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PAPER

Analysis of polycyclic aromatic hydrocarbons in tree-rings of Masson pine (*Pinus massoniana* L.) from two industrial sites in the Pearl River Delta, south China

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Concentrations of polycyclic aromatic hydrocarbons (PAHs) were examined and potential sources of PAHs were identified from the dated tree-rings of Masson pine (*Pinus massoniana* L.) near two industrial sites (Danshuikeng, DSK and Xiqiaoshan, XQS) in the Pearl River Delta of south China. Total concentrations of PAHs ($\sum$PAHs) were revealed with similar patterns of temporal trends in the tree-rings at both sites, suggesting tree-rings recorded the historical variation in atmospheric PAHs. The differences of individual PAHs and of $\sum$PAHs detected in the tree-rings between the two sites reflected the historical differences of airborne PAHs. Regional changes in industrial activities might contribute to the site-specific and period-specific patterns of the tree-ring PAHs. The diagnostic PAH ratios of Ant/(Ant + PA), FL/(FL + Pyr), and BaA/(BaA + Chr)) revealed that PAHs in the tree-rings at both sites mainly stemmed from the combustion process (pyrogenic sources). Principal component analysis further confirmed that wood burning, coal combustion, diesel, and gasoline-powered vehicular emissions were the dominant contributors of PAHs sources at DSK, while diesel combustion, gasoline and natural gas combustion, and incomplete coal combustion were responsible for the main origins of PAHs at XQS. Tree-ring analysis of PAHs was indicative of PAHs from a mixture of sources of combustion, thus minimizing the bias of short-term active air sampling.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), composed of two or more fused benzene rings, are ubiquitously environmental pollutants. Multiply anthropogenic emissions of PAHs into the atmosphere were much more important than the natural sources.[1] Low-molecular weight PAHs (≤ 3 rings, LMW-PAHs) usually occurred in the atmosphere as a vapour phase, whereas high-molecular weight PAHs (≥ 5 rings, HMW-PAHs) were bound to particles, while intermediate molecular weight PAHs (4 rings, IMW-PAHs) were partitioned between vapour and particulate state depending on the atmospheric conditions.[2] Urban environments have been revealed with much higher concentrations of atmospheric PAHs than rural regions.[3] Generally, PAHs in both urban and rural atmospheres were associated with fine particles and then deposited.[4,5] The deposition of PAHs from the atmosphere controlled the concentrations of most PAHs in plants.[6]

Due to their carcinogenicity and mutagenicity, 16 PAHs were classed as priority pollutants.[7] Despite great progress in improving air quality in the past decades, atmospheric PAHs

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Environmental impact

This paper addresses the potential usage of tree-rings from Masson pine to retrieve the history of airborne PAHs over the past 50 years, to distinguish the possible sources of PAHs, and to elucidate the efficiency of Masson pine as a biomonitor for the emission of PAHs. Hence, the technique involved in this research could minimize the bias of short-term active air sampling of PAHs. In addition, results in this study are important for guiding refinements in environmental legislation or steering responsible industry management practices and are expected to be helpful in optimising regional industrial policies and combustion technology adoption.
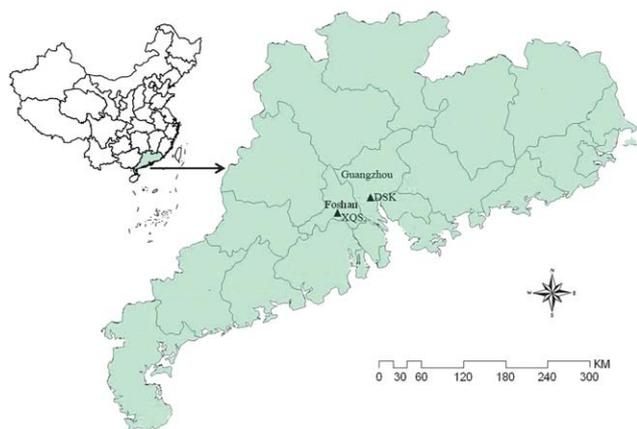
still pose a considerable threat to human health across the globe. Consequently, the monitoring of PAHs in the atmosphere is of great international importance for guiding refinements in environmental legislation or steering responsible industry management practices and consumer behavior. Biomonitoring PAHs using different plants, such as lichens,[8] mosses,[9,10] maize,[11] deciduous tree species,[12–17] conifer,[18–22] etc. offered practicable passive samplers with low cost as an alternative to conventional monitoring using high volume air samplers. Compared with the broadleaved trees, conifer species have been more frequently identified as a reliable means of monitoring organic pollutants in the atmosphere due to their wide distribution and their special properties of needles (e.g. large leaf surface, enriched epicuticular and intracuticular waxes) to effectively absorb and retain organic pollutants.[23] However, in most cases these plants could only be sampled to reveal current status (levels) of airborne PAHs. Detection of historically accumulative PAHs from multiple industries using the same type conifer species were less reported. Long-term atmospheric PAHs monitoring data, which was urgently necessary for regional retrospective detection of PAHs, was not easily available in many areas.

