

# DISTRIBUTION AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN CAMPHOR (*CINNAMOMUM CAMPHORA*) TREE BARK FROM SOUTHERN JIANGSU, CHINA

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## Introduction

PAHs are primarily derived from anthropogenic sources (fossil fuels and combustion) and natural sources (oil seeps, bitumen, coal, plant debris, forest and prairie fires). As semi-volatile organic pollutants, PAHs are present in both gas and particle phases in the atmosphere. In recent years, some plants have been used to passively sample the atmosphere, including lichen, moss, plant leaves and tree bark. Due to its large surface area, high lipid content and long life cycle, tree bark is a good passive sampler for persistent organic compounds<sup>1</sup>. Located in the lower reaches of Yangtze River, Jiangsu province is now one of the most prosperous provinces in China, especially Southern Jiangsu. With the rapid economic development and the quick urbanization process, the pollution in the Yangtze River Delta has increasingly aroused the public concern. The objective of this paper was to investigate the distribution and possible sources of PAHs in Southern Jiangsu.

## Materials and methods

Standards of 16 USEPA priority PAHs were analyzed. Because of the high volatility of Naphthalene and easy losses during the experiments, it was not taken account in this study. All camphor tree bark samples (n=33) were collected in August 2012 in Southern Jiangsu (Fig. 1). Approximately 18 g of the bark sample was extracted in an Accelerated Solvent Extraction (ASE) with a mixture of acetone and hexane (V/V = 1:1).



Fig.1 Map of the sampling sites in the Southern Jiangsu.

All samples were analyzed by GCMS-QP2010 plus (Shimadzu, Japan). The analytical column was a Rtx-5MS capillary column (30 m×0.25 mm i.d.; 0.25 μm film thickness; Restek). The GC oven temperature was programmed from 60 °C (1 min) to 160 °C at 10 °C/min, increased to 260 °C at 8 °C/min, then to 300 °C at 6 °C/min and held for 8 min. The injector and detector temperatures were 250 °C and 300 °C, respectively.

## Results and discussion

### *Concentrations and composition of PAHs in tree bark*

Concentrations of PAHs in camphor tree bark from Southern Jiangsu are given in Table 1. Among the PAHs, Phe,

Fl and Pyr concentrations were the highest, contributing 13.8-56.4%, 5.6-29.1% and 4.1-20.7% to the total PAHs respectively. The sum of the three compounds represented 43.8-80.8% of total PAHs. Pereira Netto et al.<sup>2</sup> and Hwang et al.<sup>3</sup> reported separately that Phe, Fl and Pyr were also the predominant PAHs in tree bark in Brazil and pine needles in Korea and United States. The  $\Sigma_{15}$ PAHs concentrations in tree barks ranged from 6.18 to 1556 ng/g dw, with an average value of 407 ng/g dw. Maximum PAH levels were found in site 21 (1556 ng/g dw), this site was at the roadside in the suburban of Wuxi city and close to some textile factories. The second highest concentrations were sample #18 (1294 ng/g dw) and #19 (1184 ng/g dw). Sample #19 was collected in the downtown commercial district and close to the road, while #18 was located in rural area near Taihu Lake. Therefore, the sources of PAHs were complicated. Besides the distance to the point source, the meteorological parameters and photolytic and biological degradation of certain PAHs may also affect their levels and their relative distributions. Generally, the concentrations of PAHs in the suburban areas were the highest, following by urban and rural areas (not including #18). The suburban area usually had some PAHs sources such as infrastructure construction activities, industrial emissions and biomass burning, indicating that the influence of speeding up urbanization process. However, the PAHs detected in the urban area might be caused by vehicle emissions, commercial and residential activities.

Table 1 Summary of PAHs concentrations in camphor tree bark from Southern Jiangsu (ng/g dw).

compund	range	Mean $\pm$ std. err.	median
Acenaphthylene (Acy)	0.158-4.69	2.04 $\pm$ 1.26	1.96
Acenaphthene (Ace)	0.690-12.0	3.21 $\pm$ 2.26	2.46
Fluorene ( Flu )	1.443-38.6	15.7 $\pm$ 8.89	14.1
Phenanthrene ( Phe )	2.107-340	121 $\pm$ 82.9	115
Anthracene ( An )	0.153-14.2	4.39 $\pm$ 3.58	3.80
Fluoranthene ( Fl )	0.347-359	91.4 $\pm$ 93.4	60.3
Pyrene ( Pyr )	0.256-323	64.6 $\pm$ 74.8	39.4
Benzo[ <i>a</i> ]anthracene (BaA)	0.077-61.4	10.3 $\pm$ 15.6	3.12
Chrysene (Chr)	0.028-209	35.9 $\pm$ 46.3	19.3
Benzo[ <i>b</i> ]fluoranthene (BbF)	0.025-137	20.6 $\pm$ 31.9	5.76
Benzo[ <i>k</i> ]fluoranthene (BkF)	0.033-66.1	7.85 $\pm$ 13.1	2.15
Benzo[ <i>a</i> ]pyrene ( BaP )	0.065-97.6	13.0 $\pm$ 21.1	3.23
Indeno[1,2,3- <i>cd</i> ]pyrene ( IcdP )	0.025-48.7	4.12 $\pm$ 8.88	0.66
Dibenzo[ <i>a,h</i> ]anthracene ( DahA )	0.0019-39.0	6.46 $\pm$ 7.39	5.18
Benzo[ <i>ghi</i> ]perylene ( BghiP )	0.010-60.8	6.97 $\pm$ 12.4	0.89
3 ring	4.67-410	146 $\pm$ 97.4	141
4 ring	0.745-906	202 $\pm$ 225	123

