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Temporal patterns and potential sources of polycyclic aromatic hydrocarbons in xylem of *Pinus kwangtungensis*

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ABSTRACT

The temporal patterns and the possible sources of polycyclic aromatic hydrocarbons (PAHs) in the xylem formed from 1883 to 2007 of Kwangtung pine (*Pinus kwangtungensis*), growing in the Nanling Mountains of Southern China, were detected whether dendrochemistry was sufficient to monitor historical changes in regional airborne PAHs. The total concentrations of 17 PAHs (ΣPAHs) distributed in the xylem of *P. kwangtungensis* did not progressively increase over time. Temporal patterns of high molecular weight PAHs (HMW–PAHs) coincided to a certain extent with the historical–socioeconomic changes in China. Based on the compositional analysis, PAHs absorbed by and accumulated in the xylem of *P. kwangtungensis* in the Nanling Mountains might be of pyrogenic origin. Although the possible sources of xylem PAHs were diverse over the studied period, principal component analysis could not convincingly distinguish the main contributors to xylem PAHs. Using only xylem of *P. kwangtungensis* was not adequate for retrospective monitoring of airborne PAHs in the atmosphere of the Nanling Mountains. Sampling other trees along a gradient and combining other meteorological and socioeconomic index data might provide more reliable information on historical changes in regional airborne PAHs.

Keywords: *Pinus kwangtungensis, polycyclic aromatic hydrocarbons, source analysis, temporal pattern, xylem*

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1. Introduction

Airborne polycyclic aromatic hydrocarbons (PAHs) are among the most wide–spread organic contaminants. Due to their carcinogenic, mutagenic, and teratogenic effects on organisms, PAHs have been closely monitored. Conventional monitoring of PAHs by high volume air samplers is often expensive for routine and long–term monitoring. A low–cost alternative method for routine, spatial, and/or temporal monitoring of airborne PAHs is bio–monitoring via "passive samplers" including mosses, tree leaves and needles (Lehndorff and Schwark, 2004; Liu et al., 2005a; Prajapati and Tripathi, 2008; Ratola et al., 2009; Ratola et al., 2010; Ratola et al., 2011; Ratola et al., 2012). However, the geographic distribution of some plant species might sometimes restrict the utility and application of these "passive samplers" in larger regional scale monitoring on PAHs. Furthermore, easily sampled leaves and needles of plants indicate only the current levels of airborne PAHs during plant's life–span, and cannot reveal historical changes in airborne PAHs. Importantly, uptake behaviors towards PAHs are usually species–dependent (Piccardo et al., 2005; Ratola et al., 2011). Currently, regional and historical changes in environmental PAHs are mainly determined from the analysis of soil sediment cores (Liu et al., 2005b; Guo et al., 2011). Research on historical changes in airborne PAHs by dendrochemistry has been relatively scarce (Wang et al., 2004; Kuang et al., 2011; Yin et al., 2011; Zou et al., 2011). Temporal patterns as well as the concentrations of PAHs revealed in tree rings were species–depended even in these limited reports, which might cast doubts regarding the accuracy of dendrochemistry in tracing the historical changes in environmental pollutants (Bellis et al., 2002).

The atmosphere has been identified as a major pathway for the transportation, transformation and deposition of airborne PAHs (Lehndorff and Schwark, 2004). After being emitted into the atmosphere from point sources, PAHs might be present in both vapor and particulate phases (Venkataraman and Friedlander, 1994). PAHs associated with fine particles could be transported long distance and existed in the environment for a long period of time (Lehndorff and Schwark, 2004). High mountains or plateaus could serve both as condensers and barriers/sinks for PAHs. Lighter PAHs that have traveled a long distance could be deposited in the "condensed phase" as elevation increased (Wania and Mackay, 1996; Yang et al., 2013).

PAHs may also enter the plants from the atmosphere via particle and gas phase deposition onto the waxy cuticle on the leaf and stem surface or by uptake through the stomata and translocated by phloem (Meredith and Hites, 1987). Although plants are able to take up PAHs into the root system followed by their translocation via xylem, root uptake of PAHs from soil was limited due to the solubility of PAHs in soil water (Wang et al., 2004). Airborne PAHs are the primary source of PAHs that accumulate in vegetation (Simonich and Hites, 1994). The high contents of lipophilic compounds in the xylem of conifers endow tree trunks with a great capability to accumulate and store atmospheric PAHs over time.

In the present study, we analyzed PAHs in the xylem of one Kwangtung pine (*Pinus kwangtungensis*) in the Nanling Mountains of southern China. The overall goal was to determine the potential of tracing historical changes in airborne PAHs by dendrochemistry. The specific objectives were: (1) to determine the temporal distribution of PAHs in the xylem of *P. kwangtungensis* formed over the past 100 y, (2) to find possible chronological changes in environmental pollution through marking sources emitting PAHs, and (3) to assess the feasibility of using *P. kwangtungensis* to trace the historical changes in airborne PAHs.

