

Atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) to a coastal site of Hong Kong, South China



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HIGHLIGHTS

- ▶ Particle phase concentrations and meteorological factors influenced PAH deposition.
- ▶ Higher PAH particle scavenging efficiencies occurred during the dry season.
- ▶ Rainfall frequency decreased the particle washout ratios before reaching constant.
- ▶ The contribution of atmospheric deposition to the coastal sediments was 30%–40%.

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ABSTRACT

Dry and wet deposition of atmospheric particles is a dominant pathway for PAHs to the coastal environments. Very few studies have been conducted to quantify the contribution of atmospheric deposition to PAH levels in the coastal regions. In this study, PAHs were analyzed in samples collected during a year-round campaign using atmospheric (gas and particle) and depositional samples at a coastal site South China. The average PAH particle deposition fluxes observed calculated $260 \pm 190 \text{ ng m}^{-2} \text{ d}^{-1}$. Remarkable seasonal variations were recorded in the total PAH deposition fluxes, with higher deposition fluxes in the dry seasons and lower fluxes in the wet seasons. The temporal trend of deposition fluxes was influenced by PAH concentration in the aerosols and changes in meteorological parameters, such as temperature, rainfall, and wind speed etc. Dry deposition velocities of individual PAH compound ranged from 0.02 to 1.03 cm s^{-1} , and there was a decrease pattern in dry deposition velocity with increasing molecular weight of PAHs. The annual mean washout ratio, defined as the ratio between the particle-associated concentrations of PAHs in precipitations and aerosols, was 3.4×10^5 in this study. Washout ratios decreased with increasing rainfall frequency and reached a consistent level afterward. The contribution of atmospheric deposition to PAH concentrations in the sediments was estimated to be 30%–40% in the coastal regions of South China.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced in the atmosphere as by-products of incomplete combustion of almost any fuels. Therefore, they are ubiquitous in the environment, mainly at higher concentrations close to the urban or industrialized areas (Brown et al., 1996; Mastral and Callen, 2000; Nielsen et al., 1996; Rehwagen et al., 2005) and they have been studied with

regard to their high toxicological effects due to their well-known carcinogenic and mutagenic properties (Lee et al., 1981; Williams, 1990). Once emitted, PAHs can redistribute between the gas and particle phases and transfer from the atmosphere and deposit onto the earth's surface (Wang et al., 2011). The atmospheric input of semi-volatile organic compounds (SVOCs) to the aquatic environment has been investigated since the early 1970s (Bidleman and Olney, 1974). During the past several decades, numerous studies have been undertaken to determine the level of PAHs phase transfer between atmospheric and aquatic compartments around the world (Dickhut and Gustafson, 1995a; Duce et al., 1991; Hoff et al., 1996). Because of the persistent characteristics of PAHs,

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marine sediments have been one of the most important reservoirs of PAHs (Yang et al., 2005). Once bound to the sediments, PAHs can re-enter the water column and circulate in the ecosystems through resuspension and other processes. Due to the close proximity site to densely populated and industrialized areas, higher PAH levels are often found in the coastal regions (Gigliotti et al., 2005). Moreover, coastal regions are the major bases of animal husbandry and aquaculture. Not only the environment is impacted by the pollutants emitted into the coastal region, but also the human health can be affected.

Currently, a widely used device to study the distribution of PAHs in sediment is a grab sampler or stainless steel static gravity corer to collect surface sediments and sediment cores, then determining the PAH concentrations in the samples in combination with a statistics analysis, such as compositional analysis or principal component analysis (PCA), to assess the input sources and possible transport pathways (Liu et al., 2005; Luo et al., 2008). Previous researches suggested that atmospheric deposition could be a prevailing input pathway for PAHs in the coastal sediments of South China by the statistical analysis (Mai et al., 2003). However, research work on the quantitative contribution of the atmospheric PAH deposition to marine sediments in the coastal regions is limited. An example of the study is a survey determining the concentrations of PAHs in the northern continental shelf of the South China Sea (Luo, 2004). In order to calculate the contribution of atmospheric deposition of PAHs into the coastal sediments, an adjacent site was chosen to collect air and depositional samples. The sampling site, Hok Tsui (22.24°E, 114.24°N) is situated at the southeastern tip of Hong Kong Island, and has been represented a regional background site with a small influence from the local pollutant sources (Liu et al., 2007; Zheng and Fang, 2000). Thus, Hok Tsui is a suitable site to quantify the contribution of depositional fluxes of PAHs to the coastal environments in south China.

Here the results are presented from a year-round atmospheric and deposition sampling from December 2003 to December 2004. The main objectives of this study were to (1) investigate the PAH atmospheric concentrations and potential emission sources at a coastal site in South China; (2) determine the depositional fluxes of PAHs and their seasonal trends; (3) estimate the dry deposition velocity and washout ratio of particulate PAHs at the sampling site; (4) assess the transport pathways for the depositional PAHs and calculate the contribution of atmospheric deposition to PAH concentrations in the surrounding marine sediments.

