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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Non-polar organic compounds in aerosols in a typical city of Eastern China: Size distribution, gas-particle partitioning and tracer for $PM_{2.5}$ source apportionment" *by* Deming Han et al.

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Response to the Interactive comment on "Non-polar organic compounds in aerosols in a typical city of Eastern China: Size distribution, gas-particle partitioning and tracer for PM2.5 source apportionment" by Deming Han et al.

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Discussion paper

Anonymous Referee 1

This study analyzed the molecular composition of non-polar organic compounds (NPOCs) in PM2.5 and their size distributions at Jiujiang city. The target NPOCs include n-alkanes, PAHs, and hopanes. Diagnostic ratios and PMF model were applied to the compositional data to evaluate the sources and atmospheric processing of PM2.5. In general, this work is well organized and written. However, I still think this work lacks novelty, and would not recommend this manuscript to be accepted for publication at Atmos. Chem. Phys., although a lot of chemical and data analysis work have been done.

Response: To the best of our knowledge, this study was the first one which systematically researched the size-specific distributions (0.01-18 $\mu$m), photo-degradation and gas-particle partitioning of NPOCs (PAHs, alkane, hopane and sterane), combined diagnostic ratios of special species and receptor model assessing the effect of partitioning on the source apportionment of PM2.5 aerosol. The new information on the profiles of PM2.5-associated NPOCs, size-specific distributions, effect of gas-particle partitioning to the aerosol identification provided by this study, would help us accurately identify the potential sources of aerosols and then asses the contributions from each source.

General comments: 1. PMF model was utilized to apportion PM2.5 components to factors/sources. However, the author did not provide any information about the method in the manuscript or supporting information. Which version of PMF model (PMF2 or EPA PMF 5.0) was used for source apportionment? How did the author determine the factor number? How did the author deal with the missing values or measurements blow detection limit? Measurement uncertainty was required for PMF input, where were these data from or how were they calculated? Are there any uncertainty analysis related to the PMF modeling? Are the PMF results valid?

Response: Considering the limitation of article length, some detailed description was

not added in the original manuscript. According to the suggestion of anonymous Referee 1, the description of PMF analysis would be added in the Section S1 ("PMF analysis and uncertainty assessment") of the revised version of Supplementary material (line 26-52). The detailed added information was as following:

"Positive matrix factorization (PMF) is considered an advanced algorithm among various receptor models, which has been successfully applied for source identification of environmental pollutants. PMF has the following advantages: each data point is given an uncertainty-weighting; the factors in PMF are not necessarily orthogonal to each other and there is no non-negativity constraint with PMF. In the present study, PMF 5.0 (US EPA) was used to apportion the contributions of different sources to PM2.5 in the atmosphere. The matrix X represents an ambient data set in which i represents the number of samples and j the number of chemical species. The goal of multivariate receptor modeling is to identify a number of sources (p), the species profile (f) of each source and the amount of mass (g) contributed by each source to each individual sample as well as the residuals (eij), as equation (S1) (see Fig.1). The PMF solution minimizes the objective function Q based on these uncertainties (u), as equation (S2).

The input data files of PMF consist of concentrations and uncertainty matrices, and the uncertainty data were calculated as equation (S3) as suggested by PMF User Guide. The missing values were represented by average values, while measurements below MDL (method detection limit) were replaced by two times of the corresponding MDL values. The "weak" variables were down-weighted, while "bad" variables were omitted form the analysis process.

The model was run 20 times with 25 random seeds to determine the stability of goodness-of-fit values. It is necessary to test different numbers of sources to find the optimal number of sources which produces the most reasonable results. If the number of sources is estimated properly, the theoretical Q value should be approximately the number of degrees of freedom or the total number of data points. Five to eleven factors were examined, and eight factors were found to be the most appropriate and most rea-

sonably interpretable. Q (True) is the goodness-of-fit parameter calculated including all points, while Q (Robust) is the goodness-of-fit parameter calculated excluding points not fit by the model, Q (Robust) and Q (True) were 1,752.4 and 1,812.9, respectively. Additionally, approximately 98

2. Page 23, line 449-457. This manuscript stated that the PMFP and PMFT profiles are similar, and should be attributed to the fact that the major NPOCs are enriched in particle phase. This might not apply for factor 6, 7 and 8 (Figure 8f, g and h). The impact of G-P partitioning process will mainly affect the factors highly loaded with low molecular weight species. So the author might need to discuss the impacts of G-P partitioning on these factors.

Response: The lower molecule weight species in gas-particle partitioning were more susceptible to influence of the ambient temperature, hence light NPOCs show large fugacity from aerosol surfaces. In the present research, factor 8 was recognized as "Light NPOCs" for the characterization of high load of light NPOCs compounds. However, due to PM2.5 aerosols in this study was mainly conducted in the cold period of high-frequency haze episodes, the resolved factor profiles between PMFP and PMFT model were similar, even for the light NPOCs factor. The discussion of impact gas-particle partitioning on these factor can be seen detailedly in line 448-456 in the Section of "3.4.3 Assessing impacts of gas-particle partitioning on source apportionment" in this original manuscript.

