**Atmospheric
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Unravelling airborne polycyclic aromatic hydrocarbons (PAHs) in southern China using tree-rings of 100-yr old *Pinus Kwangtungensis*

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Abstract

Reliable perennial biomonitoring of airborne polycyclic aromatic hydrocarbons (PAHs) is urgently necessary to detect long-term impacts of anthropogenic emission, in response to industrial policies and combustion technology adoption. One hundred records of airborne PAHs were novelly demonstrated by analyzing the tree-rings of Kwangtung pine (*Pinus kwangtungensis*) formed from 1883 to 2007 at Naling Mountains of southern China. The total concentrations of PAHs ($\sum$PAHs) detected in the tree xylem did not progressively increase against the time. Temporal increase of high molecular-weight PAHs (HMW-PAHs) coincided well to the historical-socioeconomic status in China, suggesting HMW-PAHs in old trees growing at high mountains were more indicative of regionally historical changes in airborne PAHs compared with $\sum$PAHs. Compositional analysis indicated airborne PAHs absorbed and accumulated in tree tissues were pyrogenic origination. Principal component analysis revealed PAHs inputs were quite historically diversiform and unevenly distributed in the atmosphere of Nanling Mountains of southern China. Dendroanalysis of old trees grown at geographically sink locations could be a useful biomonitoring technique for unravelling historical changes in PAHs composition and intensity in the atmosphere, in relation to regional industrial development and fuel consumptions.

1 Introduction

Airborne polycyclic aromatic hydrocarbons (PAHs) are among the most widely spread organic contaminants globally. As being target pollutants for their carcinogenic, mutagenic and teratogenic effects on organisms (Perera, 1997), PAHs should be closely monitored their occurrence and intensity for the sake of human exposure risk and public health. However, conventional monitoring of PAHs by using high volume air samplers is expensive to be implemented for routine and long-term monitoring. In recent studies, biomonitoring methods have been proved to offer a low cost alternative for routine,

spatial and/or temporal monitoring of airborne PAHs, by using passive samplers including mosses, grasses, crops, and broad-leaved trees species sorbing PAHs from dry and wet deposition (Kaupp et al., 2000; Müller et al., 2001; Librando et al., 2002; Hwang et al., 2003; Lehndorff and Schwark, 2004; Liu et al., 2005b). However, the specific leaf properties of some plant species and their limited geographic distribution might restrict their utility and application in regional and/or even global monitoring and comparative studies on airborne PAHs. Conifer species with similar needle properties have thereby been identified as a reliable means of monitoring PAHs in the atmosphere, due to their wide distribution and their effective needles absorbing and retaining organic pollutants, such as, *Pinus sylvestris* (Holoubek et al., 2000), *Picea abies* (Weiss, 2000), *Pinus nigra* and *Pinus pinaster* (Piccardo et al., 2005). The needles of these species can be easily sampled to reveal current status (level) of atmospheric PAHs, but difficultly to detect historical changes in PAHs emission in the surrounding environment. A more reliably perennial biomonitoring method is urgently necessary to retrospect to the atmospheric PAHs, in response to industrial policies and combustion technology adoption. However, little research has been reported on assessing regionally historical changes in airborne PAHs due to the lacking of long-term atmospheric PAHs monitoring, particularly in developing countries. Recent studies have used in situ sampling of soil sediments (Liu et al., 2005a) and tree-ring bark pocket (Wang et al., 2004), to retrospectively reveal historical changes in PAHs in China.

After being emitted into the atmospheres from point sources, PAHs may be presented both in the vapor and particulate phases (Venkataraman and Frendlander, 1994). Atmosphere was a major pathway for the transportation and deposition of airborne PAHs (Bidleman, 1998). Particularly, the particle-associated high molecular-weight PAHs (e.g. more than 4 rings PAHs, HMW-PAHs) could undergo long-range atmospheric transport and exist in the environment for a long time after deposition (Blais et al., 1998; Sanusi et al., 1999). High mountains served both as condenser for vapor phase PAHs and as barrier/sink for particulate associated less volatile PAHs. Thus, some organic compounds like PAHs could actually increased in "condensed phase"

