

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-913

Anonymous Referee #1

Referee comment on "Direct observations indicate photodegradable oxygenated volatile organic compounds (OVOCs) as larger contributors to radicals and ozone production in the atmosphere" by Wenjie Wang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-913-RC1>, 2021

The authors of this manuscript conducted a dedicated field measurement in Guangzhou city to investigate the role of OVOCs in productions of radicals and O₃ based on a box model simulation constrained by the observation data. They found that photolysis of non-formaldehyde OVOCs contributed to large fractions (22-44%) of the total RO_x radicals' production to significantly accelerate O₃ formation, which is of great importance for comprehensively understanding the ozone chemistry and developing effective control strategies in polluted areas. Therefore, I strongly recommend the manuscript to be published in the journal. The following minor comments are suggested to be considered for improving the manuscript:

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.

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?

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?

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.

The photolysis of OVOCs usually have multichannel with different contribution to RO_x 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 RO_x radicals, whereas the later channel contributes to 2 molecules of RO_x. Therefore, using the total photolysis frequency of each OVOC with k_i value of 2 (in equation E2) must largely overestimate its contribution to RO_x 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).

Minor comments:

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

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

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".

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

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.