However, for the factor 6 and 7, namely "Biomass burning" and "Shipping and diesel exhaust", which were characterized by inorganic salts (Cl- with K+) and heavy metals (Ni with V), respectively. The tracers for these factors could not be partitioned between phases, despite several light NPOCs species took relative medium to high factor loads, their impacts caused by gas-particle partitioning should be ignored.

3. From the title, it seems that the manuscript focused on the size distribution, G-P portioning of NPOCs, and the application of NPOCs on source apportionment of PM2.5.

While this study did not measure the gas-phase NPOCs, the gas-particle portioning is only simulated basing on Pankow's theory, and could not be validated. As such, it might not be appropriate to put G-P partitioning in the title, or we can say "G-P partitioning simulation", or "the impacts of G-P portioning on source apportionment". Size distribution was measured for NPOCs, which should be related to other parts of this manuscript. For example, does the size distribution help to explain the PMF results?

Response: We still think the original "Non-polar organic compounds in aerosols in a typical city of Eastern China: Size distribution, gas-particle partitioning and tracer for PM2.5 source apportionment" was a proper title, for two main reasons. 1). The size-distribution and gas-particle partitioning of NPOCs was really two major research contents in this study. The gaseous phase of NPOCs for the corresponding 13-staged aerosols were not measured in this study, because of it is still almost impossible of collecting different size-specific aerosol and the corresponding gaseous NPOCs simultaneously. In fact, we adopt the classical gas-particle partition model to simulate the abundance of gaseous NPOCs and explored the particle fraction ($\varphi$) of NPOCs with typical organic matter parameters in urban, rural and background areas. Just as PAHs, alkanes, hopanes and steranes could be called as "NPOCs" in this study, though not all kinds of NPOCs species were analyzed. 2). The NPOCs were used as tracers for the source identification of PM2.5 through specific specie ratios and receptor model, but not source apportionment of NPOCs themselves. If the title was changed to "gas-particle partitioning simulation" or "the impacts of gas-particle partitioning on source apportionment", either it lost the key section of "source identification of PM2.5" or it is wrong for this study.

The size-specific distributions of NPOCs have important influence on their gas-particle partitioning and photo- degradation. Also, combining the characterized species ratios and model extractions, size-specific distributions of NPOCs have relation to aerosols source identifications. The size-distribution of NPOCs was tightly related to the parts of Sections of "Degradation of organics", "Gas-particle partitioning" and "PMF source

apportionment" in this study.

4. Diagnostic rations of n-alkanes, PAHs and hopanes were intensively used to evaluate the sources of NPOCs in previous work. The criteria of diagnostic ratios are qualitative and confusing.

Response: Despite diagnostic ratio was relatively a bit empirical and rough when used for the source identification in some cases, it could easily provide useful information in most situations. Additionally, the combined use of diagnostic ratios of NPOCs and PMF model would provide mutual authentication.

5. Besides the above comments, the lack of enough novelty is the main issue for this work. The size distribution and diagnostic ratios of NPOCs in typical Chinese cities were intensively investigated (Bi et al., 2005; Zhou et al., 2005; Wang et al., 2009a, b, 2011; Duan et al., 2012). The impacts of G-P portioning of semi-volatile organic compounds (SVOCs) on PMF source apportionment have been observed and validated by Xie et al. (2013, 2014), and the method of using gas + particle phase SVOCs have been intensively applied in PMF source apportionment studies (Gao et al., 2015; Wang et al., 2016; Zhai et al., 2016). Moreover, this work did not provide any new phenomenon or viewpoints that add our knowledge on size distribution or G-P partitioning of NPOCs, or sources apportionment using NPOCs data.

Response: China is suffering severe atmospheric pollutions including haze pollution. Due to the heterogeneous development of industrial, economic, geomorphic and environmental conditions, different cities were facing different environmental pressure and situation. Currently, researches of NPOCs were focused on megacities in Eastern China, while most medium cities were ignored. Undoubtedly, systematically analyzing aerosols bound NPOCs and learning their tracers for the source apportionment of PM2.5 in a typical medium city, has great academic and practical values without doubt.