with elevation above sea level (Wania and Mackay, 1996) and deposed after long distance transportation. As well known, plants might take up organic chemicals either by aboveground tissues from the atmosphere (Sabljic et al., 1990) or by roots from the soil (Wang and Jones, 1994). For PAHs, roots uptake and translocation via xylem have been shown negligible (Paterson and Mackay, 1994; Kipopoulou et al., 1999). Stoma and lenticel of trees were pathways for gas-phase PAHs diffusing into the living cells of tree xylem and for particle-phase PAHs entrapping into growth rings (Meredith and Hites, 1987). Airborne PAHs have been proven to be the primary source to be accumulated in vegetation (Simonich and Hites, 1994). Additionally, high content of organic matters (e.g. turpentine, colophony) in xylem of conifer species make their growth rings have great capability of accumulating PAHs when the PAHs were absorbed from the atmosphere and of preserving them over time. Mechanism of airborne PAHs accumulation in tree trunk tissue was well documented by Wang et al. (2004). Therefore, the analysis of PAHs accumulated in tissues of plants naturally grown at high mountains may provide reliable information on regional emission of PAHs, in couple with regional metrological information. We here summarized the processes of airborne PAHs from point sources to plant tissues in Fig. 1 after Lehndorff and Schwark (2004). In the present study, we analyzed PAHs in the tree-rings of Kwangtung pine (*Pinus kwangtungensis*) sampled from Naling Mountains in southern China: (1) to examine the temporal distribution of PAHs in the xylem of *Pinus kwangtungensis* which was formed over the past 100 yr; (2) to elucidate potential input sources of PAHs in the tree-rings. The expected results will demonstrate the potential of tree-rings analysis to unravel regionally historical changes in airborne PAHs at a regional scale.

2   Materials and methods

2.1   Site description

Nanling Mountain range, 2100 m a.s.l., is an important boundary in south China be-
tween the temperate continent in the north and subtropical regions in the southeast
coast (Lee et al., 2005). It covers more than 1000 km from west to east across Guangxi-
Guangdong-Hunan-Jiangxi provincial border. Annual ambient air temperature in Nan-
ling Mountain range is between –6.9 and 39.1 °C, with an annual average temperature
and rainfall of 17.5–20.3 °C and 569–2200 mm, respectively (Liu et al., 2005b). Re-
searchers found that Naling Mountain was a key recipient for long-range transport of
air pollutants from northern China to the southern coastal region, particularly in the
winter (Chan et al., 2002; Wang et al., 2003). PAHs contents in mosses from Nanling
Mountain revealed that the distribution patterns of PAHs in the moss samples matched
well with those in bulk atmosphere deposition in the adjacent source areas (Liu et al.,
2005b).

At the southern side of the mountains lies the Pearl River Delta of Guangdong
province. Rapid industrialization and urbanization has put the Delta one of the severely
polluted regions since the 1980s when China's opening and reforming policy was
adopted. High levels of atmospheric PAHs have been frequently documented in the
Delta in recent years (Guo et al., 2003; Mai et al., 2003; Tang et al., 2006; Wang et al.,
2006; Ren et al., 2007; Li et al., 2009).

2.2   Tree collection and tree-ring sample preparation

Kwangtung pine, a unique species in China, only grows on the mountains ranging from
800–1600 m above sea level and sunny crags ranging from 1000–1800 m above sea
level in Nanling Mountain range. At the beginning of 2008, forests at the core zone of
Nanling Mountains were seriously destroyed by the unexpected Ice-snow Disaster in
south China, which destructively damaged numerous old trees in the mountains. By

taking this opportunity, we selected a Kwangtung pine open-growing at a crag 1400 m above sea level and sampled a disc (about 20 cm in thickness) at 1.3 m height above ground and brought back to laboratory for processing.

Upon returning to the laboratory, the disc was immediately mounted and polished to reveal the annual growth rings, using a machine tool fitted up with a clean and sharp graver. The ring-width series of the tree-ring were dated from the outside to the piths with Windendro™ system (V 6.1D, Canada). After dating, tree-ring tissues representing 10-yr growth intervals (except for the first and the last sample, representing 15-yr and 2-yr intervals, respectively) were carefully sliced from the heart-wood to the sap-wood with an electric clean micro-chisel, in order to gain enough mass for PAHs analysis. A total of 23 chipping samples were sliced from the disc, which represented more than 100 yr (1883–2007) history. The chipping samples were freeze-dried for 36 h and finely ground to pass a 0.2 mm screen.

2.3 PAHs extraction, purification and analysis

All the extraction, purification and analysis were carried out according to published methods (Liu et al., 2005b) in the National Key Laboratory of Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The details of extraction, purification and analysis were described below.

