

Compositional fractionation of polycyclic aromatic hydrocarbons (PAHs) in mosses (*Hypnum plumaeformae* WILS.) from the northern slope of Nanling Mountains, South China

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Received 5 February 2005; accepted 15 May 2005

Abstract

High mountains may serve both as condenser for vapor phase persistent organic pollutants (POPs) and as barrier/sink for particulate associated less volatile POPs. The fractionation of POPs along altitudinal profiles is of interest in understanding the role of high mountains in the atmospheric transport of POPs. In the present study, polycyclic aromatic hydrocarbons (PAHs) in a selected moss species, *Hypnum plumaeformae* WILS, from two altitudinal profiles on the northern slope of Nanling mountains in Southern China were analyzed and compared with those in air samples. The total PAH concentration in the mosses was 310–1340 ng g⁻¹ dry weight, with phenanthrene being the most abundant. The distribution patterns of PAHs in the moss samples matched well with those in bulk atmosphere deposition in the adjacent source areas. The PAH distribution pattern in the mosses was a composite of both particle-associated and vapor phase PAHs, with heavy PAHs are susceptible to uptake/retention by mosses than light PAHs. A plot of log ($C_{\text{moss}}/C_{\text{air}}$) against log K_{oa} gave a good linear relationship in the log K_{ao} range of 6.7–10.2. It is suggested that the widely spread moss, *H. plumaeformae* WILS, can be used as an effective tool in the biomonitoring of atmospheric PAHs pollution in East Asia. The concentrations of most PAHs in the mosses generally declined with increasing altitude. In addition, there was a shift in compound pattern with an increase in the proportion of light PAHs (2–3 rings), a decrease in heavy PAHs (5–6 rings) and a relatively stable content of 4-ring PAHs. A combination of particulate scavenging and cold condensation are proposed as the major mechanisms for the compositional fractionation of PAHs along the altitudinal profile.

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Keywords: Moss; High mountains; Polycyclic aromatic hydrocarbons (PAHs); Monitoring; Atmospheric deposition; Fractionation; Long-range transport; Southern China

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds found in the environment, mainly derived from biomass burning, incomplete fossil fuel combustion, petroleum leakage/evaporation, and the early diagenesis of organic matter. Owing to their hydrophobicity, PAHs may partition and accumulate in organisms and many are known to be carcinogenic and mutagenic (Aas et al., 2001). In the atmosphere, PAHs may be present both in the vapor and particulate phases, especially aerosols with an aerodynamic diameter less than $2\ \mu\text{m}$ (Venkataraman and Frenlander, 1994), which may be absorbed readily by plant leaves. As a large group of persistent organic pollutants (POPs), PAHs can undergo long-range atmospheric transport, and exist in the environment for a long time.

Selected POPs are long-range transported from temperate mid-latitudinal source areas into the cold Polar Regions on our globe as a consequence of consecutive air-surface exchange and atmospheric transport (Wania and Mackay, 1996). Temperature dependence of some organochlorine compounds was observed in mosses in Andean mountains (Grimalt et al., 2004) and snow in western Canada (Blais et al., 1998), for example, and some compounds (e.g. HCB) can actually increase in “condensed phase” with elevation above sea level. This phenomenon, to some extent, mimics the latitudinal distribution of HCH and HCB in tree bark (Simonich and Hites, 1995) and HCH in seawater (Wania and Mackay, 1996). Particle-associated POPs, such as heavy PAHs (e.g. 5–7 rings) are also found in the air (Sanusi et al., 1999, AE), water (Vives et al., 2004), soil and sediment (Grimalt et al., 2004) of remote high mountain environments, indicating the ability of fine aerosols to undergo a long-range air transport and deposition of PAHs.

Vegetation samples, such as tree bark, pine needles and mosses (Bacci et al., 1990; Jones et al., 1992; Simonich and Hites, 1994; Lead et al., 1996; Grimalt et al., 2004; Hellström et al., 2004), can “sample” and integrate POPs from the atmosphere and can be used to compare the composition along gradients e.g. with altitude. They receive vapor phase POPs which partition to their surfaces, and also capture particulate-associated POPs (Finizio et al., 1997; McLachlan, 1999; Kipopoulou et al., 1999; Holoubek et al., 2000; Franzaring et al., 2000; Wolterbeek, 2002; Klein et al., 1999; Barber et al., 2004; Bartkow et al., 2004). In particular, epiphytic moss has no roots, no circulatory system and no cuticle layer (Lead et al., 1996; Grimalt et al., 2004), and the uptake of POPs from soil hence is less significant. Therefore, mosses are particularly efficient at absorbing/retaining atmospherically derived trace substances.