NPOCs as one important class of particles were rather chemically stable, which have been reported by numerous researchers, several researchers use them as tracers for





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PM2.5 source apportionment. Just as reviewer suggested (Table C1), there were numerous researches about molecular compositions, sized distributions of organic compounds and their effects on G/P partitioning have been published. However, these researches have their unique research interests, showed different focuses to our manuscript (Table R1), e.g. Wang et al., (2011b), Wang et al., (2009) and Wang et al., (2015) analyzed the concentrations of NPOCs and researched their characterizations. Wang et al., (2011a) reported concentrations, characterization and the size specific (0.4-9.0 $\mu$m) distributions of n-alkanes, PAHs and hopanes in three different typical sites, they neither evaluated their gas-particle partitioning of these compounds, nor investigated their sources and the corresponding contribution. Xie et al., (2014) evaluated the gas-particle partitioning process of six species of PAHs, twelve species of n-alkanes, hopanes and steranes, explored the partitioning impacts on their source apportionment, and got five NPOCs species profiles (odd alkane, light SVOCs, n-alkane, PAHs and sterane).

This manuscript systematically provides new information on the profiles and characterizations of PM2.5-associated NPOCs, evaluated their size-specific distributions and impacts on the gas-particle partitioning, found the effects of gas-particle partitioning and degradation were not apparent o the source apportionment. As best as our knowledge, this is the first research systemically analyzing the characterization, size-specific distribution, gas-particle phase partitioning of NPOCs, and exploring effects of partitioning between tracers for the aerosol source identifications. Based on this manuscript, it will help us to identify the more accurate sources of aerosols and asses the contributions from each source, provide information for further targeted optimized emission control strategies.

Table C1 Comparison between related studies with this manuscript (see Fig.2)

We thank Referee 1 for his good suggestions in the anonymous refereeing process and his/her careful reading our article.

Reference: 1) Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z., Wang, Z., 2009a. Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. Atmospheric Chemistry and Physics J1 - ACP 9, 8869-8882.

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3) Wang, G., Kawamura, K., Xie, M., Hu, S., Li, J., Zhou, B., Cao, J., An, Z., 2011. Selected water-soluble organic compounds found in size-resolved aerosols collected from urban, mountain and marine atmospheres over East Asia. Tellus B 63, 371-381.

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$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{(S1)}$$

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad \text{(S2)}$$

$$\begin{cases} Unc_i = \frac{5}{6} \times MDL_i & C_i \leq MDL_i \\ Unc_i = \sqrt{(C_i \times Error\ Fraction)^2 + \left(\frac{1}{2} \times MDL_i\right)^2} & C_i > MDL_i \end{cases} \quad \text{(S3)}$$

**Fig. 1.**

**Table C1** Comparison between related studies with this manuscript

| ID | Studies | Sampling site | Sampling duration | Analysis method | PAHs | n-Alkanes | Hopanes | Steranes | Size-distribution | Gas-particle partitioning | Source identification | Remark |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ① | Wang et al., 2011a; ACP | Baoji city, China | 11-14, Jan. 12-20, Feb. 12-24 Apr. 2008 | Ultrasonication Extraction+GC/MS | 16 species | C18-C36 | 5 species | / | TSP; 0.4-9.0 μm, nine stage; | / | / | |
| | | Mount Tai, China | 22-29 Jun. 2006; 12-24 Jan. 2008 | | | | | | | | | |
| | | Okinawa Island, Japan | 18 Mar. -12 Apr. 2008 | | | | | | | | | |
| ② | Wang et al., 2011b; EST | Nanjing city, China | 1-17 Jan. 2007 12-14 Oct. 2007 | Ultrasonication Extraction+GC/MS | 16 species | C18-C34 | / | / | 0.4-9.0 μm, nine stage; | / | / | |
| ③ | Wang et al., 2009; Tellus, B | The same to study ① | The same to study ① | Ultrasonication Extraction+GC/MS | / | / | / | / | 0.4-9.0 μm, nine stage; | / | / | Mainly about sugar, sugar-alcohol, carbonxylic acid |
| ④ | Wang et al., 2015; EST | Nanjing city, China | Jul. 2004 - Jan. 2005 | Solvent extraction+ GC/MS | / | C18-C36 | / | / | / | / | Tracers for source identification | |
| ⑤ | Wang et al., 2006; EST | 14 Chinese cities | 2 days in winter + 2 days in summer, 2003 | Ultrasonication Extraction+GC/MS | 18 species | C16-C35 | C27-C32 | / | / | / | / | Other sugars and so on |
| ⑥ | Gao et al., 2015; AE | Guizhou city, China | 28 Nov. - 23 Dec. 2009 | Ultrasonication Extraction+GC/MS | 13 species | / | 4 species | / | / | / | Factor identification + correlation analysis | |
| ⑦ | Xie et al., 2014; EST | Denver, USA | Aug. 2012- Jul. 2013 | / | 6 species | 12 species | 5 species | 5 species | / | / | PMF model | Extracted five species profiles |
| | This manuscript; ACP | Jiujiang city, China | Sep. - Dec. 2016 | TD-GC/MS, without solvent extraction | 15 species | 30species, C11-C40 | 5 species | 5 species | 13 stage, 0.01-18 μm | Partitioning between all these NPOCs | Tracers + PMF model | Extracted 8 factors for $PM_{2.5}$ aerosols |

**Fig. 2.**



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