Comments on ACP ms – VOCs in Shanghai

The authors have made lots of efforts to revise this manuscript according to the comments from reviewers. Additional information and discussions were provided, and the English writing was improved. However, some of the questions were not fully elaborated in terms of the research highlight, the rationality of the methods, and the result interpretations. Therefore, I think the current manuscript is not ready for publication until the below comments are addressed.

1. The authors emphasized that the VOCs characteristics and their impacts on O_3 and SOA under different land-use types remained a gap and highlighted that the multi-site measurements would be able to fill this gap. In fact, the abundance, compositions, sources, and the O_3 and SOA chemistry have been extensively investigated not only in Shanghai but also around the globe. Several studies have measured VOCs in the same locations (line 240-244). Despite the different TVOC concentrations, the results in this study were consistent with previous studies, including the VOC compositions and source contributions. Therefore, I wonder what new insight this work would bring in addition to comparing the reported results. What's more, a similar study has been published, which measured VOCs at the same 3 sites concurrently and investigated the VOC characteristics, sources, and secondary formation potentials (Wang et al., 2022).

2. The causation between land-use and VOC sources was confusing. For example, in line 63-64, "the land-use types influence not only the VOC concentrations but also the sources, especially the anthropogenic sources". Actually, the spatial variations of VOC abundance and compositions were due to the different major emission sources in different land-use types. Meanwhile, the definition of different land-use types in this study was based on the functional types of the areas, which include different source sectors inside. Thus, the results in this study are mostly attributable to different emission sources, and they can hardly be concluded to the impacts of the different land-use types directly as in the Discussion section. Besides, though the term "land-use" was repeatedly emphasized throughout the manuscript, the relation between the findings and the land-use types was weak.

3. Line 150-152: The meteorological parameters were measured at one weather station, while the meteorological factors were different among the 3 sites in the results (Figure 1). The authors need to clarify the data source.

4. The COD values were used to estimate the divergence of TVOC concentrations among sites. What were the thresholds of high and low similarity? The values 0.20, 0.33, and 0.36 seem to be small, as CODs of 0.269 and 0.783 were used to determine the similar and dissimilar sites in the cited paper (Wongphatarakul et al., 1998).

5. The sensitivity analysis is confusing. Firstly, why were background values needed in the calculation? What were the "specific $PM_{2.5}$ gradients" in line 213? What were the "corresponding VOC concentrations" in line 220? Secondly, how to derive equations 14 and 15? Which parameter in the calculation indicates sensitivity? Most importantly, why do we need to analyze the sensitivity of VOCs to $PM_{2.5}$ instead of the other way around? Line 220-221: "the concentration of VOCs was greatly affected by the variations of $PM_{2.5}$ concentration." And Line 229.

6. As shown in Figure 1, two prominent peaks of VOC concentrations were observed at JS. In spite of the peaks, the TVOC level at JS was comparable and even lower than that at PD. While the authors only discussed the mean TVOC concentrations at 3 sites, the special events were concealed.

7. Line 248-249: Why were the average $PM_{2.5}$ concentrations comparable among 3 sites, whereas the O_3 levels were higher at QP than at the other sites?

8. Line 257: How to infer that "The termination and titration ($NO + O_3 \rightarrow NO_2 + O_2$) were more efficient"?

9. Line 250-260: Pearson correlation coefficient was applied to estimate the correlations of VOCs and O_3 and VOCs and $PM_{2.5}$. The Pearson correlation coefficient is to measure the linear correlation between two datasets. However, O_3 and $PM_{2.5}$ have non-linear relationships with VOCs. Hence, the feasibility of this estimation should be justified.

10. Line 305-306: haze days were defined as "visibility < 10 km and RH > 80 %". Given the high RH, how to distinguish haze from fog?

11. Line 313-314: Why JS and PD had stagnant weather while QP didn't? How to define stagnant weather, and what were the weather conditions on haze days?

12. Line 316-317: The authors attributed the elevated VOC concentrations on haze days to enhanced emissions. Is there any evidence for the enhanced emissions, especially the vehicle exhausts?

13. Figure 5: How to define the different thresholds of VOC ratios? If the reference values were obtained from previous studies, are they comparable and suitable for this study?

14. Line 355 and 367: What do you mean by "during the VOC pollution"?

15. The source profiles apportioned from PMF results were highly doubtful. The problems are not limited to the followings. 1) Industrial source was not resolved at QP, while the biogenic source was not resolved at JS and PD. Are the source apportionment results comparable among these sites? 2) From Figure 6c, a high proportion of 1,2,3-trimethylbenzene was apportioned to the biogenic source at QP. The proportions of aromatics were even higher than isoprene in the biogenic source. 3) Isoprene, as a tracer for biogenic sources, was apportioned to the industrial source at JS and paint solvent usage at PD. 4) At QP, C_2 species were apportioned to vehicle exhausts, while they were also tracers for coal combustion. In addition, coal combustion at QP contained a large proportion of ethylbenzene, which was not explained. 5) Line 413-414: Fuel evaporation was identified by C_3-C_7 species. However, high proportions of aromatics, such as benzene at JS, and isopropylbenzene at PD, were also apportioned to this source. In addition, the contributions of fuel evaporation to TVOC at QP (20.15%) were much higher than those of the other sites. What could be the reason for that? 6) How about the correlations between every two sources (G-Space plot)?

16. According to the PSCF results, regional transport of VOCs, especially from northern regions, also contributed to the VOC concentrations at 3 sites. While the VOCs were apportioned to local sources in the PMF model, which part of the VOCs was accountable for the regional transport?

17. Line 472-473 and 497: How to quantify the percentage of OFP and SOAFP to O_3 and $PM_{2.5}$ concentrations?

18. As discussed in line 500-504, large uncertainty existed for the SOAFP method. Indeed, the OFP and SOAFP methods are only based on the reference reactivity of VOCs, which species with high reactivity tend to have larger secondary yields. The results herein are rather general and widely known. It is hard to tell what new findings we can get from this method.

Reference

Wang, S., Zhao, Y., Han, Y., Li, R., Fu, H., Gao, S., . . . Chen, J. (2022). Spatiotemporal variation, source and secondary transformation potential of volatile organic compounds (VOCs) during the winter days in Shanghai, China. Atmospheric Environment, 286, 119203. doi:https://doi.org/10.1016/j.atmosenv.2022.119203

Wongphatarakul, V., Friedlander, S. K., & Pinto, J. P. (1998). A comparative study of PM2.5 ambient aerosol chemical databases. Journal of Aerosol Science, 29, S115-S116. doi:https://doi.org/10.1016/S0021-8502(98)00164-5