This paper reports the altitudinal (300–1750 m.a.s.l.) variation of PAH concentrations and compositional

distribution patterns in a moss species, *Hypnum plumaeforme* WILS, from 300–1750 m.a.s.l. on the northern slope of Nanling mountains, Southern China. This location receives continental cold airflow (Asian monsoons) blowing down to South China coastal regions in winter, and is also influenced by marine climate in summer time.

2. Sampling

2.1. Regional background

Nanling mountain range is located in southern China straddling from west to east across the Guangxi-Guangdong-Hunan-Jiangxi provincial border for more than 1000 km (Fig. 1). The mountain range is an important boundary for temperate and subtropical region in South China (Lee et al., 2005). The annual ambient air temperature in the Nanling Mountain ranges between -6.9 and $39\ ^\circ\text{C}$, with an annual average temperature and rainfall of 17.5 – $20.3\ ^\circ\text{C}$ and 569 – 2200 mm, respectively. The area is a key recipient for long-range air pollutant transport from northern China to the southern coastal region, particularly during the winter monsoon period (Chan et al., 2002; Wang et al., 2003a, b). In the south of the Nanling range, lies the Pearl River Delta (PRD) region of Guangdong Province. The PRD forms one of the most urbanized areas in China, with a total population of more than 30 million and covers an area of $41,700\ \text{km}^2$. Frequent atmospheric pollution episodes were recorded in wintertime in the PRD (Chan et al., 2002; Lee and Hills, 2003). In particular, the observed high PAH concentrations in aerosols over Hong Kong in winter were

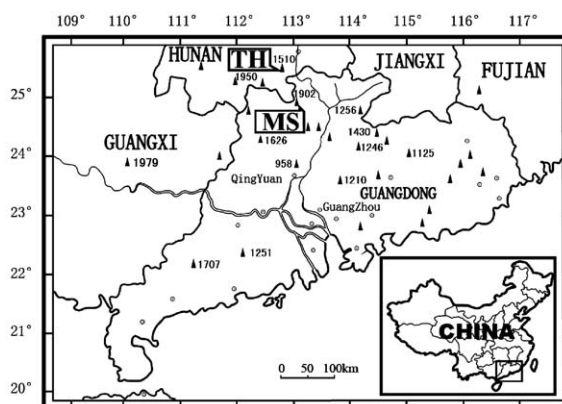


Fig. 1. Schematic map showing the sampling sites and Nanling mountain ranges. Shaded triangles represent mountain peaks. Heights of major mountain peaks are denoted in meter above sea level (m.a.s.l.). MS: Manshan profile, TH: Tianhu profile.

suggested to be related to the possible long-range atmospheric transport of pollutants from the inner continent (Guo et al., 2003). Therefore, it is of interest to know how PAHs carried by the cold airflow is attenuated in the Nanling mountains.

2.2. Moss sampling

The moss *Hypnum plumaeformae* WILS is commonly found in dense mats in Nanling Mountain and the PRD region (Lee et al., 2005). The mat structure and density will affect pollutant trapping and retention (Sucharová and Suchara, 1998; Lee et al., 2005). The mosses were sampled in January 2003 when winter wind was at its maximum. Sampling sites were recorded with a global positioning system (GPS) device. Samples were collected at 13 different elevations on Tianhu profile (TH) and 9 on Mangshan profile (MS), both on the northern slope of Nanling Mountains (Table 1). One composite sample was collected for each altitude, and mosses were picked by hand, and stored frozen in polyethylene bags prior to PAH analysis in laboratory.

2.2.1. Air sampling

A high-volume air sampler (Anderson-type) was used to collect air samples for 12 h from the Nanling

mountains at five stations (2 samples for each station) between 1000 and 1400 m.a.s.l. at a sampling flow of 0.465 l/min. The atmospheric particle phases were collected on a 20.3 × 25.4 cm Whatman glass micro-fiber filter (GFF) (grade GF/A, 20.3 × 25.4 cm) and a polyurethane foam plug (PUF) (length 8.0 cm, diameter 6.25 cm, density 0.035 g cm⁻³) absorbed vapor phase PAHs. The GFF was baked at 450 °C for 6 h prior to use, and PUF plugs were pre-extracted with dichloromethane (DCM) for 24 h. Exposed GFFs and PUFs were stored in glass jars below -20 °C until analysis.

