

Manuscript title: Evolution and chemical characteristics of organic aerosols during wintertime PM_{2.5} episodes in Shanghai, China: Insights gained from online measurements of organic molecular markers

Point-by-point response to comments

We sincerely thank the referee for the comments concerning our manuscript. They are valuable in helping us improve our manuscript. Our point-by-point response is provided below and marked in blue text.

- 1) I think the introduction part is not sufficient to raise the scientific question. Numerous field studies have been conducted in Shanghai over the past decades. The limitations of these previous studies should be clearly discussed, and the ways in which this study can address these limitations need to be stated.

Response: Thanks for your suggestion. We will give more detail discussions on the findings and limitations of previous field studies conducted in Shanghai in the revised manuscript.

- 2) TAG is the key instrument of this paper. However, I did not see much information about its operation in this paper. For example, how much was the TD temperature? Was the derivatization agents used in TAG? If so, what are the agents?

Response: Although the operation of the TAG instrument was described in detail in our earlier publications, we agree with the reviewer that more essential operation information needs to be included in the current manuscript to facilitate readers' comprehension of our work.

In brief, the CTD temperature program was set to be firstly held at 45 °C for 2 min, then increased to 330 °C in 6 min, and lastly held at 330 °C for 12 min. During this thermal desorption step, polar organic compound in PM_{2.5} deposit on the CTD underwent in-situ derivatization under a helium stream saturated with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA). MSTFA was the derivatization agent used in this study. More detailed information related to our TAG system is provided in our previously published papers (He et al., 2020; Wang et al., 2020; Zhu et al., 2021).

- 3) The same comments also apply to other instruments. The method section is too brief.

Response: Other instruments are more commonly deployed in field studies and better known to the atmospheric measurement community. The working principles of these instruments mentioned have been described in our previously published papers. For example, the performance of AMS during this field campaign is reported in Huang et al. (2021). Qiao et al. (2014) and Zhou et al. (2016) have described the working principles of OC/EC analyzer and MARGA adopted in this study and their performances during this field campaign is available in Zhou et al. (2022). In addition, detailed information related to the VOC measurements by the GC-FID adopted in this study is given in Liu et al. (2019) and Wang et al. (2015). We will add these references in the revised manuscript.

- 4) Table S1 lists the range and average concentrations of the 98 quantified organic compounds. How did the authors quantify their concentration? Through standard injection? How were these compounds identified? Is the identification method very reliable? Or it is just a search through NIST MS database? Such information should be clearly presented.

Response: Below is a detailed explanation of how we identify and quantify the 98 compounds and this information will be added to the supplementary information document. In our study, calibration curves were first established before using the TAG system to measure ambient samples. To be specific, 5 µL of ISs was mixed with 0-5 loops (5 µL/loop) of external standards and co-injected into CTD cell for GC-MS identification and quantification. This yielded a five-point calibration curve for each analyte. Calibration curves were established by fitting the normalized peak areas of external standards to their corresponding IS with respective concentrations. During the ambient measurements, 1 loop (5 µL) of IS was also injected into each aerosol sample by the auto-injection system equipped in the TAG. The target organic compounds in aerosol samples were identified by the retention time and mass spectrum, which were obtained from their authentic standards. Then we calculated peak area ratios of target organic compounds against their corresponding IS (listed in Table S1) for each ambient sample and used the above-mentioned calibration curves to quantify their masses in real aerosol samples. The details of the TAG calibration and

quantification method have been given in several of our previously published papers (He et al., 2020; Wang et al., 2020).

- 5) TAG can operate in one-hour resolution. Why it was operated with a time resolution of 2 hours (Line 80)? In Table 2, it stated that TAG's time resolution was 1 hour. Which number is correct?

Response: Yes, the TAG system can be operated in one-hour resolution as reported by other papers (Isaacman et al., 2014), if a short GC program is adopted. Figure R1 (see below) shows the temperature status of three components in the TAG system. Note that during part of sample analysis stage, the CTD is not ready for sample collection mode. Sampling can only start when the CTD temperature has dropped to 35°C. As such, the time allocated to sample collection would be less than 1 hour if an hourly time resolution is adopted, such as in previous studies by Goldstein and coworkers. In our work, we have adopted a longer GC program and a full hour for sample collection. The combined time for each cycle of sample collection and analysis is 2 hours. We will correct the related information in Table 1.