2. Materials and methods

2.1. Sample program

The sampling site is located at the tip of the southeastern Hong Kong Island, surrounded by the South China Sea (Fig. 1). Sampling was carried out on a bi-weekly basis for a one year period, from December 2003 to December 2004 (Li et al., 2010a). A bulk particle deposition (wet and dry) collection was achieved using a stainless steel funnel with an area of 0.049 m², attached to a filter holder in a blinded screen house (Li et al., 2010a). The bulk deposition samples were filtered *in situ* through pre-cleaned (4 h at 450 °C) 90 mm diameter glass microfiber filters (GFF) (Whatman Type GF/F, nominal pore size 0.7 μm). Prior to the first sampling, the inner surface of the stainless steel funnel was washed with distilled water and wiped with pre-cleaned cotton wool (Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions with dichloromethane (DCM)). After sampling, the inner surfaces of the stainless steel funnels were wiped again with the pre-cleaned cotton. The cotton wool and filter were combined to measure the depositional fluxes of particle-bounded PAHs.

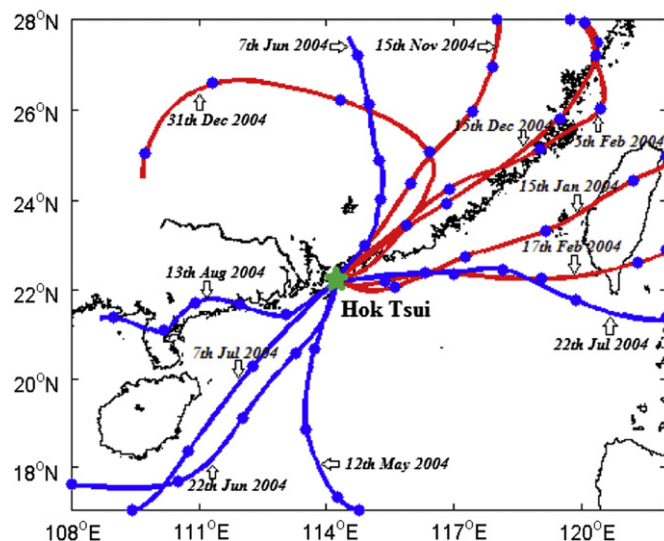


Fig. 1. Backward air trajectory (48 h) plots on the sampling days (12th May 2004, 7th Jun 2004, 22nd Jun 2004, 7th Jul 2004, 22nd Jul 2004, 13th Aug 2004, 15th Nov 2004, 31st Dec 2003, 15th Dec 2003, 15th Jan 2004, 5th Feb 2004, 17th Feb 2004) in summer and winter.

Simultaneously, active air sampling was carried out using a modified high volume air sampler (Hi-Vol) with a flow rate of 0.217–0.228 m³ min⁻¹ adjacent to the passive deposition sampler. Details of the sampler have been described previously (Li et al., 2006). Twenty-four hours samples were collected at the beginning and the end of the sampling period on a bi-weekly basis. The air was drawn through a pre-cleaned (4 h at 450 °C) quartz microfiber filter (QFF, Whatman QM-A, 20.3 × 25.4 cm) to collect particles and then through a polyurethane foam plug (PUF) (length 8.0 cm, diameter 6.25 cm, density 0.035 g cm⁻³) to collect compounds present in the gas phase. During the sampling, meteorological parameters, including ambient temperature, relative humidity, wind speed and wind direction, rainfall were all recorded *in situ* with a portable meteorological apparatus.

2.2. Extraction and analysis

An analytical method used for the extraction and clean-up of PAHs in GFF and PUF was expounded in previous publications (Li et al., 2006). Briefly, deuterated PAH standards (acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂) were added to the GFF and PUF as recovery surrogates, and they were Soxhlet extracted (4–6 cycles h⁻¹) with DCM for 48 h, the extracts were then fractionated and cleaned up using a mixed silica gel/alumina column.

GFFs and PUFs were analyzed for PAHs by GC-MSD (HP-5890 series II GC, HP-5972 MSD, equipped with a 30 m × 0.25 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 PAHs (17 in total) were quantified: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Nielsen et al.), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pery), indeno[1,2,3-cd]pyrene (Ind), dibenzo[a,h]anthracene (DiB) and benzo[g,h,i]perylene (BghiP).

