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3 **Identification, abundance and seasonal variation of anthropogenic**
4 **organic aerosols from a mega-city in China**

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1 **Abstract:** PM_{2.5} aerosols were collected in Nanjing, a typical mega-city in China, during
2 summer and winter 2004 and were characterized for aromatic and cyclic compounds using a
3 GC/MS technique to understand the air pollution problem. They include polycyclic aromatic
4 hydrocarbons (PAHs), hopanes, phthalates and hydroxy-PAHs (OH-PAHs). PAHs, hopanes and
5 OH-PAHs presented higher concentrations in winter (26–178, 3.0–18, and 0.013–0.421 ng m⁻³,
6 respectively) than in summer (12–96, 1.6–11, and 0.029–0.171 ng m⁻³, respectively) due to an
7 enhanced coal burning for house heating and atmospheric inversion layers developed in the cold
8 season. In contrast, phthalates are much more abundant in summer (109–368 ng m⁻³, average 230
9 ng m⁻³) than in winter (33–390 ng m⁻³, average 170 ng m⁻³) due to an enhanced evaporation from
10 plastics during the hot season and the subsequent deposition on the pre-existing particles.
11 Generally, all the identified compounds are more abundant in nighttime than in daytime due to
12 inversion layers and increased emissions from heavy-duty trucks at night. PAHs, hopanes and
13 phthalates in Nanjing aerosols are 5–100 times more abundant than those in Los Angeles, USA,
14 indicating a serious air pollution problem in the city. Concentrations of OH-PAHs are 1–3 orders
15 of magnitude less than their parent PAHs and comparable to those reported from other
16 international cities. Source identification using diagnostic ratios of the organic tracers suggests
17 that PAHs in Nanjing urban area are mainly derived from coal burning, whereas hopanes are
18 more attributable to traffic emissions.

19 **Keywords:** Organic aerosols; Hopanes; Phthalates; Hydroxylated PAHs; Source reconciliation

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1 **1. Introduction**

2 Emissions from fossil fuel combustion and biomass burning in China have a significant
3 impact on the local air quality and global climate changes (Kaufman et al., 2002; Menon et al.,
4 2002; Richter et al., 2005). Increased summer floods in the south and droughts in the north have
5 been linked to the anthropogenic aerosols in the remote populous industrial regions that alter the
6 regional atmospheric circulation (Menon et al., 2002). Roughly one-fourth of global
7 carbonaceous aerosols are generated in China (Cooke et al., 1999), where the emission of
8 carbonaceous aerosols is continuously increasing due to the fast growth of the fossil fuel
9 consumption. China is the biggest user of coals in the world, consuming 1.2 billion tons of coal
10 in 2002, most of which are burned without any serious controls (China Statistic Yearbook, 2003).
11 In addition, emissions from vehicle exhausts is aggravating Chinese urban air quality. The
12 number of vehicles doubled in the country between 1995 and 2002, resulting in a steep increase
13 in the concentrations of nitrogen dioxide, volatile organic compounds, particles, and ozone in the
14 urban areas, especially in the mega-cities (Akimoto, 2003; Zhang et al., 2004).

15 In the past decades, numerous studies have focused on inorganic compositions of
16 aerosols from China, because the deserts in the west are recognized as the sources of Asian dust
17 storms (Parrington et al., 1983; Bergin et al., 2001; Vancuren and Cahill, 2002) and the SO₂
18 emissions from coal combustion in the country are thought as the origins of East Asian acid rains
19 (Swinbanks, 1989; Akimoto and Narita, 1994; Triendl, 1998; Akimoto, 2003). However, only a
20 few measurements have been made for organic aerosols from the country with an increase in
21 recent years (Zheng et al., 1997; Guo et al., 2003b; Bi et al., 2005). Furthermore, most of these
22 studies were carried out in southern and northern China, characterizing only a limited number of
23 compounds.

1 For shedding light on the status of air pollution in China, a comprehensive survey during
2 summer and winter 2004 was conducted in Nanjing, a typical mega-city in East China with more
3 than 4 million residents and several huge industrial regions, where serious air pollution has been
4 a long-term problem. In our previous work, seven classes of organic compounds in PM_{2.5}
5 aerosols from Nanjing were quantified on a molecular level (Wang and Kawamura, 2005). Here,
6 we report additional four classes of anthropogenic organic compounds in the fine particles, that
7 is, polycyclic aromatic hydrocarbons (PAHs), phthalates, and hopanes, as well as hydroxylated
8 PAHs. It should be noted that it is the first time to characterize phthalates and hydroxylated
9 PAHs in the aerosols from China, which would be very useful for the proper evaluation of
10 Chinese air quality.

11 **2. Experimental Section**

12 *2.1 Sample collection, Extraction and Derivatization*

13 Sampling procedures were described elsewhere (Wang and Kawamura, 2005). Briefly,
14 two PM_{2.5} high volume air samplers were set up on the rooftop of a three-story building on the
15 campus of Nanjing University. A week-term of sampling (n = 28) was performed on day/night
16 basis in summer and winter 2004. Afterwards, the filter aliquots were extracted three times with
17 dichloromethane (DCM) each for 10 min under ultrasonication, and filtrated through a pipette
18 packed with quartz wool to remove filter debris and other particles. The extracts were
19 concentrated by a rotary evaporator, and continuously blown down to dryness using purified
20 nitrogen gas. Then, 50 μL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1%
21 trimethylsilyl chloride and 10 μL of pyridine were added into the extracts, and heated at 70°C for
22 3 hr to convert OH functional group of hydroxyl PAHs into trimethylsilyl (TMS) ethers. Finally,
23 40 μL of 1.43 ng μL^{-1} C₁₃ n-alkane in hexane was added into the sample as an internal standard.

