



# Non-polar organic compounds in aerosols in a typical city of Eastern China: Size distribution, gas-particle partitioning and tracer for PM<sub>2.5</sub> source apportionment

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**Abstract.** Aerosol-associated non-polar organic compounds (NPOCs), including 15 polycyclic aromatic hydrocarbons (PAHs), 30 n-alkanes, 2 iso-alkanes, 5 hopanes and 5 steranes, were identified and quantified in PM<sub>2.5</sub> samples using thermal desorption–gas chromatography/mass spectrometry (TD-GC/MS) method. The samples were collected in a typical city of Eastern China. The total concentrations of NPOCs were 31.7–388.7 ng m<sup>-3</sup>, and n-alkanes were the most abundant species (67.2%). The heavy molecular weight PAHs (4- and 5-ring) contributed 67.88% of the total PAHs, and the middle chain length n-alkanes (C<sub>25</sub>–C<sub>34</sub>) were the most abundant in n-alkanes. PAHs and n-alkanes were majorly distributed in 0.56–1.00 μm fraction. Σ(hopanes+steranes) were associated with the 0.32–1.00 μm fraction. Analysis showed that 83.0% of NPOCs were originated from anthropogenic sources, especially pyrogenic sources such as fossil fuel combustion and biomass burning. The ratio–ratio plots indicated that NPOCs in local area were affected by photochemical degradation and emissions from mixed sources. Gas-particle partitioning model showed that the particle-phase fraction (φ) of light molecular weight NPOCs ranged from 2.4% to 62.5%, while that of heavy NPOCs accounted for more than 90.0%. The data based on single particle phase and the data based on gas-particles phases incorporated with other PM<sub>2.5</sub> compounds were used as input data for positive matrix factorization (PMF) model, respectively. Eight factors were extracted for both cases: secondary aerosol formation, vehicle exhaust, industrial emission, coal combustion, biomass burning, ship emission, dust and light NPOCs. This study provides new information on the profiles of PM<sub>2.5</sub>-associated NPOCs, size-specific distributions, photodegradation and their gas-particle partitioning. This will help us accurately identify the potential sources of aerosols and then assess the contributions from each source.



## 29 1. Introduction

30 In recent years, severe atmospheric pollution characterized by haze has been occurring in developing countries (Yadav et  
31 al., 2013; Wang et al., 2015), affecting visibility, optical radiation and human health (Shen et al., 2015; Sulong et al., 2017).  
32 China has experienced numerous severe and long-lasting haze episodes since winter in 2013, which has affected over 600  
33 million local residents and covered a quarter of the country's land area (Huang et al., 2014; Hao and Liu, 2015). In  
34 essence, haze episode is caused by the distribution of particle matters with different sizes in atmosphere, leading to  
35 decrease in visibility (Xie et al., 2017). Carbonaceous aerosols contain a large amount of particle matters, accounting for  
36 30–50% of PM<sub>2.5</sub> mass concentrations (Yadav et al., 2013; Wang et al., 2016). Carbonaceous aerosols have significant  
37 influence on environmental and physical processes, including dry/wet deposition, cloud condensation nucleation, and  
38 heterogeneous reactions (Li et al., 2017; Feng et al., 2006).

39 Since carbonaceous aerosols can affect ambient environment significantly, it is crucial to investigate aerosol-associated  
40 organic compounds. Because non-polar organic compounds (NPOCs) can provide specific information on the  
41 identification of aerosol sources (Rajput and Sarin, 2014; Wang et al., 2016), they are now of special interest to  
42 researchers. n-Alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes are four typical NPOC species,  
43 and are frequently used to apportion sources of ambient particulate matters (Xu et al., 2013; Zhao et al., 2016). n-Alkanes  
44 are emitted from natural and anthropogenic activities, including particulate abrasion products from leaf surfaces of  
45 vegetation and fossil fuel combustion. Notably, fossil fuel combustion is characterized by the release of C<sub>22</sub>–C<sub>25</sub>  
46 n-alkanes, while particulate abrasion products from leaf surfaces is characterized by the predominance of >C<sub>29</sub> odd  
47 n-alkanes (Yadav et al., 2013). PAHs are mainly emitted from anthropogenic activities, including biomass burning, coal  
48 combustion, fossil fuel combustion and industrial processes (Ma et al., 2011; Zhang et al., 2015). Hopanes and steranes  
49 are from unburned fossil fuels and lubricant oils, and they are often found in vehicle exhausts, ship emissions and coal  
50 combustion emissions.

51 PAHs are typical semi-volatile organic compounds, which can partition between gas and particle phases in ambient  
52 atmosphere (Ma et al., 2011; He and Balasubramanian, 2009). The gas-particle partitioning behavior of semi-volatile  
53 organic compounds can be used in their removal process, which is performed through wet/dry deposition, long-range  
54 transport and reaction with atmospheric oxidant. Recently, research has shown that n-alkanes, hopanes and steranes are  
55 also semi-volatile and subject to gas-particle partitioning (Xie et al., 2013; Xie et al. 2014; Wang et al., 2016). Furthermore,  
56 lighter, more volatile compounds show larger partitioning tendency. Additionally, another crucial factor affecting  
57 particle-bound concentrations of NPOCs is their aerodynamic diameter (Wang et al., 2009). The size-specific



distributions of compounds are dependent on their physical-chemical properties, gas-particle partitioning and photodegradation (Okonski et al., 2014; Chen et al., 2016b). Thus, characterization of the size-specific distribution of NPOCs is crucial for understanding their formation, assessing their possible environmental fate and offering proper management (Kleeman et al., 2008; Wang et al., 2009). Although several studies (Hien et al., 2007; Wang et al., 2009) have focused on the size distribution of PAHs, much less attention has been given to other NPOC species.

NPOCs are typically assumed to be stable and nonreactive (Feng et al., 2006; Ma et al., 2011). However, recent research (Xie et al., 2013; Wang et al., 2016) has shown that NPOCs can be oxidized by  $\cdot\text{OH}$  radicals,  $\text{RO}_2\cdot$  radicals and  $\text{O}_3$  over atmospherically relevant time scales. PAHs, n-alkanes, hopanes and steranes can undergo photochemical oxidation, increasing the production of secondary organic aerosol (Robinson et al., 2006; May et al., 2012). For example, PAHs can react with  $\cdot\text{OH}$  radicals, and through adding carbonyl groups to the carbon skeleton, the free ends of C-C scission products remain tethered together, which prevents fragmentation and leads to more functional groups on the single product (May et al., 2012). Hence, the low-volatility species which can condense into particle phase are formed, and subsequently undergo oligomerization reactions following condensation.

To develop strategies for controlling atmospheric pollution caused by particulate matter, receptor-based models (e.g., positive matrix factorization, PMF) have been widely applied to quantitatively apportion sources of particulate matter (Wang et al., 2009; Li et al., 2016; Huang et al., 2017). However, the output factors of receptor model are not necessarily emission sources, because there exist some atmospheric processes like photodegradation or gas-particle partitioning. Considering the gas-particle partitioning of NPOCs, Xie et al. (2013) adopted both gaseous and particulate NPOCs in PMF model and successfully extracted seven factors. More recently, Wang et al. (2016) used data of NPOCs combined with those of organic/elemental compounds (OC/EC), inorganic compounds and elemental compounds as input for PMF model, and they found that total (gas+particle) bound concentrations enabled more reasonable source profiles than single particle phase.

In this paper, we conducted a comprehensive study on  $\text{PM}_{2.5}$ -associated NPOCs in a typical city of Eastern China. Specifically, we: (1) quantified the concentrations of NPOCs (n-alkanes, PAHs, hopanes and steranes) through thermal desorption–gas chromatography/mass spectrometry (TD–GC/MS) method; (2) determined the size-specific distributions of NPOCs from 0.01 to 18  $\mu\text{m}$ ; (3) analyzed the degradation of NPOCs; (4) explored the gas-particle partitioning of NPOCs and assessed its effects on  $\text{PM}_{2.5}$  source apportionment.