2. Material and Methods

2.1. Site description

The Nanling Mountain range (112°30'–113°04'E, 24°–24°57'N), 2 100 m above sea level (asl), is an important boundary in Southern China between the temperate to the subtropical regions to the southeast (Lee et al., 2005). The range extends more than 1 000 km from west to east across the Guangxi–Guangdong–Hunan–Jiangxi provincial borders. The Mountains have an annual temperature and rainfall of 17.5–20.3 °C and 569–2 200 mm, respectively, during the past 30 years (Liu et al., 2005a). The Nanling Mountains are a key recipient of air pollutants (mainly stemmed from industrial and vehicular sources) transported from northern China to the southern coastal region, particularly in winter (Chan et al., 2002). The distribution patterns of PAHs in moss samples from the Mountains matched well with bulk atmospheric deposition patterns in the adjacent areas (Liu et al., 2005a), where airborne PAHs were mainly stemmed from industrial emissions (e.g. petroleum refineries, coal–fired power plants, auto manufacture) and vehicular exhausts (Fu et al., 2003; Mai et al., 2003; Xu et al., 2006; Cai et al., 2007; Wang et al., 2011; Wang et al., 2013).

2.2. Xylem collection and preparation

At the beginning of 2008, an ice and snow storm occurred in southern China, which seriously damaged numerous old trees in the Mountains. Taking this opportunity, we destructively sampled one old Kwangtung pine tree growing on a crag 1 400 m asl. One disc (about 20 cm in thickness) at a height of 1.3 m above ground level was cut from the tree and transported to the laboratory for processing. In the laboratory, the disc was immediately mounted and polished to reveal the annual growth rings. After the tree rings were dated using the Windendro^{TM} system (V 6.1D, Canada), chips of xylem representing 10–year growth intervals (except for the first and the last samples, which represented 15–year and 2–year intervals, respectively) were carefully sliced from the heart–wood to the sap–wood (one chip per time interval) with a clean, electric micro–chisel to obtain a sufficient mass for PAH analysis. A total of 23 chips, representing a more than 100–year history (1883–2007), were sliced from the disc. The chips were freeze–dried for 36 h and finely ground to pass through a 0.2–mm screen and were then used for PAH measurements.

2.3. PAH measurements

The extraction, purification and analysis of xylem PAHs were performed according to published methods (Kuang et al., 2011) in the National Key Laboratory of Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The experimental quality was controlled by laboratory blanks and recovery standards (SRM 1649A, NIST, Gaitherbury, USA). The following 17 PAHs were detected with a GC–MSD system in the tree ring samples: naphthalene (Nap), acenaphthylene (Acpy), acenaphthene (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 method detect limit (MDL) of each PAHs species was in the range of 0.6–2.6 ng kg^{-1} DW (Table 1). The PAH concentrations in this study were presented on a dry weight basis.

2.4. Data analysis

After the measurements, the following parameters were calculated: (1) the concentration of the total PAHs detected (ΣPAHs), (2) the percentage of individual PAHs with different numbers of benzene rings relative to ΣPAHs, (3) the ratio of low molecular weight PAHs (with 2 to 3 rings, LMW–PAHs) to high molecular weight PAHs (with 4 to 7 rings, HMW–PAHs), and (4) the ratio of the sum of major combustion–specific PAHs (ΣCOMB) to ΣPAHs in the tree ring samples (combustion–specific PAHs include FL, Pyr, BaA, Chr, BbF, BkF, and BaP). Finally, principal component analysis (PCA) was used to explore the similarities or differences among the samples and to facilitate the assessment of emission 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 >0.10 were considered.

3. Results and Discussion

3.1. Temporal patterns of PAHs in the xylem

The individual concentrations of all PAHs are presented in Table 1. The concentrations of ΣPAHs and HMW–PAHs as well as the fractions of LMW–PAHs and HMW–PAHs to ΣPAHs in the dated tree rings of Kwangtung pine are plotted against time in Figure 1. Unexpectedly, ΣPAHs did not progressively increase from the oldest tree rings to the youngest ones; the highest levels were found in xylem formed in 1883–1895 and the lowest in tissue from 1946–1950 (Figure 1A). Unlike ΣPAHs, the HMW–PAHs patterned an increasing tendency from the old to the young xylem with a first peak found in tissue formed during 1951–1955 and a second larger peak found in tissue formed since the 1980s (Figure 1B). The fractions of the LMW–PAHs and the HMW–PAHs relative to ΣPAHs showed that the LMW–PAHs were the dominant component of ΣPAHs in the xylem formed before 1980 (Figure 1C).