1 2.2 Gas chromatography-mass spectrometry quantification

2 Gas chromatography-mass spectrometry (GC-MS) quantification of compounds was
3 performed on a Hewlett-Packard 6890 GC coupled to a Hewlett-Packard 5973 MSD. The GC
4 separation was performed on a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., 0.5 μm
5 film thickness) with GC oven temperatures programmed from 50°C (holding for 2 min), increase
6 to 120°C at 15°C min⁻¹, and to 300°C at 5°C min⁻¹ with final isotherm held at 300°C for 16 min.
7 The sample was injected on a splitless mode at the injector temperature of 280°C. The mass
8 spectrometer was operated on an electron impact mode (EI) at 70 eV and scanned from 50 to 650
9 dalton. GC-MS response factors were determined using authentic standards. Average recoveries
10 of all the standards were better than 80%. Field blank filters were also treated by the same
11 procedure above, and no significant contamination was found. Data reported here were all
12 corrected for the blanks.

13 3. Results and discussion

14 3.1 PAHs

15 Seventeen PAHs were detected in the samples studied with total concentrations of 39 ng
16 m⁻³ (range, 12–96 ng m⁻³) in summer and 86 ng m⁻³ (26–178 ng m⁻³) in winter (see Table 1).
17 PAHs are much more abundant in nighttime than in daytime due to the accumulation process
18 caused by the inversion layers at night (see Figure 1a). In addition, heavy-duty diesel trucks are
19 allowed by local government to work only at night, emitting more pollutants into the air.
20 Benzo(*b*)fluoranthene (BbF) was found as the dominant PAH in all the aerosol samples studied,
21 contributing around 40% of total PAHs, followed by indeno(1,2,3-*cd*)pyrene (IP) and
22 benzo(*ghi*)perylene (BghiP) (see Figures 2a and 2b). This molecular distribution is consistent
23 with that reported by Yang et al (2005). Relative abundance of pyrene was found much higher in

1 winter than in summer mainly due to their decreased volatilization under cold ambient conditions
2 (Figure 2b). As seen in Figure 2, the similar molecular distributions between day and night and
3 summer and winter samples suggest that there is no significant difference in the emission sources
4 for PAHs throughout the year. Because benzo(*a*)pyrene (BaP) is less stable than benzo(*e*)pyrene
5 (BeP), it is selectively decomposed over BeP under high ambient temperature (Nielsen, 1984;
6 Finlayson-Pitts and Pitts Jr., 2000). The ratios of BaP to BeP are 0.90 ± 0.2 in summer and $1.5 \pm$
7 0.5 in winter, respectively, indicating an enhanced selective photo-oxidation of BaP over BeP in
8 hot seasons.

9 The current concentrations of PAHs are around one third of those reported by a previous
10 study on Nanjing aerosols collected in 2001 (annual concentration was 214 ng m^{-3}) (Yang et al.,
11 2005), suggesting an improvement of the local air quality. One of potential reasons is that the
12 local government eliminated the two-stroke motor-cycle for personal traffic, which emitted
13 tremendous amount of dirty exhausts because in its engine gasoline including lubricant oils were
14 burned at very low combustion efficiency (Wang et al., 2003). Moreover, more and more natural
15 gas is replacing coal for cooking and heating, and the number of diesel buses is decreasing due to
16 a new subway constructed recently. Therefore, the number of sources for PAHs is reducing in
17 Nanjing. Annual concentrations of PAHs in the city (63 ng m^{-3}) are comparable to those in
18 Qingdao (88 ng m^{-3}) (Guo et al., 2003b), but are much lower than those in Guangzhou (234 ng
19 m^{-3}) (Bi et al., 2003). PAHs in mainland China are much more abundant than in Hong Kong (23
20 ng m^{-3}) (Guo et al., 2003a), Los Angeles (12 ng m^{-3}) (Rogge et al., 1993) and London (17 ng m^{-3})
21 (Baek et al., 1992). Additionally, it should be noted that concentrations of volatile organic
22 compounds and nitrogen oxides are sharply increasing in Chinese urban areas due to the fast

1 growth in the number of motor vehicles, although NO_x emissions are constant in North America
2 and decreasing in Europe (Akimoto, 2003; Richter et al., 2005).

3 To assess the different sources of PAHs present in the examined aerosol samples, relative
4 concentrations of IP to BghiP and BghiP to BeP were compared for the samples studied and
5 shown in Table 2. Several studies (Grimmer et al., 1983; Zheng and Fang, 2000; Yassaa et al.,
6 2001) reported that the concentration ratios of IP/BghiP are attributable to different emission
7 sources. The ratios close to 0.22, 0.50 and 1.3 are typically indicative of gasoline, diesel and coal
8 sources, respectively. In our study, IP/BghiP was 1.2 ± 0.3 in summer versus 1.4 ± 0.3 in winter,
9 indicating that coal burning is the major source of PAHs. Furthermore, the average ratio in
10 nighttime was slightly lower than in daytime (see Table 2), which can be explained by an
11 additional emissions from heavy-duty diesel trucks that are only allowed to work in nighttime in
12 the city. Ohura et al. (2004) reported that the relative concentrations of BghiP/BeP in emissions
13 from gasoline and coal combustions are 2.0 and 0.8, respectively. From Table 2, it is clear that
14 BghiP/BeP ratios in winter (1.1 ± 0.4) are lower than those in summer (1.4 ± 0.2). The ratios are
15 close to that of coal burning emission, further suggesting that PAHs in Nanjing are mainly
16 derived from coal burning, especially in winter.