2.3. Atmospheric particle deposition sampling

Dry and wet air depositions of particle bound PAHs were collected using a glass filter setup under a 25 cm diameter funnel made of stainless steel. The sampling site is at a suburban meteorological station located in Luhu Park in the north part of Guangzhou city, the Pearl River Delta, which corresponded with the moss sampling locations. Using the open apparatus to collect both dry and wet atmospheric particle deposition samples were collected on a monthly basis from April 2001 to March 2002. Before and after the sampling program, the GFFs were treated as air samples.

Table 1
Locations of the moss sampling sites

	Sample name	Altitude (m)	Latitude	Longitude
	TH-01	300	N25°38'45.8"	E112°50'38.4"
	TH-02	400	N25°37'43.0"	E112°50'29.3"
	TH-03	500	N25°36'59.6"	E112°50'10.9"
	TH-04	610	N25°36'27.3"	E112°50'03.0"
	TH-05	710	N25°35'59.7"	E112°49'43.9"
	TH-06	825	N25°35'43.6"	E112°49'54.1"
TH Series	TH-07	900	N25°35'28.3"	E112°49'49.0"
	TH-08	900	N25°32'52.0"	E112°49'25.7"
	TH-09	1000	N25°32'42.0"	E112°49'54.4"
	TH-10	1100	N25°32'04.8"	E112°50'15.1"
	TH-11	1200	N25°31'50.8"	E112°50'18.9"
	TH-12	1300	N25°31'33.3"	E112°50'11.7"
	TH-13	1400	N25°31'15.6"	E112°50'14.5"
	MS-01	480	N25°01'29.8"	E112°49'38.0"
	MS-02	500	N24°59'02.3"	E112°51'32.5"
	MS-03	680	N24°58'56.7"	E112°54'58.0"
	MS-04	850	N24°59'02.2"	E112°55'52.2"
MS-Series	MS-05	1000	N24°58'18.0"	E112°56'33.0"
	MS-06	1200	N24°57'31.8"	E112°57'25.1"
	MS-07	1400	N24°57'03.5"	E112°58'59.9"
	MS-08	1600	N24°56'09.2"	E112°59'04.1"
	MS-09	1750	N24°55'49.4"	E112°59'13.6"

3. Chemical analysis

3.1. Moss

The green part of the moss was separated and thoroughly washed with tap water, and then with deionized water (DIW) until no particles were adhered to the surfaces (Lee et al., 2005). The mosses were air dried at 16 °C in a dark clean room with an air-conditioner. The dried mosses were then ground to about 0.2 mm. We analyzed the remaining water content in selected 'dried' mosses, these were within 0–1.5% by weight. In the following text, concentrations (in ng g^{-1} dw) were not corrected by the limited residual water content in the moss powder.

3.1.1. Extraction

A Dionex ASE 300 (Dionex Co., USA) was employed. Five grams of moss powder was mixed with 5 g of anhydrous sodium sulfate (baked for 4 h at 600 °C in oven before use), packed in a 33 ml stainless extracting cell. The samples were spiked with a known aliquot of naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 as analyte surrogates. Dichloromethane (DCM) and acetone (1:1, V:V) was used as solvent; the system pressure was kept at 1500 psi, and the temperature set to 100 °C during the full process of extraction. The ASE was conducted for two cycles, each lasting for 5 min of heating time, and 5 min of static extraction time. Five grams of activated copper slices was added to the extracts to remove elemental sulfur.

3.1.2. Cleanup

The moss extract was concentrated to 1 ml with a rotary evaporator at 30 °C. It was loaded on a multiple layer chromatographic column packed with 2 g anhydrous sodium sulfate, 5 g aluminum oxide (extracted by DCM for 72 h, heated for 12 h in 250 °C), 5 g florisil (baked for 8 h at 450 °C in an oven) and 10 g silica gel (extracted by DCM for 72 h, heated for 12 h in 150 °C), and eluted with 60 ml of DCM. The eluent was volume reduced on an evaporator, and the solvent exchanged to 1 ml of hexane. A gel permeation chromatography (GPC) column (10 mm i.d., packed with 10 g of S-X3 Biobeads, dipped by dichloromethane in advance, Accustandard Co., USA) was used to eliminate lipids. After extract loading, the GPC column were eluted with 80 ml *n*-hexane: DCM (V: V, 1:1) at a flow rate of 0.5 ml min^{-1} . The first 35 ml eluent was discarded, and the following 45 ml which contains PAHs were collected and concentrated on an evaporator to 200 μl . For each sample, 1 μg of hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) was added as internal standard prior to GC-MSD analysis.

