



Characterization of Polycyclic Aromatic Hydrocarbons in Cloud Deposition at Mount Heng in Southern China

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ABSTRACT

Cloud water samples were collected during March to May 2009 at Mount Heng (27°18'N, 112°42'E, 1269 m A.S.L.), a high altitude site in southern China. The samples were analyzed by GS-MS to investigate the distribution, transport pattern, scavenging ratios and possible sources of PAHs. During the observation campaign, the concentration of total (in both particle and dissolved phase) PAHs in cloud water ranged from 323.0–5660 ng L⁻¹, with an average of 1589 ng L⁻¹. BbF was the most abundant compound, contributing to 14.50% of the total PAH concentration, followed by PhA, FluA, Pyr, BaA and Chr. Particle scavenging (Wp) was the dominate removal mechanism, accounting for over 77% of the total scavenging. Significant negative relationship was found between logWp and supercooled vapor pressure of PAHs, suggesting that particle scavenging by cloud water is more efficient for higher molecular weight PAHs. During the observation period, air mass was suggested to mainly originate from south or southeast of China based on back trajectory analysis, while air masses coming from northern China had highest PAH concentration. Diagnostic ratio and principal component analysis indicated that PAHs in cloud water at Mount Heng might originate from multiple sources.

Keywords: Cloud water; PAHs; Scavenging ratio; Transport pattern; Source analysis.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of widespread environmental pollutants, and they have been detected in various environmental compartments such as surface water, particulate matter, soils, sediments and even in food (Soclo *et al.*, 2000; Tao *et al.*, 2004; Lohmann *et al.*, 2009; Li *et al.*, 2010; Alomirah *et al.*, 2011). In recent years, PAHs have been of great concerns as they are

bioaccumulatable and can cause mutagenic and carcinogenic effects (Vaananen *et al.*, 2003; Wang *et al.*, 2010; Li *et al.*, 2013; Xia *et al.*, 2013; Tiwari *et al.*, 2015; Zhang *et al.*, 2015a). Significant emission abatement of PAHs has been proposed during the international convention processes, e.g., the 1979 Geneva Convention on Long-range Trans-boundary Air Pollution. Though a reduction of PAHs emission has been reported in European countries and U.S. since 1990 (Xu *et al.*, 2006; Ravindra *et al.*, 2008), the PAH emission in developing countries including China are expected to increase continuously due to economic development and rapid growth in energy consumption (Li *et al.*, 2013). For instance, the annual PAH emission in China was estimated to be about 114 Gg y⁻¹ in 2004, contributing the 20% of the global total emission (Zhang and Tao, 2009).

Although the natural sources such as forest fires and volcanoes can contribute to PAH burden, human activities like vehicle emission, domestic heating and industrial

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emissions are by far the major sources of PAHs (Park *et al.*, 2002; Li *et al.*, 2014; Vasilakos *et al.*, 2007). Once released into the atmosphere, PAHs can redistribute between gas and particle phases according to particle size, vapor pressure and meteorological conditions (Lohmann and Lammel, 2004; Wu *et al.*, 2014; Cheruiyot *et al.*, 2015). In general, high molecular weight PAHs (4–6 rings) tend to be more concentrated in particle phase, while the ones with lower molecular weight (2–3 rings) are often concentrated in gas phase (Olivella, 2006; Tian *et al.*, 2009). Due to their persistence, PAHs can undergo long-range atmospheric transport from their original sources through the grasshopper effect or global distillation, and they have been detected in high altitude sites in some previous studies (Fernández *et al.*, 2002; Arellano *et al.*, 2011). Compared to urban environment, remote mountain areas, particularly for those located in free troposphere, are unique environments to investigate the long range transport and global distribution of PAHs. Since 2000s increased number of researches have been conducted on measurement of pollutants at mountain regions, however, limited work has been done for cloud. Cloud plays an important role in redistribution and transport of atmospheric pollutants (Wang *et al.*, 2015). During the evolution of cloud, the cloud droplets can accumulate particulate and gaseous PAHs (Li *et al.*, 2010). Based on the scavenging mechanism of cloud, PAHs in cloud can become the source of PAHs for terrestrial and aquatic systems (Simcik, 2004).

Only a few studies concerning cloud water have been conducted and these studies were mainly conducted in Asian countries including China (Guo *et al.*, 2012), Korea (Kim *et al.*, 2006) and Japan (Watanabe *et al.*, 2001). Even less information on PAH characteristics in cloud water have been obtained, particularly for the regions with high altitude in the free troposphere. In this study, a preliminary analysis of PAH pollutant characteristics was done at Mount Heng (1269 m A.S.L.), China to fill this knowledge gap. Taking advantage of cloud events happened in this high altitude site, 22 cloud samples were collected by Caltech

Active Strand Cloud Water Collector (CASCC) during the observation campaign. The objectives of the present study were (1) to gain a primary understanding on the distribution of PAHs in cloud at Mount Heng and (2) to examine the possible sources and transport patterns of PAHs in the region.

EXPERIMENTAL WORK

Site Description and Sample Collection

Mount Heng, located in Hunan Province, China, covers an area of 181.5 km². Influenced by tropical and Asian humid continental monsoon, and cloud and precipitation events happened frequently in this region. Two major developed regions - Pearl River Delta (PRD) and Yangtze River Delta (YRD) located adjacently to Mount Heng. Particularly, the two most important city of each region: Guangzhou and Shanghai situated 400 km to the south and 900 km to the east of Mount Heng, respectively. Our sampling site located at the meteorological station of Mount Heng (27°18'N, 112°42'E), which is at the summit of the mountain with an altitude of 1269 m A.S.L. (Fig. 1). Local pollution is negligible since most of the residents work in tourism or related services. This sampling site is a unique site for free atmospheric chemistry measurement (Sun *et al.*, 2010; Nie *et al.*, 2012; Zhou *et al.*, 2012a; Zhou *et al.*, 2012b; Nie *et al.*, 2014).