17 Actually, coals are commonly used in Chinese families for house cooking and heating in
18 both rural and urban areas, in which combustion efficiency is very low. Around 5000 tons of
19 PAHs were emitted annually in China from the combustion of household honeycomb-briquette
20 that are made of coal, in which benzo(*b,k*)fluoranthene gives the highest emission factor (Chen et
21 al., 2005). That is the reason why BbF is dominant in Nanjing samples. BbF was also reported as
22 the predominant particle-associated PAH in previous studies on Chinese continental (Guo et al.,
23 2003b; Wang et al., 2005; Yang et al., 2005) and coastal marine aerosols (Simoneit et al., 2004)

1 and the soot deposits from Chinese household coal-burning stoves (Wornat et al., 2001).
2 Therefore, it can be proposed that BbF is a dominant PAH in atmospheric aerosols all over China,
3 which is different from the cases in any other countries, where BghiP is the most abundant solid
4 phase PAH due to the emissions from vehicular engines.

5 Aerosol data from Hong Kong suggest that BbF is the dominant PAH in cold seasons,
6 whereas BghiP is the most abundant PAH in hot seasons. In fact, PAHs in Hong Kong are
7 mainly derived from local vehicular exhaust in summer. However, northerly and northwesterly
8 winds dominate over Hong Kong in winter, transporting PAHs that are influenced by coal
9 burning from mainland China. In contrast, easterly and southeasterly winds prevail in summer
10 and bring a relatively clean oceanic air over Hong Kong. Thus, unlike PAHs in winter aerosols
11 dominated by BbF, PAHs in Hong Kong summer aerosols are dominated by BghiP. Such a
12 seasonal changes in the PAH compositions obtained in Hong Kong could be a strong evidence to
13 support our proposal that BbF is a dominant PAH in Chinese aerosols, which can be thought as a
14 fingerprint for coal burning in China.

15 *3.2 Hopanes*

16 Hopanes are pentacyclic hydrocarbons of the triterpene group that are believed to derive
17 primarily from bacteriohopanols in bacterial membranes and to produce in sediments over
18 geological time (Oros and Simoneit, 1999). They are abundant in crude oils and enriched in
19 lubricant oil fraction. A series of hopanes were detected in the samples studied (see Table 1) with
20 higher concentrations in winter ($8.6 \pm 4.3 \text{ ng m}^{-3}$) and lower concentrations in summer (4.7 ± 3.0
21 ng m^{-3}), which is probably caused by coal burning for house heating and inversion layer in cold
22 seasons. Diurnal variations showed higher concentrations of hopanes at night in both seasons.
23 The current concentrations are about 20% of those in 2001 reported by the previous study (Yang

1 et al., 2005) due to the same reason mentioned above. As shown in Figure 3, 17 α (H),21 β (H)-30-
2 norhopane (C₂₉ $\alpha\beta$) and 17 α (H),21 β (H)-30-hopane (C₃₀ $\alpha\beta$) are the most abundant hopanes,
3 followed by 17 α (H),21 β (H)-22S-homohopane (C₃₁ $\alpha\beta$ S) and 17 α (H),21 β (H)-22R-homohopane
4 (C₃₁ $\alpha\beta$ R), which is consistent with the results reported by Yang et al (2005). In addition to
5 being emitted during coal combustion process, hopanoid hydrocarbons (C₂₇–C₃₅) that are
6 abundant in lubricant oils are also emitted into the air from internal combustion engines
7 (Simoneit and Mazurek, 1982; Kawamura et al., 1995). Concentrations of hopanes in Nanjing
8 city are comparable to those reported from Tokyo in 1988–1989 (0.7–15 ng m⁻³, average, 5.5 ng
9 m⁻³) (Kawamura et al., 1995).

10 Hopanoid hydrocarbons are specific biomarkers of petroleum (Simoneit, 1984; Peters and
11 Moldowan, 1993) and coal (Oros and Simoneit, 2000). Diagnostic ratios of hopanes (i.e. C₂₉ $\alpha\beta$ /
12 C₃₀ $\alpha\beta$, C₃₁[S/(S+R)] and C₃₂[S/(S+R)]) from vehicular exhausts and coal burning emissions are
13 listed in Table 2. The three ratios for Nanjing aerosols are closer to those in vehicular exhausts
14 than in coal burning emissions, indicating that hopanes in the samples are more attributable to
15 traffic emissions than coal burning.