Environmental PAHs are mostly derived from anthropogenic emissions. Atmospheric deposition of PAHs has progressively increased in southern China, particularly since the late 1970s when the Open–door and Economic Reform policies were implemented (Xu et al., 2006; Wang et al., 2007; Wang et al., 2010; Guo et al., 2011; Wang et al., 2011). For example, the concentrations of ΣPAHs recorded in the sedimentary cores sampled from the Pearl River Estuary increased from ~200 ng g^{-1} in the 1960s to ~800 ng g^{-1} in the late 1990s (Liu et al., 2005b). In the present study, the temporal changes in ΣPAH in the xylem of Kwangtung pine did not exactly reflect the sedimentary PAH deposition in the same region (Liu et al., 2005b), neither matched the temporal patterns recorded in the tree rings of Longpetiole beech (*Fagus longipetioleta*) from Southeastern China (Wang et al., 2004).

Although the physiological mechanisms controlling PAH behavior in plant tissues have been partly elucidated (Wang et al., 2004), we should consider that the highest concentrations of ΣPAHs and the larger fraction of the LMW–PAHs in the oldest xylem might be the results of the higher concentrations of environmental LMW–PAHs and some biogenic sources of LWM–PAHs i.e. Nap (Krauss et al., 2005). Whether xylem chemicals (in particular the content of lipophilic compounds) have influence on the accumulation or the translocation of PAHs due to their radial redistribution are still not sure, but it is true that the content of chemicals in conifer xylem (this study) is significantly higher than that in broadleaved species adopted by Wang et al. (2004) and Zou et al. (2011). Tree species, environmental variables as well as PAH properties could affect the absorption and accumulation of PAHs (Simonich and Hites, 1994; Barber et al., 2002). The higher

concentrations of LMW–PAHs in the oldest xylem of Kwangtung pine might be ascribed to the PAH characteristics, the structural properties of xylem as well as the xylem chemical content. The LMW–PAHs are usually more abundant in the atmosphere and have more rapid atmospheric diffusion than the HMW–PAHs (Mader and Pankow, 2002), thus can be easily diffused through the cuticle and ultimately absorbed whereas the HMW–PAHs remain mostly embedded within the cuticle. Additionally, PAHs predominantly bound to particles can be readily washed off from the leaves since their slow desorption from particle and the low diffuse rate through leaf cuticle. Tree xylem can be divided into heartwood and sapwood. The LMW–PAHs might be tightly contained in the dead cells of the heartwood and could not be easily volatilized. At the same time, the much higher lipid content in heartwood than in sapwood might also capture more PAHs by the oldest xylem. These aspects might lead to an inconsistently temporal pattern of ΣPAHs with those already reported (Wang et al., 2004; Liu et al., 2005b).