## 85 2. Materials and methods

### 86 2.1 Sampling sites and sample collection

87 Jiujiang city is located in 113°57'–116°53' E and 28°47'–30°06' N with elevation of 32 m in Jiangxi Province of Eastern  
 88 China. It is characterized by a subtropical monsoon climate. Jiujiang is the second largest city in Jiangxi Province, with  
 89 approximately 4.83 million resident population and over 700 thousand motor vehicles in 2015. Preliminary statistics  
 90 indicate that the gross industrial standard coal consumption in Jiujiang amounted to 7.80 million tons in 2015. In Jiujiang,  
 91 petrochemical industry, which can process approximately five million tons of crude oil per year, is located at the  
 92 northeast part of the city and in upwind direction. In addition, Mount Lu (elevation of 1474 m), located at the south of  
 93 Jiujiang, blocks the transport of air masses from Northern China Plain region to southern area, leading to the  
 94 accumulation of particulate matters in the city area, especially in winter seasons.

95 Five PM<sub>2.5</sub> sampling sites were selected for routine air quality measurements in Jiujiang city (Table 1), including Shihua  
 96 (SH), Xiyuan (XY), Shili (SL), Wuqierqi (WQ) and Jiujiangxian (JJ). High-volume air samplers (YH-5, Qingdao, China)  
 97 loaded with a quartz fiber filter were used. Prior to use, they were prebaked at 550 °C for 4 h to eliminate residual organic  
 98 compounds. PM<sub>2.5</sub> sampling at these five sites were performed synchronously for five continuous days per month from  
 99 Sep. to Dec. 2016, in addition to the extensive sampling period (Dec. 1–16).

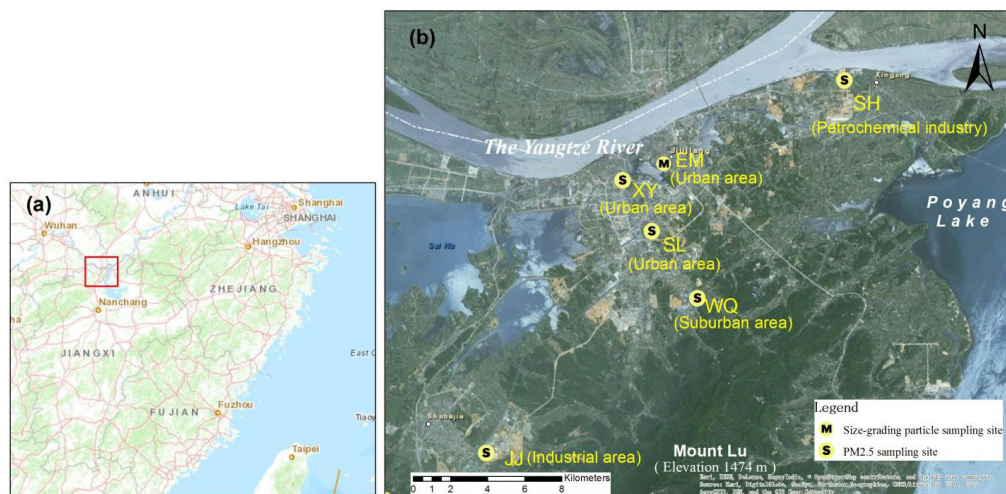
100 **Table 1.** Detailed description of the six sampling sites in this study

| Site | Type             | Surrounding area  | Height | Main pollutants        | Sampling time                                |
|------|------------------|---|--------|------------------------|--|
| SH   | Residential area | 1.7 km to petrochemical industry; 600 m to traffic road | ~12 m  | Petrochemical industry | Sep. 9-13; Oct. 11-15; Nov. 10-14; Dec. 1-16 |
| XY   | Urban area       | 500 m to traffic road; 1 km to wharf                    | ~23 m  | Vehicle; ship          | Sep. 9-13; Oct. 11-15; Nov. 10-14; Dec. 1-16 |
| SL   | Urban center     | 500 m to traffic road                                   | ~20 m  | vehicle                | Sep. 9-13; Oct. 11-15; Nov. 10-14; Dec. 1-16 |
| WQ   | Suburban area    | 1.3 km to the city center                               | ~17 m  | vehicle                | Sep. 9-13; Oct. 11-15; Nov. 10-14; Dec. 1-16 |
| JJ   | Industrial area  | Located in industrial area; 500 m to highway            | ~20 m  | Industry emission      | Sep. 9-13; Oct. 11-15; Nov. 10-14; Dec. 1-16 |
| EM   | Urban area       | 500 m to traffic road                                   | ~20 m  | vehicle                | Dec. 1-16                                    |

101 The sampling site of size-specific aerosols was located at a five-story building of Jiujiang Environmental Monitor  
 102 Station (EM site). Airborne particle samples were collected for 23 h using a Nano-Micro-orifice Uniform Deposition  
 103 Impactor (MOUDI) sampler (Model 122R, MSP Cor, USA), at air flow rate of 30 L/min. Detailed instrument operation,  
 104 quality assurance and control method can be found in our previous work (Chen et al., 2016b). Briefly, this sampler can  
 105 collect particles within 13 size fractions: 0.01–0.018, 0.018–0.032, 0.032–0.056, 0.056–0.1, 0.1–0.18, 0.18–0.32,



0.32–0.56, 0.56–1.0, 1.0–1.8, 1.8–3.1, 3.1–6.2, 6.2–9.9, 9.9–18  $\mu\text{m}$ . Prior to sampling, each filter tray was washed with distilled water and ethanol. Two kinds of quartz fiber filters (diameters of 47 and 90 mm, respectively) were prebaked at 550 °C for 4 h, wrapped in aluminum foil and then sealed in clean polyethylene bags. Leak and flow tests were conducted according to manufacturer's instructions: leak test was done with a duration of 60 s with leak rate < 10 Pa/s at initial pressure of  $55 \pm 5$  kPa. The mass concentrations of particle matters were determined by subtracting the filter weight before and after sampling. A well calibrated digital balance within a precision of 0.01 mg (Sartorius SE2, Germany) was used. The collected particle samples were stored at controlled temperature ( $-20$  °C) and relative humidity until analysis.



**Fig. 1.** Location of aerosol sampling sites in Jiujiang, Eastern China

## 2.2 Analysis of aerosol samples using TD–GC/MS

Fifty-seven NPOC species (Table S1) were identified by using an in-injection port thermal desorption union (TDU, Shimadzu, Japan), coupled with gas chromatography/mass spectrometer (GC/MS, QP2010 Plus, Shimadzu, Japan). Compared with traditional solvent extraction method, TD–GC/MS method (Ho and Yu, 2004; Ho et al., 2008) has advantages such as solvent and sample filtration, labor saving, and less contamination from solvent impurities. A filter aliquot (1 cm<sup>2</sup>) from quartz fiber was cut into small pieces on a clean glass dish, and then they were inserted into the TD tubes (CAMSCO, USA). Both sides of the samples were surrounded with pre-baked, silane-treated glass-wool plugs, to enhance the cryofocusing of the analytes and prevent heavy and polar compounds from entering the GC column. The sample processing time in TD tube was set to 45 min, and the TD tube was electronically cooled to  $-10$  °C. The desorption and interface temperatures were set to 295 and 280 °C, respectively. Helium (99.999%) was used as carrier gas for the thermally desorbed organic compounds, with gas flow rate of 1.12 mL/min. GC was used under splitless



126 injection mode, and the initial oven temperature was set to 40 °C with an isothermal hold time of 5 min. Stepwise  
127 programmed linear temperature ramping included 10 °C/min to 120 °C (held for 2 min), and then 20 °C/min to 300 °C  
128 (kept for 20 min). A Rtx-5MS capillary column (Restek, USA, L × I.D. 30 m × 0.25 mm, df 0.25 µm) was used to  
129 separate desorbed organic compounds. Mass range was m/z 50–500 and scanned at 0.5 s/scan. The ion was produced  
130 from electronic impact ionization (EI) at 70 eV, and then was separated by high performance quadrupole mass filter.

### 131 2.3 Determination of OC/EC and other constituents

132 OC and EC were analyzed (a round punch of 0.538 cm<sup>2</sup>) using the thermal–optical– transmittance (TOT) method  
133 (NIOSH protocol, Desert Research Institute, USA). The instrument included a temperature- and atmosphere-controlled  
134 oven and a laser of 680 nm wavelength to generate an operational EC/OC split. The instrument was heated stepwise from  
135 start to 250 °C (60 s), 500 °C (60 s), 650 °C (60 s) and finally 850 °C (90 s) in the helium atmosphere for OC  
136 volatilization, and from start to 550 °C (45 s), 650 °C (60 s), 750 °C (60 s) and finally 850 °C (80 s) in the helium  
137 atmosphere containing 2% oxygen for EC oxidation.