2.3. Quality assurance and quality control (QA/QC)

All chemical standards were purchased from Accustandard Co., U.S.A. Quality assurance and quality control were determined using

laboratory blanks and field blanks. Lab and field blanks were extracted and analyzed in the same way as the samples. There was no significant difference (*t* test significance <95%) between analyte concentrations in the lab and field blanks, indicating that contamination was negligible during the transport, storage, and analysis of the samples. Method detection limits (MDLs) were derived from the blanks, and quantified as three times the standard deviation of the mean blank concentrations. When compounds were not detected in blanks, three times the instrumental detection limits (IDLs) were used for calculating the MDLs. In addition, peaks were only integrated when the signal-to-noise ratio was ≥ 3 ; otherwise, they were considered non-detectable (n.d.). The mean recoveries for standards in field samples were 65%–106% and PAH concentrations reported in this paper were corrected for the recovery efficiency and blanks.

3. Results and discussion

3.1. Ambient air concentration levels

The 17 PAHs in total were detected in the air (gaseous and particulate phases) samples, and a summary of individual and total PAHs concentrations is presented in Table 1. The mean value of total PAH concentration in the gaseous phase was 8.5 ng m^{-3} , with a range of $3.1\text{--}29 \text{ ng m}^{-3}$, while in the particulate phase, total PAHs concentration varied from 0.11 to 8.8 ng m^{-3} , with an arithmetic mean of 1.9 ng m^{-3} . By comparison, total PAH concentrations at another sites in Hong Kong reported previously were 1.4 ng m^{-3} (particle) in Hok Tsui, which was sampled in 1993 (Zheng and Fang, 2000) and 90.81 ng m^{-3} (gas + particle) in urban atmosphere influenced mainly by an emission from traffic exhaust (Lee et al., 2001). Moreover, results in this study were comparable to the other coastal sites, which were 51 ng m^{-3} (gas) and 0.84 ng m^{-3} (particle) in Galveston Bay (Park et al., 2001), 19.70 ng m^{-3} (gas) and 1.05 ng m^{-3} in the coastal areas of tropical and subtropical Atlantic Ocean (Del Vento and Dachs, 2007), respectively. Compared with these two regions, PAH contamination in this coastal site of Hong Kong was in a low to medium level. In general, PAH compounds with three and four aromatic rings (i.e. Phe, Fla, Pyr) were dominant in the gaseous phase, while higher molecular weight PAHs (i.e., BaP, Ind, BghiP) were more likely to remain in the particulate phase. The average of particulate PAHs observed in

Galveston Bay and Atlantic Ocean were approximately 18%, and less than 5% of the data reported in this study, respectively.

The differences of particulate PAH concentrations between the seasons were significant ($p < 0.01$, one-way ANOVA). The concentrations of PAHs in winter (from November to February) were almost 3.5 times higher than those in summer (from May to August). As there were no local pollution sources of PAHs close to the sampling site, backward trajectories were generated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (Rolph, 2003) to indicate the potential long range transport paths of PAHs in the atmosphere. Forty eight hours of predominant backward trajectories in winter and summer are shown in Fig. 1. High PAH concentrations were observed when the air masses traveled passing mainland China before reaching Hok Tsui during the winter monsoon period. In contrast, low concentrations of PAHs were observed in summer when the air masses came from the ocean or southwest of the sampling site (Li et al., 2007). For example, on the 15th Jan 2004, 17th Feb 2004, PAH concentrations were relatively low when the air masses passed through the South China Sea. On the 7th Jun 2004, the air masses passed through the Pearl River Delta (PRD) areas resulting in the elevated concentrations of PAHs. It suggested that industrial and other emissions in China mainland north of Hong Kong and the PRD region could be the major regions of the PAH emissions for the downwind areas, including Hong Kong. On the contrary, PAH levels from the South China Sea were much lower than from mainland China, and the air masses were relatively clean.

The concentrations of some marker compounds and their ratios can provide some indications on the possible emission sources (Budzinski et al., 1997; Sicre et al., 1987; Yunker et al., 2002). Fig. 2 illustrates a plot of Flua/(Flua + Pyr) against Ind/(Ind + Bgp) for the particle samples in winter and summer (Yan et al., 2009; Yunker et al., 2002). There were significant differences for these ratios between the winter and summer. A predominant influence of grass, wood and coal combustion in winter was in accordance with the condition in South China area where coal consumption accounts for more than 50% of the total energy consumption (Duan et al., 2007). However, it seems like the petroleum combustion was prevalent in the summer, and it probably indicated that the emission from gasoline and diesel engine (i.e., ship traffic) in the South China Sea were the main source and they can be transported to the studied site.

Table 1
The concentration ranges and means of PAHs in air (gas and particle) and deposition samples.