3.2. Air samples

Briefly, the PUF plugs and GFFs were Soxhlet extracted with DCM for 24 h. Clean-up was done by a column packed with 2 g anhydrous sodium sulfate, 5 g alumina, and 10 g silica gel (5% deactivated), eluted with 60 ml *n*-hexane and DCM (1:1, V:V). The subsequent steps were similar to that described for the moss samples.

3.3. Analysis

PAHs compounds were separated on a $30 \text{ m} \times 0.25 \text{ mm}$ i.d. HP-5 capillary column (film thickness $0.25 \mu\text{m}$) and analyzed using a Hewlett-Packard 5890 gas chromatography and 5972 mass selective (GC-MSD) detector operated in the electron impact mode (70 eV). The instrumental conditions were as follows: injector temperature, 280 °C; ion source temperature, 180 °C; temperature program: 60 °C (2 min), 60–290 °C at $3 \text{ }^\circ\text{C min}^{-1}$, 290 °C (30 min). The carrier gas was helium at a constant flow rate of 1.5 ml min^{-1} . 1 μl sample was injected in splitless/split mode. Mass range m/z 50–500 was used for quantitative determinations. Data acquisition and processing was controlled by HP Chemstation software.

The following 16 PAHs were selected as target compounds in the analysis: naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[*a*]anthracene (BAA), chrysene (CHR), benzo[*b*]fluoranthene (BBF), benzo[*k*]fluoranthene (BKF), benzo[*a*]pyrene (BAP), indeno [123-*cd*]pyrene (INP), dibenzo[*ah*]anthracene (DAH), and benzo[*ghi*]perylene (BGP).

3.4. Quality assurance (QA) and quality control (QC)

The method blanks showed no detected target compounds. Three field duplicates showed quite uniform PAHs concentrations with a standard deviation of 5–8%. Surrogates were added to all samples (including QA samples). The mean surrogate recoveries for 21 moss samples were as follows: naphthalene-d8: 49.3%, acenaphthene-d10: 60.6%, phenanthrene-d10: 90.9%, chrysene-d12: 95.2%, perylene-d12: 99.2%, and for air and deposition samples, the recoveries were 40–101%. In our study, the instrument detect limit (IDL) for PAHs was 0.13–0.92 ng on the GC-MSD, and the method detect limit (MDL) was calculated to be within $3.3\text{--}7.8 \text{ ng g}^{-1}$ dw.

4. Results and discussion

4.1. PAH concentrations in mosses

A summary of PAH concentrations in the mosses is given in Table 2. All the 16 USEPA priority PAHs were

detected in the moss samples. PHE was the most abundant PAH, followed by NAP, BBF, FLA, CHR, PYR and INP. Other PAH compounds contributed less than 6% of the total PAH concentration. The total PAH concentrations varied from 310 to 1210 ng g⁻¹ dw, with a mean of 640 ng g⁻¹ dw. This was at the same level as those in mosses from rural areas in Košetice (Holoubek et al., 2000), but lower than those from urban Valašské and Vresová (averages 3060 and 3670 ng g⁻¹ dw, respectively), and those in *Hylocomium splendens* from urban Warsaw, Poland (830–3570, average 2370; Orliński et al., 2002).

4.2. Comparison of PAH concentrations in mosses and atmosphere

Compound octanol-air partition coefficients (K_{oa}) can be used to describe both gas-particle partitioning and air-plant partitioning of lipophilic organic compounds as follows (Finizio et al., 1997; Paterson et al., 1993):

$$\log K_p = m \log K_{oa} + b, \quad (1)$$

$$\log(\text{BCFv}) = n \log K_{oa} + c, \quad (2)$$

where K_p is the particle-gas partition coefficient (m³ μg); BCFv is the ratio of volumetric concentrations; m , n , b and c are constants. Heavy PAHs (5–6 rings) are less volatile compounds with high K_{oa} values, tending to be associated with atmospheric particles, whilst light PAHs (2–3 rings) with high sub-cooled liquid vapor pressures