Extraction of PAHs from the tree-ring samples was performed with a Dionex ASE 300 (Dionex Co., USA). About 10 g of tree-ring powder (dry weight, dw) was mixed with 5 g of anhydrous sodium sulfate (barked for 4 h at 600 °C in oven before use) and packed in a 33 ml stainless extracting cell. The samples were spiked with a known aliquot of naphthalene-d8, acenaphthane-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 as analyte surrogates. The extraction used Dichloromethane (DCM) and acetone (1:1, v/v) as solvent under the conditions of 1500 psi and 100 °C. 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. The tree-ring 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 evaporated and solvent-exchanged to 1 ml of hexane. A gel permeation chromatography (GPC) column (10 mm i.d., packed with 10 g of S-X3Biobeads, dipped by dichloromethane in advance, Accustandard Co., USA) was used to eliminate lipids.

The GPC column was eluted with 80 ml n-hexane: DCM (1:1 v/v) 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 to a final volume of 200 µl under a gentle stream of nitrogen. For each sample, eight microliters of 50 µg ml^{-1} hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) was added as internal standard prior to GC-MSD analysis.

PAHs compounds were separated on a 30 m × 0.25 mm i.d. HP-5 capillary column (film thickness 0.25 µm) and quantified 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 °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 mode. Mass range m/z 50–500 was used for quantitative determinations. Data acquisition and processing was controlled by HP Chemstation software.

For quality control, the analysis also include a procedural blank (solvent with a clean GF/F filter), a spiked blank (PAH standards spiked into solvent with a clean GF/F filter), a sample duplicate, and a SRM 1649A reference sample were processed. The procedural blank samples contained no detectable target compounds. The relative percent difference for individual PAHs identified in paired duplicate samples ($n = 2$) was all <13 %. Recoveries of all the PAHs in the SMR 1649A sample were between 59 and

117 % of the certified values. The instrument detect limit (IDL) for PAHs was 0.03–0.13 ng g^{-1} on the GC-MSD, and the method detect limit (MDL) was calculated to be in the range of 0.6–2.6 ng g^{-1} dw.

2.4 Data analysis

The following parameters were calculated: (1) the concentrations of the detected PAHs ($\sum$PAHs); (2) the percentage of different benzene ringed individual PAHs to $\sum$PAHs; (3) the ratios of low molecular-weight PAHs (2–3 rings PAHs, LMW-PAHs) to high molecular-weight PAHs (4–7 rings, HMW-PAHs); 4) the ratios of the sum of major combustion specific PAHs ($\sum$COMB) to $\sum$PAHs in the tree-ring samples (combustion specific PAHs include FL, Pyr, BaA, Chr, BbF, BkF, and BaP). The PAH compositional ratios used in the source assessment included PA/Ant and FL/Pyr. Finally, principal component analysis (PCA) was used to explore the similarities or differences among the samples with complex compositional information and facilitate the assessment of input sources. PCA with varimax rotation was performed using the software package SPSS (SPSS 11.5). Only the principal components with eigenvalues >1.0 were retained, and only the principal component loadings with absolute values greater than 0.10 were considered.

3 Results

3.1 Historical patterns of PAHs in the tree-rings

Seventeen PAHs were detected in the tree-ring samples: Naphthalene (Nap), Acenaphthylene (Acpy), Aacenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenz[a,h]anthracene (DBA), Indeno[1,2,3-cd]-pyrene (IND), Benzo[g,h,i]-perylene (BghiP), and Dibenzo(ghi,pqr)perylene (PER). The $\sum$PAHs and HMW-PAHs

concentrations in the dated tree-rings of Kwangtung pine were plotted against the time in Fig. 2. The levels of ∑PAHs did not progressively increase from the oldest tree-ring samples to the youngest ones, with the highest concentrations appeared in the earliest tree-rings formed in the period of 1883–1895 (591.83 ng g^{-1} dw) and the lowest appeared in the period of 1946–1950 (107.51 ng g^{-1} dw). The levels of ∑PAHs fluctuated at 200 and 400 ng g^{-1} dw in the tree-rings formed in the period of 1900–1980 and 1980–2007, respectively, and temporally increased from 121.52 ng g^{-1} dw to the maximum of 436.02 ng g^{-1} dw in the xylem formed from 1966 to the recent years (Fig. 2a).