In this study, we analyzed 16 EPA priority PAHs in the tree-rings of Masson pine (Pinus massoniana L.) sampled near two industries in the Pearl River Delta of south China: 1) to examine the time trend of PAHs in the tree-rings formed over the past 50 years to retrieve the history of airborne PAHs; 2) to distinguish the potential sources of PAHs detected in the xylem using selected PAH ratios and principal component analysis (PCA); and 3) to elucidate the potential of tree-rings of Masson pine as a biomonitor for different point emissions of PAHs, thus minimizing the bias of short-term active air sampling.

2. Materials and methods

2.1. Site description

Masson pine trees were sampled from Danshuikeng Forest Park (DSK) in Huangpu district of Guangzhou and Xiqiaoshan Forest Park (XQS) in Nanhai district of Foshan, respectively (Fig. 1). Huangpu district has been a dominating industrial center in Guangzhou since the 1960s. Up to now, high densities of petroleum refineries, coal-fuelled power plants and auto manufacture have spread through this district. The total amount of car manufacture, crude-oil refining and power generation were more than 30 million, 10 million tons, and 70 billion kilowatt-hours, respectively, in 2008.[24] Gas and particulate pollutants released from industries have posed a serious threat to local vegetation. For instance, a large-scale decline of Masson pines was observed near industrial sites in recent years. Though the causes for the decline in number of pines have not clearly been understood, pine needles collected from DSK have shown fairly high heavy metal concentrations compared to those from a remote rural site.[25] In Nanhai district, ceramic manufacture has flourished since the late 1990s and Nanhai has become one of the largest ceramic centers in China.[26] A high density of industries with more than 90 ceramic factories and 300 burning kilns were estimated within 80 km^2 of this region.[27] These industries released lasting-increasing amounts of pollutants. Damages on vegetation close to ceramic manufacture[28] and decreased tree-ring growth of Masson pine at XQS were confirmed.[29]

2.2. Tree collection and tree-ring sample preparation

At each forest park, one open-growing Masson pine tree without visible injury, of similar size (around 40 cm in diameter at breast height), similar age (about 50 years old), and similar exposure to light was selected and cut down. A disc (about 20 cm in thickness) at breast height was carefully sampled with saw by manpower from the tree stem and brought back to the laboratory in a paper bag for further processing.

Upon returning to the laboratory, the disc was immediately mounted and polished (2–3 cm depth from the surface of the disc) to minimize external contamination and to reveal annual growth rings using a machine tool fitted with a clean and sharp graver. The tree-rings were then dated from the sapwood to heartwood by Windendro™ system (V 6.1D, Canada). After dating, tree-ring tissues representing 5 year growth intervals were carefully sliced from sapwood to heartwood with an electric clean micro-chisel, in order to gain enough mass of xylem for PAHs analysis. A total of 12 chipping samples representing about 60 years (1946–2005) history at DSK and a total of 10 samples representing about 50 years (1956–2005) history at XQS were sliced from the disc, respectively. All 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[10] in the National Key Laboratory of Geochemistry, Guangzhou Institute of Geochemistry, CAS. The details of extraction, purification and analysis are described below.