Cloud samples were collected during March to May 2009 by a Caltech Active Strand Cloud Water Collector (CASCC) designed by the California Institute of Technology, U.S. (Fig. 2). CASCC was operated at 24.5 m³ min⁻¹, and the drop cut size was 3.5 μm (50% collecting efficiency). Based on the inertial impact of 508-μm Teflon strands, cloud drops were pulled into a 500-mL Teflon bottle. The collecting period for each sample was one hour and a total of 22 cloud samples were collected during the observation campaign.

Before sampling, the CASCC was carefully cleaned using high-purity deionized water, and cloud samples were filtered through fiberglass filters (0.45 μm pore size) to remove suspended matter after sampling and then preserved in

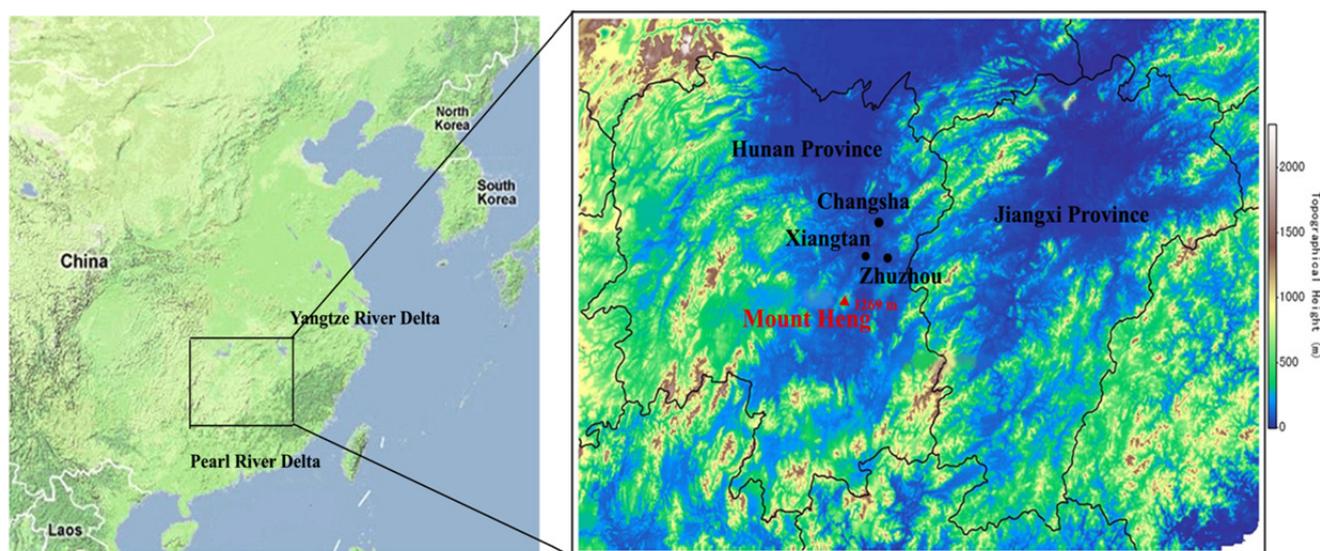


Fig. 1. Location of Mount Heng and the nearby geographical condition.

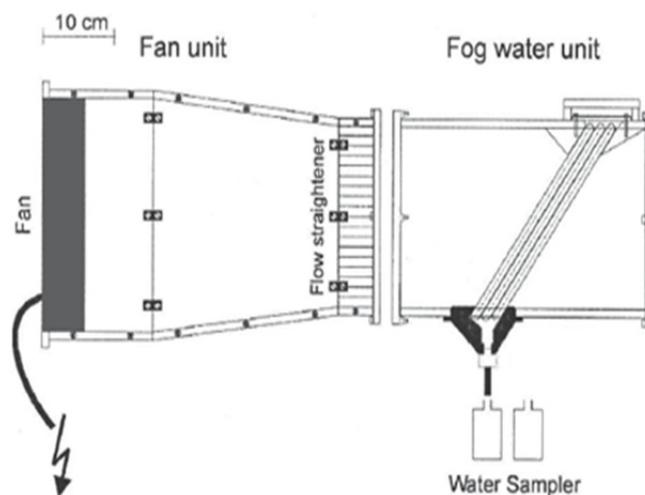


Fig. 2. Instrument structure of CASCC.

pre-cleaned Teflon bottles. The fiberglass filters and Teflon bottles were stored at -20°C and 4°C , respectively and transported to the laboratory at Shandong University for chemical analysis.

Sample Analysis

Cloud water samples were extracted using liquid-solid extraction using C18 extraction disks (47-mm diameter, 0.5-mm thickness) with 47-mm quartz filters. The dissolved phase was enriched using C18 disks, and the particulate phase was retained on quartz filters. Samples were spiked with 10 μL surrogate analytes (2-fluorobiphenyl and p-terphenyl-d14) before extraction to determine the analytical recovery efficiencies. To wash and condition the C18 disks, 5 mL of ethyl acetate, 5 mL of methanol and 5 mL of ultrapure water were used (Wang *et al.*, 2015).