Unlike ∑PAHs, temporal patterns of HMW-PAHs in the tree-rings progressively increased from the piths to the sap-woody of Kwangtung pine, with two peaks over the studied time scale. The total concentrations of HMW-PAHs patterned with a slight fluctuation of less than 10.0 ng g^{-1} dw in the tree-rings before the 1950s, then notably increased with a first peak in the xylem samples of 1951–1955, and finally dramatically peaked in those of 1991–1995 (Fig. 1b).

Temporal percentages of LMW-PAHs and HMW-PAHs to ∑PAHs revealed that LMW-PAHs were the dominant component of ∑PAHs (e.g. accounted for more than 80 % of ∑PAHs) in the tree xylems over the studied time scale expect for the period of 1951–1955. On the contrary, the historical changes in the percentages of HMW-PAHs (e.g. from about 10 % before the 1950s to more than 50 % of ∑PAHS after the 1980s) verified the progressive contributions of HME-PAHs to ∑PAHs in the tree xylems (Fig. 1c).

3.2 Temporal changes in PAHs ratios

Values of LMW-PAHs/HMW-PAHs, ∑COMB/∑PAHs, PA/Ant and FL/Pyr ratios in the xylem samples formed at different periods were plotted in Fig. 3. Ratios of LMW-PAHs/HMW-PAHs in the samples formed before the 1950s were much higher (most were above 10.0) than those after the 1950s (most were below 5.0) except for the period of 1966–1970 (Fig. 3a). On the contrary, values of ∑COMB/∑PAHs increased synchronously with the decreasing patterns of LMW-PAHs/HMW-PAHs in the tree-rings against the time, with values of below 0.1 before the 1950s and of above 0.2 after the

1950s (Fig. 3b). Through the studied time scale, values of PA/Ant were most less than 10.0 (Fig. 3c), while values of FL/Pyr were above 1.0 (Fig. 3d).

3.3 Principal component analysis

According to the temporal variations of ∑PAHs in the tree-ring samples, we divided the tree-rings into three periods (before the 1950s, from 1950 to 1980, and after the 1980s) to carried PCA. In the first period, two principal components (PC1 and PC2) were identified and accounted for 88.2 %, 10.2 %, respectively, of the total variance. PC1 had high loading for Ant, Flu, PA, FL, Pyr, Chr. PC2 was dominated by Nap, Pyr, BaA, Chr, BkF, FL (Fig. 4a). In the second period, three components (PC1, PC2 and PC3) were obtained and explained 63.2 %, 20.5 %, 9.4 %, respectively, of the variance of data. PC1 were characterized by Nap, Pyr, FL, PER, Chr and BaA. PC2 had high loading for BaP, DBA, BkF, BaA. PC3 was predominately weighted in Ant, Acpy, and Acp (Fig. 4b). The last period were identified with four components. PC1 explaining 37.1 % of the variance was highly weighted in Ant, Acpy, Acp and Flu. PC2 was responsible for 32.8 % of the total variance and dominated by Pyr, IND, PER, Pyr, and BaP. PC3 explained 15.5 % of the variance with high loading for FL, Chr, DBA. PC4 explaining 9.4 % of total variance had its highest loadings on PA, BbF, NaP and BkF (Fig. 4c).

4 Discussion

4.1 Historical changes in airborne PAHs reflected by tree-ring analysis

Environmental PAHs were most released from anthropogenic sources such as combustion of fossil fuels, domestic heating, waste incineration, industrial processes and, importantly, motor vehicle exhaust (Luo et al., 2004). PAHs in plant tissues could be the results of both origin sources and environmental processes (Wang et al., 2004).

In the present study, the temporal changes in $\sum$PAH indicating un-expectantly highest concentrations in the earliest tree-rings of Kwangtung pine did not match those with historically progressive increase revealed by analyzing sedimentary core from the Pearl River Estuary of south China (Liu et al., 2005a), nor tree-rings of Longpetiole beech (*Fagus longipetioleta*) from southeastern China (Wang et al., 2004). The absolute domination of LMW-PAHs to $\sum$PAHs was responsible to the highest levels of $\sum$PAHs in the earliest xylems of Kwangtung pine (Fig. 1a, c). This might result from: (1) the characters of individual PAHs. LMW-PAHs are high volatile compounds remaining as gases in media, while HMW-PAHs are low volatile compounds agglomerated into or adsorbed onto particles (Mader and Pankow, 2000). The rapider diffusion of LMW-PAHs that traveling easily in the air than HMW-PAHs thus causing more LMW-PAHs reached the sites and trapped in the tree-rings. Simultaneity, we here could also speculate that in the older days the pollution sources were relatively farer than the present days; (2) the specific structural properties of tree-rings. Tree-rings can be divided into heartwood and sapwood. Heartwood formation occurred by the death of parenchyma cells in a zone of transition between sapwood and heartwood and consisted entirely of dead cells, while sapwood kept zoetic. The highest concentrations of $\sum$PAHs were mainly ascribed to the high contents of LMW-PAHs (accounted for over 90 %, Fig. 2c) tightly wrapped by the dead cells in heartwood and restricted their volatile loss from the growth rings. In the sapwood, the 2–3 rings PAHs can volatize from the tree-rings, as being indicated by the lower percentages of those compounds in the tree-ring far away from the heartwood (Fig. 2c).