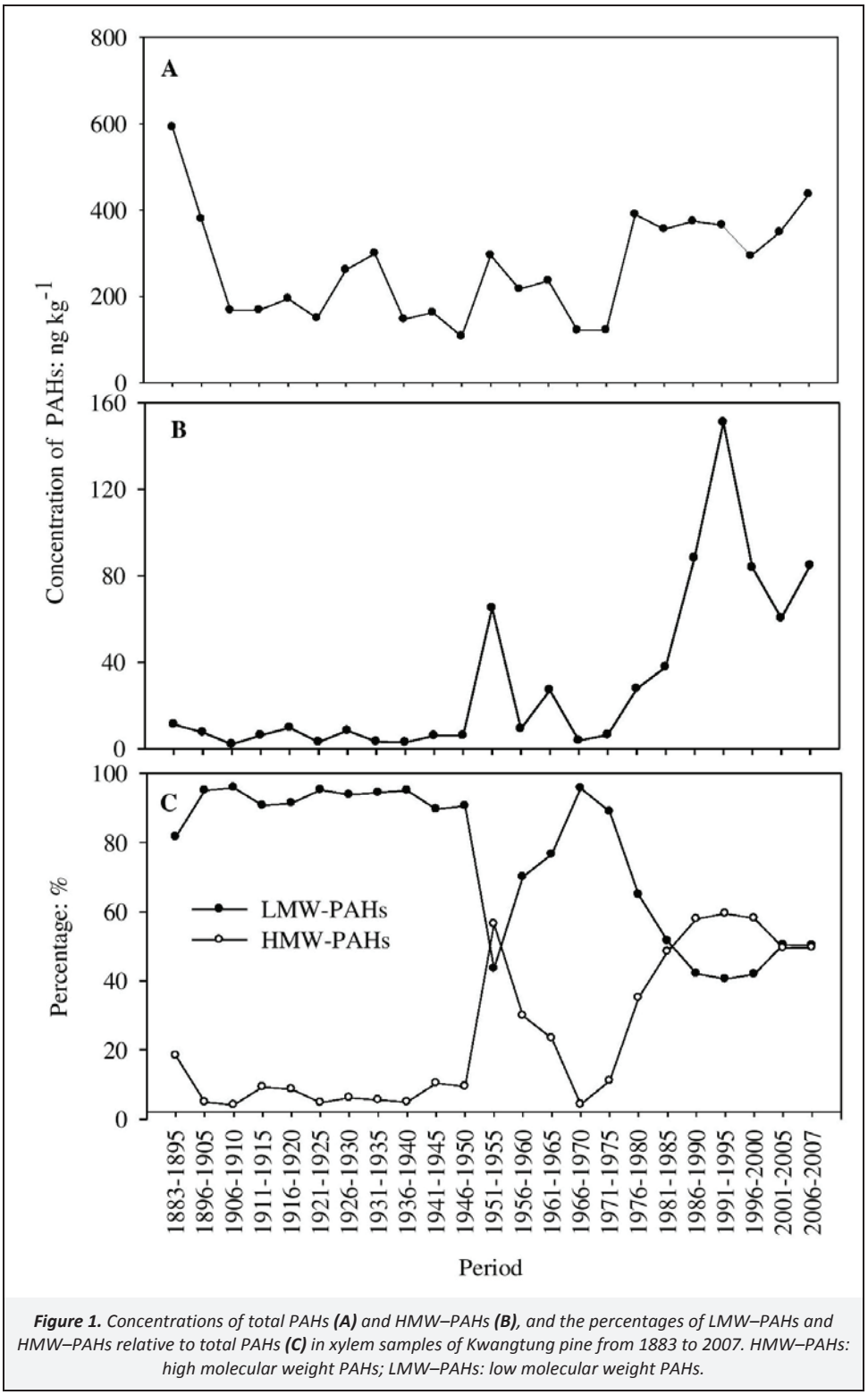

Figure 1. *Concentrations of total PAHs* ***(A)*** *and HMW–PAHs* ***(B)****, and the percentages of LMW–PAHs and HMW–PAHs relative to total PAHs* ***(C)*** *in xylem samples of Kwangtung pine from 1883 to 2007. HMW–PAHs: high molecular weight PAHs; LMW–PAHs: low molecular weight PAHs.*

Table 1. *Concentrations of PAHs in the xylem of Kwangtung pine formed at different periods in Nanling Mountains (ng kg^{-1} DW) and the method detection limit (MDL) of the PAHs (ng kg^{-1})*

Year	Nap	Acpy	Acp	Flu	PA	Ant	FL	Pyr	Chr	BaA	BbF	BkF	BaP	DBA	IND	BghiP	PER
1883–95	209.81	5.15	9.94	35.78	205.82	16.67	9.96	10.65	31.22	45.70	0.20	3.63	4.82	1.50	0.85	0.01	0.12
1896–05	212.18	2.58	2.67	19.24	112.97	10.81	3.01	2.39	4.12	1.75	0.85	0.15	4.42	1.21	0.65	0.01	0.10
1906–10	111.06	1.07	1.05	8.15	36.91	2.64	1.72	1.02	1.38	0.79	0.06	0.13	0.43	0.82	0.44	0.03	0.04
1911–15	110.82	0.95	0.93	5.69	31.91	2.59	1.46	0.91	1.20	6.05	0.17	0.22	2.82	1.38	1.31	0.10	0.07
1916–20	85.13	4.56	2.38	16.87	61.91	6.99	2.02	1.14	2.40	1.60	0.27	0.25	3.72	3.67	1.52	0.12	0.05
1921–25	86.29	1.03	1.47	8.69	41.77	3.48	0.99	0.61	1.52	1.09	0.07	0.22	1.87	0.65	0.12	0.01	0.01
1926–30	137.17	2.34	1.86	12.12	81.61	10.04	0.15	0.04	1.32	6.33	0.15	0.11	0.50	7.41	0.04	0.02	0.01
1931–35	121.14	6.60	5.61	26.62	108.71	14.02	3.30	1.66	4.24	4.14	0.41	0.10	0.10	2.25	0.29	0.02	0.01
1936–40	65.46	1.11	1.30	10.45	53.86	7.30	1.53	1.04	1.82	0.05	0.38	0.02	1.33	1.05	0.03	0.00	0.00
1941–45	61.06	4.99	2.69	25.71	45.34	6.24	2.94	0.65	6.50	0.86	0.84	0.04	1.06	0.29	3.48	0.08	0.10
1946–50	47.88	0.78	0.61	5.56	39.30	3.25	1.38	0.78	1.26	0.77	1.46	0.06	1.14	2.84	0.35	0.05	0.04
1951–55	73.09	1.06	1.36	8.62	39.06	5.41	16.22	10.83	12.50	62.08	2.71	6.54	1.58	51.61	2.39	0.18	0.06
1956–60	68.88	7.41	6.15	11.56	22.06	36.04	10.44	6.71	1.42	37.28	0.20	0.42	0.40	7.04	0.98	0.06	0.00
1961–65	90.51	1.37	2.31	15.83	62.67	8.37	0.94	0.49	8.91	17.92	0.12	0.81	0.20	25.04	0.67	0.15	0.04
1966–70	65.94	0.85	0.83	6.75	36.69	5.32	0.89	0.51	0.02	0.14	0.21	0.01	0.12	2.12	1.10	0.02	0.01
1971–75	42.31	1.10	1.27	11.68	47.12	4.71	2.10	0.92	2.66	1.48	0.44	0.16	0.22	4.55	0.48	0.35	0.05
1976–80	147.67	1.66	1.82	16.54	77.39	8.04	29.61	22.35	15.02	42.10	1.17	0.89	0.19	20.73	4.03	0.28	0.34
1981–85	113.36	1.24	1.24	8.92	52.56	5.99	15.87	30.25	27.85	60.61	17.10	5.98	0.57	11.68	1.53	0.22	0.59
1986–90	57.40	30.66	15.51	14.06	23.94	15.74	16.34	24.05	27.62	60.29	21.23	12.31	1.10	14.64	37.81	0.38	0.69
1991–95	65.71	0.97	1.07	8.78	67.23	4.23	12.79	20.91	26.34	6.06	21.36	8.83	31.73	29.54	57.06	1.26	1.17
1996–00	76.89	0.94	1.05	6.69	34.19	3.37	25.17	24.67	23.58	13.55	48.96	7.40	5.18	13.68	6.21	1.51	0.83
2001–05	102.95	1.45	1.27	8.28	57.64	4.38	55.63	20.55	20.97	15.01	17.40	6.71	1.58	6.95	26.33	0.29	1.03
2006–07	77.79	20.15	12.89	20.62	65.97	22.01	23.92	23.79	26.83	57.34	31.98	8.28	1.85	6.61	31.33	3.54	1.13
MDL	1.97	1.13	1.17	1.70	2.60	0.71	2.06	1.52	0.74	1.31	1.24	0.90	0.60	0.61	0.99	0.94	0.45