Preconcentration of PAHs in liquid phase was conducted using solid phase extraction on C18 cartridge. Before concentrating samples, C18 cartridges were preconditioned by 3 mL of ethyl acetate and 3 mL of methanol. After sample enrichment, the cartridges were dried by nitrogen flow for 15 min. PAHs in cartridges were then eluted using acetone/n-hexane (1:1, v/v) solvents, and the volume of the eluate was reduced to 1 mL under a gentle nitrogen flow.

The quartz filters were extracted using Accelerated Solvent Extractor (DIONEX ASE 300) to enrich PAHs compounds. 33 mL acetone/n-hexane (1:1, v/v) solvents were used to elute PAHs, and the volume of eluant was reduced to 1 mL under a gentle nitrogen flow.

PAHs analysis for all collected samples was conducted by gas chromatography with mass selective detection (GC-MS, SHIMADZU 2010plus). The GC-MS was equipped with a 60 m DB-5 ms capillary column and operated in the ion monitoring mode (SIM). The chromatographic conditions were based the research published before (Li *et al.*, 2016). A mass range between 50 and 500 m/z was used for quantitative determinations. 16 US-EPA priority PAHs were analyzed during the process, namely acenaphthene (Ane), acenaphthylene (Acy), fluorene (Flu), phenanthrene (PhA), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr),

benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (InP), dibenzo(a,h)anthracene (DbA) and benzo(g,h,i)perylene (BP).

The particulate and gaseous phases of the ambient air samples were collected by a medium volume sampler (KC-300, Qingdao Laoshan Electronic Instrument Company) during the observation campaign, and PAHs were analyzed by GC-MS. The results were described in our previous study (Li *et al.*, 2016).

Quality Control (QC)/Quality Assurance (QA)

Field blanks which were collected simultaneously with other samples at the sampling sites were used to determine if there was any background contamination. Laboratory blanks including method blanks (solvent) and spiked blanks (standards spiked into solvent) were analyzed using the same procedure as samples. The detection limits calculation was described by Hwey-Lin Sheu *et al.* (1996) and QC/QA results suggested that the contaminants did not interfere with the recognition and quantification of PAHs. Surrogate standards (2-fluorobiphenyl and p-terphenyl-d14) were added to all the samples to monitor procedural performance. The mean recoveries (%) for surrogates in all samples were 60–70%. To quantify the PAHs, six-point calibration curves were conducted to determine the linearity of the responses. The correlation coefficient of calibration curve was greater than 0.99. The concentration of naphthalene is not reported for its low recoveries and interference in analytical procedure.

RESULTS AND DISCUSSION

Concentrations of PAHs in Cloud Deposition

Descriptive statistics for all valid observations of individual PAHs in cloud samples collected at Mount Heng are summarized in Table 1. During the observation campaign, the concentration of total (dissolved + particle) PAHs in cloud water samples ranged from 323.0 to 5660 ng L^{-1} , with an average of 1589 ng L^{-1} . BbF was the most abundant compound with a mean concentration of 230.5 ng L^{-1} ,

Table 1. Statistical description of individual PAH concentrations in cloud samples at Mount Heng.

Species	PAHs concentrations (ng L ⁻¹)								
	dissolved phase			Particle phase			Total (dissolved + particle)		
	range	mean	SD	range	mean	SD	range	mean	SD
Acy	1.12–14.18	5.02	3.21	1.12–15.82	4.44	4.12	2.45–19.98	9.47	4.82
Ane	18.35–77.03	35.16	14.93	1.94–47.35	10.02	12.00	22.03–86.06	45.18	18.83
Flu	21.80–98.67	44.49	17.58	1.94–33.07	9.30	8.88	29.14–108.6	53.79	20.07
PhA	30.81–273.1	101.65	57.41	7.56–192.6	44.35	46.09	52.96–330.1	146.0	82.95
AnT	2.22–33.70	16.19	7.02	1.55–92.65	10.69	18.97	7.79–109.6	26.88	20.96
FluA	10.68–114.7	47.47	28.81	6.67–325.4	92.16	91.94	26.74–395.9	139.6	106.1
Pyr	8.68–154.7	61.34	34.71	5.08–572.1	87.84	124.3	30.25–699.3	149.2	141.8
BaA	5.56–291.4	95.31	67.10	0.61–279.8	65.03	67.58	18.02–466.7	160.3	113.3
Chr	3.89–96.93	49.59	25.79	2.14–420.8	75.01	98.29	18.02–513.4	124.6	106.7
BbF	1.67–67.75	21.67	15.10	0.92–917.4	208.8	234.0	12.48–971.5	230.5	248.2
BkF	1.75–59.62	14.88	14.55	1.22–183.5	63.95	57.37	5.51–238.6	78.83	66.96
BaP	2.22–77.92	21.82	17.50	1.22–442.5	71.23	99.55	11.81–501.9	93.05	108.8
InP	1.53–35.00	9.22	7.52	1.53–659.2	122.8	163.4	3.06–677.4	132.1	166.6
DbA	1.67–8.79	3.58	1.84	1.79–127.7	21.93	30.66	3.57–130.8	25.51	30.95
BP	1.75–142.6	20.70	29.85	1.22–793.7	153.4	186.5	7.40–831.2	174.10	203.50
ΣPAHs	118.7–1386	548.1	265.5	43.69–4738	1041	1149	323.0–5660	1589	1291

contributing to 14.50% of the total concentration. PhA, FluA, Pyr, BaA and Chr comprised a second set of major compounds with their average concentrations over 100 ng L⁻¹. In previous studies, it was reported that the solubility of lower molecular weight (LMW) PAHs was much higher than higher molecular weight (HMW) PAHs in water phase (Lee and Lee, 2004; Sahu *et al.*, 2004). The mean concentration of HMW PAHs, however, was 2.78 times higher than LMW PAHs in cloud water samples due to the particle inside. Six potential carcinogenic PAHs (including BaA, BbF, BkF, BaP, Ind and DbA), as proposed by the International Agency for Research on Cancer (IARC), were detected at relative high concentrations, contributing to over 45.33% of the total PAHs.