Generally, LMW-PAHs were chiefly originated from low- or moderate-temperature combustion process (such as biomass burning and domestic coal burning) while HMW-PAHs were mainly from the high-temperature combustion process (such as vehicular exhaust and industrial coal combustion) (Mai et al., 2003). The temporal increases of the concentrations and proportion of HMW-PAHs in the tree-rings formed after the 1950s (Fig. 2b, c) matched well the socioeconomic status of south China. The period of 1951–1955 was an apparently important threshold since which the HMW-PAHs

accounted more and more in the ∑PAHs except for a sharp decrease during 1966–1975. These fluctuations coincided with the historical events happened in China. Since the foundation of People's Republic of China in 1949, industrial productions were gradually recovered and anthropogenic emission progressively increased, which contributed to the first HMW-PAHs peak in the tree-rings within the same periods. The decline of HMW-PAHs in tree-rings formed in 1966–1975 would be mostly likely due to the dramatic halt of industrial production during the so-called "Cultural Revolution" period between 1966 and 1976, during which Chinese industrial development almost stagnated. Since the late 1970s when Open-door and Economic Reform policy were implemented, China has undergone a rapid transition from agriculture-based economy to industry- and technology-based economy, with annual energy consumption increase by about 5.3 % over the period 1980–1991 (Byrne et al., 1996). The rapid industrialization and urbanization caused progressively atmospheric emission of PAHs in China (Xu et al., 2006; Wang et al., 2007; Zhang et al., 2007) could be reflected by the synchronously increasing concentrations of HMW-PAHs in the tree-rings. Although the absorption and accumulation of PAHs by vegetation depended on various factors such as tree species, environmental variables as well as the atmospheric PAHs concentrations (Simonich and Hites, 1994; Barber et al., 2002), our results clearly suggested that HMW-PAHs compared with ∑PAHs in issues of old trees growing at high mountain were much more indicative of the regionally historical changes of airborne PAHs.

4.2 Evaluation of tree-ring PAHs sources (petrogenic vs. pyrogeni)

Pyrogenic PAHs are combustion of organic matter, anthropogenic industrial activity, or natural fire, while petrogenic PAHs are mainly derived from crude oil and its refined products (Barker et al., 1991). The ratios of LMW-PAHs to HMW-PAHs have been used to attempt to discriminate the origins (petrogenic vs. pyrogenic) of PAHs (Tam et al., 2001; Yuan et al., 2001). A large proportion of HMW-PAHs was a typical characteristic of a combustion origin (pyrogenic), while the enrichment of LMW PAHs was common in petrogenic sources (Boehm and Farrington, 1984). In the tree-ring

samples, LMW-PAHs accounted for more than 80 % of ∑PAHs before the 1950s, while HMW-PAHs accounted for more than 50 % in the samples formed after the 1950s (in particular after the 1980s) (Fig. 2c). The lower values of LMW-PAHs/HMW-PAHs (lower than 1.0) in the tree-rings formed since the 1950s (Fig. 3a) implied significant pyrogenic PAHs had been absorbed and accumulated in the tree xylems. As observed in Figs. 2, 3a and b, the abrupt increase of HMW-PAHs loading after the 1950s indicated more pyrogenic PAHs were emitted into the atmosphere since then. High concentrations of HMW-PAHs in aerosol samples from the Pearl River Delta which were probably a prevailing pyrogenic source for PAHs (Mai et al., 2003) gave further support to this tree-ring analysis. Ratio of ∑COMB to ∑PAHs was another useful PAH source indicator (Prahl and Carpenter, 1983). The ∑COMB/∑PAHs values in the xylems formed before the 1950s were much lower than those after the 1950s (Fig. 3b), providing further evidence of higher absorptions of combustion-originated PAHs from the atmosphere by the tree since the 1950s.