A Dionex ASE 300 (Dionex Co., USA) was used for extraction of PAHs from the tree-ring samples. About 10 grams of tree-ring powder (dry weight, DW) was mixed with 5 g of

Fig. 1 Location of the sampling sites in the Pearl River Delta. Danshuikeng Forest Park (DSK) is near dense petrochemical industries and coal fuelled power plants in Guangzhou. Xiqiaoshan Forest Park (XQS) is close to several coal- and oil-fired ceramic manufacturers in Nanhai of Foshan.

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anhydrous sodium sulfate (barked for 4 h at 600 °C in oven before use) and packed in a 33 ml stainless steel 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 a mixture of dichloromethane (DCM) and acetone (1 : 1, v/v) as the solvent under the conditions of 1500 psi and 100 °C. The ASE was conducted for two cycles, each lasting 5 min heating time and 5 min static extraction time. Five grams of activated copper slices were 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-X3 Biobeads, 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 microlitres of 50 μg mL^{-1} hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) was added as an internal standard prior to GC-MSD analysis.

PAHs 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}. A 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. EPA 16 PAHs were selected as target compounds in the analysis.

For quality control, the analysis also include a procedural blank (solvent with a clean GF/F filter), a spiked blank (16 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 percentage difference for individual PAHs identified in paired duplicate samples (*n* = 2) were all < 13%. Recoveries of all the PAHs in the SRM 1649A sample were between 59 and 117% of the certified values. The instrument detect limit (IDL) for PAHs was 0.03–0.13 ng 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. Both IDL and MDL were estimated in a way typical for the determination of trace contaminants. The IDL was obtained with a GC-MSD system by seven successive injections of a standard with a level of 20 pg μL^{-1} for each PAH, and then the standard deviation and t-factor were used to calculate the IDL for each PAH. The MDL for each PAH was further calculated using IDL under the average dry weight of samples.

2.4. Data analysis

The percentage of different benzene ringed individual PAHs to total EPA 16 PAHs ($\sum$PAHs) and concentration ratios of various PAHs were calculated in this study. 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 0.1 were considered.

3. Results

3.1. Concentrations of PAHs in the tree-ring samples

Concentrations of individual PAH and $\sum$PAHs in the tree-rings formed at different periods from the two industrial sites are shown in Table 1. All the EPA 16 PAHs were detected in the tissue samples from DSK, while PAHs were mainly found with LMW-PAHs and IMW-PAHs in the tree-ring samples from XQS. The 5-ringed DBA and 6-ringed IND and BghiP were not detected across all the woody tissues at XQS.

Temporal changes in $\sum$PAHs in the tree-rings patterned similarly at the both sites, with decreasing trends from the older tree-rings to the younger ones. However, $\sum$PAHs showed relatively small fluctuation in the tissues formed since the 1980s at both sites (with about 300 and 100 ng kg^{-1} DW at DSK and XQS, respectively). In the tree-ring samples formed during the same periods, $\sum$PAHs at DSK were always revealed to be much higher than those at XQS.

3.2. Temporal changes in molecular distributions of PAHs

The temporally relative percentages of the detected PAHs were grouped into three portions (LMW-PAHs, IMW-PAHs and HMW-PAHs) and plotted against the periods, see Fig. 2. It can be seen that the temporal distributions of PAHs in the tree-rings had site-specific and period-specific variations. At DSK, the LMW-PAHs were the dominant components (*e.g.* accounted for more than 70% of $\sum$PAHs) in the xylem over the time scale except in the period of 1981–1985. Fractions of the other two portions of PAHs, although accounting for less than 30% of $\sum$PAHs, patterned with highly synchronous fluctuations in the tree-rings except the period of 1971–1975. At XQS, the fractions of LMW-PAHs in the tree-rings almost progressively increased from the older tree-rings to younger ones, with notably high percentage in the latest xylem. Unlike the fluctuating compositional patterns of HMW-PAHs at DSK, the factions of 5–6 rings PAHs in the tree-rings at XQS showed a decreasing trend from the heartwood (formed in the period before the mid-1970s) to the sapwood (formed recently). The threshold of the temporal changes for 4 rings PAHs appeared at 1976–1980, when the percentage peaked.