On average, the concentration of particle phase PAHs was approximately 1.90 times higher than that of dissolved phase PAHs, and the distribution of PAHs in two phases are presented in Fig. 3. In dissolved phase, PhA, BaA and Pyr were the predominant PAHs, accounting for 18.55%, 17.39% and 11.19% of the total PAHs, respectively. In particle phase, BbF was the most abundant compound, contributed to 20.06% of the total concentration. The second most abundant compounds were BP and InP, accounting for 14.74% and 11.80% of the total PAHs, respectively. The relative high PAH concentration remained in particle phase indicated the behavior of PAHs in cloud water could be determined by adsorption to particle instead of dissolution mechanism. The distribution coefficient (K_p), calculated by the ratio of PAH concentrations in particle phase (ng L⁻¹) to those in the dissolved phase (ng L⁻¹), are presented in Fig. 4. Qualitatively, the K_p value of individual PAH increased with the increase of the molecular weight, and good correlation was found between K_p value and PAH concentration in particle phase. These results supported the view of previous studies that HMW PAHs had a relative high hydrophobicity and could bound to particle more effectively (Zhang *et al.*, 2007; Yan *et al.*, 2012).

The distribution of individual PAHs in cloud water

observed at Mount Heng was consistent with our previous study conducted at Mount Tai (the highest mountain at northern China, 1534 m A.S.L.) and Mount Lu (another high mountain site located in southern China, 1165 m A.S.L.) which reported that the most abundant PAH compounds in cloud were PhA and Flu (Li *et al.*, 2010, Wang *et al.*, 2015). However, the observed PAH concentrations at Mount Heng (mean: 1589.05 ng L⁻¹) were 5.25 and 2.50 times higher than those reported at Mount Tai (mean: 302.6 ng L⁻¹) and Mount Lu (mean: 635.4 ng L⁻¹), respectively. The results obtained at these mountain regions can provide an overall picture of PAHs associated with cloud water in free troposphere of China.

Scavenging Ratios of PAHs by Clouds

PAHs, as a group of typical semi-volatile organic contaminants, can partition between gas and particle phases after being released into the atmosphere by natural and anthropogenic processes. During the course of their transport, PAHs can be removed from atmosphere by wet and dry deposition, which introduce atmospheric PAHs into various aquatic systems (Cheruiyot *et al.*, 2015). Cloud is an important processor for atmospheric PAH deposition, where gas phase PAHs could be dissolved in cloud droplets and particle-bound PAHs can be directly scavenged by cloud droplets.

The scavenging ratios of PAHs by cloud water can be described by the equations suggested by Ligocki *et al.* (1985a, b):

$$W_T = \frac{C_{\text{cloud}}}{C_{\text{air}}} = W_p \varnothing + W_g (1 - \varnothing) \quad (1)$$

where W_T , W_p and W_g are total-, particle- and gas-scavenging ratios, respectively. The particle-scavenging ratio W_p is defined as $C_{p,\text{cloud}}/C_{p,\text{air}}$ where $C_{p,\text{cloud}}$ is the

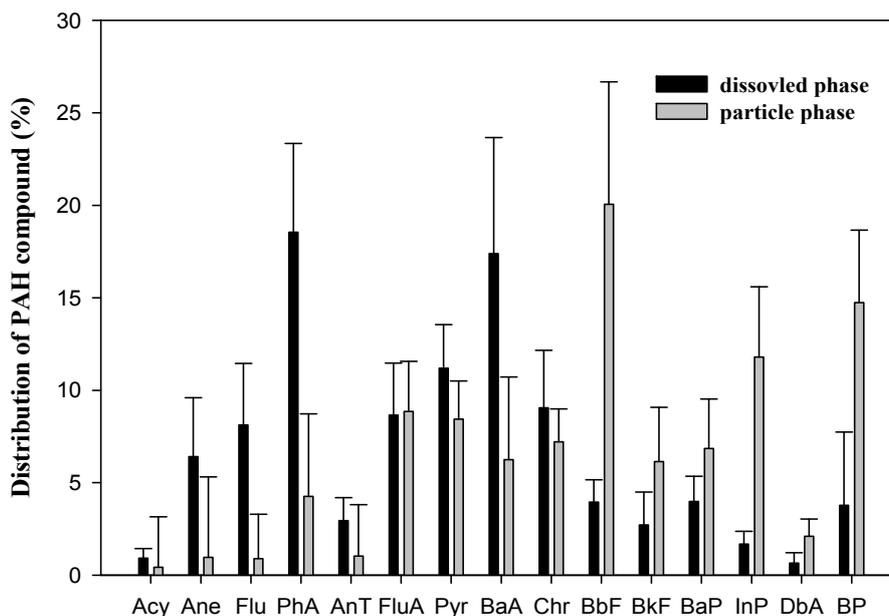


Fig. 3. Distribution of individual PAHs in dissolved phase and particle phase.

