

Responses to Reviewer #1

Major comments:

How did you calibrate the concentrations of acetaldehyde, propionaldehyde, n-butanal, n-pentanal, n-hexanal, methacrolein, and methyl vinyl ketone measured by the GC-MS technique? These OVOCs may be unstable in cylinders. Additionally, the preconcentration procedure for the GC-MS technique may cause loss of the OVOCs especially under high RH condition because of their relatively high Henry constant with respect to NMHCs. The authors are suggested to present the detail information about the calibration in the section of Material and Methods.

Reply: Many thanks for your suggestion. Cylinder standard gases were employed to calibrate the online GC-MS/FID system. A 63-chemicals mixture standard (Spectra Gases) was used to calibrate C2–C6 carbonyls, methanol, and halocarbons.

Concentrations of acetaldehyde, acetone, propionaldehyde, n-butanal, n-pentanal, n-hexanal, methacrolein, and methyl vinyl ketone were calculated according to their calibration curves. We agree with you that the GC-MS technique may have some uncertainty in measuring OVOCs. Therefore, we compared OVOC concentrations measured by GC-MS and PTR-ToF-MS. The measurement results of the two instruments are quite similar. Therefore, we think the uncertainty of the GC-MS technique is acceptable. This gives us confidence to use GC-MS data. I added the detailed calibration procedure of GC-MS in Supplement.

Line 131-133: We compared concentrations of common OVOC species measured by both GC-MS and PTR-ToF-MS. The agreement of measurement results from the two instruments are quite consistent (Figure S1).

Line 25-38 in Supplement: Cylinder standard gases were employed to calibrate the online GC-MS/FID system. A 63-chemicals mixture standard (Spectra Gases) was used to calibrate C2–C6 OVOCs and halocarbons. The calibration curves

for each species were acquired by diluting the mixture standard gas into five concentration gradients. The coefficients of determination (r^2) for all calibration curves are larger than 0.995. Ambient concentrations of C2–C6 OVOCs were calculated according to their calibration curves. It is worth noting that these OVOCs may be unstable in cylinders. Additionally, the preconcentration procedures for the GC-MS technique may cause loss of the OVOCs especially under high RH condition because of their relatively high Henry constants. We compared OVOC concentrations measured by GC-MS and PTR-ToF-MS. The measurement results of the two instruments are quite similar (Figure S1). Therefore, the uncertainty of the GC-MS technique is acceptable. This gives us confidence to use OVOC data from GC-MS.

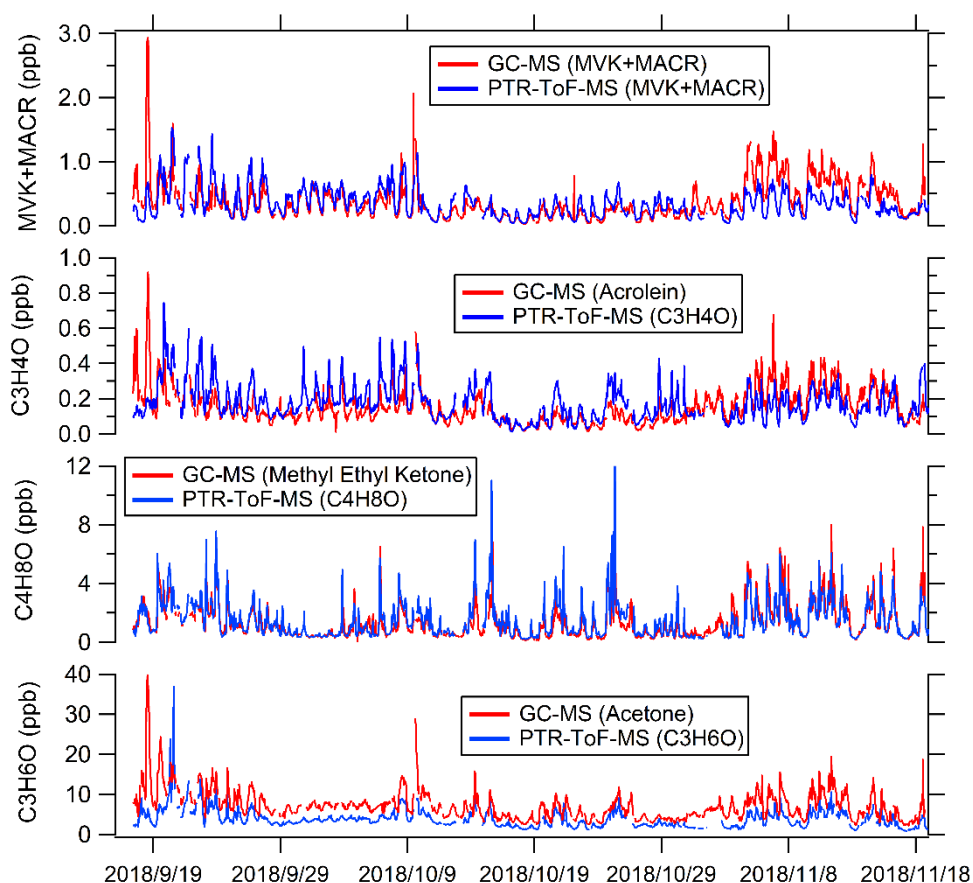


Figure S1. Comparison of typical OVOC concentrations measured by both GC-MS and PTR-ToF-MS.