A PA/Ant value of less than 10.0 and a FL/Pyr value of greater than 1.0 have been used to indicate pyrogenic origins of PAHs (Baumard et al., 1998). The plots shown in Fig. 3c and d provided more evidences of the predominance of combustion-originated PAHs that tree absorbed from the atmosphere after the 1950s. Our results were consistent with the findings about PAHs in the sedimentary core from the Pearl River Estuary, which were mainly of pyrogenic origin since the 1950s (Liu et al., 2005a).

4.3 Source apportionment by PCA

Numbers of principal components revealed by PCA increased with China's socioeconomic development (2, 3, 4 components in the period before the 1950s, 1950–1980, after the 1980s, respectively), implying the sources of airborne PAHs were progressively complicated. In the period before the foundation of People's Republic of China (before the 1950s), the dominance of Ant, Flu, PA, FL, Pyr, Chr was identified in PC1. According to Fang et al. (2004), high loading on Ant, Flu, Pyr and PA were the source fingerprints of wood combustion. Therefore, wood combustion-related operations, e.g.

home cooking burning wood might be associated with this factor. Nap was marker of in-completed combustion-related emission (Simsick et al., 1999). Ant, Pyr, BaA, Chr, BkF, FL were the typical markers of coal burning (Randolph and Joel, 2003). Thus, PC2 with high loading on those PAHs was likely related to in-completed coal combustion. Wood burning and coal combustion might be the main sources of the airborne PAHs accumulating in the tree tissues of this period.

During the period from PR China's foundation to 1980, three possible contributors of PAHs were revealed in the xylems by PCA analysis. The first one which had high weight on Nap, Pyr, FL, PER, Chr and BaA could responsible for coal combustion (Park et al., 2002). The second one was dominated by high BaP, DBA, BkF, BaA and moderate Chr, FL, BbF. Chr was dominance of diesel emission (Bourotte et al., 2005), BbF, BkF, DBA were gasoline emission (Esen et al., 2008), while BaA was a tracer for natural gas. Therefore, vehicular-related transportation was likely responsible for the contributor. The third component with high loading on PA, Acpy, Ant and Acp was possibly contributed from wood combustion.

Since China's Open-up and Reform policy (after the 1980s), the process of industrialization and urbanization has been accelerated coupled with lasting increase of energy consumption nationally (Xu et al., 2006). Potential contributors to PAHs in the tree-rings were more diversiform identified by PCA. The first potential contributor was highly weighted on 3–4 rings PAHs (Acp, Acpy, Ant, Flu and BaA). According to Bourotte et al. (2005), the presence of 3–4 rings PAHs was indicative of the dominance of diesel emission. Diesel-related emission was responsible for the first resource. The second potential resource with high loading on Pyr, IND, PER, BaP, BaA and DBA could trace to smelting and power plants. As identified by Fang et al. (2004), high Pyr, PER, BaP, IND and DBA were likely related to exhaust emissions from "stationary" sources. BaP, BaA and PER were found derive in large amount for the products of steel (Kulkarni and Venkataraman, 2000). DBA was related to thermal power plant which used coal as fuel (Fang et al., 2004). The deducing coincided well with the status with the extensive locations of smelteries and the increasing expands of thermal power plants during the last

decades in Guangdong province. The third component dominated by FL, Chr, DBA, BaP and Pyr could be considered as coal-related combustion emissions as identified by Esen et al. (2008). The recent status that industrial coal would be the dominant energy consumption in China (Xu et al., 2006) gave further interpretation of the result. The last factor highly weighted by PA, BbF, BkF, PER, IND, and Acpy could be a representative of traffic-related sources. BkF and Acpy could responsible for diesel combustion because elevated levels of BkF and Acpy were indicative of diesel vehicles (Randolph and Joel, 2003). BbF was an indicator of gasoline emissions (Mai et al., 2003), BbF, BbK, IND were vehicular transportation (Esen et al., 2008). Therefore, vehicle powered by gasoline and diesel was the contributor to the airborne PAHs. The result was consistent to the sharp increase of vehicle number (710 000 to 9 490 000) from the mid 1980s in China (Liu et al., 2005a).