may largely exist in the vapor phase in the atmosphere under ambient conditions. Air-plant transfers of POPs may be: (a) kinetically limited with respect to gas phase uptake; (b) approaching or close to gas phase-plant equilibrium; (c) essentially controlled by particle phase deposition (McLachlan, 1999). A higher K_{oa} will lead to a higher particle-bound fraction in the air, and a corresponding higher contribution of particle-bound deposition (McLachlan, 1999). Higher K_{oa} compounds will also take longer to reach gas phase/plant equilibrium. The PAH distribution patterns in the mosses, vapor phase and particulate phase in the air (as the average of 5 samples) are compared in Fig. 2. The compounds from NAP to ANT existed primarily in vapor phase; CHR to BGP mainly existed in the particulate phase, and were seldom detected in the vapor phase; FLA to BAA showed comparative contents in both vapor and particulate phases. PAHs in *H. plumaeformae* WILS comprised of both light PAH (2–3 rings) and heavy PAH (5–6 rings), showing the mixed compositions of those supplied principally by gas phase (dominated by light PAH), and particle phase (dominated by mid to heavy PAH) deposition. As the moss samples were thoroughly washed by DIW prior to PAH analysis, it thus can be assumed that *H. plumaeformae* WILS is capable of retaining PAHs delivered by particle deposition, besides air-plant partitioning and dynamic gaseous deposition. This implies that, *H. plumaeformae* WILS broadly acts as a “passive sampler” of PAHs present in the air. However, this does not occur with equally efficiency across the compound range of PAHs. The percentage of 2–3, 4, 5–6 ring PAHs in the atmosphere was 62% > 21% > 17%, respectively, while on average, 27% < 35% < 38% was observed in *H. plumaeformae* WILS. The moss, therefore, tended to retain heavier PAHs more efficiently.

A series of moss to air (averaged total) PAH concentration ratios were calculated and plotted against the reference K_{oa} values (Harner and Shoeib, 2002; temperature of 2 °C) in Fig. 3. A good correlation between $\log(C_{\text{moss}}/C_{\text{air}} \text{ PAHs})$ and $\log K_{oa}$ was found in the $\log K_{oa}$ range of 6.7–10.2. This correlation generally agreed with other studies (Tremolada et al., 1996; McLachlan et al., 1995), although the slopes varied possibly owing to the difference in ambient temperature (5–10 °C in our paired air and moss sampling sites) and plant species. Partitioning for high K_{oa} compounds (in this study, those with $\log K_{oa} > 10.2$) does not follow the same relationship which has been noted in previous studies (Tremolada et al., 1996; McLachlan, 1999). This is possibly because high K_{oa} compounds need a long time to reach equilibrium, and particle-bound deposition may be the controlling process.

The average ratios of BKF/BBF in moss and atmosphere were both 0.24, and the ratios of FLA/PYR in moss and atmosphere were 1.21 and 1.22, respectively.

Table 2
Concentrations of 16 individual PAHs and ΣPAH in mosses (*Hylocomium plumaeformae* WILS.) from the northern slope of NanLing mountains (ng g⁻¹ dw) ($n = 22$)

PAH	Min	Max	Mean
NAP	50	180	105
ACY	n.d.*	24	5.6
ACE	n.d.	6.1	1.6
FLU	n.d.	31	10
PHE	22	340	120
ANT	n.d.	30	9.5
FLA	13	130	66
PYR	20	104	54
BAA	4	33	13
CHR	18	120	55
BBF	25	260	80
BKF	5.8	68	20
BAP	0.8	47	19
INP	14	170	45
DAH	n.d.	23	5.1
BGP	n.d.	140	37
Total PAHs	310	1340	640

*n.d.: not detect.