PAH concentration of particle phase in cloud water (ng m^{-3}) and $C_{p,\text{air}}$ is the concentration of the compound of interest bound to airborne particles (ng m^{-3}). Likewise, the gas scavenging ratio W_g is defined as $C_{d,\text{cloud}}/C_{g,\text{air}}$ where $C_{d,\text{cloud}}$ is the dissolved concentration of PAHs in cloud water (ng m^{-3}) and $C_{g,\text{air}}$ is the gaseous concentration in air (ng m^{-3}). ϕ is the fraction of PAHs associated with particles in the air, defined as $C_{p,\text{air}}/(C_g + C_{p,\text{air}})$, which were obtained through the field measurement. As presented in Table 2, the total scavenging ratios (W_T) varied among individual PAH compounds, ranging from Flu (2.75×10^4) to InP (8.98×10^5). The W_T values obtained in this study were consistent with the result found at Mount Lu for cloud sample (W_T : 4.69×10^3 to 7.93×10^4 for PAHs), and those reported at Hong Kong, China (W_T : 10^5 for PAHs) (Liu *et al.*, 2013), Athabasca oil sands region, Canada (W_T : 10^2 – 10^5 for PAHs) (Zhang *et al.*, 2015b), Guangzhou, China (W_T : 10^3 – 10^4 for PAHs) (Guo *et al.*, 2014), Singapore (W_T : 10^4 – 10^5 for PAHs) (He and Balasubramanian, 2009), Lake Michigan, USA (W_T : 10^2 – 10^7 for PAHs) (Offenberg and Baker, 2002), Chesapeake Bay region, USA (10^3 – 10^5 for PAHs) (Poster and Baker, 1996) and Mumbai, India (W_T : 10^3 – 10^5 for PAHs) (Sahu *et al.*, 2004) regarding precipitation. The variation of W_T values from different studies could be caused by several factors such as meteorology, sampling environment and sample styles (precipitation or clouds).

In this study, the observed W_g and W_p values for individual PAHs varied from 2.08×10^4 (AnT)– 4.14×10^5 (BbF) and 2.23×10^4 (Flu)– 9.30×10^5 (BbF), respectively (Table 2). The W_g and W_p values for HMW PAHs were generally much higher than those for LMW PAHs. The relative importance of gas and particle scavenging on the total removal of contaminants from the atmosphere depends on the relative contribution of the terms $W_p\phi$ and $W_g(1-\phi)$ (Eq. (1)). As presented in Table 2, the contribution of gas scavenging was more important for LMW PAHs. In contrast,

particle scavenging contribution was more significant for HMW PAHs. For the total PAH compounds, particle scavenging was the dominate removal mechanism, accounting for over 77% of the total scavenging, while gas scavenging was much less important. These results were in consistent with a previous study which suggested that particle phase was an important contribution to deposition (Li *et al.*, 2010). Significant negative relationship was found between $\log W_p$ and supercooled vapor pressure (PL^0) of PAHs (Fig. 5, $p < 0.01$), suggesting that particle scavenging by cloud water is more efficient for higher molecular weight PAHs, which tend to bound to the particle phase in atmosphere.

Transport Pattern of Cloud Deposition

In previous studies, PAH concentration in precipitation always decreased significantly with increasing cumulative rainfall since most PAHs can be scavenged during the initial stage of precipitation. However, PAHs measured in cloud water could present a relatively stable process (Li *et al.*, 2010). In this study, no significant correlation was observed between PAHs concentrations in cloud and cloud water amount or cloud duration (results were not presented), which was consistent with our previous finding. These results indicated the transport pattern of air mass could have more important influence for cloud deposition. In order to investigate origins of air masses, 72 h back trajectory was calculated using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (version 4.7) with FNL meteorological datasets at a height of 1269 m A.S.L. (Fig. 6).

All the air masses were classified into five major categories: N - air masses originating from continental areas in northern China, travelling to the station across North China Plain; E - air masses coming from oceanic areas of east China, reaching the station across Yangtze River Delta region; S - air masses originating from the south or southeast of mostly marine