The temporal pattern of the HMW–PAHs in the xylem of Kwangtung pine, to a certain extent, reflected the socioeconomic development of southern China. For example, the appearance of the first peak (1951–1955) corresponded with the foundation of the People's Republic of China in 1949 and the subsequent increase in industrial production (i.e. iron and steel, coal etc.) in many regions nearby Nanling Mountain (the Pearl River Delta, Yangtze River Delta). The subsequent decline in HMW–PAHs in xylem formed from 1966 to 1975 corresponded with the dramatic halt in industrial production during the so–called "Cultural Revolution". Since the mid–1980s, the Pearl River Delta has undergone a rapid transition from an agriculture–based economy to an industry–and technology–based economy. Consequently, the social–economies have rapidly developed in the Pearl River Delta. For instance, the gross domestic product increased from ~4.5 in 1952 to ~110 in 1985 and to ~1 070 billion RMB in 2000; the power generation increased from ~0.1 to ~16.7 and to ~129.2 billion kw h^{-1} in the corresponding years (Guangdong Year Book, 2001). Coupled with this development, emissions of PAHs were dramatically increased (Xu et al. 2006), leading to the temporal accumulation of PAHs deposited in the soils (Liu et al., 2005b). The second peak of HMW–PAHs in the xylem formed from 1991 to 1995 probably reflected this transition. However, it should be noted that PAHs in plant tissues can be influenced by many complex factors besides the atmospheric PAH concentrations. The possible influence of tree age on the accumulation or translocation of PAHs in plant tissue should be taken into consideration, since younger trees have less dense crowns and lower total surface of needles which influence the uptake of PAH. The increase in HMW–PAH concentrations observed in this study might be attributed to natural processes, the entry of PAHs in needles and anthropogenic influence, etc. Inadequate scientific explanation on the low value of HMT–PAHs during 1956–1960 and 1966–1975 also showed the uncertainties when evaluate the atmospheric PAHs pollution in direct utilization of xylem PAHs. Therefore, a combination of more tree species and larger sample size, in comparison with data from soils, atmosphere, and the regional socioeconomic data from the same regions might overcome the uncertainty and strengthen the persuasiveness of tracing historical changes in airborne PAHs using coniferous dendrochemistry (like Kwangtung pine in this study).

3.2. Potential sources (petrogenic vs. pyrogenic) of xylem PAHs

The diagnostic ratios of LMW–PAHs/HMW–PAHs, ΣCOMB/ΣPAHs, and PA/Ant, are plotted in Figure 2. The ratios of LMW–PAHs/HMW–PAHs in the samples formed before the 1950s were much higher (most were >10.0) than those formed after the 1950s (most were <5.0) except for the period of 1966–1975 (Figure 2A). In contrast, most of the ΣCOMB/ΣPAHs ratios increased with chronological time, with values less than 0.1 before the 1950s (except for 1 xylem sample) and with values larger than 0.2 after the 1950s (expect for 3 xylem samples, Figure 2B). Through the studied time scale, values of PA/Ant in 6 of 11 xylem samples formed before the 1950s and in 9 of 12 xylem samples formed after the 1950s were less than 10.0 (Figure 2C).