	Gas (<i>n</i> = 23)			Particle (<i>n</i> = 23)			Deposition (<i>n</i> = 23)		
	Mean \pm S.D. (ng m^{-3})	Range (ng m^{-3})	<i>n_d</i>	Mean \pm S.D. (ng m^{-3})	Range (ng m^{-3})	<i>n_d</i>	Mean \pm S.D. ($\text{ng m}^{-2} \text{d}^{-1}$)	Range ($\text{ng m}^{-2} \text{d}^{-1}$)	<i>n_d</i>
Ace	0.16 ± 0.12	<LOD–0.51	22	<LOD	<LOD–0.03	18	4.2 ± 3.1	<LOD \pm 12	20
Acy	0.23 ± 0.13	<LOD–0.48	22	0.01 ± 0.01	<LOD–0.01	3	1.9 ± 2.8	<LOD \pm 11	11
Flu	0.88 ± 0.45	0.25–2.0	23	0.01 ± 0.01	<LOD–0.03	17	27 ± 39	3.5 ± 140	24
Phe	4.5 ± 2.3	1.9–9.6	23	0.16 ± 0.10	0.04–0.38	23	120 ± 100	20 ± 370	24
Ant	0.27 ± 0.20	0.07–0.87	23	0.01 ± 0.01	<LOD–0.02	22	11 ± 14	1.2 ± 64	24
Flua	1.5 ± 3.2	0.23–16	23	0.23 ± 0.34	0.01–1.4	23	23 ± 15	5.0 ± 68	24
Pyr	0.86 ± 1.2	0.19–6.3	23	0.17 ± 0.27	<LOD–1.2	22	10 ± 7.2	2.9 ± 29	24
BaA	0.01 ± 0.02	<LOD–0.10	20	0.07 ± 0.11	<LOD–0.37	23	4.3 ± 2.0	2.2 ± 11	24
Chr	0.06 ± 0.04	<LOD–0.20	20	0.18 ± 0.22	<LOD–0.93	23	6.5 ± 4.3	2.0 ± 14	24
BbF	0.01 ± 0.01	<LOD–0.03	14	0.36 ± 0.47	0.01–2.1	23	26 ± 68	2.5 ± 340	24
BkF	0.01 ± 0.01	<LOD–0.02	12	0.12 ± 0.14	<LOD–0.50	22	4.4 ± 2.8	<LOD \pm 12	23
Bep	0.02 ± 0.02	<LOD–0.03	12	0.12 ± 0.13	<LOD–0.45	19	11 ± 13	<LOD \pm 68	23
BaP	0.01 ± 0.01	<LOD–0.02	6	0.05 ± 0.06	<LOD–0.20	18	5.5 ± 14	0.56 ± 70	24
Pery	0.01 ± 0.01	<LOD–0.01	6	0.01 ± 0.01	<LOD–0.04	15	0.73 ± 1.1	<LOD \pm 5.7	21
Ind	0.01 ± 0.01	<LOD–0.01	1	0.20 ± 0.28	<LOD–1.24	21	4.5 ± 3.3	0.56 ± 12	24
DiB	<LOD	<LOD	0	0.03 ± 0.05	<LOD–0.24	14	4.1 ± 3.7	<LOD \pm 13	22
BghiP	0.01 ± 0.01	<LOD–0.01	1	0.17 ± 0.17	<LOD–0.73	23	4.3 ± 3.2	<LOD \pm 11	23
Total	8.5 ± 5.8	3.1–29		1.9 ± 2.0	0.11–8.8		260 ± 190	70–670	

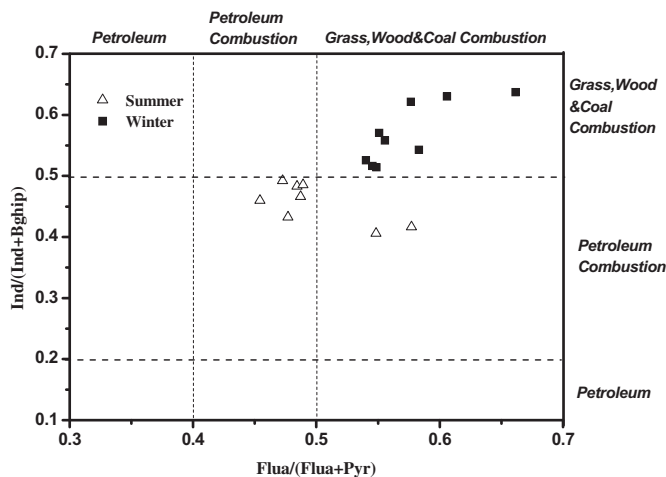


Fig. 2. Plots of isomer ratios $\text{Ind}/\text{Ind} + \text{Bgp}$ against $\text{Flua}/\text{Flua} + \text{Pyr}$ in particulate phase for source identification.