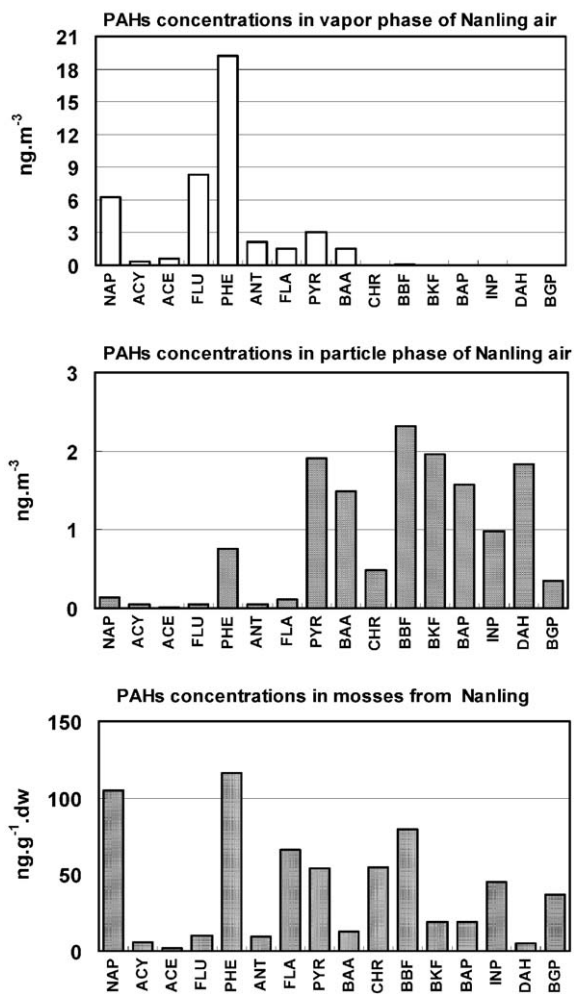


Fig. 2. Comparison of PAH distribution patterns in vapor and particulates phases in the air (as an average of five samples) and mosses (average).

As these pairs of PAHs have the same molecular weights, their identical ratios in the air and the moss may suggest that *H. plumaeformae* WILS has no obvious selectivity in capturing these compounds from the air.

ANT was reported to be more liable to photodegradation than PHE (Gschwend and Hites, 1981). The average ratio of PHE/ANT was 20 in moss, and 12 in the atmosphere. This may imply that ANT has been subjected to continuing photodegradation process in the moss (Wild et al., 2005). Notwithstanding, there is more degradation of lighter compounds in/on plants, and this may be another mechanism for the heavier compounds becoming selectively enriched in plants (Wild et al., 2005).

Apart from the above paired air-moss sample, the PAH distribution patterns in moss were further compared with regional atmospheric data in the PRD

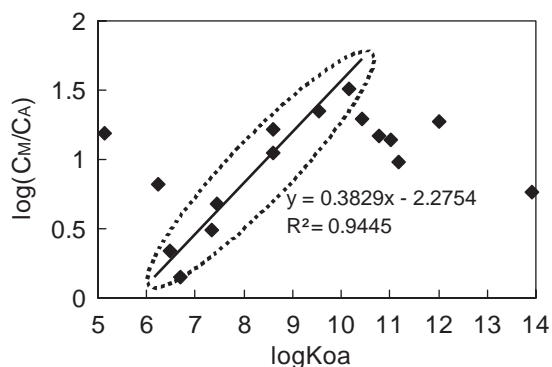


Fig. 3. Plot showing the correlation between $\log(C_{\text{moss}}/C_{\text{air}})$ and $\log K_{\text{oa}}$ of PAHs. The encircled dots were samples used for the regression equation calculation.

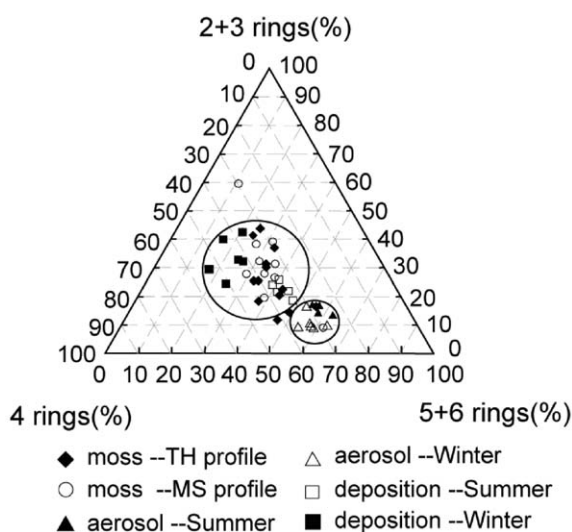


Fig. 4. Comparison of PAH compositions in mosses in Nanling, aerosols and particulate deposition in the Pearl River Delta. The three ends represent PAHs with 2+3, 4, and 5+6 aromatic rings in the structures, respectively. The two circles denote the area represent atmospheric deposition (large circle) and aerosol (small circle), respectively.

(Zhang et al., 2003). As shown in Fig. 4, PAHs in the mosses displayed a similar distribution pattern as in atmospheric particulate deposition, suggesting that atmospheric particulate deposition is a major pathway for PAHs into *H. plumaeformae* WILS.