5 Conclusions

More than one hundred records of airborne PAHs novelly were demonstrated by analyzing the tree-rings of *Pinus kwangtungensis* at Naling Mountains in southern China. The total concentrations of PAHs ($\sum$PAHs) detected in the tree xylem did not progressively increase against the time. Temporal increase of high molecular-weight PAHs (HMW-PAHs) coincided well to the historical-socioeconomic status in China, suggesting HMW-PAHs in old trees growing at high mountains were more indicative of regionally historical changes in airborne PAHs compared with $\sum$PAHs. Compositional analysis indicated airborne PAHs absorbed and accumulated in tree tissues were pyrogenic origination. Principal component analysis revealed PAHs inputs were quite historically diversiform and unevenly distributed in the atmosphere of Nanling Mountains of southern China. Dendroanalysis of old trees grown at geographically sink locations could be a useful biomonitoring technique for unravelling historical changes in PAHs composition and intensity in the atmosphere, in relation to regional industrial development and fuel consumptions.

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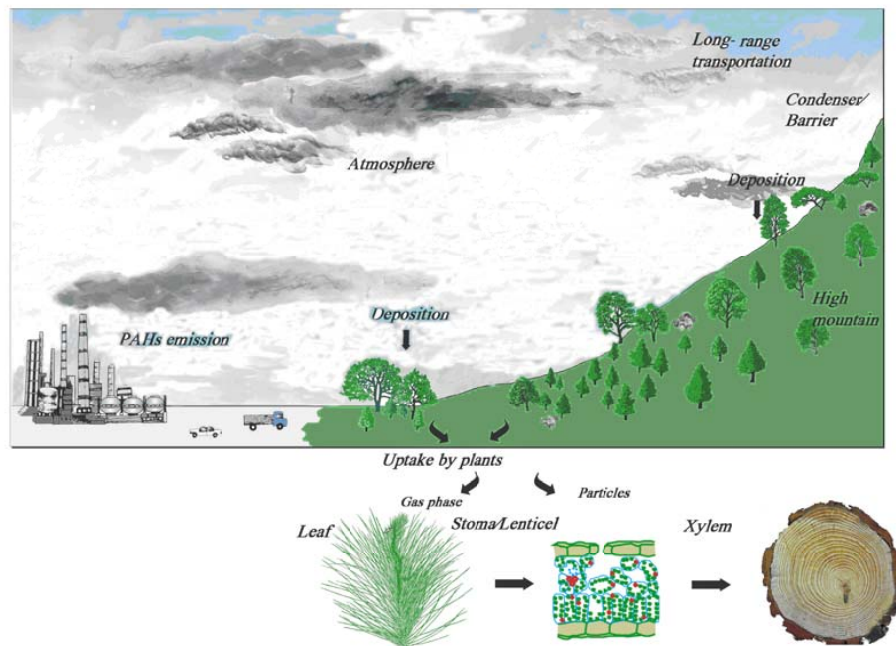