3.2. PAH deposition fluxes and their variation with controlling factors

The PAH deposition fluxes ranged from 71 to 670 $\text{ng m}^{-2} \text{d}^{-1}$, with an average value of 260 $\text{ng m}^{-2} \text{d}^{-1}$. In accordance with the deposition profiles reported by the others (Poor et al., 2004; Wang et al., 2011), Phe (43.5%), Flu (10.4%), BbF (10.0%) and Flua (8.6%) were the major components on an annual basis. The average flux of BaP was $5.5 \pm 14 \text{ ng m}^{-2} \text{d}^{-1}$ which is lower than those reported in the PRD region with a geometric mean of $6.6 \text{ ng m}^{-2} \text{d}^{-1}$ (Li et al., 2010a), but higher than the report in Tuckerton, U.S.A with the mean value of $4.8 \text{ ng m}^{-2} \text{d}^{-1}$ (Gigliotti et al., 2005). In comparison with the compound composition in the aerosol samples, the proportion of 3-ring PAH in the deposition samples was higher than that in the particulate phase of the air while the others were lower.

Coarse particles, such as construction dust, fly ash, re-suspended soil dust and other debris in air, possess high deposition velocities and they can adsorb the vapor PAHs, which in turn may introduce the relatively higher concentration of low molecular weight PAH in the deposition fluxes than those in the aerosol samples (Li et al., 2009; Tang et al., 2006).

The PAH depositional fluxes measured over a one-year period are plotted as a time-series in Fig. 3. Previous study reported that a better way to examine potential seasonal variations of the PAH deposition fluxes in the PRD region was to divide the whole year results into two distinct seasons, wet season from April to September, and dry season from October to March. In this study, the atmospheric deposition of PAHs exhibited statistically significant seasonal differences, and the deposition fluxes tended to be higher in the dry seasons than the wet seasons. In general, the seasonal variations of the particle-phase semi-volatile organic compounds (SVOCs) deposition fluxes could be affected by several factors, such as the variability of PAH concentration in aerosol, temperature, precipitation and wind speed (Fig. 3). The PAH concentration in aerosols was the most important factor, which directly affect the variation of the particulate deposition fluxes (Wania et al., 1998). The aerosols with higher concentrations of PAHs were found in the dry season, revealing that high aerosol concentrations induced high deposition fluxes. Moreover, the Asia Brown Cloud (ABC), also called Asia haze, a mixture of aerosol, ash, soot and other particles, hovered over most of the tropical Indian Ocean, South, Southeast and East Asia. It generally appeared in January to March due to low temperature, low wind speed, less precipitation and the formation of atmospheric inversion (Li et al., 2010a). The ABC could induce the high levels of atmospheric particle PAHs, and consequently contribute to the high particulate deposition fluxes of PAHs in South China.

Besides the PAH concentrations in aerosols, temperature is considered to be another crucial factor in controlling the behaviors of PAHs, such as the partitioning between gas and particle. In this study, a significant correlation between the ambient temperature

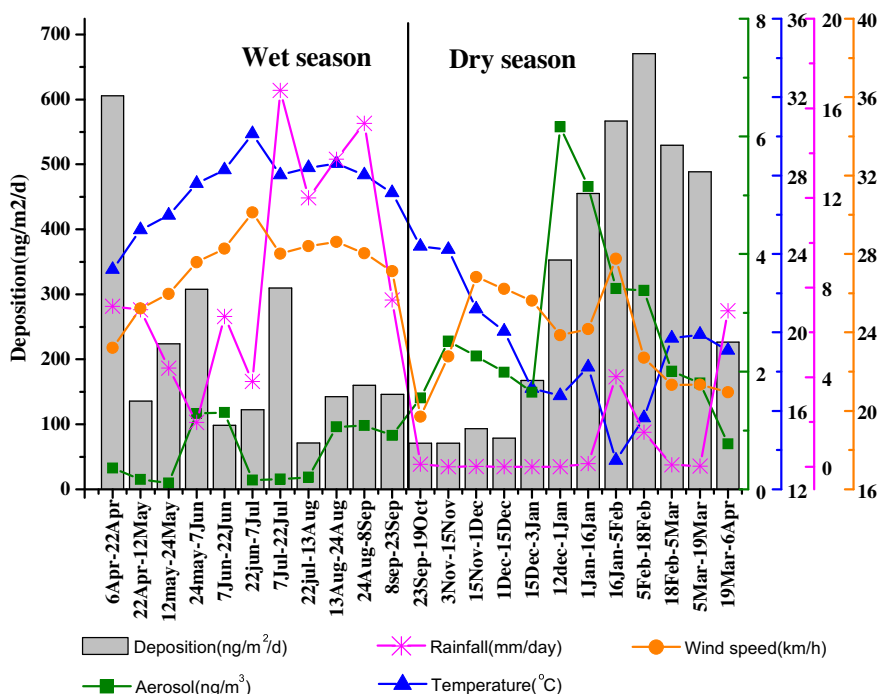


Fig. 3. Seasonal variations of PAHs in deposition and aerosol samples with changes of temperature, rainfall and wind speed.