4.3. Fractionation of PAHs along the mountain slopes

It was reported that the concentrations of organochlorine compounds in mosses from Andean Mountains were temperature dependent (Grimalt et al., 2004), increasing with altitude; similar trends were also

observed in fishes from high mountain lakes in Europe (Vives et al., 2004). On the contrary, the total PAH concentrations in *H. plumaeformae* WILS from the northern slopes of Nanling Mountains show generally decreased with altitude (Fig. 5a), largely owing to the decrease of 4- and 5–6 ring PAH concentrations, whilst the 2–3 ring PAH concentrations showed no significant increase. In particular, a sharp decrease of total PAH concentration was observed at 900 (TH profile) and 850 m.a.s.l. (MS profile). An increase of total PAH concentration related to the increase of 2–3 ring PAH at 1400 m.a.s.l was found in both profiles (Fig. 5a).

The correlation between each PAH compound and altitude in TH profile was examined further. As shown

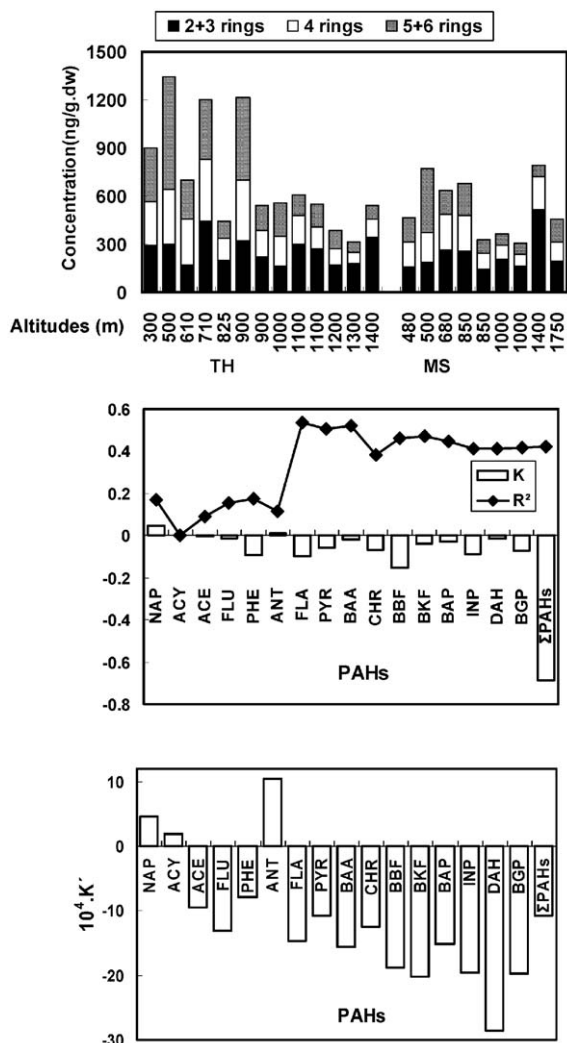


Fig. 5. The altitudinal profiles of PAH concentrations in mosses from Nanling (a); the correlation coefficients of individual PAH compounds (R^2) and slopes (K) with altitude (b); and their relative rates of decrease (c).

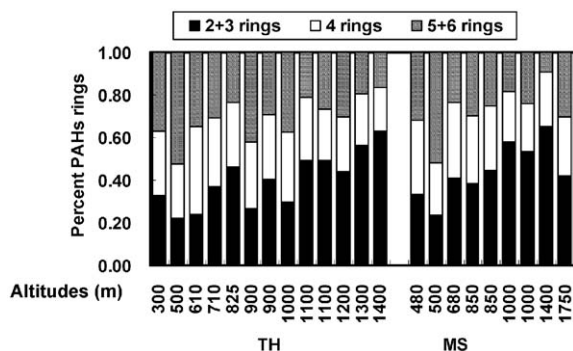


Fig. 6. Compositional fractionation of PAHs along two altitudinal profiles in the Nanling mountains.