16 3.3 Phthalates

17 Phthalates are widely used plasticizers in the polyvinyl chloride (PVC) and other plastic
18 materials. These additives can be released into the air from the matrix by evaporation because
19 they are not chemically bonded to the polymer. Emission rates of phthalates increase as a
20 function of temperature (Fujii et al., 2003). Phthalates that are ubiquitous in atmospheric
21 environment are carcinogenic and endocrine-disrupting (Sidhu et al., 2005; Swan et al., 2005).
22 To our knowledge, however, there is no information about phthalates in Chinese aerosols. This is
23 the first time to report the concentrations of solid-phase phthalates in the atmosphere. Three

1 kinds of phthalates were detected in the aerosols with total concentrations of 230 ng m^{-3} (range,
2 $109\text{--}368 \text{ ng m}^{-3}$) in the summer and 170 ng m^{-3} in the winter ($33\text{--}390 \text{ ng m}^{-3}$). The higher values
3 in the summer indicate their enhanced evaporation under high ambient temperature. Bis(2-
4 ethylhexyl) phthalate is predominant, accounting for more than 50% of total phthalates (see
5 Table 1), whereas diisobutyl and di-*n*-butyl phthalates are less abundant. Phthalates in Nanjing
6 aerosols are 1-2 orders of magnitude more abundant than those reported from Texas and Kansas,
7 USA (2.1 ng m^{-3}) (Weschler, 1984), Sweden (3.7 ng m^{-3}) (Thuren and Larsson, 1990) and Paris,
8 France (8.2 ng m^{-3}) (Teil et al., 2006), suggesting a serious air pollution in Nanjing urban area
9 and the potential adverse health impact on local population. Among the three phthalates,
10 diisobutyl and di-*n*-butyl phthalates are linearly correlated well ($r^2 = 0.86$, $p > 0.01$), suggesting
11 their common source.

12 *3.4 Hydroxylated PAHs*

13 Unlike PAHs, very little attention has been paid to hydroxylated PAHs (OH-PAHs),
14 although these compounds are more toxic than the corresponding PAHs due to their direct-
15 carcinogenicity (Dong et al., 2000; Finlayson-Pitts and Pitts Jr., 2000). OH-PAHs in atmosphere
16 can be the results of direct emission from combustion sources, such as diesel engines, and/or
17 formation in the atmosphere by the hydroxyl radical oxidation of PAHs (Atkinson et al., 1987).

18 Totally, 10 OH-PAHs were detected in the Nanjing samples (see Table 1 and Figure 4).
19 In general, these PAH derivatives are 1–3 orders of magnitude less abundant than their parent
20 PAHs. Concentrations of total OH-PAHs in winter (average, 214 pg m^{-3}) are twice higher than
21 those in summer (78 pg m^{-3}), which is probably resulted from the higher level of PAH precursors
22 and the accumulation process of inversion layers. In addition, hydroxylated PAHs are less stable
23 than their parent PAHs and can be easily degraded under high ambient temperature, leading to

1 their lower abundance in summer than in winter. 2-Hydroxyl-9-fluorenone, 1-hydroxyl-
2 benz(*a*)anthracene, 12-hydroxyl benzo(*a*)pyrene and 11-hydroxybenz(*b*)fluoranthene are major
3 components in both seasons, whereas others are minor (Table 1). In general, concentrations of
4 the major OH-PAHs are around 20 pg m⁻³ in summer and 50 pg m⁻³ in winter. There is no
5 significant linear correlation between the concentrations of the OH-PAHs and their parent PAHs,
6 because their abundances in the air are determined by many factors such as temperatures,
7 meteorological conditions, oxidant concentrations and their ambient lifetimes.

8 Although very few studies on hydroxy-PAHs in the atmosphere have been documented,
9 our results agree with the previously published values. For instance, Galceran et al. (1995)
10 reported that annual concentration of 2-hydroxy-9-fluorenone in aerosols from Barcelona, Spain
11 was 3–75 pg m⁻³. Nishioka et al. (1988) reported concentrations for hydroxy-nitro-PAHs in
12 urban air particulate extracts between 10 and 600 pg m⁻³. However, all the published studies
13 were limited to the measurement of the lower molecular weight hydroxy-PAHs containing 3
14 rings or less. In the current work, we report for the first time the atmospheric high molecular
15 weight hydroxy-PAHs with 4- or 5-ring (e.g., 1-hydroxylbenz(*a*)anthracene (4-ring), 11-
16 hydroxybenzo(*b*)fluoranthene (5-ring)) (Table 1).

17 **4. Conclusion**

18 PAHs, hopanes, phthalates and hydroxylated PAHs in PM_{2.5} aerosols from Nanjing were
19 characterized on a molecular level, along with their diurnal and seasonal variations. BbF was
20 found to be the dominant PAH in all the samples. Based on this study, together with the previous
21 reports on PAH compositions in aerosols from different Chinese regions and different Chinese
22 coal emissions, we propose that BbF is the most abundant solid-phase PAH in the atmosphere all
23 over China, and thus BbF can be used as a fingerprint compound for coal burning in the country.

1 PAH concentrations in Nanjing are still much higher than those in some cities in
2 developed countries, although the current levels become lower due to the replacing of coal by
3 some clean energy sources and the upgrading of the municipal traffic system. Diagnostic ratios
4 of the PAHs demonstrate that emission from coal burning is the main sources in the urban area.
5 However, hopanes in the aerosols are more attributable to the traffic emissions. Phthalates in the
6 Chinese aerosols are found to be 1–2 orders of magnitude more abundant than those in
7 developed countries, further suggesting that air pollution is still serious in the city, and an impact
8 on the local human health is probably significant. Additionally, a wide range of hydroxy-PAHs
9 (2- to 5- ring) were detected in Nanjing aerosols. PAHs, hopanes and OH-PAHs are more
10 abundant in winter than in summer not only due to the accumulation process of inversion layers
11 but also due to more coal burning for house heating in the cold season. In contrast,
12 concentrations of phthalates are higher in summer than in winter due to the enhanced evaporation
13 and the subsequent deposition on the pre-existing particles during summer. In general, the
14 quantified compounds are more abundant in nighttime than in daytime due to the emissions from
15 the heavy-duty trucks and the inversion layers.