and the deposition fluxes ($r^2 = 0.49$, $p < 0.005$) was found. In addition, the contribution of the lighter PAHs to the total PAHs, 63% in the dry season, was significantly higher than the wet season, with a proportion less than 52%. This profile could be attributed to the vapor-particle partitioning for SVOCs driven by temperature (Teil et al., 2004). Furthermore, the wind speed, intensity and the rate of precipitation could also affect the washout ratio or dry deposition speed, which influence the variation of deposition fluxes. Previous researches reported significant correlations between the deposition fluxes of PAHs and rainfall or wind speed (Li et al., 2009; Tasdemir and Esen, 2007). In this study, the mean of daily precipitation in the wet season was more than 8.8 mm day^{-1} , and less than 1.1 mm day^{-1} in the dry season. The frequent rainfalls in the wet season probably facilitated the transport of PAHs from air to ground and aquatic environments. However, no significant correlations between the deposition fluxes and the rainfall or wind speed were found in this study.

3.3. Dry deposition velocities and washout ratio

The dry deposition velocities of PAHs and washout ratio can be calculated by combination of the particulate PAH depositional fluxes and PAH concentration data in the aerosols. During the deposition sampling period, only two aerosol samples were collected at the beginning and the end of the sampling time on a bi-weekly basis. This could lead to uncertainties in the velocity calculation. Dry and wet depositional fluxes (F_T) can be divided into the dry deposition fluxes (F_D) and wet deposition fluxes (F_W): $F_T = F_D + F_W$. A particle-phase dry deposition velocity (V_D , cm s^{-1}) were derived from the measured dry deposition fluxes (F_D) and particle phase ambient concentrations (C_{ap}): $V_D = F_D/C_{ap}$. The washout ratio is defined as the ratio between the particle-associated concentrations of chemical in precipitation and aerosol concentrations of compound in the atmosphere (Dickhut and Gustafson, 1995b). Efficiencies of particle washout (W_p) from the atmosphere by precipitation were empirically calculated by following parameters; wet deposition fluxes (F_W), particle phase ambient concentration (C_{ap}), and rainfall (V_R , m day^{-1}): $W_p = F_W/C_{ap}/V_R$.

The overall average dry deposition velocity was $0.21 \pm 0.08 \text{ cm s}^{-1}$ in this study. This result was in line with those reported for PAHs, PCBs and BDE-209, such as $0.45 \pm 0.35 \text{ cm s}^{-1}$ for PAHs and $0.74 \pm 0.23 \text{ cm s}^{-1}$ for PCBs (Esen et al., 2008), and $0.28 \pm 0.01 \text{ cm s}^{-1}$ for BDE-209 (Li et al., 2010b). However, the bulk deposition velocities were approximately ten times lower than the dry PAH deposition velocities reported by Bozlaker et al. (2008) and Vardar et al. (2004). The discrepancy among these deposition velocities could be attributed to the differences in the sampling collection procedures, sampling sites and particle size distribution. The longer duration of sampling times and higher sampling height might cause the lower dry particulate deposition velocities (Kajiwara et al., 2008; Shannigrahi et al., 2005). The dry deposition velocities for individual PAH compound are shown in Fig. 4 (The C_{ap} of Ace and Acy is lower than the limit of detection (LOD), therefore the V_D of Ace and Acy are not presented). The calculated average dry deposition velocities for each PAH ranged from 0.02 to 1.03 cm s^{-1} , varied in a wide range of V_D nearly 2 orders of magnitude depending on the physical properties of particles and meteorological conditions (Zhang et al., 2012). Previous studies reported that the higher molecular weight (MW) PAHs were more likely to be partitioned with fine particles while the contribution of coarse particles to the deposition fluxes was important (Tasdemir and Esen, 2007). There was a decrease of the dry deposition velocity with the increase of PAH MW in this study. The results, in line with the previous findings, indicated that a greater fraction of the high

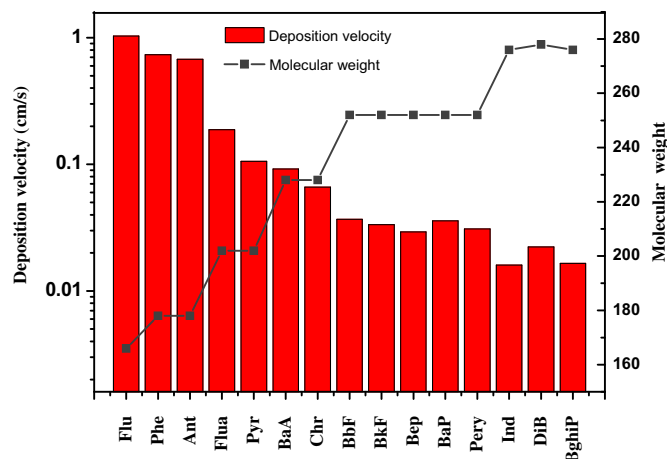


Fig. 4. Average dry deposition velocities of PAH compounds associated with particles.