138 Elemental compositions, including Na, K, Ca, Mg, P, Fe, Ti, Al, Pb, Cu and Zn, were determined by energy dispersive  
139 X-ray fluorescence (ED-XRF) spectrometry (Epsilon 5, Netherlands). Water soluble inorganic ions, including cations  
140 (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>) and anions (Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>), were detected by ion chromatography (IC, ISC-90,  
141 Dionex, USA).

### 142 2.4 Quality assurance and quality control

143 Prior to sampling in each site, the five PM<sub>2.5</sub> samplers were calibrated by environmental monitor station. PM<sub>2.5</sub> samplers  
144 were placed on the rooftop at EM site with distance between any two samplers <3 m, collecting for 12 h, then the added  
145 mass was calculated. Field blanks were collected by keeping blank filters in the sampler for the same duration at  
146 sampling site. Additionally, both transport and laboratory blank filters were analyzed, and all the data reported in this  
147 study were corrected according to the results.

148 The internal standards of n-tetracosane d<sub>50</sub> (n-C<sub>24</sub>D<sub>50</sub>), naphthalene-d<sub>8</sub>, acpnaethene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, and  
149 chrysene-d<sub>12</sub> were spiked into each sample. This was done to account for the loss of components from sample filters  
150 associated with the instrument instability due to changes in laboratory environmental conditions. SRM 2260, SRM  
151 2260A and SRM 1494 (NIST, USA) were used as calibration standards for PAHs, n-alkanes and hopanes/steranes,  
152 respectively. Six-point calibration curves of NPOCs were constructed through adopting different calibration solutions,  
153 namely 0, 0.05, 0.25, 0.50, 1.0 and 2.0 µg L<sup>−1</sup> for PAHs, hopanes and steranes, while 0, 0.10, 1.0, 5.0, 10.0 and 20.0 µg



L<sup>-1</sup> for n-alkanes, to the field blank filters and loaded into TD tubes. Ratios of the average peak area values ‘A’ for represented samples ‘S’ to the corresponding internal standard ‘IS’, namely AS/AIS; and ratios of average concentration ‘C’ for represented samples to the corresponding internal standard (CS/CIS), were generated via using Shimadzu software with the slope of the curve being the RRF (relative response factor). The calibration curves for most target compounds were highly linear ( $r^2 > 0.99$ ), demonstrating the consistency and reproducibility of this method. The method detection limit (MDL) was determined at the 99% confidence level.

## 2.5 Diagnostic parameters and isomeric ratios

Different diagnostic parameters were adopted in this study to explore natural and anthropogenic contributions. The parameters include carbon preference index (CPI), the carbon number of the most abundant n-alkane ( $C_{max}$ ), contributions from natural wax n-alkanes (WNA%) and petrogenic n-alkanes (PNA%), higher plant n-alkane average chain length (ACL), and molecular diagnostic ratios (MDRs) for PAHs (Yadav et al., 2013; Zhao et al., 2016).

(1) CPI is defined as the ratio of the total concentration of odd n-alkanes to that of even n-alkanes (Eq. (1)). It reflects the comparison between natural and anthropogenic contributions.

$$CPI = \frac{\sum_{i=11}^{39} C_i}{\sum_{j=12}^{40} C_j} \quad (1)$$

where i and j represent odd and even carbon numbers, respectively, and C represent the concentrations of carbon n-alkanes.

(2) WNA% is calculated as Eq. (2). Note that negative value of  $[C_i - (C_{i-1} + C_{i+1})/2]$  was replaced by zero.

$$WNA\% = \frac{\sum WNA_{C_n}}{\sum NA_{C_n}} = \frac{\sum_{i=11}^{39} [C_i - (C_{i-1} + C_{i+1})/2]}{\sum_{n=11}^{40} C_n} \quad (2)$$

(3) Aerosol-associated n-alkanes can originate from plant wax or petroleum combustion, and the percentage of petrogenic n-alkanes (PNA%) can be calculated as:

$$PNA\% = 100\% - WNA\% \quad (3)$$

(4)  $C_{max}$  represents the carbon number of the most abundant n-alkane, and it is regarded as the most important indicator of biogenic inputs. In general,  $C_{max} = 31$  indicates effects from leaf abrasion products, whereas  $C_{max} = 29$  implies effects from road dust, as well as vehicle and industrial emissions.

(5) ACL can indicate emissions of n-alkanes from plants which are related to temperature and humidity. It is defined as counted carbon atoms per carbon molecule, depending on the odd n-alkanes from higher plant. ACL can be estimated through Eq. (4) as follows:





$$ACL = \frac{23 \cdot C_{23} + 25 \cdot C_{25} + \dots + 39 \cdot C_{39}}{C_{23} + C_{25} + \dots + C_{39}} \quad (4)$$

(6) MDRs for PAHs source apportionment include ANT/PHE ratio, PYR/FLU ratio, IcdP/BghiP ratios (namely, ANT/(ANT+PHE) ratio and FLU/(FLU+PYR) ratio), and IcdP/(IcdP+BghiP). If ANT/(ANT+PHE) < 0.1, petroleum origins are suggested; if the ratio > 0.1 pyrogenic sources are indicated. If FLU/(FLU+PYR) < 0.4, petroleum sources are suggested; if the ratio > 0.4, pyrogenic sources are indicated (Kuang et al., 2011; Chen et al., 2016a). Note that the ratio ranging from 0.4 to 0.5 also suggests fuel combustion. If 0.2 < IcdP/(IcdP+BghiP) < 0.5, fuel combustion is suggested; if the ratio > 0.5, grass, wood and coal combustion should have contributed to particulate matters (Chen et al., 2016a).

## 2.6 Gas-particle partitioning model

Gas-particle partitioning is an important mechanism that affects the fate and transport of NPOCs (Pankow, 1994; Kim et al., 2011). To understand the partitioning behavior of NPOCs, we evaluated the distribution of NPOCs between gas and particle phases in the atmosphere. The gas-particle coefficient  $K_p$  ( $\text{m}^3 \mu\text{g}^{-1}$ ) for each compound species was calculated using the following equations:

$$K_p = \frac{F/PM}{A} = \frac{R \cdot T}{10^6 \cdot MW_{OM} \cdot \xi_{OM} \cdot P_L^o} \quad (5)$$

$$P_L^o = P_{L,0}^o \cdot \exp \left[ \frac{\Delta H_0}{R} \left( \frac{1}{298} - \frac{1}{T} \right) \right] \quad (6)$$

where F and A represent the concentrations of NPOC in gas and particle phases ( $\text{ng m}^{-3}$ ), respectively; PM is the measured mass concentration of particulate matter, *i.e.*,  $\text{PM}_{2.5}$  in this study ( $\mu\text{g m}^{-3}$ ); R is the ideal gas constant ( $8.314 \text{ m}^3 \text{ Pa}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$ ); T is the ambient temperature (K);  $MW_{OM}$  is the mean molecular weight ( $\text{g mol}^{-1}$ ), and is  $200 \text{ g mol}^{-1}$  in this study (Xie et al., 2013);  $\xi_{OM}$  is the activity coefficient of each compound in the absorbing phase and assumed to be unity in this calculation (Xie et al., 2013);  $P_L^o$  and  $P_{L,0}^o$  are subcooled vapor pressures at T and 298 K, respectively (Pa);  $\Delta H_0$  is vaporization enthalpy of the liquid at 298.15 K. The measured  $P_L^o$  and  $\Delta H_0$  were extracted from previous literatures (And and Hanshaw, 2004; Wang et al., 2016).