16

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Table 1. Statistic summary for concentrations of anthropogenic compounds in Nanjing aerosols, ng m⁻³

	summer				winter			
	daytime (n=7)		nighttime (n=7)		daytime (n=7)		nighttime (n=7)	
	range	mean	range	mean	range	mean	range	mean
I. PAHs (abbreviation)								
Phenanthrene (Phe)	0-0.7	0.2 ± 0.2	0-0.7	0.2 ± 0.3	0-1.8	0.3 ± 0.7		
Anthracene (Ant)	0-0.5	0.2 ± 0.2	0-0.8	0.3 ± 0.3	0-1.9	0.3 ± 0.7		
Fluoranthene (Fluor)	0.1-2.2	1.0 ± 0.7	0.4-1.8	1.2 ± 0.5	0.8-7.9	2.1 ± 2.6	0.5-18	4.2 ± 6.4
Pyrene (Pyr)	0.5-2.1	1.0 ± 0.6	0.4-1.7	1.1 ± 0.5	1.5-9.1	5.7 ± 2.4	2.0-19	10 ± 7.0
Benz(<i>b</i>)fluorenen (BF)					0-5.8	0.8 ± 2.2		
Benz(<i>a</i>)anthracene (BA)	0-0.7	0.2 ± 0.3	0-2.6	0.9 ± 1.1	0-13	4.0 ± 4.2	0-16	7.8 ± 5.7
Chrysene/triphenylene (Chr/Tr)	0.5-5.3	1.8 ± 1.6	0.6-4.6	2.3 ± 1.4	3.3-8.9	6.7 ± 1.9	3.4-19	10 ± 5.8
Benzo(<i>b</i>)fluoranthene (BbF)	4.1-38	12 ± 12	5.0-36	22 ± 13	14-43	29 ± 11	11-69	41 ± 23
Benzo(<i>e</i>)pyrene (BeP)	0.6-6.0	1.7 ± 1.9	0.9-5.9	3.4 ± 2.0	1.8-6.2	3.4 ± 1.5	0.9-8.5	4.9 ± 3.0
Benzo(<i>a</i>)pyrene (BaP)	0.6-5.6	1.7 ± 1.8	0.6-5.1	2.8 ± 1.8	2.1-6.7	4.4 ± 1.6	2.2-12	6.4 ± 3.6
Perylene (Per)	0.1-1.3	0.4 ± 0.4	0.1-1.7	0.6 ± 0.6	0-0.9	0.3 ± 0.4	0-2.6	1.3 ± 0.8
Indeno(1,2,3- <i>cd</i>)pyrene (IP)	1.1-12	3.3 ± 4.0	1.5-11	5.0 ± 4.2	1.8-11	5.5 ± 3.1	2.1-15	7.1 ± 5.4
Dibenz(<i>a,h</i>)anthracene (DBA)	0.1-2.2	0.6 ± 0.7	0.2-9.3	2.4 ± 3.4	0.5-2.0	0.9 ± 0.5	0.2-3.1	1.4 ± 1.0
Benzo(<i>ghi</i>)perylene (BghiP)	0.9-10	2.7 ± 3.3	1.2-9.4	4.9 ± 3.4	1.0-9.4	4.0 ± 2.7	1.8-12	5.4 ± 3.7
Anthanthrene (Anta)	0.1-1.0	0.3 ± 0.3	0.1-0.7	0.4 ± 0.2	0-0.5	0.2 ± 0.2	0-3.3	1.1 ± 1.1
Coronene (Cor)	0.4-6.5	1.8 ± 2.1	1.0-6.1	3.3 ± 2.2	0-6.2	1.9 ± 2.1	0.7-7.0	2.7 ± 2.4
Dibenzo(<i>a,e</i>)pyrene (DBP)	0-3.2	0.6 ± 1.2						
Subtotal	12-96	29 ± 30	13-87	50 ± 30	38-96	69 ± 21	26-178	104 ± 63
II. Hopananes (abbreviation)								
17α(H)-22,29,30-Trisnorhopane (C ₂₇ α)	0.1-0.3	0.1 ± 0.1	0.1-0.4	0.2 ± 0.1	0.4-0.7	0.5 ± 0.1	0.2-1.4	0.7 ± 0.4
17β(H)-22,29,30-Trisnorhopane (C ₂₇ β)	0-0.2	0.1 ± 0.1	0-0.5	0.1 ± 0.2	0.1-2.8	0.6 ± 1.0	0.1-0.4	0.2 ± 0.1
17α(H)21β(H)-30-Norhopane (C ₂₉ αβ)	0.2-0.6	0.3 ± 0.1	0.5-2.1	1.2 ± 0.5	0.4-1.9	1.1 ± 0.5	0.6-3.5	2.0 ± 1.0
17β(H),21α(H)-30-Norhopane (C ₂₉ βα)	0-0.1	0.1 ± 0.1	0-0.2	0.1 ± 0.1	0.2-4.5	0.9 ± 1.6	0.1-0.7	0.4 ± 0.2
17α(H),21β(H)-Hopane (C ₃₀ αβ)	0.4-1.1	0.7 ± 0.2	0.9-3.7	2.1 ± 0.9	0.4-3.0	1.6 ± 0.7	0.9-5.5	3.0 ± 1.6
17β(H),21α(H)-Hopane (C ₃₀ βα)	0-0.1	0.1 ± 0.1	0.1-0.5	0.3 ± 0.1	0.2-0.7	0.3 ± 0.2	0.2-0.6	0.4 ± 0.2
17α(H),21β(H)-22 <i>S</i> -Homohopane (C ₃₁ αβ <i>S</i>)	0.2-0.7	0.3 ± 0.2	0.4-1.3	0.9 ± 0.3	0.5-1.0	0.7 ± 0.2	0.3-1.9	1.1 ± 0.6
17α(H),21β(H)-22 <i>R</i> -Homohopane (C ₃₁ αβ <i>R</i>)	0.2-0.5	0.3 ± 0.1	0.3-0.9	0.7 ± 0.2	0.3-0.7	0.4 ± 0.1	0.2-1.3	0.7 ± 0.4
17β(H),21α(H)-Homohopane (C ₃₁ βα)	0-0.2	0.1 ± 0.1	0.1-0.4	0.3 ± 0.1	0.1-0.7	0.2 ± 0.2	0.1-0.4	0.2 ± 0.1
17α(H),21β(H)-22 <i>S</i> -Bishomohopane (C ₃₂ αβ <i>S</i>)	0.2-0.5	0.3 ± 0.1	0.3-1.0	0.7 ± 0.2	0.3-0.7	0.5 ± 0.1	0.2-1.2	0.6 ± 0.3
17α(H),21β(H)-22 <i>R</i> -Bishomohopane (C ₃₂ αβ <i>R</i>)	0.1-0.5	0.2 ± 0.1	0.2-0.8	0.5 ± 0.2	0.3-0.6	0.4 ± 0.1	0.2-1.2	0.6 ± 0.3
Subtotal	1.6-4.6	2.7 ± 1.0	3.0-11	7.1 ± 2.7	4.8-13	7.3 ± 2.8	3.0-18	9.9 ± 5.3
III. Phthalates								
Diisobutyl phthalate	2.8-43	14 ± 17	1.0-49	9.7 ± 19	7.5-31	13 ± 8.5	4.6-27	15 ± 7.7
Di- <i>n</i> -butyl phthalate	5.2-89	26 ± 32	1.8-64	14 ± 25	6.4-26	12 ± 6.8	3.4-34	16 ± 11
Bis(2-ethylhexyl) phthalate	95-357	175 ± 92	128-253	228 ± 104	57-333	132 ± 96	25-247	151 ± 82
Subtotal	109-368	216 ± 84	136-358	252 ± 93	72-390	158 ± 111	33-301	181 ± 99
IV. Hydroxylated PAHs^a								
2-Hydroxynaphthaquinone			0-25	9 ± 11	1-9	6 ± 4	0-3	1 ± 2
9-Hydroxylfluorene	2-14	7 ± 6	0-6	2 ± 2	0-5	2 ± 3	0-5	2 ± 3
2-Hydroxylfluorene	0-12	4 ± 7			0-30	10 ± 17	0-108	42 ± 58
9-Hydroxylphenanthrene	0-5	3 ± 2	0-6	2 ± 3	0-6	3 ± 3	0-161	54 ± 93
2-Hydroxyl-9-fluorenone	0-8	3 ± 4	2-51	27 ± 20	27-50	38 ± 11	13-110	55 ± 50
1-Hydroxypyrene	0-3	1 ± 1			0-17	6 ± 9	0-16	5 ± 9
1-Hydroxylbenz(<i>a</i>)anthracene	10-15	13 ± 3	7-22	13 ± 7	21-42	34 ± 11	0-23	13 ± 12
2-Hydroxylchrysene	0-12	6 ± 6	0-7	3 ± 3	22-27	26 ± 2	0-17	7 ± 9
12-Hydroxylbenzo(<i>a</i>)pyrene	0-65	31 ± 33			43-115	78 ± 36	0-55	26 ± 27
11-Hydroxylbenzo(<i>b</i>)fluoranthene	0-4	1 ± 2	0-90	30 ± 40	0-7	2 ± 5		
Subtotal	29-99	69 ± 36	42-171	87 ± 59	179-250	220 ± 37	13-421	208 ± 205
Total	131-389	247 ± 81	176-453	309 ± 119	144-478	234 ± 120	61-496	295 ± 163
PM _{2.5} mass, μg m ⁻³	56-187	128 ± 58	43-176	135 ± 48	97-162	124 ± 22	40-153	113 ± 42
Total/PM _{2.5} mass, %	0.1-0.5	0.2 ± 0.1	0.1-0.6	0.3 ± 0.2	0.1-0.4	0.2 ± 0.1	0.2-0.4	0.3 ± 0.1