Table 1 Concentrations of PAHs in the tree-rings formed at different periods at the two different industrial sites (ng kg^{-1} DW). DSK, Danshuikeng; XQS, Xiqiaoshan

Site	Year	Nap	Acpy	Acp	Flu	PA	Ant	FL	Pyr	Chr	BaA	BbF	BkF	BaP	DBA	IND	BghiP	∑PAHs
DSK	1946–50	80.565	0.977	0.996	7.236	54.823	7.381	1.231	1.111	1.750	1.365	0.026	0.201	0.277	0.290	0.421	0.006	158.655
	1951–55	89.929	0.802	0.741	6.921	43.118	5.424	0.998	0.620	2.930	1.085	0.025	0.055	0.448	0.285	0.191	0.013	153.584
	1956–60	159.575	1.883	4.649	8.986	23.155	3.770	1.128	0.197	11.299	33.932	3.426	1.181	1.188	16.194	46.789	0.125	317.476
	1961–65	148.536	7.849	8.437	28.994	111.867	24.897	3.938	2.654	8.734	38.742	3.211	8.101	8.016	54.007	4.390	0.302	462.676
	1966–70	141.205	2.717	2.117	21.743	86.167	10.352	4.354	1.682	6.411	4.255	0.182	0.968	0.229	7.077	6.223	0.008	295.689
	1971–75	110.980	0.860	0.694	5.633	64.277	9.442	1.549	1.298	1.707	1.821	0.011	0.201	0.612	76.414	1.978	0.481	277.958
	1976–80	185.534	1.154	1.036	9.031	63.228	8.782	2.022	1.351	3.899	5.434	0.463	0.370	0.940	12.462	0.866	0.008	296.579
	1981–85	74.016	3.429	4.139	15.115	48.344	10.782	6.291	6.450	18.503	59.354	2.412	6.130	17.820	50.248	9.080	0.743	332.855
	1986–90	150.466	3.848	4.872	17.906	58.933	8.750	4.922	3.475	2.693	9.667	0.723	1.404	6.340	3.614	4.736	0.052	282.402
	1991–95	161.583	3.774	2.678	16.045	69.237	10.755	4.073	4.391	4.020	7.625	0.053	0.054	0.087	0.280	0.573	0.026	285.255
	1996–00	172.352	2.282	2.607	9.113	21.479	5.937	2.384	3.006	8.633	15.685	0.443	1.515	2.758	2.345	6.883	0.114	257.536
	2001–05	191.407	1.539	1.677	10.277	52.277	6.488	2.710	2.822	2.430	0.934	0.007	0.044	0.150	0.204	0.061	0.010	273.036
XQS	1956–60	24.348	3.282	4.671	18.457	28.303	3.056	1.342	2.104	10.325	5.544	11.534	42.589	< 0.02	< 0.02	< 0.02	< 0.001	155.554
	1961–65	17.810	2.837	3.090	11.359	16.737	2.752	1.980	2.182	3.936	4.705	21.315	11.100	< 0.02	< 0.02	< 0.02	< 0.001	99.803
	1966–70	14.884	3.695	2.890	15.359	23.675	2.562	13.051	1.640	1.982	3.612	11.742	7.915	< 0.02	< 0.02	< 0.02	< 0.001	103.006
	1971–75	17.124	3.366	2.070	14.116	19.228	2.687	18.488	3.480	1.153	1.410	24.614	8.236	< 0.02	< 0.02	< 0.02	< 0.001	115.971
	1976–80	6.485	0.996	1.460	8.750	17.590	2.772	2.650	0.378	6.594	5.401	6.123	0.990	0.530	< 0.02	< 0.02	< 0.001	60.719
	1981–85	14.355	1.752	1.008	13.356	17.841	2.294	0.480	0.703	4.706	5.603	4.794	2.950	0.475	< 0.02	< 0.02	< 0.001	70.318
	1986–90	18.087	2.035	1.531	21.908	24.999	3.321	0.946	0.838	3.516	9.307	7.193	2.799	1.056	< 0.02	< 0.02	< 0.001	97.535
	1991–95	19.027	1.889	1.421	26.646	27.744	4.520	0.984	1.054	1.304	1.392	0.690	0.374	9.378	< 0.02	< 0.02	< 0.001	96.422
	1996–00	22.862	2.409	1.978	23.175	26.207	3.116	1.355	1.889	1.334	4.281	5.222	5.384	8.459	< 0.02	< 0.02	< 0.001	107.670
	2001–05	14.449	2.831	2.334	19.921	27.198	3.726	2.071	1.860	5.031	1.124	4.866	4.794	6.159	< 0.02	< 0.02	< 0.001	96.363

