

## **Mass spectral characterization of secondary organic aerosol from urban lifestyle sources emissions by Zhu et al.**

### General comments: Summary of research question and contribution of work

This research work has been submitted for consideration as a “research article”. The authors aim to quantify atmospheric physicochemical processing of primary gas and particle-phase cooking and vehicular emissions, focusing on organic aerosols. The team uses a suite of instruments, to initially dilute (Dekati dilutor), oxidize (GO: PAM reactor), and detect (HR-ToF-AMS for organic aerosols; SMPS for particle size distributions and numbers; SO<sub>2</sub>, CO, and CO<sub>2</sub> gas phase monitors) the primary emissions from Chinese cooking (frying-based) and vehicular tests (gasoline direct injection engine used with gasoline fuel). For cooking, the authors varied the dish type (and the associated operating conditions, four types of dishes cooked) while for the engine operation, the authors varied the running speeds and torques (five combinations). The authors report data for equivalent photochemical ages (EPA) up to 2.1 days for cooking tests, and up to 4.2 days for vehicle tests. The authors note that for cooking, the type of cooking (operating condition) matters more than the EPA (extent of oxidation) for the mass spectral similarity analysis, and vice-versa for vehicular emissions. Next, the authors apply the IGOR PMF PET tool to identify primary and secondary components of the aged cooking and vehicular emissions. For cooking tests, the authors found only two PMF factors: one primary and one secondary. However, for vehicular tests, the authors found three factors: one primary and two secondary factors. Finally, the authors apply averaged mass spectra of some, and not all, obtained factors to ambient datasets collected in Shanghai. The authors show that using these lab-based primary and secondary cooking and vehicular factors in ME-2 analysis improves diurnal patterns for some factors (LO-SOA in winter, MO-OOA in summer), and allows extraction of an other-POA factor with a diurnal pattern peaking in the evening and extracted only in winter, possibly associated with biomass burning and coal combustion.

While the paper addresses a relevant and longstanding question of atmospheric chemistry (constraining secondary organic aerosols), **the present scientific and technical quality of the paper is lacking in multiple aspects. I recommend that this manuscript be reconsidered for publishing after major revisions.**

### Major Comments

- 1) The paper presents the cooking tests and results as original work of this paper, and references published work (Zhang et al., 2020) incorporating those tests and results mostly in the Methods section (exception being Line 196). However, the ACP similarity report revealed large sections of this paper discussing the cooking results (for example, Lines 172-176, 207-221) are almost verbatim from published work (Zhang et al., 2020), **a clear and unfortunate case of self-plagiarism**. The authors should add explicit references and paraphrasing (if taking verbatim text) to all such portions of the paper.
- 2) The authors present the use of mass spectral similarity analysis in the methods section and discuss five categorizations to be used in the rest of the paper. However, they often deviate from using the categories to describe results. For example, in lines 159-170, 176. they use

phrases such as “almost resembled”, “different”, “similar”, and “almost the same variation” to describe mass spectral comparisons instead of using the five qualitative categories introduced in the paper in Sect. 2.3. The authors should address these inconsistencies by making sure all comparisons are presented in terms of the defined categories. Otherwise, Sect. 2.3 should be removed and all references to the categories removed in the paper. Similarly, the authors need to pick nomenclature/abbreviations for distinct factors and stick to them throughout. As an example, Fig. 3 refers to vehicle SOA factors as LO-SOA and MO-SOA, but the text below (lines 237) refers to those factors as LO-OOA and MO-OOA. Adding a nomenclature table at the end of the manuscript would also be helpful.

