

Reviewer 1

This study presented concurrent measurements of detailed mass spectra of aerosol particles and gases in an urban environment in Wuhan, a megacity in central China. The authors emphasized the two most intensive anthropogenic sources, the traffic source and cooking, and in details investigated the primary emission, secondary production/transformation of organic aerosols and gases, under the influence of two typical meteorological conditions. The results and analysis provide insights and improve the understanding on the organic aerosol-gas conversion and SOA formation, for the important sources on high population exposure in a typical anthropogenically polluted environment. Because the concurrent measurements in both phases are rare, in particular for the region in central China, it is also a very valuable dataset. I would recommend for its publication after addressing the following minor comments.

We thank reviewer for the insightful and positive comments. We have now addressed all comments and revised our previous manuscript accordingly. Reviewer's comments are in black italics. Our reply is in red, and the corresponding changes in the texts are highlighted in yellow.

1) It will be useful to add some diagnosis for the PMF results from measured VOCs. More discussions on the choice of PMF factors should be given for VOCs. The conventional PMF analysis on VOCs only used a few species. Here a bunch of species are used. The difference regarding the species input for PMF should be given, and what is the advantages and disadvantages between both approaches.

We thank the reviewer to point this out. The detailed diagnosis for the PMF factors from the PTR measurement is now added in Text S2 and Figure S4.

The discussions regarding the different method using PTR measurements compared to conventional GC-MS measurements on the VOCs are added.

“Here 109 species of VOCs from the PTR-TOF-MS were used, which are mostly oxygenated or contain cyclic functional groups, in contrast with the GC-MS measurement which contains many aliphatic hydrocarbon compounds and usually only dozens of species were used for the PMF analysis (Zheng et al., 2021). These may lead to some unsolved primary VOC sources for the current analysis using the PTR-measured VOCs, if the source contained crucial markers of aliphatic species, but this method may have great advantage in comprehensively resolving factors of secondary VOCs. This may explain the less primary but more secondary VOC factors compared to conventional PMF-resolved VOC sources (Cai et al., 2010).”

Line 210-216.

2) It is interesting to see a substantial fraction of secondary oxygenated VOCs and even for oVOCs, a few factors can be resolved with different levels of oxidation. This reflects the feature of PTR measurement using proton as ion source, which prefers to measure oVOCs. Some discussions will need to discuss the nature of oVOCs you observed rather than primary hydrocarbons, which may place some limitation for the conclusion here.

The limitation using PTR-measured VOCs for the PMF analysis is now discussed as the answer to the above question.

3) It would be useful to point out what the policy maker could benefit from current study, such as the potential benefits to regulate the nighttime and daytime emissions. The importance in

controlling the highly oxidized species in the daytime may be emphasized. This will help increase the impacts of this study.

The related discussions are now added according to reviewer's suggestions.

“The particular regulation should be placed to avoid the formation of daytime highly-oxidized species when high solar radiation, which may contribute to the reactive oxygen species and exert adverse health impacts (Tao et al., 2003; Verma et al., 2009).”

Line 377-379.

Other technical correction:

Line 26, needing to define O/C

It has been revised.

“...in a higher oxidation state (oxygen-to-carbon, O/C = 0.72)...”

Line 26-27.

Line 41, before? Needing changing a word.

It has been revised.

“This raises challenges for source-oriented environmental policy making, until explicit understanding on the formation mechanism of SOA from different sources.”

Line 41.

Line 42, allow the online attribution

It has been revised.

“The application of detailed mass spectra of organic aerosols allows the online source attribution of organic aerosol (OA).”

Line 42.

Line 69, in a typical region of mixed sources of ...

It has been revised.

Line 74, initializing

It has been revised.

Line 75, The cluster analysis

It has been revised.

Line 102, VOC compound

It has been revised.

Line 103, at which temperature?

We have now added temperature.

“The vapor saturation concentration (equilibrium vapor pressures) (C^*) of each VOC compound at 25 °C is estimated using the parameterization based on elemental ratio and molecular weight.”

Line 102-104.

Line 121, the model fits the data well

It has been revised.

Line 149, high temperature

It has been revised.

Line 127, electrical mobility diameter

It has been revised.

Line 130, need a slope value for the PM closure

We have added the slope value.