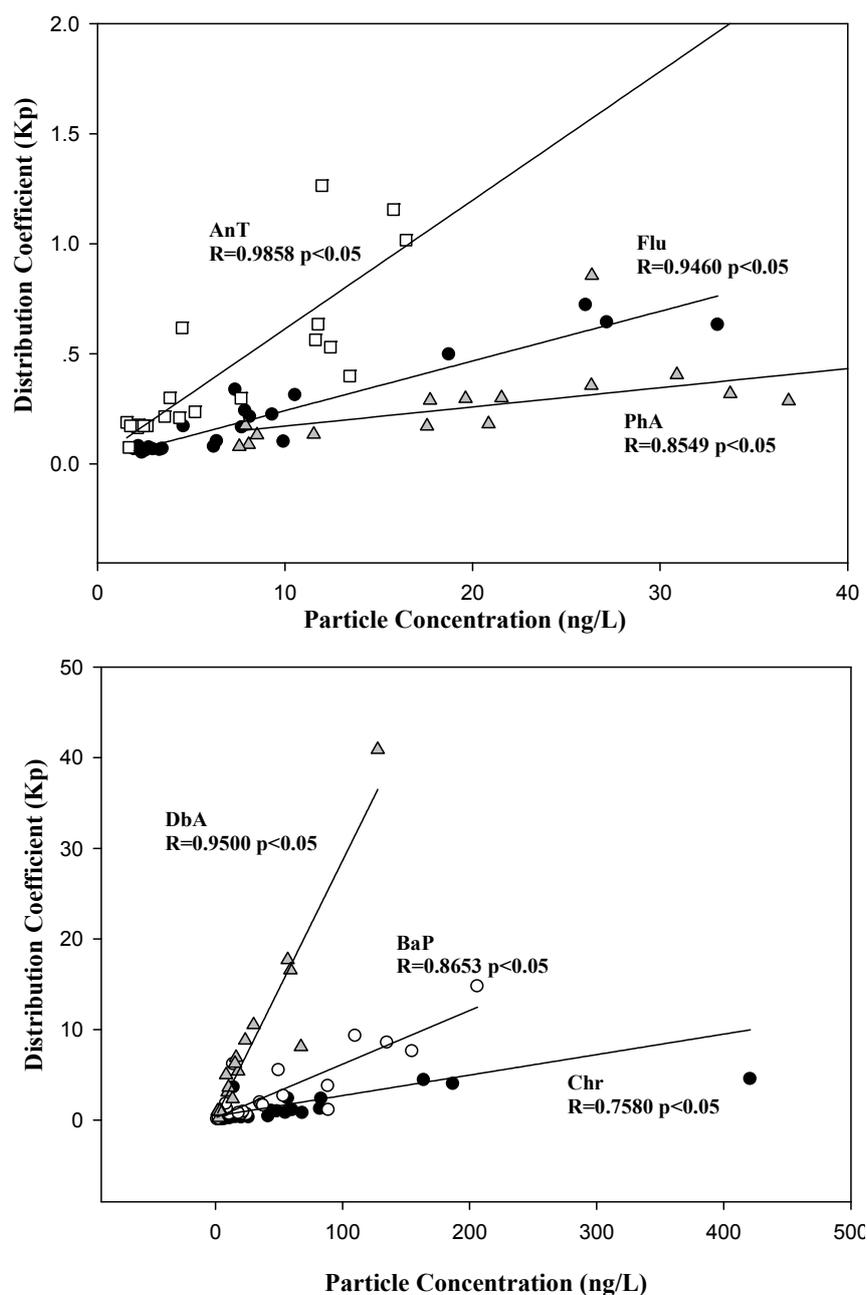


Fig. 4. Relationship between K_p of individual PAH and PAH concentration in particle phase.

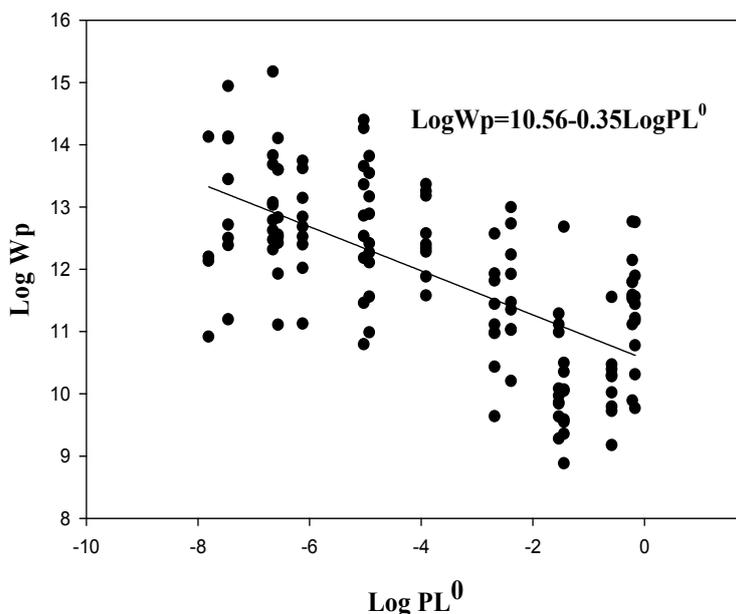
origin and traveling to the station across Pearl River Delta region; SW - air masses coming from south-western coastal areas away from sampling site; L - air masses influenced by pollution sources of local province. The air mass associated with trajectory passed over two categories defined above was omitted, and 20 cloud samples were taken into account.

Among the five categories of air masses, category S was the dominate one, accounting for 35% of the total, followed by the categories SW (25%), N (15%) and L (15%). E was the category contributing to the least proportion (10% of the total). The air masses of N category, originating from northern China where there was heavy pollution, had the highest PAH concentration (2341 ng L^{-1}) among the five categories. The PAH concentration of SW category (1608

ng L^{-1}) was the second highest. Air masses travelling across two most developed regions of China (Yangtze River Delta region - E category and Pearl River Delta region - S category) had comparable PAH concentrations, which were 1047 (S category) and 1115 (E category) ng L^{-1} , respectively. The PAH concentration of L category group was 1180 ng L^{-1} . For N, SW, S and L category group, the proportion of individual PAHs were similar as each other. For these categories, PhA, BaA and BbF were the major compounds, accounting for nearly 35% of PAHs concentration. For E category, BaA accounted for 13.20% of the PAHs concentration, while Pyr and FluA accounted for 11.45% and 10.59% of the total PAHs, which is different from the other four categories.

Table 2. The PAHs particulate, gaseous scavenging ratios, and their relative contributions to the total scavenging processes.

Species	Scavenging ratios			Relative contribution	
	Gas scavenging (W_g)	Particle scavenging (W_p)	Total scavenging (W_T)	The contribution of Gas phase (%)	The contribution of Particle phase (%)
Acy	5.85×10^4	5.34×10^4	5.69×10^4	68.45%	31.55%
Ane	1.40×10^5	1.08×10^5	1.33×10^5	79.46%	20.54%
Flu	3.03×10^4	2.23×10^4	2.75×10^4	64.75%	35.25%
PhA	5.08×10^4	1.72×10^5	5.34×10^4	97.87%	2.13%
AnT	2.08×10^4	1.37×10^5	3.49×10^4	87.89%	12.11%
FluA	4.27×10^4	7.33×10^4	5.82×10^4	49.33%	50.67%
Pyr	6.25×10^4	8.10×10^4	7.29×10^4	43.79%	56.21%
BaA	1.75×10^5	1.98×10^5	1.90×10^5	34.13%	65.87%
Chr	3.07×10^5	5.13×10^5	4.26×10^5	42.26%	57.74%
BbF	4.14×10^5	9.30×10^5	8.20×10^5	21.36%	78.64%
BkF	3.80×10^5	4.11×10^5	4.03×10^5	24.76%	75.24%
InP	1.28×10^5	9.19×10^5	8.98×10^5	2.70%	97.30%
BP	2.42×10^5	4.80×10^5	4.61×10^5	8.22%	91.78%
sum	2.05×10^6	4.10×10^6	3.63×10^6	22.68%	77.32%