- 3) There is literature out there that has evaluated evolution of mass spectra of vehicle emissions such as Kroll et al., 2012. Kroll and co-workers focus on diesel emissions, a major missing gap in this study. Could the authors use mass spectra from such studies for their PMF/ME-2 analysis and quantify the effect of including/excluding such mass spectra in their work? The review by Gentner et al., 2017 might be a useful source to add relevant papers to the literature review in this paper. It is also important to note that the authors have drawn broad conclusions on vehicular emissions based on one vehicle type (one engine) and one fuel. How representative are measurements based on this combination for the entire fleet of Shanghai? This could be discussed in detail in the limitations section (see (7)).
- 4) The PMF/ME-2 analysis presented in this paper has multiple shortcomings, both in terms of descriptions in the methods section, as well as the analysis and presentation of results.
  - a. In the methods section, there is no mention of how the authors conducted ME-2 analysis on the datasets in this study. The Igor PET tool runs on PMF2.exe and does not have a ME-2 option.
  - b. PMF analysis based on mass spectral similarity analysis only has previously been shown to generate spurious factors (Ulbrich et al., 2009). Other analyses such as time-series correlations with external tracers need to be presented to justify PMF/ME-2 factors. However, such correlations have been presented only for MO-OOA factor in summer and LO-SOA factor in winter, and not for other factors. Similarly, the other-POA factor could be a mix of the HOA and the COA factors (in the same 2-D plane as defined by the two vectors), and this should be checked using the scalar triple product. Refer to Ulbrich et al, 2009 for more details.
  - c. The authors use PMF to separate POA and SOA factors from aged HOA and COA detected in this study. However, using single MS to represent entire time series data in a test is an obvious limitation of PMF that has not been explicitly recognized. I suggest the authors recognize this as a limitation explicitly. It is also unclear how the references for the application of the PMF technique (line 118) are relevant since they are applying PMF on ambient and not lab datasets. Also, it is unclear how this analysis was conducted. Were different EPA tests combined for each type (vehicle operation, food dish) and then PMF conducted? Or was PMF conducted separately for each experiment?
  - d. Why was other-POA in winter not identified as associated with a specific POA component such as BBOA or CCOA, given ambient source apportionment results

from Chinese cities (including Shanghai) are readily available from earlier literature? The low levels of contributions at  $m/z$  60,  $m/z$  73, and  $m/z$  115, which are tracers of biomass burning and coal combustion make the argument that this other-POA factor is associated with biomass burning or coal combustion weak. What reference profile does the mass spectral similarity analysis suggest this factor resembles? What evidence do we have with respect to time series correlations?

- e. In Section 3.3, the authors compare their approach (of using constrained POA and SOA) to the completely unconstrained PMF approach. However, the improvement of ME-2 for primary factors over unconstrained PMF has already been presented in recent work such as Zhu et al., 2018. So, a more appropriate question to address would be: how much of an improvement do we observe in the ME-2 method when both primary and secondary factors are constrained (compared to when only the primary factors are constrained)? Given the PMF and ME-2 runs the team has already conducted, such a comparison should not be hard to perform, and will give much more substantial insight into the importance of the approach compared to the current presentation. Another result that could arise from this comparison is that constraining the secondary factors could be overconstraining the PMF runs, which leads to factor mixing and reduced number of factors. Interestingly, Zhu et al., 2018 were able to separate coal combustion and biomass burning cleanly in winter during heavily polluted periods using their only primary factor-constrained ME-2 approach.
  - f. The final choice of constraints using ME-2 was described in vague terms in lines 259-260 and lines 265-269. “Considering the actual oxidation conditions or the concentration of OH radicals, the cooking PMF POA, SOA, and the vehicle PMF LO-SOA was finally selected as the input source spectra of ME-2... In addition, the ME-2 source analysis was performed by using two primary OA factors (the cooking PMF POA, HOA resolved in three cities) and two secondary OA factors (the cooking PMF SOA, the vehicle PMF LO-SOA) as constraints based on the same ambient OA datasets as PMF model during the summer and winter observations of Shanghai.” This is insufficient explanation. Why were vehicle POA and vehicle MO-SOA factors from lab tests not selected? Why was HOA resolved in three cities selected? This seems an arbitrary choice and needs to be justified further so the approach can be replicated in the future. Also, was the average of the HOA MS from three cities selected? I did not find the MS of that factor in the paper. How similar or different is it from the lab vehicle HOA MS, and why?
  - g. Factor uncertainties, residual, and total concentrations should be reported for each PMF/ME-2 analysis.
- 5) The conclusions of the paper are very generalized and presented as applicable to broad categories of cooking and vehicular emissions in ambient environments. However, the experiments conducted by the authors are limited in their scope: cooking experiments are all frying-based, and only one gasoline engine was assessed at a few operating conditions (combinations of vehicle speeds and torques) in this study. I have a few questions

associated with this choice that questions the confidence the authors place in their PMF/ME-2-based COA and HOA concentrations and composition.