MW PAHs were associated with fine particles rather than to the low MW PAHs (Demircioglu et al., 2011; Tasdemir and Esen, 2007).

The annual mean washout ratio for $\Sigma_{17}\text{PAH}$ was 3.4×10^5 , similar to those measured in other studies (Birgöl et al., 2011), but was higher than those reported for PBDEs in the PRD regions (Zhang et al., 2009). A notable seasonal variability in the washout ratios of PAHs was also observed, with higher particle scavenging efficiencies occurring during the dry season. The washout ratios for $\Sigma_{17}\text{PAH}$ increased from the wet (1.1×10^5) to the dry (6.8×10^5) seasons. A large amount of particles were mostly suspended in the atmosphere during the dry season. Those high concentrations of the aerosol might lead to the higher washout ratios. Fig. 5 shows the washout ratios and rainfall frequency among the different molecular weight PAHs (Phe, Chr, BkF, BghiP). The washout ratios of high MW PAHs was lower than for low MW PAHs, which is in agreement with other studies (Birgöl et al., 2011). It may be due to the more distribution of low MW PAHs to larger particles (Dickhut and Gustafson, 1995b). W_p decreased with increasing rainfall frequency, and it reached a consistent level afterward. These tendencies were similar to those of PCDD/F homologs, where scavenging effectiveness of the particle-bound PCDD/F homologs were higher at the beginning of a rainfall, and then dropped with increasing rain volume (Koester and Hites, 1992).

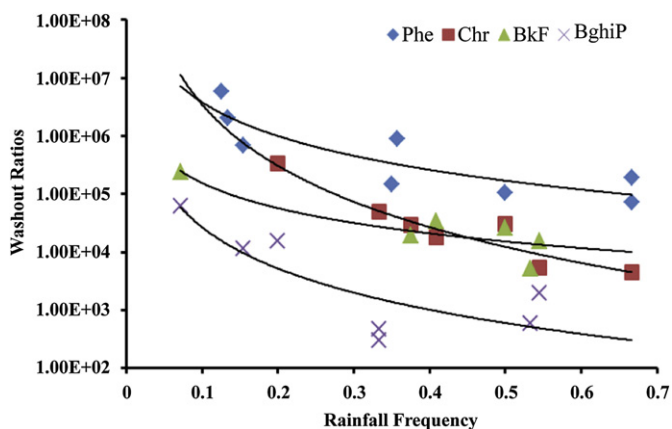


Fig. 5. Decrease in the measured particle washout ratios for Phe, Chr, BkF and BghiP with rainfall frequency (rainfall frequency means the ratio of rainy days during the corresponding sampling period).

3.4. Contributing to PAHs in sediments

To better understand the possible transport pathways for depositional PAHs, a comparison between PAHs in the sediments sampled in October 2002 from the northern continental shelf of the South China Sea (Luo, 2004) with results from this study was conducted. The mean concentrations of 15 PAHs (except for BeP and Pery) (ng g^{-1}) in surface sediments of the South China Sea were converted into equivalent deposition fluxes by calculation: $F = C_s M_s / 365 \pi R^2$, where F ($\text{ng m}^{-2} \text{d}^{-1}$) is the equivalent deposition fluxes, C_s (ng g^{-1}) is the PAH annual concentration, M_s (g) describes the dry weight of sediment samples, and R describes radius of the gravity corer. The average value of equivalent deposition fluxes was $391 \text{ ng m}^{-2} \text{d}^{-1}$, higher than the result in this study with a mean value of $250 \text{ ng m}^{-2} \text{d}^{-1}$. Moreover, significant correlations were found between individual compounds in the sediments and in the atmospheric deposition ($R^2 > 0.31$, $p < 0.05$). This indicated that although other transport pathways (i.e., river input) could contribute to PAHs enrichment in sediments, atmospheric deposition could be the dominant pathway for PAHs to reach the coastal sediments (Mai et al., 2003). Unlike the components distribution in deposition samples, BbF (17.4%), Phe (13.8%), Ind (11.4%) and Flua (10.1%) were the major components in sediments.