The ratios of LMW–PAHs/HMW–PAHs have been used to determine the origins (petrogenic vs. pyrogenic) of PAHs (Yunker et al., 2002). Although several authors have questioned the adequacy of their use for other matrices (Katsoyiannis et al., 2007), they are still used in PAH source analysis (Mai et al., 2003). Enrichment with HMW–PAHs is a typical characteristic of a combustion origin (pyrogenic, Zakaria et al., 2002). In this study, LMW–PAHs accounted for more than 80% of ΣPAHs before the 1950s, while HMW–PAHs accounted for more than 50% of the samples formed after the after the 1980s (Figure 1C). Although there are biogenic sources of PAHs (in particular LMW–PAHs) in forests (Krauss et al., 2005), the increase in the proportion of HMW–PAHs (Figure 1C) suggested an increase of PAHs derived from combustion since the 1980s. The prevailing pyrogenic sources of PAHs in aerosols (Mai et al., 2003), sediments (Liu et al., 2005b), and urban surface dusts (Wang et al., 2011) from the Pearl River Delta gave support to the xylem analysis. As another useful indicator of PAH source, the ratio ΣCOMB/ΣPAHs (Prahl and Carpenter, 1983) in the xylem, was much lower before than after the 1950s (Figure 2B), also providing evidence of pyrogenic PAHs. A PA/Ant value of less than 10.0 has been used to indicate pyrogenic origins of PAHs (Baumard et al., 1998). The plots shown in Figure 2C confirmed the predominance of combustion–originated PAHs that tree absorbed from the atmosphere after the 1950s. Our results were consistent with the findings that PAHs in the sedimentary core from the Pearl River Estuary were mainly of pyrogenic origin since the 1950s (Liu et al., 2005b).

3.3. Possible contributors to xylem PAHs

Based on to the temporal variations of xylem ΣPAHs (Figure 1), we divided the tree xylem into three periods (before 1950, from 1950 to 1980, and after 1980) for PCA in order to assess the possible contributors. Two (accounted for 88.2 and 10.2% of the total variance), 3 (accounted for 63.2, 20.5, and 9.4% of the total variance), and 4 (accounted for 37.1, 32.8, 15.5, and 9.4% of the total variance) principal components (PC) were identified in the three periods, respectively (Figure 3).

Before the 1950s, PC1 was found with dominance of Ant, Flu, PA, FL, Pyr, Chr, Acp, and BaA, which are the source fingerprints of wood combustion (Fang et al., 2004). Therefore, wood combustion–related operations (e.g. the burning of wood for home cooking) might be associated with this factor. The high loading values of Nap could indicate incomplete combustion–related emissions (Dong and Lee, 2009), while high values of Pyr, BaA, Chr, BkF, and FL are typical markers of coal combustion (Larsen and Baker, 2003). Thus, we inferred that incomplete wood burning and coal combustion might have been the main sources of the airborne PAHs accumulated in the tree rings before the 1950s.

In the period of 1950–1980, three possible contributors were found for PAHs in tree xylem. In PC1, highly weighted on Nap, Pyr, FL, PER, Chr, BaA, and BkF, might be attributed to coal combustion (Park et al., 2002). PC2 was dominated by high loading values for BaP, DBA, BkF, and BaA and moderate values for Chr, FL, and BbF. Chr is also a marker of diesel emissions (Bourotte et al., 2005); BbF, BkF, and DBA (Esen et al., 2008) are markers of gasoline emissions; BaP and BaA are markers of natural gas combustion (Kulkarni and Venkataraman, 2000). Therefore, vehicular emissions was likely responsible for this component. In PC3, the high loading values for PA, Acpy, Ant, and Acp could be explained by wood combustion.

After 1980, the four PCs indicated there were more sources of xylem PAHs over time. PC1 had high values for 3–4 ringed PAHs (Acp, Acpy, Ant, Flu, and BaA), which are markers of diesel emissions (Bourotte et al., 2005). PC2 had high values for Pyr, IND, PER, BaP, BaA, and DBA. High levels of Pyr, PER, BaP, IND, and DBA are likely related to exhaust emissions from "stationary" sources (Fang et al., 2004). Large quantities of BaP, BaA, and PER are generated in steel production (Kulkarni and Venkataraman, 2000), and DBA is related to thermal power plants that use coal as the fuel and is also a marker of gasoline emissions (Fang et al., 2004). Thus, the interpretation of the results suggested multiple PAH contributors. PC3 had high loading values for FL, Chr, DBA, BaP, and Pyr, which are markers of coal–related combustion emissions (Esen et al., 2008). PC4 had high values for PA, BbF, BkF, PER, IND, and Acpy, which indicate traffic–related sources (Larsen and Baker, 2003; Mai et al., 2003; Esen et al., 2008). Summarily, vehicles powered by gasoline and diesel might be the likely sources of airborne PAHs.