**Fig. 5.** Relationship between particle scavenging ratio (W_p) and supercooled vapor pressure (PL^0).

Source Identification

(1) Diagnostic Ratios

It is suggested that the concentrations and molecular ratios of some marker PAHs can provide a general idea about the contribution of different PAH sources in the environment (Kavouras *et al.*, 2015). Four widely used diagnostic ratios including PhA/(PhA + AnT), BaA/(BaA + Chr), InP/(InP + BP) and FluA/(FluA + Pyr) were applied in this study to analyze the PAHs collected in cloud samples, and the results are presented in Table 3.

In previous studies, the ratio PhA/(PhA + AnT) is 0.50 for gasoline, 0.65 for diesel emissions and 0.76 for coal combustion (Khalili *et al.*, 1995; Wang *et al.*, 2010). In the present study, the ratio was 0.84 for cloud samples which was higher than reference ratio (0.76), indicating that coal

combustion was the main source of PAHs at Mount Heng site. For 4-ring PAH isomer indicator BaA/(BaA + Chr), the ratio lower than 0.2 signals petrogenic sources and the ratio higher than 0.35 indicates combustion sources (Soclo *et al.*, 2000). The value analyzed in cloud sample in this study was 0.59, suggesting that incomplete combustion is the dominant source. For FluA/(FluA + Pyr), the ratio lower than 0.4 suggests the sources of unburned petroleum, the ratio higher than 0.5 signals coal and wood combustion, and the ratio from 0.4 to 0.5 suggests the combustion of liquid fossil fuels (Yunker *et al.*, 2002). The FluA/(FluA + Pyr) ratio was 0.51 for the sample in this study, highlighting the contributions from coal and wood combustion sources. Another widely used indicator is InP/(InP + BP), and the ratios of 0.18, 0.37, 0.56 and 0.62 indicate the PAH sources from

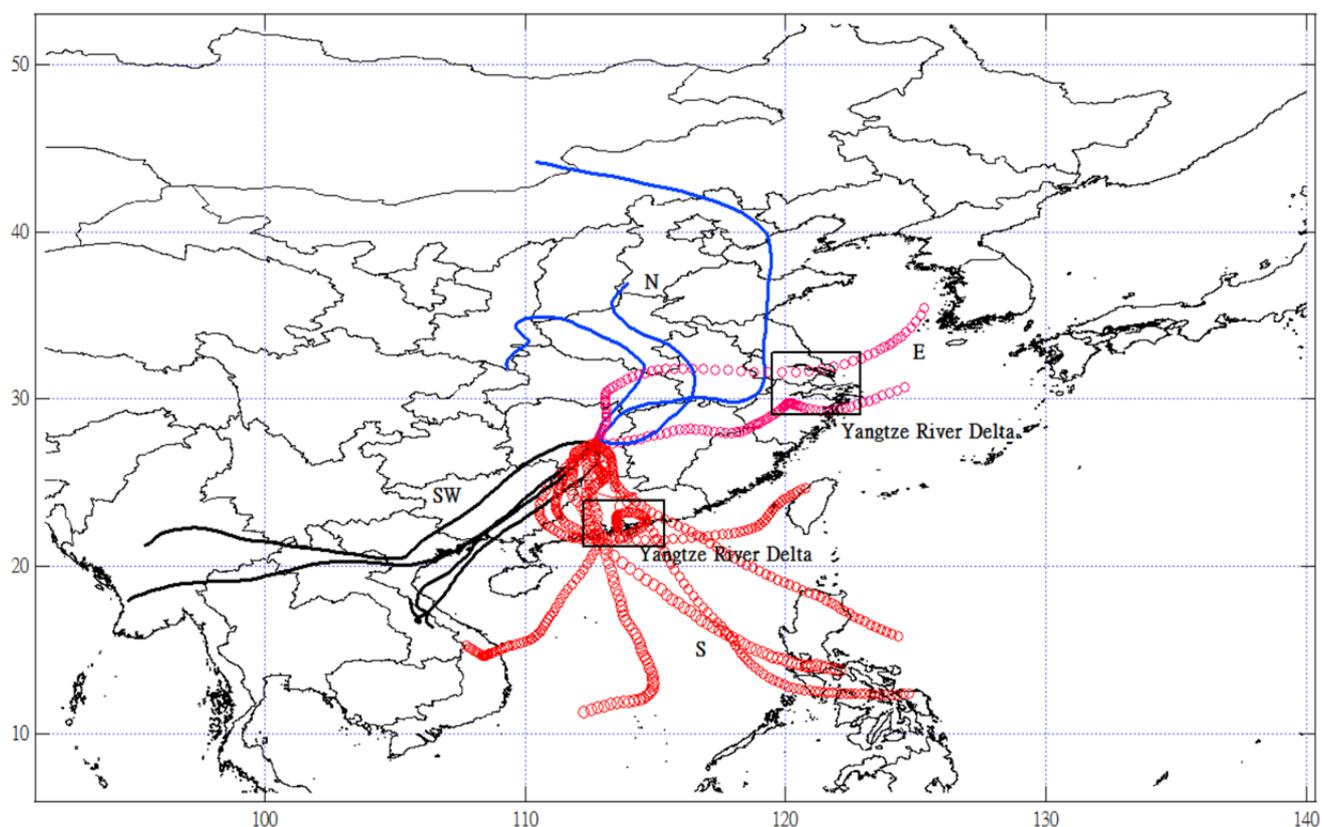


Fig. 6. 72-h backward trajectories for cloud samples at Mount Heng.