The total concentration (S) of each NPOC in gas and particle phases was calculated as Eq. (7):

$$S = F + A = \left( 1 + \frac{10^6 \cdot MW_{OM} \cdot \xi_{OM} \cdot P_L^o}{R \cdot T \cdot PM} \right) \times F \quad (7)$$

Also, Jung–Pankow model was further used to investigate gas-particle partitioning. In this model, the ratio ( $\phi$ ) of the concentration of NPOC species in particle phase to the total NPOC concentration was calculated:

$$\phi = \frac{C_p}{C_p + C_g} = \frac{c \cdot \theta}{c \cdot \theta + P_L^o} \quad (8)$$





$$\log K_p = \log \frac{c \cdot \theta}{P_M} - \log P_L^0 \quad (9)$$

where  $\theta$  represents particle surface area per unit volume of air ( $\text{cm}^2 \text{cm}^{-3}$ ) and  $c$  is a constant which depends on thermodynamics of the adsorption process, molecular weight, and surface properties ( $\text{Pa cm}^{-1}$ ). In this study,  $c = 17.2 \text{ Pa cm}^{-1}$ , and  $\theta$  is  $1.1 \times 10^{-5}$ ,  $1.5 \times 10^{-6}$  and  $4.2 \times 10^{-7}$  ( $\text{cm}^2 \text{cm}^{-3}$ ) for urban area, rural area and background, respectively.

### 3. Results and discussion

#### 3.1 Abundance of PM<sub>2.5</sub> and NPOCs

The statistical summary and the abundance of measured PM<sub>2.5</sub> and NPOC species are shown in Fig.2 and Table S2. The average PM<sub>2.5</sub> concentration in all sampling sites was  $79.3 \pm 37.7 \mu\text{g m}^{-3}$ . The average OC and EC concentrations were  $13.8 \pm 6.9$  and  $6.3 \pm 2.2 \mu\text{g m}^{-3}$ , respectively. Organic matter (OM) was the most abundant component in PM<sub>2.5</sub>, accounting for 18.8–27.8% of the total mass, which was estimated to be 1.4 times of OC concentration (Feng et al., 2006; Huang et al., 2014). Following OM,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were also abundant, accounting for 19.9–22.6%, 16.4–18.1% and 10.4–13.7% of PM<sub>2.5</sub>, respectively.

Fifty-seven NPOCs were identified in this study (Table 2), including 30 n-alkanes, 2 iso-alkanes, 15 PAHs, 5 hopanes and 5 steranes. Their total concentrations ranged from 31.7 to  $388.7 \text{ ng m}^{-3}$  (an average of  $155.9 \pm 55.4 \text{ ng m}^{-3}$ ), accounting for 0.4–2.4% of OM. This was consistent with the measurement results of NPOCs in Pearl River Delta (PRD) (Wang et al., 2016) and South China Sea (Zhao et al., 2016) in China, with percentages of 0.1–4.2% and 0.8–1.7%, respectively. n-Alkanes were the most abundant NPOCs, with concentration of  $105.3 \pm 55.1 \text{ ng m}^{-3}$ , accounting for 67.2% of NPOC concentration. PAHs was the second most abundant species, averagely accounting for 29.2% of NPOC concentration. Hopanes and steranes were minor constituents, with average concentrations of  $3.6 \pm 3.0$  and  $1.8 \pm 1.3 \text{ ng m}^{-3}$ , respectively.

The level of n-alkanes in Jiujiang was comparable to those in Shanghai (Feng et al., 2006) and Hong Kong (Li et al., 2013), but a bit higher than those in Guangzhou (Xu et al., 2013), British Columbia (Ding et al., 2009) and South China Sea (Zhao et al., 2016). However, concentrations of PAHs in Beijing and Delhi were 1.7 and 8.2 times higher than that in Jiujiang, respectively.

**Table 2.** Comparison of NPOC concentrations between Jiujiang City and other areas ( $\text{ng m}^{-3}$ )

|                 | n-Alkane <sup>a</sup>   | PAHs <sup>b</sup>               | Hopane <sup>b</sup>         | Sterane <sup>b</sup>       | Time      | Reference         |
|-----------------|---|---------------------------------|-----------------------------|----------------------------|-----------|-------------------|
| Jiujiang, China | $105.3 \pm 55.1$ (16.3–305.0); C <sub>11</sub> –C <sub>40</sub> | $45.3 \pm 17.6$ (12.3–96.5); 15 | $3.6 \pm 3.0$ (0.6–16.4); 5 | $1.8 \pm 1.3$ (0.3–7.0); 5 | 2016.9–12 | This study        |
| Shanghai, China | $32.9$ – $341.9$ ; C <sub>17</sub> –C <sub>36</sub>             | $7.8$ – $151.1$ ; 15            | /                           | /                          | 2002–2003 | Feng et al., 2006 |
| Beijing, China  | $163.0 \pm 193.5$ ; C <sub>20</sub> –C <sub>35</sub>            | $78.7 \pm 115.4$ ; 16           | $6.9 \pm 6.6$ ; 4           | /                          | 2004      | Feng et al., 2006 |



|                            |  |                          |                    |                     |                    |                    |
|----------------------------|--|--------------------------|--------------------|---------------------|--------------------|--------------------|
| Guangzhou, China           | 48.1±20.8; C <sub>19</sub> –C <sub>40</sub>            | 19.0±17.5; 18            | /                  | /                   | 2010.11            | Xu et al., 2013    |
| South China Sea            | 15.7–124.2; C <sub>15</sub> –C <sub>38</sub>           | 3.4–127.9; 22            | 0.4–19.6; 8        | 0.4–3.5; 6          | 2013.9–10          | Zhao et al., 2016  |
| Hong Kong, China           | 97.9; C <sub>29</sub> –C <sub>33</sub>                 | 13.5; 15                 | 21.5               |                     |                    | Li et al., 2013    |
| PRD <sup>c</sup> , China   | 1.6–436(64);<br>C <sub>22</sub> –C <sub>38</sub>       | 0.1–74(14.2); 17         | 0.3–21(2.3);<br>10 | 0.01–4.1(3.4<br>);5 | 2011–2012          | Wang et al., 2016  |
| British Columbia<br>Canada | 4.89–74.38(15.58);<br>C <sub>11</sub> –C <sub>40</sub> | 1.01–41.7<br>(10.82); 16 | /                  | /                   | 2005.12–2<br>007.2 | Ding et al., 2009  |
| Delhi, India               | 425±343; C <sub>12</sub> –C <sub>35</sub>              | 373±197; 17              | /                  | /                   | 2006–2009          | Yadav et al., 2013 |

<sup>a</sup>: mean concentration (concentration range); species;

<sup>b</sup>: mean concentration (concentration range); number of species;

<sup>c</sup>: including four cities in PRD: Guangzhou, Dongguang, Nanhai and Nansha.