Comparing the PCA results with the temporal adjustment of socio–economy in the Pearl River Delta, we found the inference

might not be totally consistent with the main sources during differ rent periods. For instance, during the first period (before 1950), the economy in the Delta was mainly agriculture–based which with more than 40% of gross domestic product from agricultural sectors (Guangdong Year Book, 2001). Wood burning and some coal combustion could be the main contributors to PAHs. From 1950 to 1980, gross domestic product from industrial sectors in Guangdong province increased from ~36% to ~50% (Guangdong Year Book, 2001), implying industrial emissions (coal combustion, vehicular exhausts, etc.) might be the main sources of PAHs. Since the 1980, the economy in the Pearl River Delta was highly industrial–and technological–based with only ~24% gross domestic product from agricultural sectors (Guangdong Year Book, 2001). The traffic–related and coal combustion sources of PAHs revealed by PCA is partly consistent with the tremendously annual increasing consumption of coal by industrial sectors from 293 in 1980 to 1 094 million tons of coal equivalent in 2003 (Xu et al., 2006). In summary, given the more diverse possible sources of xylem PAHs, the results of tree rings PCA were not completely consistent and did not provide enough evidence to distinguish the main contributors to xylem PAHs.

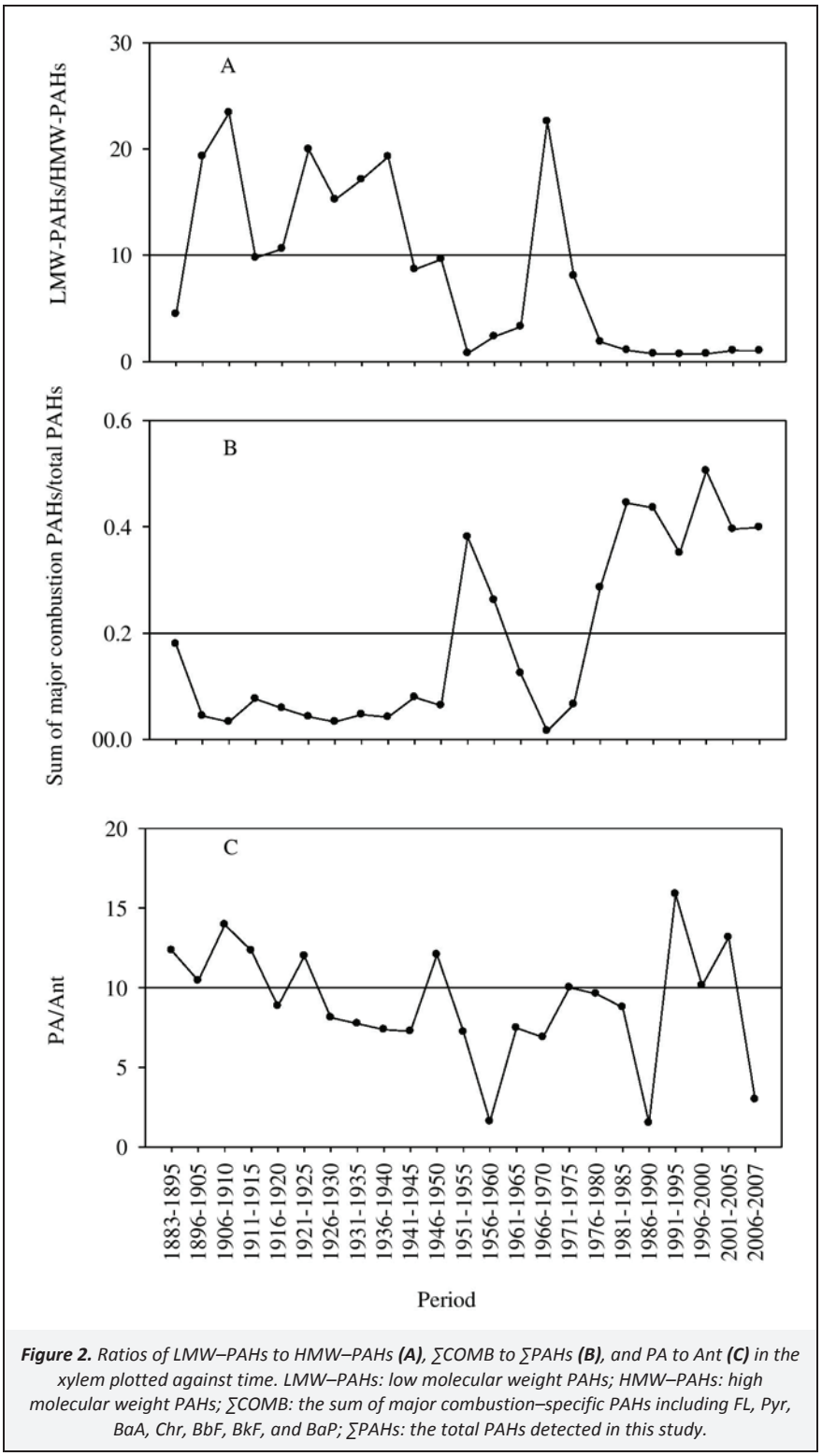

Figure 2. *Ratios of LMW–PAHs to HMW–PAHs* ***(A)****, ∑COMB to ∑PAHs* ***(B)****, and PA to Ant* ***(C)*** *in the xylem plotted against time. LMW–PAHs: low molecular weight PAHs; HMW–PAHs: high molecular weight PAHs; ∑COMB: the sum of major combustion–specific PAHs including FL, Pyr, BaA, Chr, BbF, BkF, and BaP; ∑PAHs: the total PAHs detected in this study.*