3.3. Source identification (petrogenic *vs.* pyrogenic) of PAHs in the tree-rings

Isomeric ratios of Ant/(Ant + PA), FL/(FL + Pyr), and BaA/(BaA + Chr) in the tree-ring samples formed at different periods in this study are presented in Fig. 3. Through the studied periods, most values of Ant/(Ant + PA), FL/(FL + Pyr), and BaA/(BaA + Chr) in the xylem at both sites were above 0.10, 0.50, and 0.35, respectively. Diagnostic PAH ratios of PA/Ant against FL/Pyr in the tree-ring tissues of Mason pine from both sites are also shown in Fig. 4. It could be easily found that values of PA/Ant in all the tree-ring samples from the two sites were below 10.0 and values of FL/Pyr were larger than 1.0, the zone indicating the pyrogenic origination of PAHs.

### 3.4. Pyrogenic PAHs source apportionment by PCA

The PCA-determined factors accounted for 91.4% and 90.8% of the total data variance for the tree-ring PAHs at DSK and XQS, respectively. Varimax rotated factor analysis for tree-ring data from DSK showed 4 possible factors, indicating 4 different contributing sources for the tree-ring PAHs (Fig. 5). The first factor, which explained 29.3% of the total variance, had its highest loading on Ant, Flu, PA and Acpy. The second factor explained 24.2% of the total variance and had high loading on BbF, IND, BaA and Chr. Factor 3 was responsible for 21.1% of the total variance. This factor was predominately weighted in Pyr, FL and BaP. Factor 4 explained 16.7% of total variance with high loading on DBA and BghiP.

Three factors were identified from application of PCA to XQS tree-ring data (Fig. 5). Factor 1 explained 32.8% of the total variance, and was highly loaded on Pyr, Acp, BkF and Acpy. The second factor was responsible for 31.8% of the total variance. This factor was predominately weighted in Ant, BbF, BaA and BaP. The last factor (26.3% of total variance) had high loading values of FL, Nap and Chr.

4. Discussion

Environmental PAHs were mainly produced during incomplete combustion and pyrolysis of organic materials by industry, agriculture and traffic, or in diagenetic alteration processes of natural organic matter.[30] After being emitted into the atmosphere from point and/or region sources, PAHs could reach
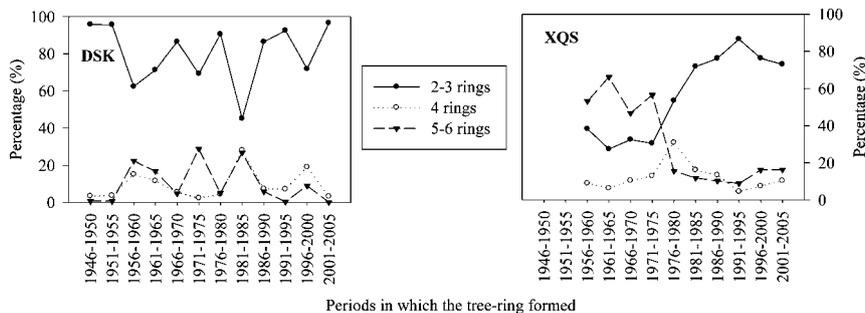
Fig. 2 Temporal molecular distributions of PAHs in the tree-rings of Masson pine from Danshuikeng (DSK) and Xiqiaoshan (XQS).
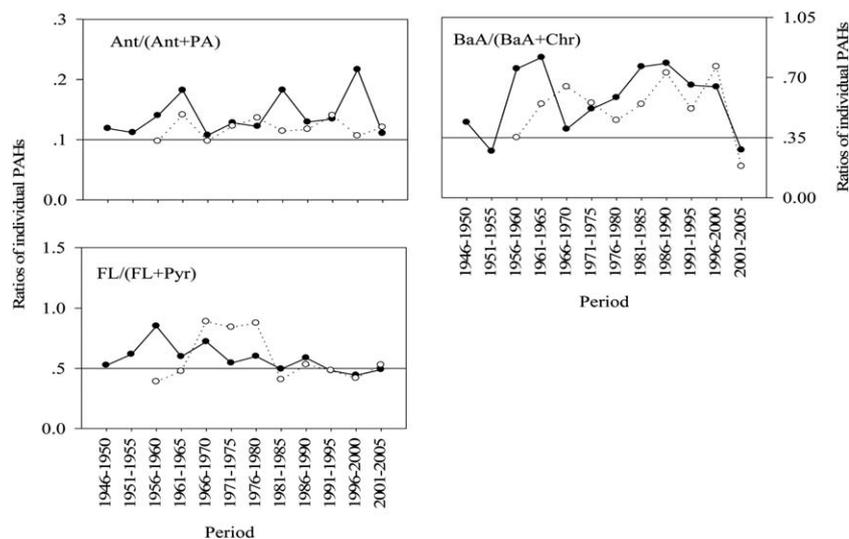
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Fig. 3 Values of isomeric ratios in the tree-ring samples at Danshuikeng (DSK, solid line) and Xiqiaoshan (XQS, dashed line).