5+6 ring	0.319-414	59.0±88.5	17.1
$\Sigma_{15}$ PAHs	6.18-1556	407±389	319

The  $\Sigma$ PAHs levels in this study were similar to those found in Mainland China <sup>4</sup>(5.1~1770ng/g dw), Palermo in Italy (33~1015ng/g dw) and Rio de Janeiro in Brazil(242~1640ng/g dw), higher than those in Portugal and Spain (22~196ng/g dw). However, Ratola et al.<sup>5</sup> reported that PAHs were more likely to be enriched in pine needles than bark. To analyze PAHs molecular distribution, the 16 identified PAHs were separated into groups according to the number of aromatic rings: the two-, and three-, four-, and five-, and six-ring PAHs. The compositions of PAHs in tree bark are shown in Fig. 2. At all sites, the three-ring (16.9-81.0%) and four-ring (12.1-59.7%) PAHs accounted for a large proportion, closed to what had been reported by Orecchio et al.<sup>6</sup>.

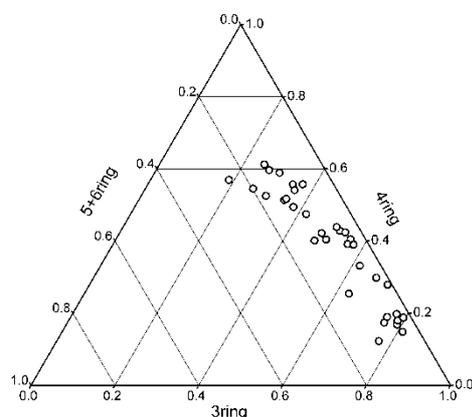


Fig.2 Triangular diagram of percentage concentration for the 15 PAHs.

#### Sources of PAHs in tree bark

The PCA results showed that two factors were responsible for the PAHs in tree bark from Southern Jiangsu (Fig. 3). The first and second components explained 73.3% and 14.5% respectively, which collectively accounted for 87.8% of the total variance. The first component was mostly loaded by six-ring of IcdP (0.965) and BghiP (0.957), five-ring of BaP (0.923), BkF (0.949), and BbF (0.880), and four-ring of BaA (0.825). IcdP, BghiP and BaP were markers of gasoline vehicle emissions while BbF and BkF were related to diesel-powered vehicles. Duval et al.<sup>7</sup> reported that BaA was the indicator of coal combustion. Therefore, the first component was associated with vehicle-related sources and coal combustion-related sources. The second component may represent combustion-related sources because of the high loading values of Acy (0.913), Ace (0.755), Flu (0.915), An (0.783), Phe (0.925), Fl (0.750) and Pyr (0.729). Fang et al.<sup>8</sup> reported that Acy, Ace, Flu and An derived from combustion. Ace and Flu might be tracers of coke oven source while Phe, Fl and Pyr were considered good markers for incineration source.

Molecular indices based on ratios of selected PAH concentrations may be used to differentiate PAHs from pyrogenic and petrogenic origins. In this study, IcdP/(IcdP + BghiP) ratios are >0.20 in all sites which showed that the combustion of fossil fuel and coal was the major source. Meanwhile, the ratio of Fl/(Fl+Pyr) ranged from 0.53 to 0.65 for all sites, suggesting coal combustion source. As shown in Fig.4, significant positive correlations were found between BaP and  $\Sigma_{15}$ PAHs ( $r=0.897$ ,  $P=0.01$ ). BaP was proved to be an important indicator of combustion-derived PAHs. To summarize, the result of diagnostic ratio was consistent with the result obtained by method of PCA. It could be inferred from the above analysis that vehicle emission (including gasoline and diesel vehicles), coal combustion and industrial emission were the major sources of PAHs in tree bark from studying area.

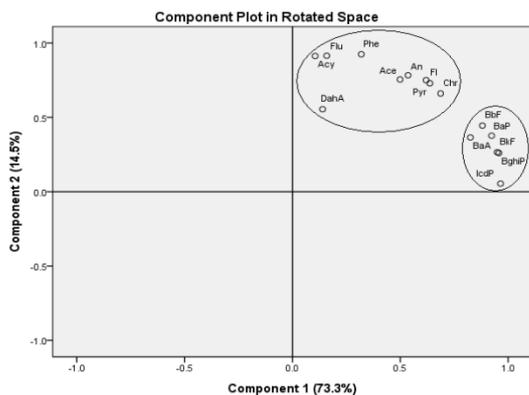


Fig.3 PCA analysis of PAHs congeners in camphor tree bark from Jiangsu Province.

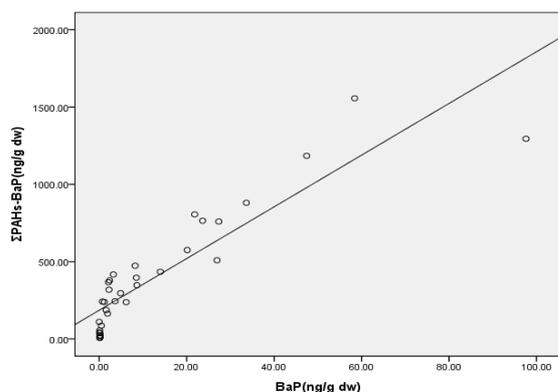


Fig.4 Correlation analysis between levels of BaP and  $\Sigma_{15}$ (PAH- BaP).

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