^a Unit of hydroxylated PAH is pg m⁻³

Table 2. Diagnostic ratios of biomarkers for source identification of anthropogenic aerosols in Nanjing

	this study				gasoline		diesel	coal
	summer		winter		nongasoline	catalyst		
	daytime	nighttime	daytime	nighttime				
IP/BghiP	1.2 ± 0.1	1.1 ± 0.4	1.5 ± 0.2	1.3 ± 0.4	0.22 ^a		0.50 ^a	1.3 ^a
BghiP/BeP	1.5 ± 0.1	1.4 ± 0.2	1.1 ± 0.3	1.2 ± 0.4	2.0 ^b			0.8 ^c
C ₂₉ αβ/C ₃₀ αβ	0.50 ± 0.05	0.56 ± 0.09	0.71 ± 0.07	0.67 ± 0.05	0.59 ^d	0.66 ^d	0.42 ^d	0.58-2.0 ^e
C ₃₁ [S/(S+R)]	0.56 ± 0.03	0.57 ± 0.01	0.61 ± 0.07	0.60 ± 0.03	0.60 ^d	0.62 ^d	0.50 ^d	0.05-0.37 ^e
C ₃₂ [S/(S+R)]	0.54 ± 0.04	0.58 ± 0.02	0.52 ± 0.05	0.51 ± 0.03	0.57 ^d	0.58 ^d	0.59 ^d	0.17-0.41 ^e