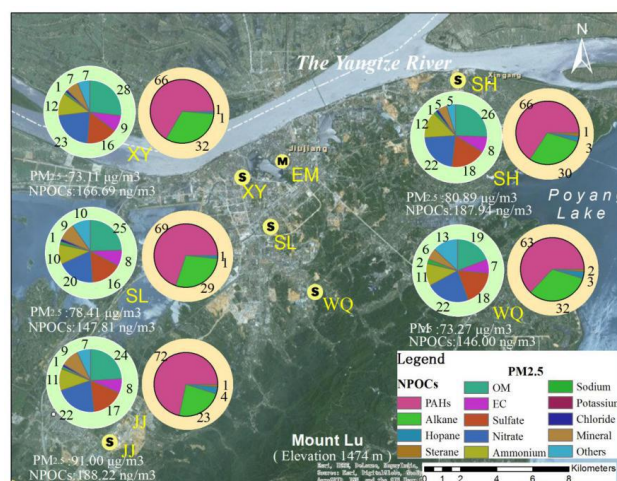


Fig. 2. Spatial distributions of NPOCs and PM<sub>2.5</sub> in Jiujiang city

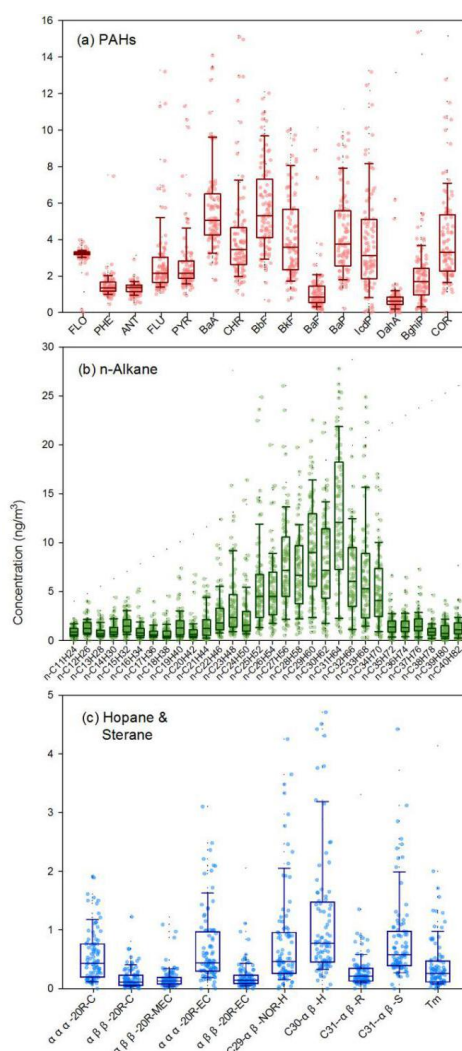
### 3.1.1 PAHs

PAHs are ubiquitous pollutants of the environment. They are originated from natural and anthropogenic sources such as biomass burning, vehicle exhausts, residential heating, waste incineration and industrial emissions. It is well established that the atmospheric concentration and lifetime of PAHs are highly dependent on their gas-particle partitioning behavior, transformation and degradation. The PM<sub>2.5</sub>-associated PAHs were shown in Fig. 3a. Their individual concentrations varied between 0.4 and 5.7 ng m<sup>-3</sup>. BbF (5.7 ng m<sup>-3</sup>) was the most abundant PAH species, followed by BaA (5.6 ng m<sup>-3</sup>) and BaP (4.2 ng m<sup>-3</sup>), together accounting for 34.2% of all PAHs, this was consistent with some previous studies in Guangzhou (Xu et al., 2013). Because of the strong carcinogenic effect of BaP, special attention should be given to it, the level of which was also higher than that indicated by the air quality guideline of WHO (1 ng m<sup>-3</sup>). Because of the vapor pressure dependent partitioning, 2- and 7-ring ring PAHs distributed majored in gas and particle phases, respectively. However, PAHs with 3–6 rings appeared in both gas and particle phases through gas-particle



247 partitioning. The total percent contribution of 4- and 5-ring PAHs was 67.9% in this study. FLU–PYR–CHR and  
248 BaA–BaP congeners of the 4-ring PAHs often indicate diesel vehicle and biomass combustion (Yadav et al., 2013),  
249 respectively, and 5-ring BkF is considered as marker of vehicle tracer. This suggests biomass burning and fossil fuel  
250 combustion have mixed effects on local pollution.

251 MDRs of atmospheric PAHs with similar molecular weight have been widely used as a useful tool for aerosol source  
252 identification. In this study, the ANT/(PHE+ANT) ratios varied in 0.28–0.68 (mean of 0.48), confirming a strong  
253 influence from pyrogenic emissions (Xu et al., 2013; Yadav et al., 2013). Most samples had FLU/(FLU+PYR) ratios of  
254 0.36–0.58, implying combined effects of pyrogenic emission and combustion of fuel, grass, wood and coal (Kuang et al.,  
255 2011; Chen et al., 2016a). The average IcdP/(IcdP+BghiP) ratio was 0.57, and in most cases the ratio > 0.50, suggesting  
256 significant impacts from the combustion of grass, wood and coal. Despite MDRs have been consistently used for source  
257 identification, it remains a rather rough method and contradictions may occur. Therefore, more samples should be  
258 collected to achieve better results.



**Fig.3.** Concentration profiles of NPOCs

259

260

### 261 3.1.2 n-Alkanes

262 Unique signatures of n-alkanes have been shown for different sources, including vehicle exhausts, tire-wear particles,  
 263 road dust, cooking oil, cigarette smoke and particulate abrasion products from leaf epicuticular waxes (Rogge et al.,  
 264 1994; Ma et al., 2011; Yadav et al., 2013; Zhang et al., 2015). A bimodal distribution of chain lengths of n-alkanes with  
 265 peaks at C<sub>20</sub>–C<sub>22</sub> and C<sub>24</sub>–C<sub>27</sub> implies vehicle exhaust sources (Zhang et al., 2015). However, a unimodal distribution of  
 266 chain lengths of >C<sub>30</sub> n-alkanes (peak at C<sub>37</sub>) represents tire-wear particle sources. The distribution pattern characterized  
 267 by large proportion of C<sub>27</sub>–C<sub>33</sub> odd n-alkanes suggests vegetation sources.



Our analysis showed that the middle-chain-length n-alkanes ( $C_{25}$ – $C_{34}$ ) were the most abundant (Fig. 3b), accounting for 72.3% of the total measured n-alkanes. Feng et al. (2006) and Xu et al. (2013) reported similar findings that  $C_{27}$ – $C_{29}$  n-alkanes dominated the distribution of n-alkanes in three metropolitan cities of China (Beijing, Shanghai, Guangzhou). In addition, a predominance of odd carbon numbered congeners ( $C_{25}$ ,  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$  and  $C_{33}$ ) was found, with  $C_{max} = 31$  in most cases and  $C_{max} = 29$  in a few cases (Fig. 3b). The  $C_{max}$  value in this study suggests that road dust, cigarette smoke and tire-wear abrasion products have all contributed to n-alkanes in Jiujiang city. However, no obvious odd/even carbon preference was observed for either  $C_{11}$ – $C_{14}$  nor  $C_{35}$ – $C_{40}$  n-alkanes.

Plant wax n-alkanes exhibit strong odd/even carbon number predominance, while n-alkanes from fossil fuel combustion do not (Feng et al., 2006). Thus, biogenic n-alkanes should have CPI values greater than unity, whereas anthropogenic n-alkanes should have CPI values close to unity. Furthermore,  $CPI < 2$  is a typical characteristic of urban environment, suggesting major contribution from petrogenic sources, e.g., vehicle exhausts and industrial emissions. The CPI values were 1.00–1.79 (average of 1.29) in this study, implying strong contributions from petrochemical sources, diesel residues and gasoline emissions. Ding et al. (2009) reported a mean CPI value of 1.5 in central British Columbia of Canada, and Xu et al. (2013) reported CPI values of 1.2–1.7 (mean of 1.4) in Guangzhou of China. The mean contribution of plant wax n-alkanes to the total n-alkanes (WNA%) was  $17.00 \pm 4.41\%$ , ranging from 7.94% to 31.31%. PNA% provides a direct insight into n-alkanes from petrogenic sources. In this study, PNA% was  $83 \pm 4.41\%$ , implying that 83% of n-alkanes were originated from anthropogenic sources. The ACL value varied from 27.45 to 30.95. This small fluctuations may suggest that emissions were similar at different sites, which was consistent with the result of Delhi in India (Yadav et al., 2013).

### 3.1.3 Hopanes and steranes

Hopanes and steranes are usually found in crude oil and engine oil, subsequently in vehicle exhausts from unburned lubricating oil residues. They are regarded as markers of fossil fuel combustion. The concentration profile of hopanes and alkanes was shown in Fig. 3c. Their total concentrations ranged from 1.1 to 20.5  $\text{ng m}^{-3}$ , and the concentration of hopanes was approximately two times of that of steranes. As expected, the total concentrations of hopanes/steranes were 6.7/2.5, 3.3/1.2 and 1.9/1.1  $\text{ng m}^{-3}$  in petrochemical industry (SH), traffic area (SL) and suburban area (WQ), respectively.

The predominant hopane analogs were  $C_{30}$ – $\alpha\beta$ –H,  $C_{31}$ – $\alpha\beta$ –S and  $C_{29}$ – $\alpha\beta$ –NOR–H, with concentrations of  $1.2 \pm 1.3$ ,  $0.8 \pm 0.7$  and  $0.8 \pm 0.9 \text{ ng m}^{-3}$ , respectively. The homohopane index ( $C_{31}$ –S/(S+R)) was 0.75, much greater than those of diesel (0.49), gasoline vehicle emissions (0.50–0.62) and petroleum (0.6), but a bit smaller than industrial bitumite coal (0.87) (Fraser et al., 2002). This implies vehicle exhausts, petrochemical emissions and coal combustion have all



contributed to particle concentrations. The concentration profiles of steranes were similar at different sites, with  $\alpha\alpha\alpha$ -20R-EC being the most abundant, followed by  $\alpha\alpha\alpha$ -20R-EC. This pattern was a bit different from that in Delhi which was dominated by C<sub>29</sub> sterane (Yadav et al., 2013).