vegetation as vapour and/or particulate state *via* dry and wet deposition. Plants could take up organic chemicals either by aboveground tissues from the atmosphere[31] or by roots from the soil.[32] For PAHs, tree roots uptake and translocation *via* xylem have been shown to be negligible.[33] Stoma and lenticel have been identified be the main pathways for gas-phase PAHs diffusing into the living cells of tree xylem and for particle-phase PAHs entrapping into the growth rings.[34] With a relatively high content of organic matter (*e.g.* turpentine, colophony) in the xylem, conifer species displayed great capability of accumulating PAHs absorbed from the atmosphere and of preserving them over time.[35] Thus, analysis of PAHs in tree-rings assigned to a distinct time in the past provided the potential to detect historical and ongoing processes of PAHs in the atmosphere where the tree grew. In the present study, the similar patterns of the temporal trends of $\sum$PAHs in the tree-rings at the both sites (Table 1) suggested that the xylem of Masson pine historically recorded the trends of airborne PAHs. At the same time, the differences of individual PAH and of $\sum$PAHs detected in the tree-rings revealed the differences of airborne PAHs levels between the two industrial environments. Concentrations of airborne PAHs at DSK might always be higher than those at XQS.

Comparison of the contribution of different PAHs (LMW-PAHs, IMW-PAHs and HMW-PAHs) to $\sum$PAHs through the

whole period from both sites could give further information on the historical changes in the profile of airborne PAHs. Generally, LMW-PAHs chiefly originated from low- or moderate-temperature combustion processes (such as biomass burning and domestic coal burning), while HMW-PAHs were mainly from high-temperature combustion processes (such as vehicular exhaust and industrial coal combustion).[36] The PAHs in plant tissues could be the results of both origin sources and environmental processes.[35] At the site of DSK, LMW-PAHs were revealed as the absolute domination species through the detected periods. HMW-PAHs were found to predominate $\sum$PAHs in the periods of 1971–1975 and 1981–1985. Thus, airborne PAHs at DSK might result from the main emission of PAHs from low- or moderate-temperature combustion processes. Simultaneously, LMW-PAHs diffusing more easily in the air than HMW-PAHs, thus causing more LMW-PAHs to reach the sites and become trapped in the tree rings, might be another cause leading to the domination of LMW-PAHs. Here we could also speculate that in the past, the pollution sources were relatively more scarce than those in the present day.