Both propionaldehyde and acetone have signals in the GC-MS. Why did you derive acetone concentration from the difference between PTR-ToF-MS and GC-MS measurements?

Reply: Many thanks for your suggestion. Given the higher accuracy of PTR-ToF-MS technology in terms of measuring OVOCs, we gave priority to utilizing the OVOCs data of PTR-ToF-MS for analysis. The difference between PTR-ToF-MS and GC-MS at least helps to reduce the uncertainty of PTR-ToF-MS induced by isomers.

Line 149-150: In this way, the uncertainty of PTR-ToF-MS induced by isomers is greatly reduced.

Line 39-46 in Supplement: Given the higher accuracy of PTR-ToF-MS technology in terms of measuring OVOCs, we gave priority to utilizing the OVOCs data of PTR-ToF-MS for analysis in this study. To reduce the uncertainty of PTR-ToF-MS induced by isomers, the concentrations of acetone were determined by the difference between the C₃H₆O concentrations measured by PTR-ToF-MS and propanal concentrations measured by GC-MS; the concentrations of MVK and MACR were determined according to C₄H₆O concentration measured by PTR-ToF-MS and the ratio of MVK to MACR measured by GC-MS.

Why did you obtain the concentrations of MVK and MACR by using the C₄H₆O concentration measured by PTR-ToF-MS and the ratio of MVK to MACR measured by GC-MS?

Reply: Many thanks for your suggestion. Given the higher accuracy of PTR-ToF-MS technology in terms of measuring OVOCs, we gave priority to utilizing the OVOCs data of PTR-ToF-MS for analysis. The ratio of MVK to MACR measured by GC-MS helps to distinguish between MVK and MACR in C₄H₆O isomers measured by PTR-ToF-MS.

Line 149-150: In this way, the uncertainty of PTR-ToF-MS induced by isomers is greatly reduced.

Line 39-46 in Supplement: Given the higher accuracy of PTR-ToF-MS technology in terms of measuring OVOCs, we gave priority to utilizing the OVOCs data of PTR-ToF-MS for analysis in this study. To reduce the uncertainty of PTR-ToF-MS induced by isomers, the concentrations of acetone were determined by the difference between the C_3H_6O concentrations measured by PTR-ToF-MS and propanal concentrations measured by GC-MS; the concentrations of MVK and MACR were determined according to C_4H_6O concentration measured by PTR-ToF-MS and the ratio of MVK to MACR measured by GC-MS.

The lifetimes of several species, e.g., isoprene and HONO are usually less than 15 min in noontime, the constrains with 1-h time resolution dataset may significantly underestimate their role in radicals' formation. The authors are suggested to present a brief discussion about the weakness of model simulation.

Reply: Many thanks for your suggestion. I agree with the reviewer about this concern. The relatively low time resolution used in model simulation is determined by the 1-h time resolution of VOC data. Model simulation with 5-min time resolution could be achieved by interpolating VOC data. We compared the OH and HO₂ concentrations simulated by the box model with 5-min and 1-hour time resolution. The difference in simulated radical concentrations between 1-h and 5-min time resolution is within 10% (Figure S3). This indicates the 1-h time resolution used in the box model is acceptable.

Lines 197-199: There is no significant difference in simulated OH and HO₂ concentrations between 1-hour time resolution and 5-minute time resolution (Figure S3).

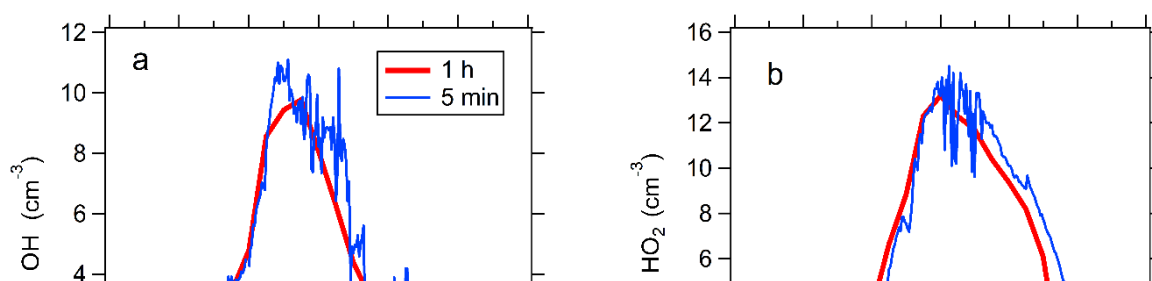


Figure S3. The simulated radical concentrations with 1-h and 5-min time resolution on October 1, 2018.