### 3.2 Size-specific distributions

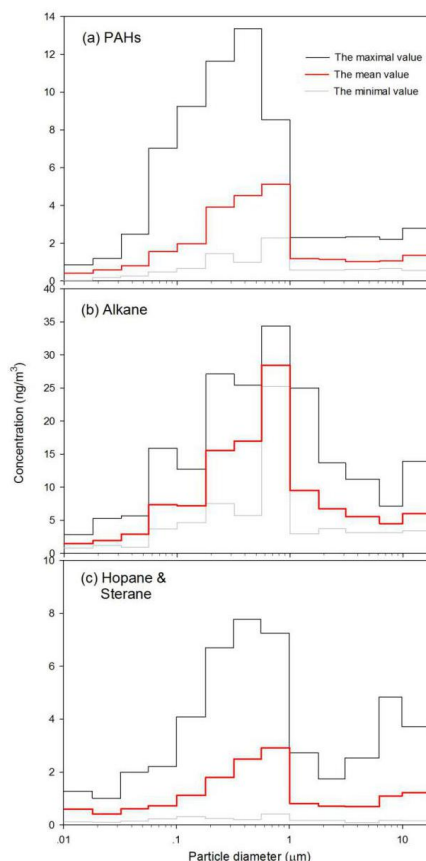
Particulate matters within 13 size fractions were collected. The size-specific distribution of NPOCs was then obtained (Fig. 4). The total concentration of PAHs (Fig. 4a) in each size fraction ranged from 0.4 ng m<sup>-3</sup> in the 0.01–0.018  $\mu$ m fraction to 5.1 ng m<sup>-3</sup> in the 0.56–1.00  $\mu$ m fraction. A bimodal distribution of the concentrations of PAHs was observed, with peaks in 0.56–1.00 and 9.90–18.0  $\mu$ m fractions, respectively. PAHs in the 0.56–1.00  $\mu$ m fraction were the most abundant. This phenomenon could be reasonably explained by that heavy molecular weight PAHs tend to be enriched in smaller particles (< 1.4  $\mu$ m) (Kleeman et al., 2008), whereas light molecular weight PAHs are speculated to adsorbed onto coarse particles by volatilization and condensation. As discussed above, the heavy molecular weight PAHs accounted for 50.6% of the total PAHs in this study. Similarly, Hien et al. (2007) found that PAHs accumulated predominantly in small size fractions (especially < 0.4  $\mu$ m) in urban aerosols. More recently, Mu et al. (2017) indicated PAHs were strongly correlated with accumulation mode particles (0.05–2.0  $\mu$ m), and PAHs in this fraction accounted for ~85% of the total measured PAHs. In fact, the relationship between the concentration of PAHs and the size particles is highly variable. This suggests not only source type but also photodegradation and gas-particle partitioning have great influences on the size-specific distribution of PAHs.

The concentrations of n-alkanes (Fig. 4b) in Aitken nuclei, Accumulation and Coarse mode particles were 1.7–3.1, 7.0–28.7 and 4.7–6.3 ng m<sup>-3</sup>, respectively. The concentrations of n-alkanes in individual fractions accounted for 1.5–24.5% of the total measured n-alkanes in all fractions. n-Alkanes in the 0.56–1.00  $\mu$ m fraction were the most abundant, whereas n-alkanes in three nano-size fractions accounted for the smallest percentages (1.5–2.5%). Notably, the concentration of n-alkanes increased with increase in fraction size. After fraction size reached 1.00  $\mu$ m, however, the concentration of n-alkanes decreased in coarse mode particles. This implies n-alkanes have a tendency to be adsorbed on fine particles. In general, condensation is more likely happen to fine particles because of their large quantity and larger specific surface area (Wang et al., 2009).

The size-specific distribution of hopanes and steranes was illustrated in Fig. 4c. Hopanes and steranes were the most abundant in the following five fractions: 0.56–1.00  $\mu$ m (2.9 ng m<sup>-3</sup>), 0.32–0.56  $\mu$ m (2.5 ng m<sup>-3</sup>), 0.18–0.32  $\mu$ m (1.8 ng m<sup>-3</sup>), 9.9–18  $\mu$ m (1.2 ng m<sup>-3</sup>) and 0.10–0.18  $\mu$ m (1.1 ng m<sup>-3</sup>). Approximately 55% of  $\Sigma$ (hopanes+steranes) were associated with the 0.10–1.00  $\mu$ m fraction. This result was consistent with that of Kleeman et al. (2008) who found the



hopanes and steranes were abundant in ultrafine size fraction during a severe winter pollution episode in Sacramento, USA.



**Fig. 4.** Mean-normalized size-specific distribution of NPOCs in the collected  $PM_{2.5}$  samples

### 3.3 Degradation of organics

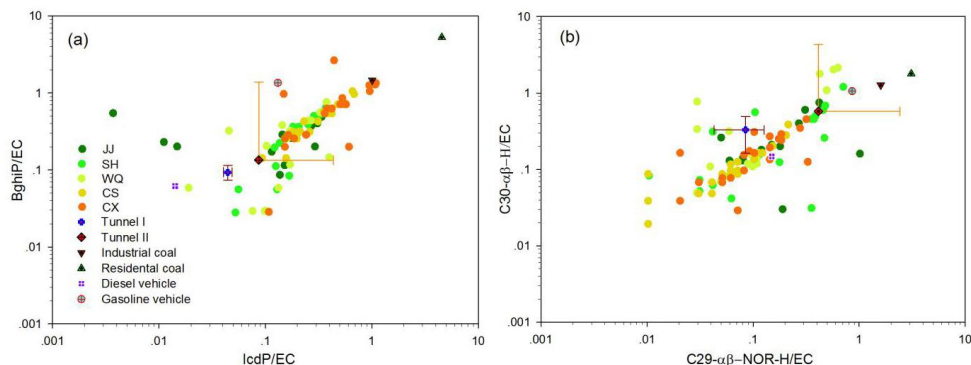
Photochemical oxidation has great influences on the mass concentration and size-specific distribution of NPOCs, and on their removal and atmospheric fate (May et al., 2012). Ratio–ratio plot was used to visually compare the distributions of critical marker species and investigate their degradation (Robinson et al. 2006; May et al., 2012). Photochemical decay could cause the ambient data to be distributed along a line emanating from the source profile, with increasing photochemical age. The more oxidation, the further ambient ratio is from the source profile. In addition to photochemical decay, the ratio–ratio plot can also be affected by mixed emissions.

In this study, IcdP/BghiP and C29- $\alpha$ -NOR/C30- $\alpha$ -H were adopted to explore the degradation of NPOCs (Robinson et al., 2006; Wang et al., 2016). EC shares common origins with PAHs and hopanes but they are subject to photodegradation.





Two pairs of PAHs and hopanes were normalized by EC. The ratio–ratio plot of IcdP and BghiP normalized by EC from different sites was depicted in Fig. 5a, together with vehicle (diesel and gasoline) exhausts, tunnel and coal burning source profiles. Most of the data points were distributed along a line, which overlapped tunnel, vehicle exhaust and industrial coal, implying ambient hopanes in this city were from vehicle emissions and coal combustion. Wang et al. (2016) reported that vehicle emissions contributed to atmospheric hopanes in four cities in PRD. There were several deviation points at left down corner, and the values were smaller than the values of tunnel and vehicle source profile, indicating mixed influence from traffic origins and degradation. Yu et al. (2011) reported a more apparent linear distributions of data sets measured in Hong Kong and PRD, which can be attributed to their single vehicle source type. In Fig. 5b, most of the data were linearly distributed, implying both biomass burning and vehicle emission contribute to hopanes. Robinson et al. (2006) found hopanes were severely depleted in Pittsburgh, USA, and they attributed this phenomenon to regional air mass transport affecting the oxidation of condensed-phase organic compounds.