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Fig. 1. A summary of airborne PAHs from point sources to conifer plant tissues (after Lehndorff and Schwark, 2004).
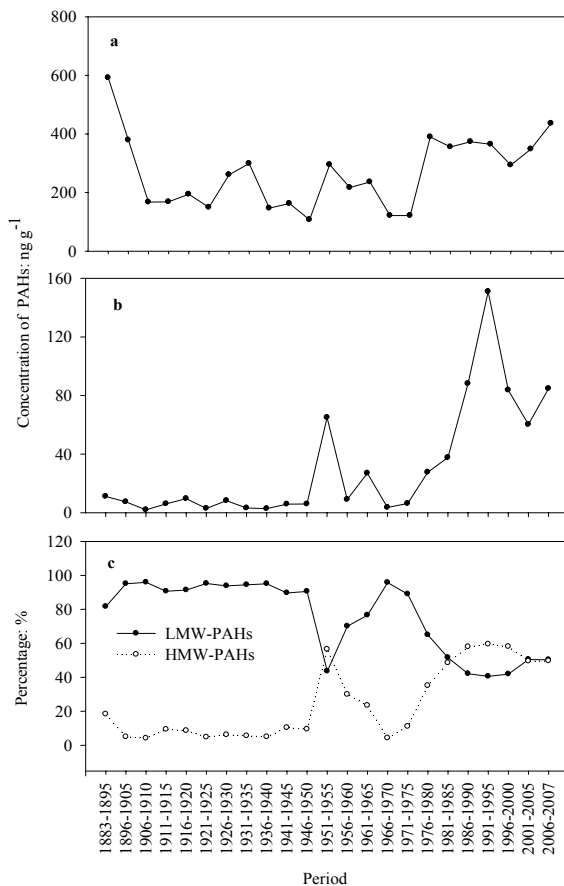
Fig. 2. Historical changes of the detected total PAHs **(a)**, HMW-PAHs **(b)** and the percentages of LMW-PAHs and HMW-PAHs to total PAHs **(c)** in the tree-ring samples of Kwangtunt pine formed from 1883 to 2007. HMW-PAHs: high molecular-weight PAHs (4–7 rings PAHs detected in this study); LMW-PAHs: low molecular-weight PAHs (2–3 rings PAHs detected in this study).
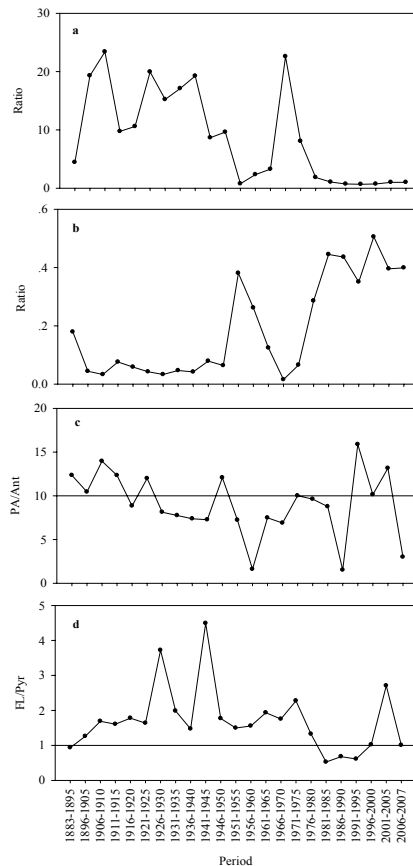
Fig. 3. Ratios of LMW-PAHs to HMW-PAHs **(a)**, ∑COMB to ∑PAHs **(b)**, PA to Ant **(c)** and FL to Pyr **(d)** in the tree-ring samples against the time. LMW-PAHs: low molecular-weight PAHs (2–3 rings PAHs detected in this study); HMW-PAHs: high molecular-weight PAHs (4–7 rings PAHs detected in this study); ∑COMB: the sum of major combustion specific PAHs including FL, Pyr, BaA, Chr, BbF, BkF, and BaP; ∑PAHs: the total PHAs detected in this study.
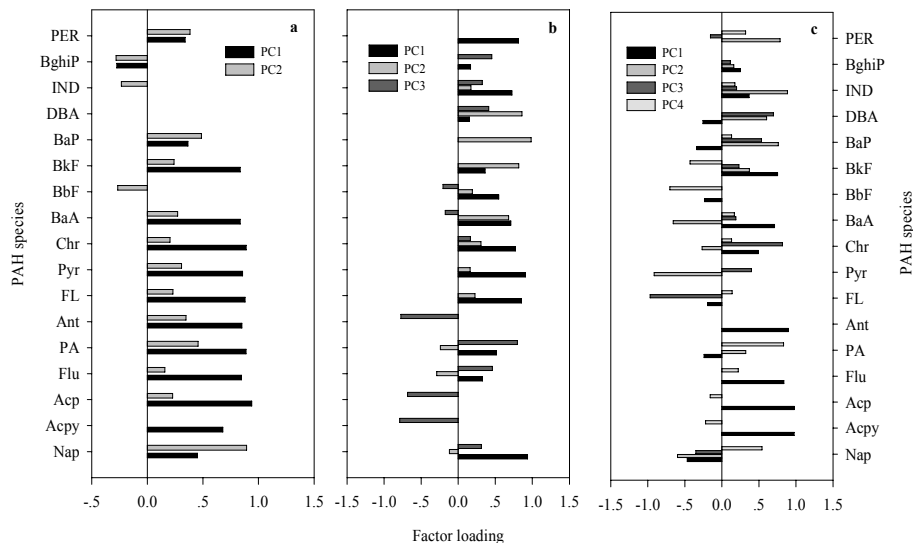
Fig. 4. Principal component analysis of tree-ring PAHs concentrations before the 1950s **(a)**, 1950–1980 **(b)**, and after the 1980s **(c)**. Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization; eigenvalue >1.00; absolute values of factor loading >0.10 list.