^a data including nongasoline and catalyst vehicles and cited from Grimmer et al. (1983); ^b data including gasoline and diesel and cited from Ohura et al. (2004); ^c data cited from Ohura et al. (2004); ^d data cited from Rogge et al. (1993a); ^e data cited from Oros and Simoneit (2000).

Figure Captions

Figure 1. Diurnal and seasonal variations of anthropogenic aerosols in Nanjing

Figure 2. Molecular distributions of PAHs during the summer and winter

Figure 3. Molecular distributions of hopanes during the summer and winter

Figure 4. Chemical structures of hydroxylated PAHs identified in the study

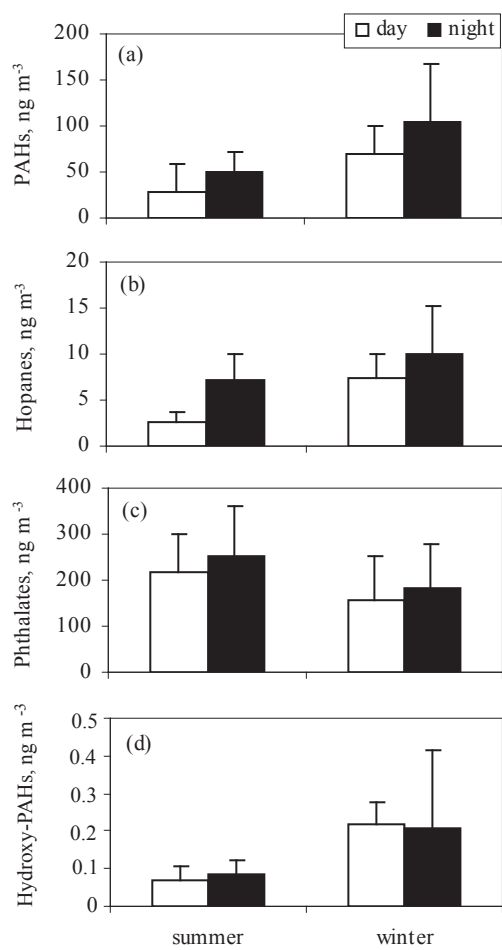


Figure 1(Wang et al.)

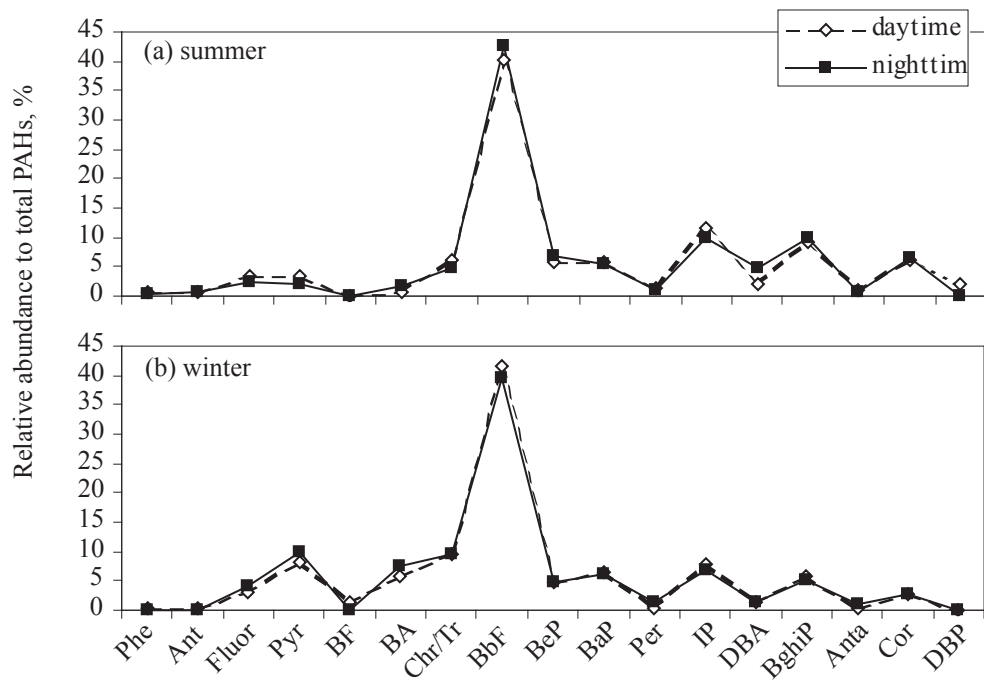


Figure 2 (Wang et al.)