in Fig. 5b, all PAHs after ACE (except ANT) displayed a negative regression slope (K), referring to a decreasing concentration with altitude. Higher correlation coefficients were observed for PAHs after FLA. In order to compare the relative extent of concentration decrease, the concentrations were normalized to the average concentration, and the relative slope (K') calculated as:

$$K'i = \frac{\Delta(C_i/\bar{C}_i)}{\Delta H}, \quad (3)$$

where C_i is the concentration of PAHs ($\text{ng g}^{-1} \text{dw}$), \bar{C}_i is the average concentration of each compound ($\text{ng g}^{-1} \text{dw}$), and ΔH is the difference between the altitudes (m) at various sampling sites. As shown in Fig. 5c, the absolute value of K' increased with molecular weight. In other words, heavier PAHs declined more rapidly with altitude. Fig. 6 summarizes the changing compositional patterns with the altitude. The altitudinal fractionation observed mimics the latitudinal fractionation of POPs, which has been shown in several recent studies (Wania and Mackay, 1993; 1996; Muir et al., 1996; Ockenden et al., 1998; Meijer et al., 2003; Jaward et al., 2004).

4.4. Pathways of atmospheric PAH transport and mechanisms of compositional fractionation

Nanling Mountains is a geographical division zone of two large watersheds in South China, i.e. the Pearl River (Zhujiang) watershed in the south, and the Yangtze River (Changjiang) watershed in the north. Both sides of the mountains are densely populated plains with severe atmospheric pollution problems, particularly on the high total suspended particulate concentrations in winter. As shown in Table 3, the compound ratios of BAP/BGP, BAP/CHR, BEP/BAP, and INP/BGP in the mosses were very close to the vehicular emission (pyrogenic) sources, while the above mentioned PHE/

Table 3
Selected PAHs ratios in mosses and atmospheric particles

	BAP/BGP	BAP/CHR	BEP ^b /BAP	INP/BGP
NL Moss	0.61	0.24	1.96	1.26
NL air	0.52	0.23		1.22
Gasoline car ^a	0.3–0.4	0.28–1.2	1.1–1.3	0.6–1.5
Diesel car ^a	0.46–0.81	0.17–0.36	2–2.5	1.30
Coal ^a	0.9–6.6	1.0–1.2	0.84–1.6	1.09
Oil refine ^a	0.65–1.7			
Wood ^a		0.93	0.44	

^aReference: Simcik et al. (1999).

^bBEP: Benzo-[e]pyrene.

ANT ratio of 12.3 indicates an input via long-range atmospheric transport (Gschwend and Hites, 1981).

PAHs are a group of compounds with a wide range of physicochemical properties, and they exist in the air both in vapor phase and particulate phase. For heavy PAHs, owing to the relatively low volatility and close associations with particles, once deposited from the air, they may be expected to cycle in the soil-water-sediment system, rather than “hoping” upward to a higher altitude under normal ambient temperatures.

Contrasting most POPs, such as organochlorine pesticides and polychlorinated biphenyls (PCBs), a large majority of PAHs in the air are pyrogenic with closely associated with particulates, especially black carbon by origin (e.g. Dachs et al., 1997), and they are still being continuously released into the environment. In winter when a lower atmospheric boundary layer is presented in the region, a near-ground high concentration of PAHs in the air may be expected (Li et al., 2004). The dense cold airflow (which is dry and strong in South China in winter) would also favor a near-ground transport of air pollutants. When the cold airflow turns upward along the mountain slopes, forest and topological scavenging of atmospheric particulates will occur, in which particulate-associated PAH would be removed first. In the meantime, cold condensation along the up-mountain profile may further enhance the removal of possible heavy PAHs in the gas phase to plants and soil surface from the air. Therefore, the distribution of PAHs may be controlled both by mechanical particle scavenging, and by temperature-dependent “cold condensation” along altitudinal profile in the mountains.

In the present study, a large majority of air particulates may be scavenged below 850–900 m.a.s.l., corresponding to the obvious total PAH concentrations gaps observed (Fig. 5a). For the more volatile 2–3 ring PAHs, an increase of PAH concentrations was found at 1400 m.a.s.l. (Fig. 5a), which may refer to the “focusing” altitude (Blais et al., 1998; Grimalt et al., 2004) for these light PAHs in the Nanling mountains (ca. 25°N with the

lowest daily temperature of –4°C, seasonal average temperature of 0°C at the 1400 m.a.s.l in winter).

Acknowledgements

This work was a contribution to the SETAC European Workshop on The Role of High Mountains in the Global Atmospheric Transport of POPs. The research was supported by the Ministry of Science & Technology of China (973:2002CB410803), NSFC (40202035), SKLOG (OGL-200204), and the Research Grants Council (RGC) of Hong Kong SAR Government (PolyU 5147/03E). GZ wishes to thank China Scholarship Council (CSC) for supporting his research in LU.

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