- a. Could a different type of cooking be a part of other-POA and frying-related COA is what the authors are referring to as primary COA?
  - b. Similarly, could a different type of vehicle emission be a part of other-POA, and gasoline-related HOA is what the authors are referring to as primary HOA?
  - c. This would also complicate the secondary COA and HOA argument. Why is there no secondary component associated with the other-POA factor? How much of the MO-OOA factor is associated with other COA (non-frying) and other HOA (non-gasoline)?
  - d. Finally, also drawing on (3), how influential could the choice of a single engine (GDI) and fuel (gasoline) be on the conclusions drawn? Is it possible that if four engines were evaluated, the results obtained would have suggested that vehicle type (together with operating condition) is more important than the EPA in determining the mass spectra? This would not be surprising, given that there are major differences in emission patterns from vehicle to vehicle (case in point being the fat tail phenomena in emissions). Is there evidence to support that only the quantities (of emissions) vary across vehicles under similar operating conditions, but not the mass spectral patterns? If not, please show this as a limitation of the study.
- 6) The authors use dilution and high concentration of OH radicals (for brief period) to measure and simulate atmospheric aging of aerosols. However, these are both limitations since: 1) dilution changes the chemistry of aging, as also observed with volatility measurements (Cain et al., 2020), and 2) high concentrations of OH radicals could lead to changes in the reaction pathways that the aerosols undergo that are different compared to pathways on exposure to low OH concentrations for longer periods of time (but resulting in the same EPA). I suggest the authors discuss these aspects in a separate section on limitations of such work, as described in (7).
- 7) To address the above limitations, I suggest the authors separate the limitations briefly described in the conclusions section (Lines 304-308) and create a separate section on “limitations and future work”, where the authors can identify all the above gaps. They can also point readers to potential future work that can emanate out of this preliminary but notable effort.
- 8) Finally, the title of the paper is misleading since “lifestyle sources emissions” would also point to volatile chemical products such as perfumes, cleaning products, and deodorants. I suggest the authors change it to “urban cooking and vehicular sources”.

After addressing comments for the major revision associated with the comments above, I suggest the authors address the following minor comments in the updated manuscript before resubmission.

#### Minor comments

- 1) In Sect. 2.1, lines 91-93, the authors describe vehicle operating conditions in terms of vehicle speeds and torques. However, given the goal of the paper is to use lab tests to describe and apportion real-world emissions, what do these rpm speeds and Nm torques mean in terms of real-life conditions? Would you describe the real-life conditions in terms of vehicle speed (in mph) and rate of gain of elevation? An equivalence of each speed-torque combination would be immensely useful in understanding how relevant these combinations are to real-life conditions. Are these combinations relevant more to flat terrains in heavy traffic? Or are they more relevant to mountainous terrains with low traffic? It is hard to draw analogies to real-life conditions based on speeds and torques only.
- 2) In Sect. 2.2, the authors should clearly state the type of aerosols being measured, whether they are NR-PM<sub>2.5</sub> or NR-PM<sub>1</sub>.
- 3) In Sect. 2.2, lines 108-110, the reference describing how CO<sub>2</sub> interference can be reduced using CO<sub>2</sub> gas phase measurements needs to be added.
- 4) Lines 118-119: The method using SO<sub>2</sub> decay for OH exposure estimation is based on Zhang et al., 2020. However, Zhang and co-workers develop the method and present the assumptions as those applicable for cooking emissions only (Refer to Supplement of Zhang et al., pg. 2). Are the same assumptions applicable on vehicular emissions?
- 5) In Fig. S2 (main manuscript line 134), the evolution at the combination of 2000 rpm and 40 Nm seems to be very suspicious. In going from EPA 2.89 days to 4.15 days, f<sub>43</sub> seems to have increased and f<sub>44</sub> to have decreased, which is counterintuitive. Can the authors check the figures are correct? And if yes, using HR-ToF-AMS data, can you shed some light on what might be happening here?
- 6) Lines 154-155: “Chinese cooking emissions” should be replaced by “Chinese cooking emissions associated with frying”. As He et al., 2010 note, the fragments noted are associated with frying but not charboiling.
- 7) Mass spectra of cooking and vehicle tests at EPA 0 (or close to zero) should be presented in the Supplement as well.
- 8) Lines 162-164: “The mass spectra at 2.89 days and 4.15 days had very similar patterns with the most prominent peaks at m/z 28 and 44, respectively, which almost resembled the mass spectra of MO-OOA resolved from ambient datasets.” Reference to Table S4 is missing!
- 9) In lines 164, 166, and elsewhere, the authors mention ambient profiles. However, the criteria used to obtain these profiles is not clear. The methods section should be updated to clarify this point.
- 10) The authors supply tables Table 1 and S2-S3 in SI for MS similarity analysis for all vehicle operating conditions and for all food types at two EPAs. Similar tables should be supplied for the remaining EPAs for vehicles conditions and all food types.