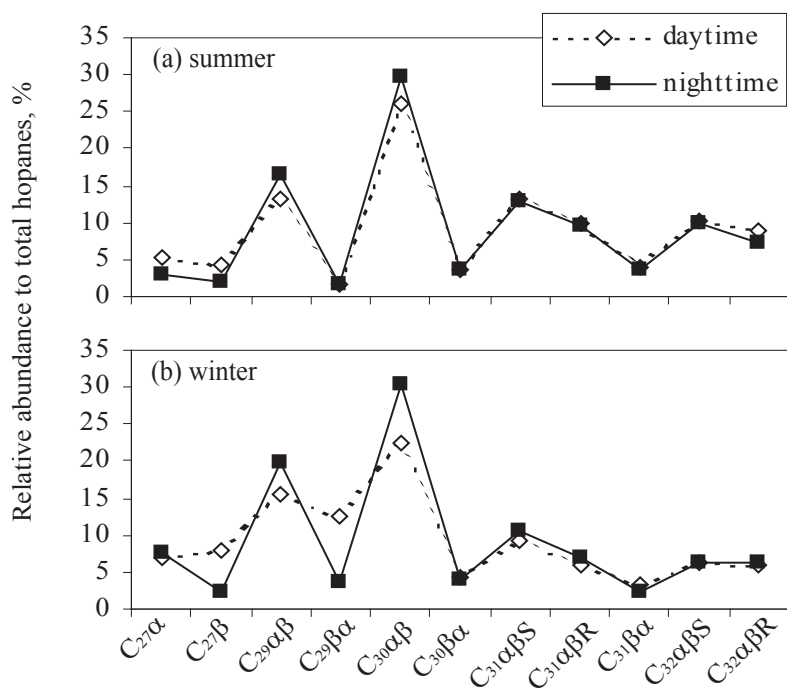


Figure 3 (Wang et al.)

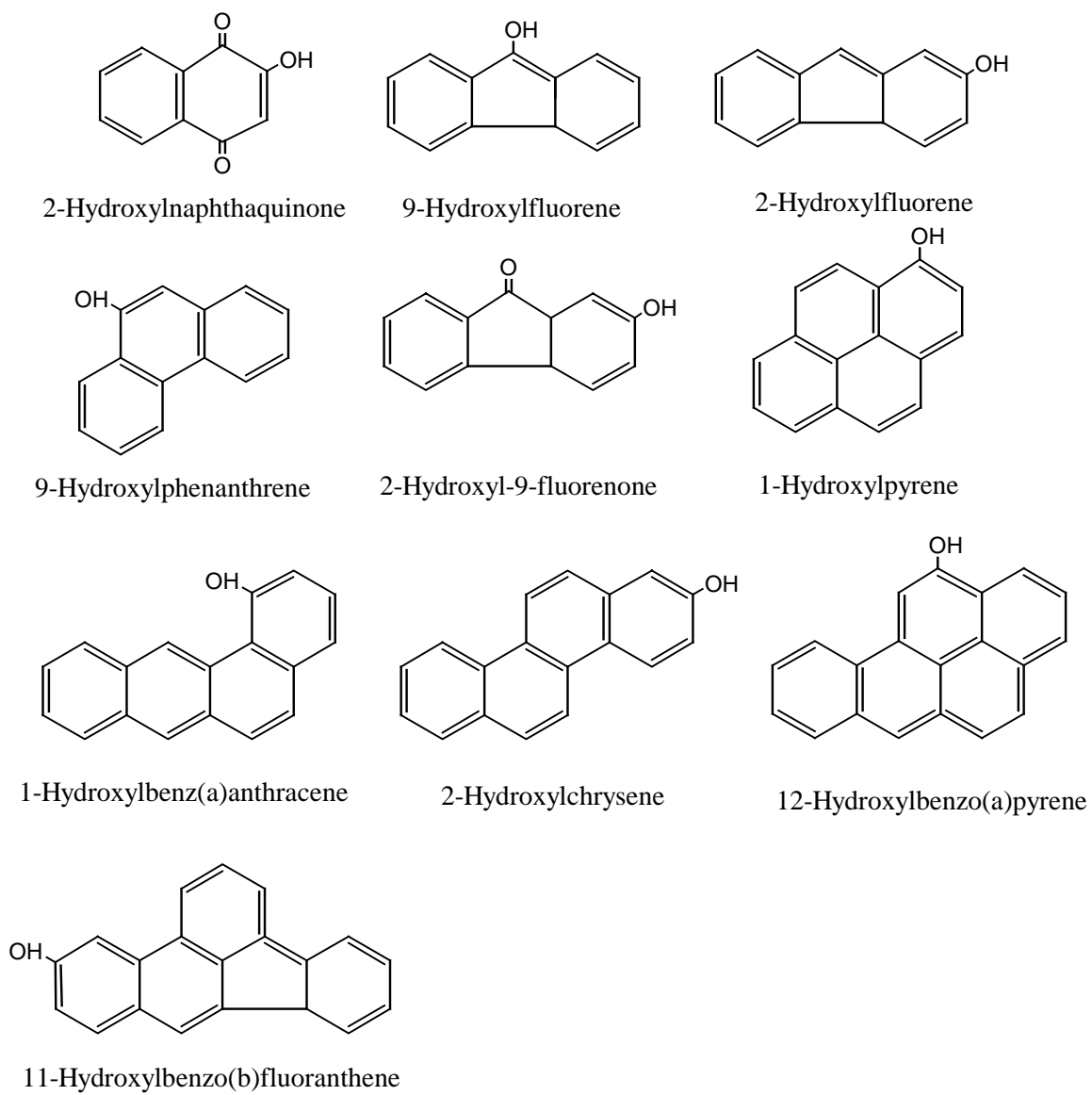


Figure 4 (Wang et al.)