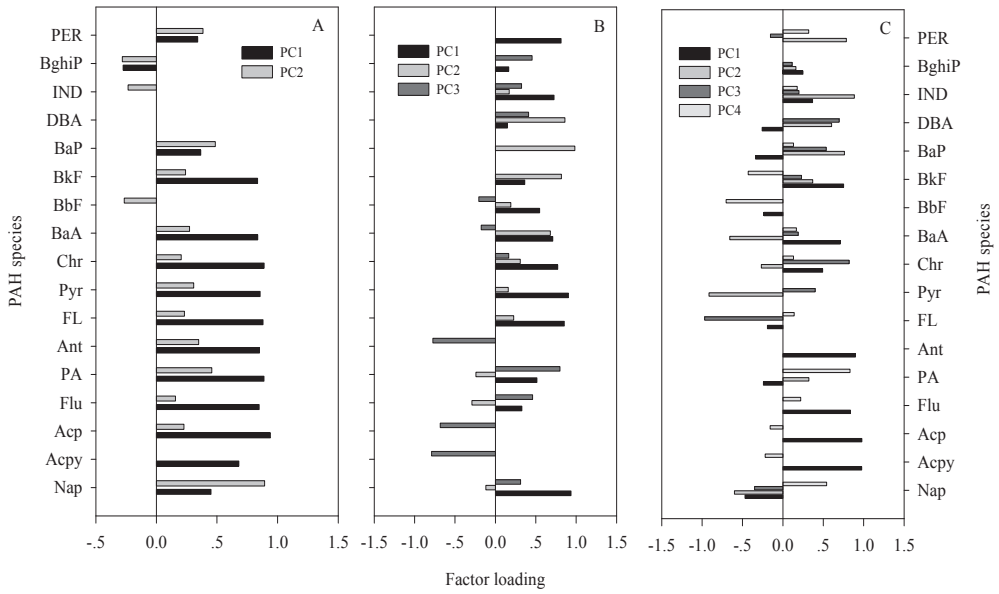

***Figure 3**. Results of principal component analysis of xylem PAH concentrations before 1950 **(A)**, from 1950–1980 **(B)**, and after 1980 **(C)**. Extraction method: principal component analysis; Rotation method: Varimax with Kaiser normalization; eigenvalue >1.00; Absolute values of factor loading >0.10 were listed.*

4. Conclusions

Airborne PAHs were detected by dendrochemistry of *Pinus kwangtungensis* xylem from the Nanling Mountains of southern China. Although the mechanism of airborne PAH accumulation in tree trunk has been partly documented previously, the total concentrations of PAHs (ΣPAHs) detected in the xylem of *P. kwangtungensis* in this study did not increase over time. Temporal patterns of high molecular weight PAHs (HMW–PAHs) to a certain extent coincided with changes in the historical–socioeconomic status in southern China. According to compositional analysis, airborne PAHs absorbed by and accumulated in the xylem of *P. kwangtungensis* in the Nanling Mountains might be of pyrogenic origin. Since the possible sources of xylem PAHs were diverse over the studied period, principal component analysis could not provide convincing evidence to distinguish the main contributors to airborne PAHs. Using only xylem of *P. kwangtungensis* was not adequate for retrospective monitoring of airborne PAHs in the atmosphere of the Nanling Mountains. Since only one tree was analyzed in this study, there must be limitation and uncertainties of the reported PAH concentrations. Sampling of other trees along a gradient and a combination of regional meteorological, socioeconomic data might overcome the limitations of dendrochemistry and provide more reliable information on the historical changes in regional airborne PAHs.

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