The photolysis of OVOCs usually have multichannel with different contribution to ROx radicals, e.g., photolysis of HCHO can produce H₂ and CO in one channel or H and HCO in another channel, the former channel makes no contribution to ROx radicals, whereas the later channel contributes to 2 molecules of ROx. Therefore, using the total photolysis frequency of each OVOC with k_i value of 2 (in equation E2) must largely overestimate its contribution to ROx radicals, especially for the carbonyls with large carbon numbers measured by PTR-ToF-MS because their photolysis mechanisms are not included into the MCM (v3.3.1).

Reply: Many thanks for your suggestion. We used the photolysis frequencies corresponding to radical formation channel, not including molecule formation channel, such as H₂ and CO formed from HCHO photolysis. For common OVOC species such as HCHO, CH₃CHO and acetone, the photolysis frequencies were calculated based on measured actinic flux combined with absorption cross sections and photolysis quantum yields reported in Jet Propulsion Laboratory (JPL) publication. For carbonyls with large carbon numbers measured by PTR-ToF-MS, absorption cross sections and quantum yields are not available, and absorption cross sections and quantum yields of species with similar structure are used as a surrogate, following the method described in Jenkin et al., (Jenkin et al., 1997) (e.g. C₂H₅C(O)CH₃ is used as a surrogate for aliphatic ketones with more carbons). Note that all of absorption cross sections and quantum yields used here corresponds to

radical formation channel, not including molecule formation channel. k_i value in equation E2 for most species is 2, but is 1 for some species. We have added this discussion in the manuscript.

Line 218-221: The photolysis frequencies of measured photodegradable species were calculated based on measured actinic flux combined with absorption cross sections and photolysis quantum yields reported in Jet Propulsion Laboratory (JPL) publication (Burkholder et al., 2020).

Line 221-223: Note that absorption cross sections and quantum yields used all correspond to radical formation channel, not including molecule formation channel.

Line 231-235: Absorption cross sections and quantum yields are not available for carbonyls with large carbon number, and absorption cross sections and quantum yields of species with similar structure are used as a surrogate, following the method described in Jenkin et al., (Jenkin et al., 1997) (e.g. $C_2H_5C(O)CH_3$ is used as a surrogate for aliphatic ketones with more carbons).

Line 217: For most OVOCs species, k_i is equal to 2 or 1.

Minor comments:

The title is suggested to be “Unexpectedly large contribution of oxygenated VOCs to atmospheric radicals and ozone production in Guangzhou”.

Reply: Many thanks for your suggestions. After careful consideration, we think that it is no need to emphasize “Guangzhou” in the title because this will limit the application of the study. In addition, we hope to highlight “the direct observations”. A recent study by Qu et al. (2021) also reported the large contribution of oxygenated VOCs to atmospheric radicals and ozone production. and this study is based on model

simulation. The strength of our study is that it is based on direct observations rather than solely from model simulations.

Reference: Qu, H., Wang, Y., et al: Chemical Production of Oxygenated Volatile Organic Compounds Strongly Enhances Boundary-Layer Oxidation Chemistry and Ozone Production, *Environmental Science & Technology*, 55, 13718-13727, 2021.

Lines 30-32, this sentence is suggested to be “a large number of oxygenated VOCs have been quantified in Guangzhou city, China.”.

Reply: Thanks. We have revised it.

Lines 32-34, the sentence is suggested to be moved after the sentence in lines 34-37. “contribute” should be “contribute to”. “comparable or larger than the contributions from nitrous acid and formaldehyde” is better rephrased as “which is comparable to or larger than the contributions from nitrous acid and formaldehyde”.

Reply: Thanks. We have revised it.

Line 39, “will underestimate P(ROX) and ozone production rate” is better to be “will underestimate the production rates of ROX and ozone”.

Reply: Thanks. We have revised it.

Line 127, the abbreviations of MACR and MVK for methacrolein and methyl vinyl ketone are suggested to be noted in brackets, or readers may not understand the meanings of the abbreviations appeared in the following.#

Reply: Thanks. We have revised it.

References:

Burkholder, J., Sander, S., Abbatt, J., Barker, J., Cappa, C., Crouse, J., Dibble, T., Huie, R., Kolb, C., and Kurylo, M.: Chemical kinetics and photochemical data for use in atmospheric studies; evaluation number 19, Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space ..., 2020.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, *Atmos. Environ.*, 31, 81-104, 1997.