On the contrary, the progressively increasing fractions of LMW-PAHs displayed changes in the profiles of airborne PAHs at XQS since the 1980s when China implemented the economic open-up and reform policy. Notably, the contribution of
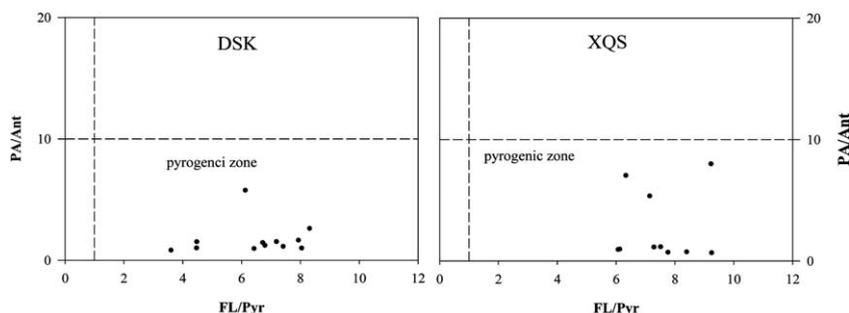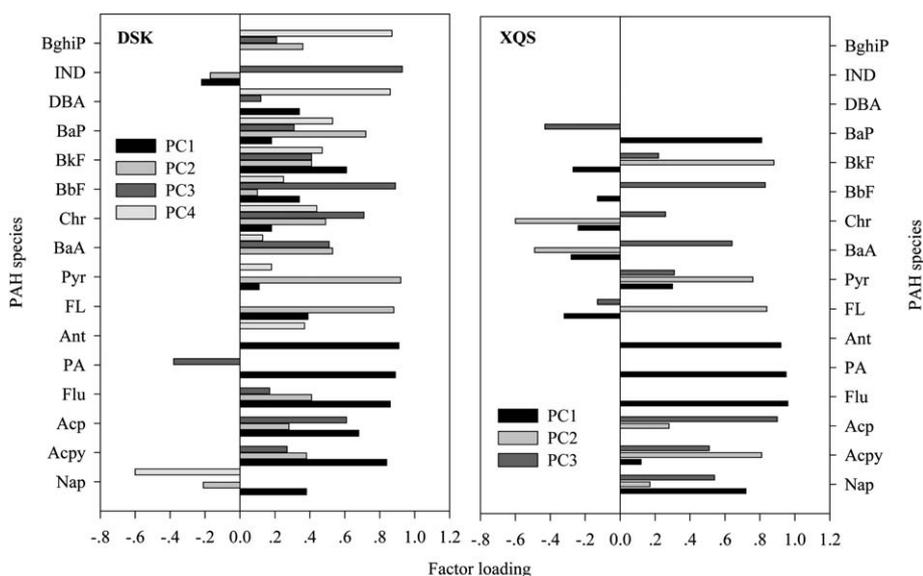

Fig. 4 Plots of PA/Ant ratios against FL/Pyr ratios in the tree-ring of Masson pine from Danshuikeng (DSK) and Xiqiaoshan (XQS).

Fig. 5 Principle component analysis of PAHs in the tree-rings of Masson pine from Danshuikeng (DSK) and Xiqiaoshan (XQS). Extraction method: principal component analysis; Rotation method: varimax with Kaiser normalization; Eigenvalue > 1.00; Factor loading with absolute value ≥ 0.1 listed.

HMW-PAHs to $\sum$PAHs at XQS, in spite of the gradually decreasing fractions of HMW-PAHs, was much higher (about 30%) than those at DSK – even 5- and 6-ringed PAHs were not detected in the tree-rings. The results might reflect the historical difference in the profile of airborne PAHs. The historical changes of energy consumption and composition gave support to explain these patterns. For example, during the period from 1990 to 2000 in Guangdong province, the total energy consumption doubled, with composition from coal consumption decreasing from 63.1% to 8.0% and with crude oil increasing from 7.0% to 53.7%.[37] The Pearl River Delta has undergone a rapid transition from a traditional agriculture-based economy to an increasingly industrial- and technological-based economy. A large number of industries as well as increasing traffic activity have been greatly expanded in the past few decades. These industrial activities might contribute to the temporal distribution patterns of PAHs in the tree-ring samples. Therefore, identification of the sources of PAHs in the tree-rings was highly desired.

PAH compositions of emissions have been revealed to be inherently variable with respect to combustion sources, and concentration ratios of various PAHs have been used for source identification.[16,38] In detail, a ratio of Ant/(Ant + PA) above 0.10 was indicative of a dominance of combustion, while a ratio below 0.10 was usually an indication of petroleum. For FL/(FL + Pyr), a ratio below 0.40 involved petroleum, between 0.40 and 0.50 were more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas ratios above 0.50 were characteristic of grass, wood or coal combustion. For BaA/(BaA + Chr) ratios, the values less than 0.20 implied petroleum origin, from 0.20 to 0.35, either petroleum or combustion, and above 0.35, combustion origin.[38] Additionally, a PA/Ant value of less than 10.0 and a FL/Pyr value of greater than 1.0 could indicate pyrogenic origins of PAHs.[39] Looking at the ratios in the present study (Fig. 3 and 4), we inferred that the PAHs detected in the tree-ring samples mainly stemmed from combustion process (pyrogenic sources). For instance,