Table 3. Diagnostic PAH ratios for cloud samples collected at Mount Heng.

Species	Value of cloud sample	Reference source emissions
PhA/(PhA + AnT)	0.84	0.5 gasoline
		0.65 diesel
		0.76 coal
BaA/(BaA + Chr)	0.59	> 0.35 combustion sources
		< 0.2 petrogenic
FluA/(FluA + Pyr)	0.51	< 0.4 unburned petroleum
		0.4–0.5 liquid fossil fuels
		> 0.5 coal and wood
InP/(InP + BP)	0.43	0.18 Cars
		0.37 Diesel
		0.56 Coal
		0.62 Wood burning

cars, diesel emission, coal combustion and wood burning, respectively (Ravindra *et al.*, 2008). In this study, the ratio was 0.43, indicating that the PAHs in cloud samples may be originated from either coal combustion or diesel emission sources.

Based on the diagnostic ratios analysis, coal and wood combustion and diesel emission were suggested to be the main sources of PAHs in cloud samples at Mount Heng. The results were consistent with our previous study on cloud water conducted at Mount Tai (Li *et al.*, 2010). The results from these high altitude background sites could give an overall picture on the possible sources of PAH in cloud in China. However, it should be cautious to interpreting the

results of diagnostic ratio analysis because the degradation property of PAH compounds can be quite different during their transportation which may change the concentrations of individual PAHs and their ratios. For example, AnT and BaA have been proved to degrade more quickly in the atmosphere than their isomers PhA and Chr, respectively (Kamens *et al.*, 1988; Schauer *et al.*, 1996; Varea *et al.*, 2011).

(2) Principal Component Analysis (PCA)

As mentioned above, there were uncertainties when using diagnostic ratios to identify PAHs sources. PCA, as an exploratory tool, has been widely used to identify the major sources of PAHs. In this study, the concentrations of

15 individual PAH compounds in cloud samples were subjected to factor analysis using SPSS version 21 (SPSS Inc.). PCA was conducted with Varimax rotation, and factors with eigenvalue >1 were considered. The results of rotated factors are listed in Table 4.

Two factors were separated, accounting for 84.05% of the total variance in the data. Factor 1, which explained 65.63% of the variance, was mostly related with individual PAHs of higher molecular weight namely FluA, Pyr, BaA, Chr, BbF, BkF, BaP, InP, DbA and BP. According to previous studies, FluA, Pyr, BaA and Chr are the major components of coal and wood combustion, and the presence of BbF, BkF, BaP, InP, DbA and BP might be from vehicular emission (Guo *et al.*, 2003; Zhang *et al.*, 2008; Chuesaard *et al.*, 2014). Thus, factor 1 could represent sources from vehicular and coal combustion emission. Factor 2, which explained 18.42% of the variance, is highly loaded on Acy, Ane, Flu and AnT. Acy and Ane have been identified to come from unburned fossil fuels emissions; PhA and AnT are major components in industry emission (Ravindra *et al.*, 2008; Li *et al.*, 2010); and Flu could be originated from different sources.

Based on the results of PCA, coal combustion, vehicular emission, industry emission and unburned fossil fuels were suggested to be the major sources of PAHs in cloud samples at Mount Heng. However, as stated earlier, the reactivity and degradation of individual PAHs could influence the results of profiles of PAH sources, so further studies are required to elucidate this issue.

CONCLUSIONS

The concentrations of PAHs in cloud samples were analyzed at Mount Heng during March to May 2009. The average concentration of total PAHs in cloud water was

Table 4. Principal component analysis for PAHs in cloud samples.

PAHs	Factor 1	Factor 2
Acy		0.775
Ane		0.860
Flu		0.846
PhA	0.769	0.475
AnT		0.767
FluA	0.960	
Pyr	0.909	
BaA	0.431	
Chr	0.946	
BbF	0.958	
BkF	0.981	
BaP	0.956	
InP	0.989	
DbA	0.958	
BP	0.982	
% of variance	65.63	18.42
Sources	coal combustion and vehicular emission	unburned fossil fuels and incense burning

1589 ng L⁻¹. Among the 16 individual PAHs, BbF was the most abundant compound, contributing to 14.50% of the total concentration, and PhA, FluA, Pyr, BaA and Chr comprised the second set of major compounds. The observed gas scavenging (Wg) and particle scavenging (Wp) values for these individual PAHs varied from 2.08×10^4 (AnT)– 4.14×10^5 (BbF) and 2.23×10^4 (Flu)– 9.30×10^5 (BbF), respectively. Wp was the dominant removal mechanism of PAHs, accounting for over 77% of the total scavenging. Significant negative relationship was found between logWp and supercooled vapor pressure of PAHs, indicating that Wp by cloud water is more efficient for higher molecular weight PAHs. Back trajectory analysis suggested that air masses mainly originated from south or southeast of mostly marine origin, while air masses of N category (coming from northern China) had highest PAH concentration. Result obtained through diagnostic ratios and PCA indicated multiple sources of PAHs in cloud water at Mount Heng.

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