**Fig. 5.** Ratio–ratio plots of two pairs of characterized species (IcdP/BghiP and C29- $\alpha\beta$ -NOR-H/C30- $\alpha\beta$ -H) normalized by EC and published source profiles. (Tunnel I: Yu et al., 2011; Tunnel II: He et al., 2009; Residential coal: Zhang et al., 2008; Industrial coal: Zhang et al., 2008; Diesel vehicle: Fraser et al., 2002; Gasoline vehicle: Fraser et al., 2002)

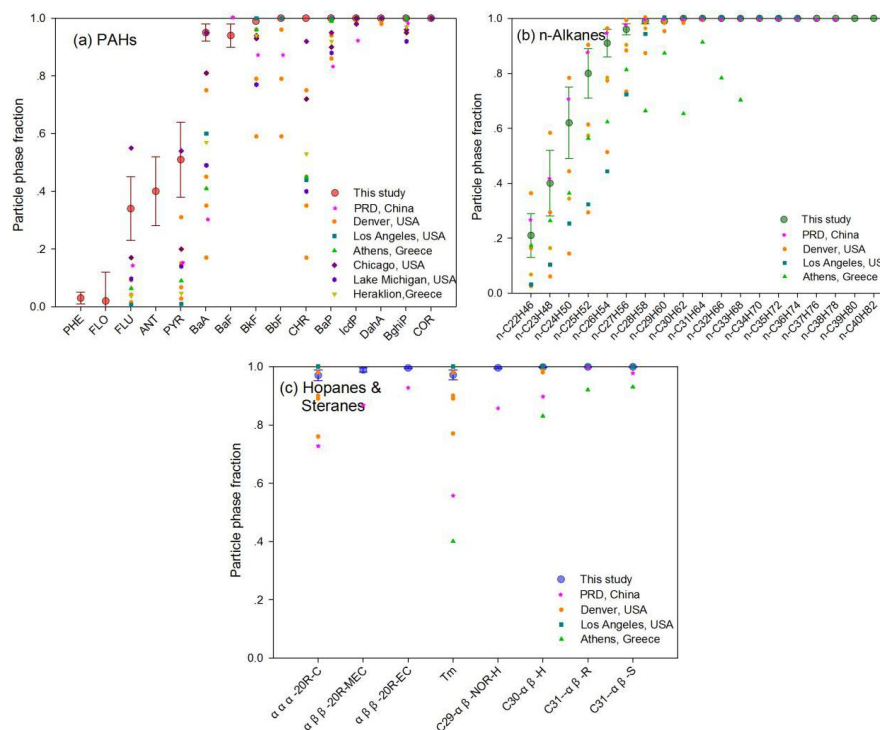
### 3.4 Impact of gas-particle partitioning on fine particle source apportionment

#### 3.4.1 Gas-particle partitioning

An important aspect of atmospheric NPOCs is their gas-particle partitioning behavior, which has effects on their fate and size-specific occurrence. Once NPOCs are emitted into the atmosphere, they subsequently partition between gas and particle phases and a partitioning equilibrium can be reached according to their vapor pressure and temperature dependencies.



361 The particle-phase fraction ( $\phi$ ) of NPOCs was calculated according to the classical gas-particle partitioning model (Fig. 6  
 362 and Fig. S1). The gas-phase fractions of LMW PAHs (e.g., FLO, PHE, ANT, FLU and PYR) were rather substantial, and  
 363 their particle-phase fractions ( $\phi$ ) ranged from 2.4% to 51.3%. Similarly, the  $\phi$  values of short chain  $C_{22}$ – $C_{24}$  n-alkanes  
 364 varied between 21.2% and 62.5%, exhibiting an increasing trend with increase in their molecular weight. However, for  
 365 the heavier molecular weight species, like PAHs with 5–7 rings, long chain n-alkanes ( $> C_{26}$ ), hopanes and steranes, the  $\phi$   
 366 values remained greater than 90.0% for all temperature ranges. The calculated  $\phi$  values of PAHs and n-alkanes were  
 367 comparable to those estimated in urban Denver, Chicago and Los Angeles in USA (Xie et al., 2013), but a bit greater than  
 368 those in PRD of China (Wang et al., 2016). The lower fractions of NPOCs in gas phase in this study compared with that  
 369 in PRD was probably because PRD area is located in a border region between subtropics and tropics. This region has  
 370 higher temperature than Eastern China area, especially in cold winter seasons, and the higher temperature can facilitate  
 371 the shift of species to gas phase.

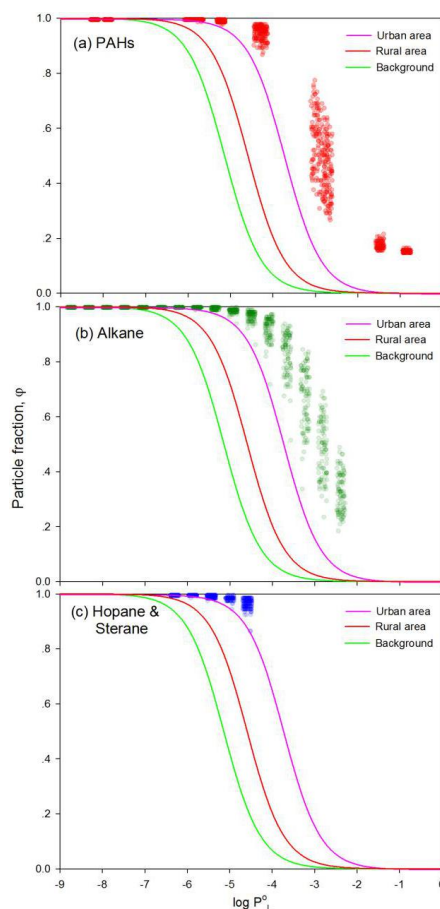


373  
 374 **Fig. 6.** Average particle-phase fractions ( $\phi$ ) of all NPOCs as in comparison with previous results

375 To further evaluate gas-particle partitioning of NPOCs,  $\phi$  values were compared with predicted ones by Jungle–Pankow  
 376 model (Fig. 7). The  $\phi$  values of LMW PAHs, short chain n-alkanes,  $\log P_{ow} > -5$  hopanes and steranes, were underpredicted  
 377 by Jungle–Pankow model. However, the  $\phi$  values predicted by Jungle–Pankow model agreed well with the calculated



ones for HMW PAHs and long chain n-alkanes. Underestimation of  $\phi$  values of PAHs by Jungle–Pankow model compared with the filed measured ones were also reported by He and Balasubramanian, (2009), and they attributed the discrepancy to the higher OM fractions in real environment than that adopted by the model.



**Fig. 7.** Comparison of  $\phi$  values between the measured and predicted results from Jungle–Pankow model

### 3.4.2 PMF source apportionment

Source apportionment analysis involves techniques that can be used to identify source species and their unique contributions, which are critical in making policies of controlling pollution. It is typically assumed the molecular markers are stable in the ambient environment, *i.e.*, being nonreactive and nonvolatile (May et al., 2012). However, many organic markers can be oxidized over atmospherically relevant time scales, and partition between gas and particle phases. As discussed above, light molecular weight NPOCs tend to shift to gas phase. Therefore, if the data of NPOCs in single particle phase are directly used as input for receptor model, this may confound the aerosol factors. To explore the impact



of gas-particle partitioning on  $PM_{2.5}$  source apportionment, the NPOCs in single particle phase and the total NPOCs in gas-particle phases were used as input data for receptor model PMF, respectively. Both input data were incorporated with elemental species, inorganic ions and OC/EC. Results based on single particle phase and the total phases were denoted by  $PMF_P$  and  $PMF_T$ , respectively. Five to eleven factors were extracted in this study to obtain reasonable results. Finally, it turned out that the results of eight factors gave the most reasonable source profiles (Fig. 8 and Fig. S2).

Factor 1 (Fig. 8a) was characterized by significant presence of Al, Ca, Mg, Ti and Fe, which are regarded as good indicator of dust (including construction dust, geological dust and road dust) (Wang et al., 2015). These elements are the major elements of dust sand, usually accumulated in the coarse mode particles. Geological dust typically contains high concentrations of crustal elements, including Fe and Mn. Hence, this factor was regarded as “dust”, with percent contributions of 8.90% and 11.0% under  $PMF_P$  and  $PMF_T$ , respectively.

Factor 2 (Fig. 8b) was characterized by the significant presence of Cu, Mn, Zn, Pb, BkF, BbF, BaF and BaP. Mn, Zn and As are related to emissions from steel production, brick, ceramic and glass making factories (Li et al., 2016; Sulong et al., 2017). Cu mainly originates from non-ferrous metal production and smelting factories. BkF, BbF and BaP are typical markers of emissions from coke industry. Several large-scale industrial parks are located in Jiujiang city, e.g., Shacheng Industry and Jiujiang Comprehensive Industry in the northern and southern areas, respectively. Therefore, factor 2 was associated with industrial emission.