PAHs in the sediments could be degraded through two main processes: non-biodegradation and biodegradation. The non-biodegradation, including hydrolysis, oxidation decomposition and photolysis etc., only potentially impacts on two- and three-ring PAHs (Zhan and Zhou, 2003). Simultaneously, previous studies showed that the removal efficiencies of two-, three- and four-ring PAHs range from 42% to 77% via the significant biodegradation after 30 d test, while five-, six-ring PAHs exhibited less than 10% disappearance even after 24 weeks test (Lei et al., 2005; Lu et al., 2011). Besides, low molecular weight (LMW) PAHs are less hydrophobic compared with high molecular weight (HMW) PAHs, and therefore they would be dissolved via the surface runoff making for a lower portion in the sediments. In contrast, HMW PAHs, which were virtually insoluble, would enrich in the sediments. Accordingly, significant differences among 3-ring, 4-ring, 5-ring and 6-ring PAHs between deposition samples and sediments were found (see Fig. 6). PAHs in the deposition samples were dominated by 3-ring compounds accounting for 63% of PAHs, while they were less than 25% in sediments. On the other hand, the proportion of high-ring compounds including 5-ring and 6-ring have remarkably increased in

Table 2

The contribution of atmospheric PAH deposition to sediments at various sites in the world.

Site	Collection period	Contributed portion (%)	References
Zhujiang River in urbanized area	Apr 2001–Mar 2002	5–18	(Li et al., 2009; Mai et al., 2002)
Lake Michigan regions	Nov 1993–Oct 1995	25–46	(Franz et al., 1998; Simcik et al., 1996)
Coastal regions in South China	Dec 2003–Dec 2004	30–40	This study

the sediments, accounting for over 45% of the total PAHs, while it was less than 20% in the air deposition samples. Based on the previous discussion, better accuracy in the contribution of atmospheric deposition of PAHs to the sediments could be acquired by comparing the deposition fluxes of individual HMW compounds (BbF, BkF, BaP, Ind, DiB, BghiP) due to their stability in both atmospheric particles and sediments. The concentration of HMW PAHs in the sediments were significantly higher than those in the atmospheric deposition ($p < 0.05$). The deposition-to-sediment portion were also calculated (i.e., $\text{portion} = F_{\text{deposition}} \times 100\% / F_{\text{sediment}}$), and the portions of HMW PAHs including BbF, BkF, BaP and DiB were 38.8%, 39.4%, 33.0% and 29.3%, respectively, whereas, Ind and BghiP only accounted for 10.1% and 13.0%, respectively. This implied the isomer pair (Ind and BghiP) may transport to the sediment by other mechanisms. Overall, the calculated results suggested that PAHs in the sediments were imported mainly via the deposition of atmospheric particle and the contribution of atmospheric deposition accounted for 30%–40%. The deposition-to-sediment portion in this study is higher in comparison with other sites in the world (Table 2). The comparison may not be critical because of the geological characteristics of the sampling area and the sampling period. The contribution of deposition-to-sediment in the Pearl River was only about 5–18%. It is a reasonable assumption that the riverine contribution was dominant for the PAHs inputs while atmospheric deposition played a minor role in the river system. Compared to the result in the Pearl River, the contributions of deposition-to-sediment was higher in Lake Michigan regions. These results indicate that the contribution of atmospheric deposition is significant to the sediments in rural or coastal areas where PAH input pathways are monotonous.

4. Conclusion

PAHs in atmospheric (gas and particle) and depositional samples were investigated in a coastal site of Hong Kong, South China. It was found that the temporal variations in the PAH deposition fluxes were influenced by PAH concentration in the aerosols and meteorological parameters. The particle washout ratios of PAHs decreased with increasing rainfall frequency and reached a consistent level afterward. The contribution of atmospheric deposition to PAH concentration in the sediments was estimated to be 30%–40% in the coastal regions of South China. Sediments can be regarded as a major sink of PAHs, therefore the present study highlights the necessity to quantify the contribution of atmospheric pollutants to the sediments and its controlling factors, which is an essential part of environmental fate research of PAHs, and thus can provide important information to environmental modeling and management.

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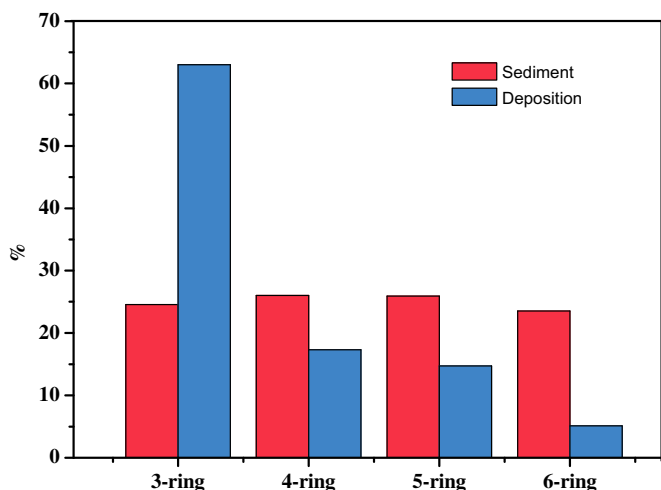


Fig. 6. The relative abundance of PAH compounds in air deposition and sediment samples.

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