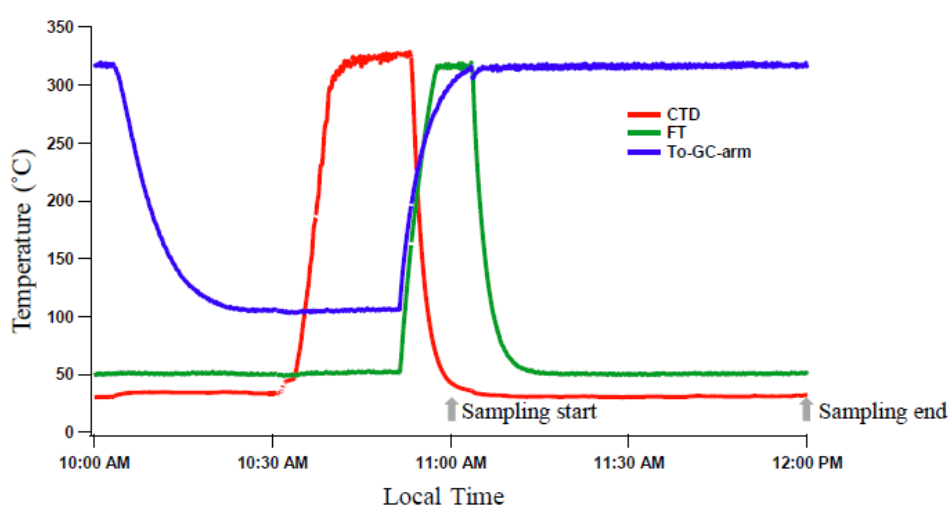


Figure R1. The temperature program of CTD, focusing trap (FT) and to-GC-arm in one analysis cycle. The next sample's start and end points are also marked, which coincide with the start and the end of the GC analysis. Adapted from He et al. (2020).

- 6) Line 265: it is stated that "transported PM₁ contained higher proportions of more-oxidized organic aerosol (MO-OOA) while less oxidized organic aerosol (LO-OOA) accounted for more PM₁ mass during local episodes." Can this statement also be supported by the AMS f44 trace?

Response: Yes, this statement is also supported by the AMS f44 tracer. We will add the figure below (Figure R2) in the revised manuscript.

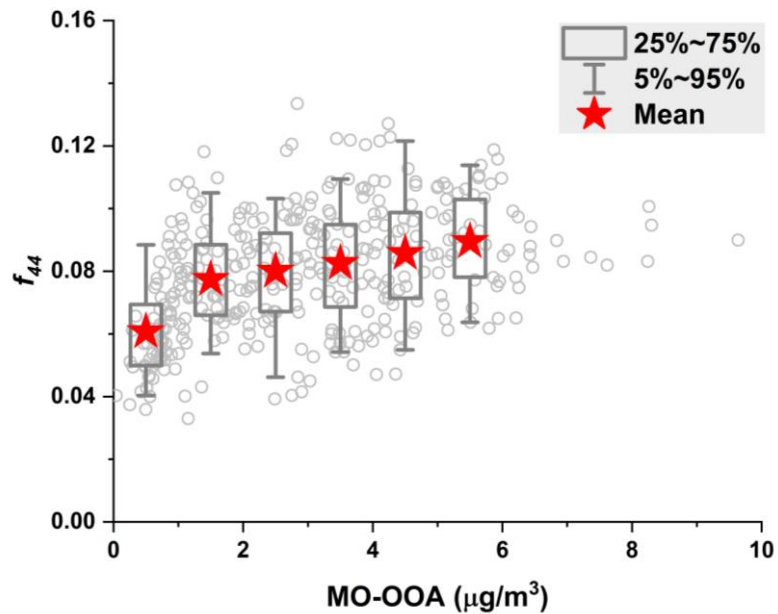


Figure R2. f_{44} as a function of MO-OOA concentration bins.

- 7) This paper uses a very traditional way to separate POC and SOC. But this study has AMS data. Why not just do a PMF analysis for AMS data and separate a SOM factor? I think this way is more accurate.

Response: We agree with the reviewer that AMS PMF is capable of separating POC and SOC using characteristic ion fragments. The reason why we use the OC/EC ratio method to estimate SOM and POM is that OC and EC were measured in $PM_{2.5}$ while AMS provides PM_1 measurements. Using POC and SOC derived from PM_1 to approximate those in $PM_{2.5}$ would bring in an uncertainty that is not straightforward in quantifying. We note that the AMS-derived source factors and POM, SOM estimated by OC/EC ratio method were well correlated, indicating that the OC/EC ratio method applied in this work overall gave reasonable estimations of POM and SOM.