Factor 3 (Fig. 8c) was characterized by large fractions of HMW PAHs (IcdP, BghiP, DahA and COR), as well as relatively high fractions of hopanes and steranes. BghiP and COR are excellent tracers of vehicle exhausts. Hopanes and steranes are related to exhausts from heavy-duty vehicles with diesel engines (Wang et al., 2016). As mentioned above, there were over 700 thousand motor vehicles in Jiujiang city in 2015, among which about 1/15 were mainly powered by diesel engines. Therefore, factor 3 was identified as “vehicle related exhausts”, with percent contributions of 12.5% and 15.0% under  $PMF_P$  and  $PMF_T$ , respectively.

Factor 4 (Fig. 8d) was characterized by the presence of well-documented indicators of secondary aerosol formation, such as  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$ , with factor fractions of 83.7%, 87.4% and 94.1%, respectively. These secondary products are formed by precursor gases ( $SO_2$  and  $NO_x$ ) via oxidation reactions (Wang et al., 2015). They are mainly emitted from biomass burning, coal combustion and vehicles.  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$  accounted for 19.9–22.3%, 16.4–18.1% and 10.4–13.7% of  $PM_{2.5}$  concentrations, respectively, which were typically derived from gas-particle conversion process as well as homogeneous and heterogeneous reactions in urban atmosphere. Furthermore, the similar spatial distribution and contribution in all sites highlight a widespread of these components. Consequently, factor 4 was identified as “secondary aerosol formation”.

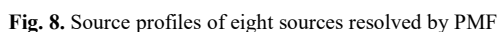


Factor 5 (Fig. 8e) was characterized by significant presence of  $C_{30}$ – $C_{40}$  n-alkanes, as well as relatively significant presence of FLU and PYR. In previous research (Wang et al., 2016), the long chain n-alkanes ( $C_{29}$ – $C_{36}$ ) were considered to come from local emissions, especially from coal combustion. PYR and FLU are frequently considered as excellent markers of coal combustion for aerosol source apportionment. Coal is the primary energy source for many industries in China. About 3.1 million tons of standard coal are consumed per year by the Jiujiang thermal power plant according to local statistics. Thus, factor 5 was identified as “coal burning”, with percent contributions of 18.7% and 16.4% under  $PMF_P$  and  $PMF_T$ , respectively.

Factor 6 (Fig. 8f) was characterized by high percentage of  $Cl^-$  and  $K^+$ , with some amounts of As, Se, Pb, OC and EC.  $Cl^-$  and  $K^+$  have been widely used as tracers of wood and biomass burning aerosol (Li et al., 2016). In the past, crop straws were disposed by local farmers in the field by burning for convenience. Although this has been extensively banned in recent years, several large-scale straw burning sites surrounding this city can still be observed by China National Satellite Meteorological Center (<http://hjj.mep.gov.cn/jgjs/>). Thus, this factor was considered as “biomass burning”, with percent contributions of 12.7% and 15.7% under  $PMF_P$  and  $PMF_T$ , respectively.

Factor 7 (Fig. 8g) was characterized by high fraction of Ni and V, which are excellent tracers of exhausts from ship and heavy-duty diesel vehicles. In fact, Jiujiang harbor is among the ten busiest harbors in Yangtze River, whose port cargo throughput is 59 million tons per year. Hence, factor 7 was identified as “shipping and diesel exhausts”.

Factor 8 (Fig. 8h) was characterized by a high load of short chain n-alkanes ( $C_{22}H_{46}$ , 76.6%;  $C_{23}H_{48}$ , 84.2%;  $C_{24}H_{50}$ , 81.1%) and LMW PAHs (about 60% for FLU, PYR, BaA and CHR). These species have several characteristics: most of their particle-phase fractions ( $\phi$ ) were less than 50%; relatively light molecular weight; strongly temperature-dependent vaporization. These compounds have been interpreted as “light NPOCs factor” in previous research (Xie et al., 2013; Wang et al., 2016). The percent contributions of this factor were 3.7% and 5.6% under  $PMF_P$  and  $PMF_T$ , respectively. Additionally, concentrations of light NPOCs factor showed an increasing trend with increase in temperature, implying the association of this factor with fossil fuel evaporation and biogenic emissions. Hence, this factor was regarded as “light NPOCs factor”.





#### 3.4.3 Assessing impacts of gas-particle partitioning on source apportionment

As stated above, using the data of single particle phase as input data for PMF model could lead to uncertainty in results, which was related to gas-particle partitioning of NPOCs in the mathematical solution. In the present study, the eight extracted factors in this study showed similar source profiles between PMF<sub>P</sub> and PMF<sub>T</sub>. This phenomenon could reasonably occur because of the major NPOCs compounds were enriched in particle phase in the present study, meanwhile, the concentrations of hopanes and steranes in gas phase were relatively low. In sharp contrast with this study, Wang et al. (2016) extracted an extra light NPOCs factor in PMF<sub>P</sub> in PRD, and they found very volatile NPOCs (like FLU) were quite variable in PMF<sub>T</sub>, but almost did not appear in PMF<sub>P</sub>. This difference could probably be due to the PM<sub>2.5</sub> source identification in this study was focused on the period of high-frequency haze episodes (late autumn and winter), while the research conducted in PRD included hot summer season which enhanced the uncertainty and variability of predicted light NPOCs.

Gas-particle partitioning has important effect on the occurrence, atmospheric lifetime and transformation of NPOCs. Also, size-specific aerosol distribution and photochemical oxidization have influence on gas-particle partitioning. For example, gas phase oxidation reaction is much faster than heterogeneous reactions, since the uptake of heterogeneous oxidant is diffusion-limited. The empirical and model predicted particle concentrations would be underestimated or overestimated, compared with filed measured values. It may add the uncertainty for the input data of receptor model. In this study, using the data of total organic compounds in gas-particle phases with other aerosol species as input data for receptor model provides an excellent tool for PM<sub>2.5</sub> source apportionment. However, reasonable caution should still be given to the more volatile organic species.

#### 4. Conclusions

NPOCs are typical molecular markers for source identification, which attract researchers' interest worldwide. To the best of our knowledge, this is the first research analyzing size-specific aerosols-associated NPOCs, conducted in a typical middle-scale city in Eastern China. Fifty-seven PM<sub>2.5</sub>-associated NPOCs including PAHs, n-alkanes, iso-alkanes, hopanes and steranes were identified and quantified using a TD-GC/MS method. The total concentrations of NPOCs were 31.7–388.7 ng m<sup>-3</sup>, with n-alkanes being the most abundant species (67.2%). The heavy molecular weight PAHs (4- and 5-ring) contributed 67.9% of the total PAHs, and the middle chain length (C<sub>25</sub>–C<sub>34</sub>) n-alkanes were the most abundant in n-alkanes. The MDRs showed that 83.0% of NPOCs were originated from anthropogenic sources, including pyrogenic source, fossil fuel combustion and biomass burning.





PAHs and n-alkanes were majorly enriched in 0.56–1.00  $\mu\text{m}$  fraction, and  $\Sigma(\text{hopanes}+\text{steranes})$  were associated with 0.32–1.00  $\mu\text{m}$  fraction. The nano-size and coarse mode particles showed low concentrations of NPOCs. The ratio–ratio plots of IcdP/BghiP and C29- $\alpha\beta$ -NOR/C30- $\alpha\beta$ -H normalized by EC implied that NPOCs in local area were affected by photochemical degradation and emissions from mixed sources. Gas-particle partitioning model showed that the calculated particle-phase fraction ( $\phi$ ) of the light molecular weight NPOCs ranged between 2.4% to 62.5%, while those of heavy PAHs, long chain n-alkanes, hopanes and steranes were high (>90.0%). Using data based on single particle phase and on gas-particle phases with other  $\text{PM}_{2.5}$  compounds as input data for PMF model, respectively, we successfully extracted eight factors from both cases. The  $\text{PMF}_T$  (the case of gas-particle phases) showed better source profiles than  $\text{PMF}_P$  (the case of single particle phase), and the light NPOCs factor contributed a bit more in  $\text{PMF}_T$  (5.6%) than in  $\text{PMF}_P$  (3.7%). This study indicates that NPOCs are useful for aerosol apportionment, and total NPOCs in two phases enable better source profiles than NPOCs in single particle phase.

#### Acknowledgement

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