judged by the temporal variation of FL/(FL + Pyr) ratios, coal combustion might contribute greatly to tree-ring PAHs at DSK before the 1990s and at XQS during 1990–2000, while liquid fossil fuel combustion might be the dominant source of PAHs at DSK after the 1990s. Based on the historical changes in BaA/(BaA + Chr) ratios, coal combustion and vehicle combustion might be the major sources of PAHs in the tree-rings at the two sites before and after the 2000s, respectively. The results coincided well with the findings in aerosol samples from the Pearl River Delta[36] and in sedimentary core from the Pearl River Estuary.[40] The recent status that industrial coal and oil shared the increasing percentage of the total energy consumption in China[41] also gave further interpretation of the results. Tree-ring analysis of Masson pine was indicative of PAHs from a mixture sources of combustion in the Pearl River Delta of south China.

In addition to the diagnostic ratios, PCA has also been employed to apportion pyrogenic PAHs sources in many studies.[4,5,36,42,43] In tree-ring samples at DSK, PCA analysis revealed 4 potential sources of environmental PAHs. The first factor had high loading on Ant, Flu, PA and Acpy (Fig. 5). High loading on Ant and Flu were the source fingerprints of wood combustion.[44] Therefore, wood combustion-related operations, *e.g.* home cooking burning wood, located within the proximity of DSK, might be associated with this factor. The second factor highly weighted in BbF, IND, BaA and Chr implied vehicular emission burning diesel might be designated as the main source of PAHs at DSK, because IND and BbF were revealed as the indicators of emissions from vehicular transportation[45] and the presence of Chr could indicate the dominance of diesel emissions.[5] In fact, the Pearl River Delta was one of the regions in China with a rapidly increasing number of automobiles since the 1980s. The third factor with high loading on Pyr, FL and BaP, the compounds of typical markers of coal combustion,[45,46] could represent a coal combustion-related source. The last factor with high loading on DBA and BghiP, the indicators of gasoline

emission,[45] suggested that gasoline-powered vehicular emission could be responsible for one of the contributors of PAHs source.

In the tree-ring samples at XQS, PCA analysis also presented three possible contributors of PAHs (Fig. 5). The first one which had high weight on BkF and Acpy could be responsible for diesel combustion because elevated levels of BkF and Acpy were indicative of diesel vehicles.[46] The second contributor had high loading on BbF, BaA and BaP. BbF was a product of high-temperature combustion, *e.g.* gasoline combustion,[36] and BaA has been considered as a tracer for natural gas.[47] Thus, this factor suggested that vehicular emissions burning gasoline and natural gas were the main sources of PAHs. The last potential contributor was predominately weighted on FL and Nap. FL was an indicator of coal combustion-related activities. Nap could be designated as incomplete combustion-related sources.[48] Therefore, this factor represented incomplete coal combustion. These contributors could be evidenced by local power plants burning coal, ceramic industries burning oil and vehicles burning diesel, gasoline and natural gas.

5. Conclusions

Concentrations, molecular distributions, source identification and apportionment of PAHs in the tree-rings of Masson pine from two industrial sites in the Pearl River Delta of south China were determined. Tree-rings of Masson pine recorded the timely trends of atmospheric PAHs. The industrial activities might contribute to the temporal distribution patterns of PAHs in the tree-ring samples. Inferred from diagnostic PAHs ratios, the PAHs detected in the tree xylem from both sites mainly stemmed from combustion processes (pyrogenic sources). Source apportionment from PCA further confirmed that PAHs in the tree-rings were dominated by wood burning, coal combustion, diesel and gasoline-powered vehicular emission at DSK, while diesel combustion, gasoline and natural gas combustion, and incomplete coal combustion were responsible for the main origins of PAHs at XQS. Tree-ring analysis of PAHs was ideally indicative to temporal changes in point emissions of PAHs, thus minimizing the bias of short-term active air sampling.

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