- 8) It seems that AMS PMF analysis was done and the results were included in Figure 3. But what are the details of this analysis. How many factors were used? How about other key parameters used in PMF? I would not report the PMF results without showing the key PMF parameters.

Response: Our recently published paper (Huang et al., 2021) has described the AMS PMF analysis in detail. In brief, a total of seven source factors were resolved by the PMF model based on AMS data collected during this period (see below in Figure R3). We will add this reference in the manuscript so that interested readers can get more detail information about the AMS PMF analysis.

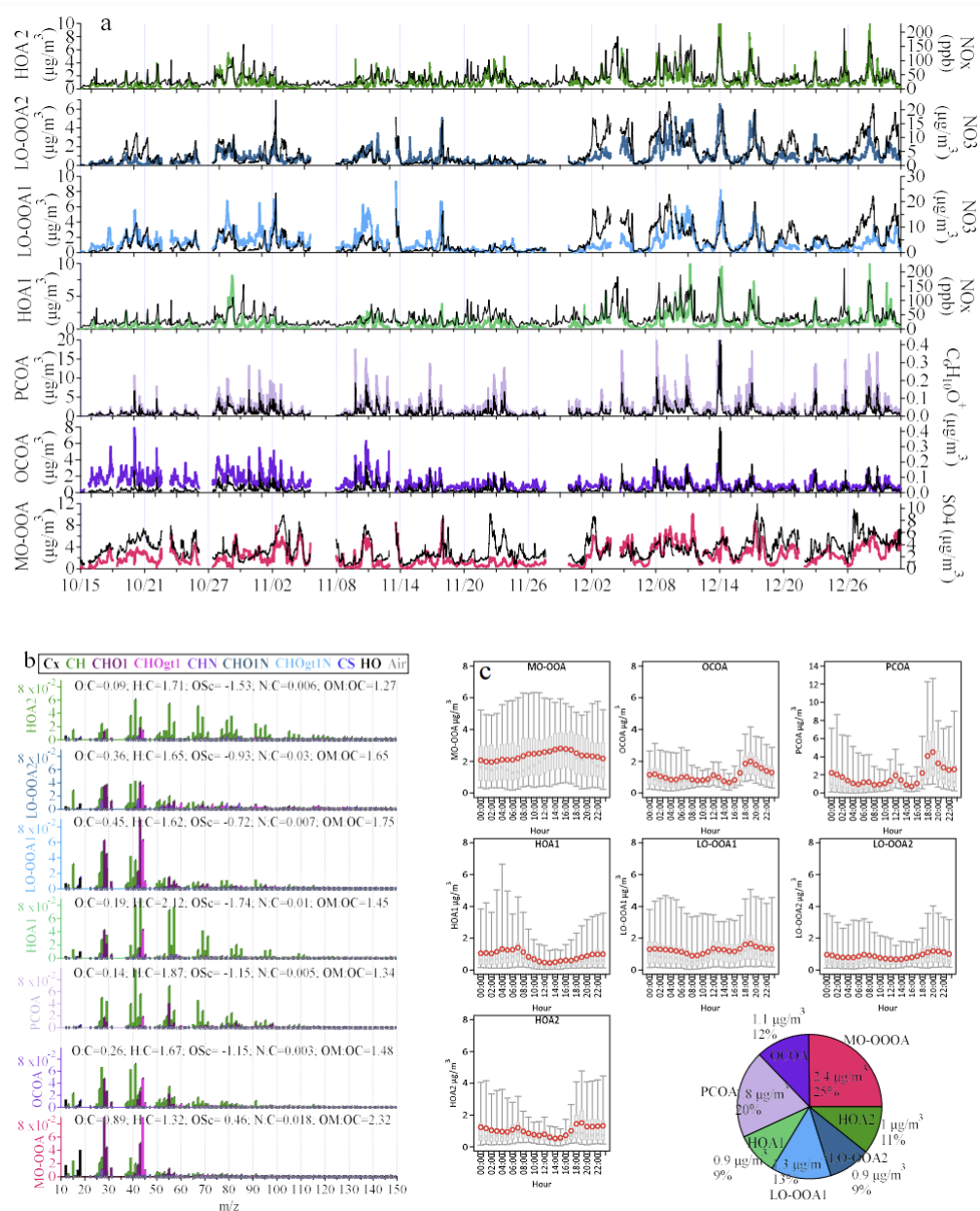


Figure R3. (a) Time series, (b) mass spectral profiles, (c) diurnal variations and fractional contributions of the OA factors from the 7-factor solution of AMS-PMF analysis. Adapted from Huang et al. (2021) figure S2.