“...the SMPS agreed well with that from the sum of compositions by the HR-ToF-AMS and SP2 ($r = 0.71$, slope = 0.90).”

Line 131.

Line 137, non-refractory

It has been revised.

Line 146, temporal evolution

It has been revised.

Line 150-154, what these different air mass histories can tell?

Some discussions are added now.

“It therefore separates the periods with more local air mass or influences from regional transport.”

Line 155-156.

The quality of Fig. 1 needs to be improved.

The figure has been improved.

The y-axis are very confusing for Fig. 1d, is the green for OA?

It has been revised.

“(d) mass concentrations of key aerosol species (the green left y-axis represents OA, the right y-axis represents other aerosol species);”

Line 159-160.

Line 168, contained some fragment markers... may have been overwhelmed

It has been revised.

Line 173, maybe needing more decimal.

It has been revised.

“This factor has a $C_3H_3O^+/C_3H_5O^+$ of 3.0 and $C_4H_7^+/C_4H_9^+$ of 2.0 (1.0 is usually for HOA),...”

Line 175-176.

Line 174, marker fragment

It has been revised.

Line 174, a major peak

It has been revised.

Line 179, account for a mass fraction?

It has been revised.

“Here the concentrations of COA in OA were in the range of 0.5–4.5 $\mu\text{g m}^{-3}$ and accounted for 23 % of **OA mass fraction** on average.”

Line 181-182.

Line 180, which was popular

It has been revised.

Line 181-182, needing to rewrite, as it already mentioned about the two factors, how could it be “further” separated.

It has been rewritten.

“**According to the oxidation state, OOA was separated into lower (OOA1) and more oxidized (OOA2) factors.**”

Line 184-185.

Line 184, the oxygenated fragment

It has been revised.

Line 186, but higher concentration

It has been revised.

It needs some emphasis that OOA1 was highly associated with the RH.

It has been revised.

Line 191, similar to what factors in those studies? The discussions here need to be specific.

We have added specific data in other cities.

“The factor OOA2 had the highest O/C of 0.72 and contained 61% oxygen-containing fragments (Fig. 2d), which is very similar to the spectra of OOA factor resolved in other cities **(0.60 and 67% in Mexico City, 0.8 and 66% in Pasadena)...**”

Line 193-194.

Line 193, at round noontime of up to ..., indicating the photochemical production

It has been revised.

Line 195, the reference here needs to be specific, what kind of agreement.

We have added specific data.

“The variation of OOA2 correlated with odd oxygen ($O_x = O_3 + NO_2$, $r = 0.70$), agreeing with previous observations that oxidized OA had strong correlation with O_x (Wood et al., 2010; Hu et al., 2016).”

Line 197-199.

Line 204-206, this sentence needs rewriting.

It has been revised.

“The first factor was dominated by aromatic compounds, such as C_6H_6 (m/z 79.054) and C_7H_8 (m/z 93.070) in Fig. 3a. They were well established markers for vehicle emissions (Gkatzelis et al., 2021) and had a good correlation with this factor ($r = 0.97$ and 0.63 , respectively Fig. S6).”

Line 217-219.

Line 207-209, the sentence needs some breakups.

It has been revised.

“This factor showed peaks in the morning and afternoon rush-hour (Fig. 3k) and was well correlated with HOA and NO_x ($r = 0.63$ and 0.53 Table S1). The concentration of this factor had a major increase during the early morning, reaching a peak value of 12.1 ± 1.3 ppb at 08:30, further corroborating the traffic source of this factor.”

Line 219-222.

Line 210, in addition to its consumption

It has been revised.

Line 212, not preferred, is more likely

It has been revised.

Line 213, for nocturnal chemistry

It has been revised.

Line 217, cooking emissions

It has been revised.

Line 219, surged?

It has been revised.

“The concentration of this factor decreased during the daytime and increased after 18:00 with a peak value at 19:00 (17.2 ± 3.0 ppb).”

Line 231-232.

Line 220, this sentence is hard to understand.

It has been revised.

“As shown in Fig. 3l, the diurnal concentration decreased strongly after emission and continued to decline throughout the night, suggesting that cooking VOCs may be major precursors and were consumed during night.”

Line 232-234.

Line 239, the mean contribution

It has been revised.

Line 243, the vapor pressure needs a reference temperature, is it in logarithmic?

It has been revised.