- 11) The authors supply four tables S4-S7 in SI for MS similarity analysis for two vehicle operating conditions and for two food types at varying EPA. Similar tables should be supplied for the remaining three vehicle conditions and for the other two food types.
- 12) Lines 173-175: “Along with the growth of OH exposure, the  $f_{43}$  of aged COA increased from 0.07 to 0.10, and meanwhile its  $f_{44}$  increased from 0.03 to 0.08 (**Fig.2b; Fig.S5**), distributing in the lower region of less oxidized organic aerosol (LO-OOA).” There is a missing reference here since the LO-OOA region is undefined. For that matter, even in Fig. S6, that region has not been defined.
- 13) The authors discuss specifics of mass spectral contributions of different mass spectra, which are hard to decipher from the figures (e.g., lines 174, 216-218). I suggest the authors add supplementary tables of contributions at key  $m/z$ s for the different tests: vehicle/cooking type and operating condition.
- 14) Line 199: In Fig. S6, add and label the line with the slope of -0.5.
- 15) Lines 219-221: The two parts of the sentence seem disconnected, and the relevance of the sentence in this paragraph is unclear. The authors could use oxidation state of aerosols as a quantitative metric. Refer to Kroll et al., 2015 for definition and use with HR-ToF-AMS.
- 16) Lines 224-226: It is unclear whether this sentence refers to vehicle LO-SOA or MO-SOA.
- 17) Fig. 3: Vehicle POA MS is missing in the figure. Need to show vehicle POA mass spectral comparison.
- 18) Like Table S9, need to add table showing angles for vehicle PMF POA. Like Table S10, need to add table showing angles for vehicle PMF MO-SOA.
- 19) Lines 244-245: This sentence is missing a figure/table reference. It is also surprising that the cooking mass spectra of deep-frying chicken was excluded because it was different. Isn't diversity in MS better and wouldn't including diverse MS better allow capturing several types of cooking OA? This also means that the other-POA factor could resemble deep-frying chicken MS. Could the authors report the results of that check?
- 20) Fig. S4, Table S11: Why is any comparison with vehicle POA MS missing in these two?
- 21) Lines 264-265: What was the basis of deciding obtained PMF contributions of COA and HOA is “far exceeding expectations”. Such claims must be backed by proper references.
- 22) Lines 288-289: Stable proportion % of COA across seasons does not imply it had stable contributions as volatility, dilution effects, and atmospheric chemistry, and interactions with other emissions all play a role in these stable proportions. I suggest that this sentence should be removed or edited to consider these factors that are likely affecting COA proportion. Attribution to stable contribution would likely involve the implementation of a volatility basis set approach.

### References for review

- 1) Gentner, D.R., Jathar, S.H., Gordon, T.D., Bahreini, R., Day, D.A., El Haddad, I., Hayes, P.L., Pieber, S.M., Platt, S.M., de Gouw, J. and Goldstein, A.H., 2017. Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions. *Environmental science & technology*, 51(3), pp.1074-1093.
- 2) He, L.Y., Lin, Y., Huang, X.F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S.J., Zhang, Y.H., 2010. Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning. *Atmospheric Chemistry and Physics* 10, 11535-11543.
- 3) Kroll, J. H., Smith, J. D., Worsnop, D. R., and Wilson, K. R.: Characterisation of lightly oxidized organic aerosol formed from the photochemical aging of diesel exhaust particles, *Environmental Chemistry*, 9, URL <https://doi.org/10.1071/EN11162>, 2012. Accessible here: [http://krollgroup.mit.edu/papers/Kroll\\_2012.pdf](http://krollgroup.mit.edu/papers/Kroll_2012.pdf)
- 4) Kroll, J.H., Lim, C.Y., Kessler, S.H. and Wilson, K.R., 2015. Heterogeneous oxidation of atmospheric organic aerosol: kinetics of changes to the amount and oxidation state of particle-phase organic carbon. *The Journal of Physical Chemistry A*, 119(44), pp.10767-10783.
- 5) Ulbrich, I.M., Canagaratna, M.R., Zhang, Q., Worsnop, D.R. and Jimenez, J.L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. *Atmospheric Chemistry and Physics*, 9(9), pp.2891-2918.
- 6) Zhang, Z., Zhu, W., Hu, M., Wang, H., Chen, Z., Shen, R., Yu, Y., Tan, R. and Guo, S., 2020. Secondary Organic Aerosol from Typical Chinese Domestic Cooking Emissions. *Environmental Science & Technology Letters*.
- 7) Zhu, Q., Huang, X.-F., Cao, L.-M., Wei, L.-T., Zhang, B., He, L.-Y., Elser, M., Canonaco, F., Slowik, J. G., Bozzetti, C., El-Haddad, I., and Prévôt, A. S. H.: Improved source apportionment of organic aerosols in complex urban air pollution using the multilinear engine (ME-2), *Atmos. Meas. Tech.*, 11, 1049–1060, <https://doi.org/10.5194/amt-11-1049-2018>, 2018.