References:

- He, X., Wang, Q., Huang, X. H. H., Huang, D. D., Zhou, M., Qiao, L., Zhu, S., Ma, Y., Wang, H., Li, L., Huang, C., Xu, W., Worsnop, D. R., Goldstein, A. H. and Yu, J. Z.: Hourly measurements of organic molecular markers in urban Shanghai, China: Observation of enhanced formation of secondary organic aerosol during particulate matter episodic periods, *Atmospheric environment* (1994), 240, 117807, 10.1016/j.atmosenv.2020.117807, 2020.
- Huang, D. D., Zhu, S., An, J., Wang, Q., Qiao, L., Zhou, M., He, X., Ma, Y., Sun, Y., Huang, C., Yu, J. Z. and Zhang, Q.: Comparative Assessment of Cooking Emission Contributions to Urban Organic Aerosol Using Online Molecular Tracers and Aerosol Mass Spectrometry Measurements, *Environ. Sci. Technol.*, 55, 14526–14535, 10.1021/acs.est.1c03280, 2021.
- Isaacman, G., Kreisberg, N. M., Yee, L. D., Worton, D. R., Chan, A. W. H., Moss, J. A., Hering, S. V., & Goldstein, A. H.: Online derivatization for hourly measurements of gas- and particle-phase semi-volatile oxygenated organic compounds by thermal desorption aerosol gas chromatography (SV-TAG), *Atmospheric Measurement Techniques*, 7, 4417–4429, 10.5194/amt-7-4417-2014, 2014.

Liu, Y., Wang, H., Jing, S., Gao, Y., Peng, Y., Lou, S., Cheng, T., Tao, S., Li, L., Li, Y., Huang, D., Wang, Q., & An, J.: Characteristics and sources of volatile organic compounds (VOCs) in Shanghai during summer: Implications of regional transport, *Atmospheric Environment* (1994), 215, 116902–, 10.1016/j.atmosenv.2019.116902, 2019.

Qiao, L., Cai, J., Wang, H., Wang, W., Zhou, M., Lou, S., Chen, R., Dai, H., Chen, C., and Kan, H.: PM_{2.5} constituents and hospital emergency-room visits in Shanghai, China, *Environ. Sci. Technol.*, 48, 10406–10414, 10.1021/es501305k, 2014.

Wang, H. L., Qiao, L. P., Lou, S. R., Zhou, M., Chen, J. M., Wang, Q., Tao, S. K., Chen, C. H., Huang, H. Y., Li, L., & Huang, C.: PM_{2.5} pollution episode and its contributors from 2011 to 2013 in urban Shanghai, China, *Atmospheric Environment* (1994), 123, 298–305, 10.1016/j.atmosenv.2015.08.018, 2015.

Wang, Q., He, X., Zhou, M., Huang, D. D., Qiao, L., Zhu, S., Ma, Y., Wang, H., Li, L., Huang, C., Huang, X. H. H., Xu, W., Worsnop, D., Goldstein, A. H., Guo, H. and Yu, J. Z.: Hourly Measurements of Organic Molecular Markers in Urban Shanghai, China: Primary Organic Aerosol Source Identification and Observation of Cooking Aerosol Aging, *ACS Earth Space Chem*, 4, 1670-1685, 10.1021/acsearthspacechem.0c00205, 2020.

Zhou, M., Qiao, L., Zhu, S., Li, L., Lou, S., Wang, H., Wang, Q., Tao, S., Huang, C., and Chen, C.: Chemical characteristics of fine particles and their impact on visibility impairment in Shanghai based on a 1-year period observation, *J. Environ. Sci. (China)*, 48, 151–160, 10.1016/j.jes.2016.01.022, 2016.

Zhou, M., Zheng, G., Wang, H., Qiao, L., Zhu, S., Huang, D., An, J., Lou, S., Tao, S., Wang, Q., Yan, R., Ma, Y., Chen, C., Cheng, Y., Su, H., & Huang, C.: Long-term trends and drivers of aerosol pH in eastern China, *Atmospheric Chemistry and Physics*, 22, 13833–13844, 10.5194/acp-22-13833-2022, 2022.

Zhu, S., Wang, Q., Qiao, L., Zhou, M., Wang, S., Lou, S., Huang, D., Wang, Q., Jing, S., Wang, H., Chen, C., Huang, C. and Yu, J. Z.: Tracer-based characterization of source variations of PM_{2.5} and organic carbon in Shanghai influenced by the COVID-19 lockdown, *Faraday Discuss.*, 226, 112-137, 10.1039/D0FD00091D, 2021.