“These VOCs with $m/z > 120$ tend to be intermediate-volatility organic compounds (IVOCs) as the estimated vapor saturation concentration ($\log_{10}C^*$, 298 K) is less than $6.5 \mu\text{g m}^{-3}$.”

Line 254-255.

Line 259, was. You need to check through the tense.

Thank you for pointing out this problem. We have revised the tense of the full manuscript.

Line 260, but increase?

It has been revised.

“During night, the O/C ratio increased with the increase moderately oxygenated fragment f_{43} ($\text{C}_2\text{H}_3\text{O}^+$).”

Line 273-274.

Line 268, showed

It has been revised.

Line 275, as intermediately involved

It has been revised.

Line 276, in the OOA2 factor

It has been revised.

Line 277, by the traffic source, via the oxidation, partitioning, further condensation

It has been revised.

“...is considered to be mainly contributed by the traffic source, via the oxidation of VOCs and partitioning to condensed phase, direct oxidation on HOA through heterogenous oxidation, or VOCs evaporated from HOA and further condensation after oxidation”

Line 290-292.

Line 291, remove or add a bracket

It has been revised.

Line 310, the concentrations are normalized

It has been revised.

Line 314, is the main driving factor

It has been revised.

Line 315, showed

It has been revised.

Line 323, reaction rate

It has been revised.

Line 356, the different

It has been revised.

Line 357, remove as

It has been revised.

References

- Cai, C., Geng, F., Tie, X., Yu, Q., and An, J.: Characteristics and source apportionment of VOCs measured in Shanghai, China, *Atmos. Environ.*, 44, 5005-5014, <https://doi.org/10.1016/j.atmosenv.2010.07.059>, 2010.
- Gkatzelis, G. I., Coggon, M. M., McDonald, B. C., Peischl, J., Gilman, J. B., Aikin, K. C., Robinson, M. A., Canonaco, F., Prevot, A. S. H., Trainer, M., and Warneke, C.: Observations confirm that volatile chemical products are a major source of petrochemical emissions in US cities, *Environ. Sci. Technol.*, 55, 4332-4343, <https://doi.org/10.1021/acs.est.0c05471>, 2021.
- Hu, W., Hu, M., Hu, W., Jimenez, J., Yuan, B., Chen, W., Wang, M., Wu, Y., Chen, C., Wang, Z., Peng, J., Zeng, L., and Shao, M.: Chemical composition, sources, and aging process of submicron aerosols in Beijing: Contrast between summer and winter, *Journal of Geophysical Research: Atmospheres*, 121, 1955-1977, <https://doi.org/10.1002/2015JD024020>, 2016.
- Tao, F., Gonzalez-Flecha, B., and Kobzik, L.: Reactive oxygen species in pulmonary inflammation by ambient particulates, *Free Radical Bio. Med.*, 35, 327-340, [https://doi.org/10.1016/S0891-5849\(03\)00280-6](https://doi.org/10.1016/S0891-5849(03)00280-6), 2003.
- Verma, V., Ning, Z., Cho, A. K., Schauer, J. J., Shafer, M. M., and Sioutas, C.: Redox activity of urban quasi-ultrafine particles from primary and secondary sources, *Atmos. Environ.*, 43, 6360-6368, <https://doi.org/10.1016/j.atmosenv.2009.09.019>, 2009.
- Wood, E. C., Canagaratna, M. R., Herndon, S. C., Onasch, T. B., Kolb, C. E., Worsnop, D. R., Kroll, J. H., Knighton, W. B., Seila, R., Zavala, M., Molina, L. T., DeCarlo, P. F., Jimenez, J. L., Weinheimer, A. J., Knapp, D. J., Jobson, B. T., Stutz, J., Kuster, W. C., and Williams, E. J.: Investigation of the correlation between odd oxygen and secondary organic aerosol in Mexico City and Houston, *Atmos. Chem. Phys.*, 10, 8947-8968, <https://doi.org/10.5194/acp-10-8947-2010>, 2010.
- Zheng, H., Kong, S., Chen, N., Niu, Z., Zhang, Y., Jiang, S., Yan, Y., and Qi, S.: Source apportionment of volatile organic compounds: Implications to reactivity, ozone formation, and secondary organic aerosol potential, *Atmos. Res.*, 249, 105344, <https://doi.org/10.1016/j.atmosres.2020.105344>, 2021.