached the curvilinear phase or equilibrium during the 3-months exposure, whereas the relatively high-er R for the HMW PAHs is related to the deposition of particle deposited PAHs. Note that the surface of SPMDs usually consists of a film mostly of oleic acid that will allow the sorption/extraction of particle deposited PAHs.

Octanol–air partition coefficient (K_{OA}) illustrates the partitioning of organic pollutants between air and environmental organic phases. The lighter PAHs (2–3 rings) typically have lower K_{OA} values would be expected to exist mainly in the vapor phase in the atmosphere, whilst heavy PAHs (5–6 rings) with high K_{OA} values tend to be associated with atmospheric particles under ambient condi-tions. The major uptake process that is responsible for the accumulation of SOCs into environmental organic phase may include: (1) equilibrium parti-tioning of the vapour-phase compounds; (2) kine-tically limited vapour-phase deposition; and (3) particle-bound deposition. Using K_{OA} as a function of the relative differences in accumulation behavior, McLachlan (1999) suggested an interpretational framework that 'explains' this pattern. Bartkow et al. (2004) found that this framework can also be used to explain the uptake of PAHs in SPMDs. Fig. 5 shows the plot of log (C_{SPMD}/C_V) values versus log K_{OA} (taken or predicted from Beyer et al., 2002) for each of the PAHs quantified at GZ01. The dominant form of uptake for the compounds Flo through Pyr is shown to be via kinetically limited deposition from the vapor phase, this correlation generally agreed with the previous studies (Muller et al., 2001; Bartkow et al., 2004). The relatively low values of (C_{SPMD}/C_V) in our data compared with
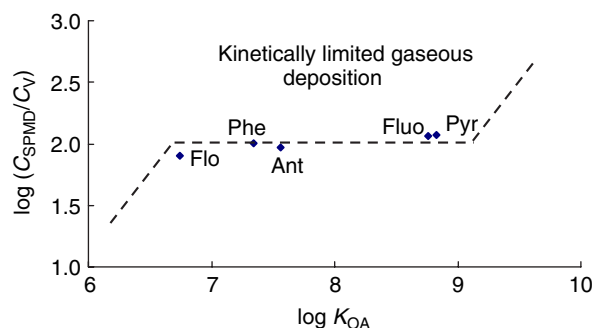

Fig. 5. Plot of log (C_{SPMD}/C_V) versus log K_{OA} for each of the PAHs quantified in the SPMDs at GZ01.
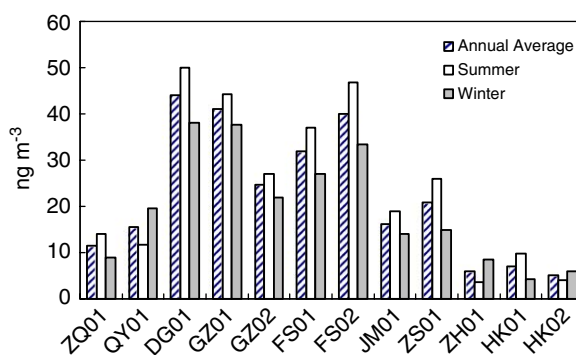

Fig. 6. SPMD-derived annual average PAHs (Flo, Phe, Anth, Fluo, Pyr) concentrations in the air in the PRD.

those reported by Bartkow et al. (2004) may be resulted from: (1) potential strong photodegrada-tion of PAHs in the SPMDs; (2) different air temperature during the deployments; (3) different size and ventilation of the Stevenson screen boxes, etc.

To estimate PAHs air concentration in other sites in the PRD, we used the unadjusted apparent sampling rates measured in Guangzhou, assuming that other environmental conditions were similar. Fig. 6 presents the SMPD-derived PAHs (sum of Flo, Phe, Anth, Fluo and Pyr) concentrations in the PRD. Annual average atmospheric PAHs concen-trations were in the range between 5 and 44 ng m^{-3}. Except for sites QY01, ZH01 and HK02, higher PAHs concentrations were found in summer than in winter. In this study, SPMD-derived PAH air concentrations were also compared with those measured using the HiVol system at station ZS01 and QY01 (Table 2). The differences between SPMD-derived air concentration of PAHs and those derived from HiVol analysis were mostly

Table 2
Comparison of SPMD-derived and measured PAH concentrations

Compounds	Atmospheric PAH concentration (ng m^{-3})			
	Actual (HiVol)		Calculated (USGS SPMD)	
	ZS01	QY01	ZS01	QY01
Flu	7	5	4	3
Phe	16	15	27	12
Anth	2	5	3	3
Fluo	2	2	4	4
Pyr	4	4	2	2

within a factor of 2 for the five individual PAH compounds, suggesting that the SPMD sampling rates acquired in Guangzhou are acceptable for estimating concentrations of atmospheric PAHs at other sites in the PRD with reasonable accuracy.

4. Conclusion

In this study, SPMDs and pine needles were employed to monitor the temporal and spatial trend of gas-phase PAHs in the Pearl River Delta. Atmospheric PAHs concentrations were higher in summer than in winter. Significant differences in atmospheric PAHs concentrations among sites were observed, higher in the centre of the Delta and lower in the South and North. The PAH compounds sampled with SPMDs and pine needle were mainly of vapor phase, whilst pine needles accumulated more of the HMW PAHs. The spatial distributions of atmospheric PAHs by SPMD and pine needle were similar in the context of their total concentrations. Apparent SPMD sampling rates was found to be higher in winter than in summer, and generally increased with decreasing temperature. Photodegradation of PAHs may result in an underestimation of true SPMD sampling rates; application of PRCs is thus strongly recommended for further studies. Good agreement was found between SPMD-derived PAH concentrations and those measured by HiViol.

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