

Review of “Direct observations indicate photodegradable oxygenated VOCs as larger contributors to radicals and ozone production in the atmosphere,” Wang et al., ACP (2021)

## Summary

This paper analyzes ground-based observations of traces gases acquired in an urban area of China during Fall 2018. The analysis focus is on oVOC observations and the contribution of oVOC to radical and ozone production. Using a box model, the study demonstrates that oVOC photolysis contributes significantly to primary radical production. The implication is that models that do not capture oVOC mixing ratios correctly (either due to missing emissions, inadequate chemical production, or other reasons) will have errors in calculation of ozone production rates and regimes. Publication is recommended following minor revisions.

## Specific Comments

L118: Does this uncertainty influence the calculation of PROx from oVOC? If so, how much? I assume it is proportional to the PROx contributions of these unmeasured compounds. A simple way to calculate the error budget for this might be to take a root-sum-square of the uncertainties weighted by their PROx contributions for each species. This might provide some insight into which species we need to focus on for improved measurements/calibration. Just a suggestion.

L190: It is unnecessary to equate this to a deposition velocity. The 24h lifetime is a standard method in 0-D box modeling to account for all types of “physical loss,” which might also include entrainment, advection, and other things. At least that’s the hand-waving justification; the truth is that it is required to limit buildup of secondary species, because a 0-D model is an approximation of a 3-D atmosphere.

L191: Over what range were the sensitivity tests conducted?

L192: change “deposition” to “physical loss”.

L255: Is this due to home heating, or from wild/agricultural fires?

L259: Multiplying the y-axis values in Fig. S2 by  $k(\text{OH}+\text{HCHO})$  or  $k(\text{OH} + \text{pyruvic})$  might improve interpretation. Then, the scale is a unitless fractional contribution to OH reactivity. Also, it should be mentioned here and in the figure captions that each point is an average over one day of the campaign (I assume).

L265: You mention the role of secondary pollution. Do the y-axis intercepts in Fig. S2 have any significance for contributions of primary emissions?

L292 – 300: It would be more pertinent here to provide some quantitative metrics for how important oVOC was as a HOx source in these previous studies (either in ppb/h or %) to compare to the present analysis.

L348: How much does OH and HO<sub>2</sub> increase between the case with oVOC constrained or not? It seems unlikely this would be a difference of 50% or more. Unless the oVOC contributions were even larger in those previous studies featuring HOx measurements?

L379: It would help less experienced readers to have some discussion/description on the conceptual definition of chain length.

L389: ChL for episode 1 is double the non-pollution value at mid-day (by eyeball).

L396: This notion of radical amplification is also discussed in Qu et al. (2021), and that should probably be referenced here.

L667: Is glyoxal included in the “others” block? Or is it not included here because it was not measured? I would expect glyoxal to be comparable to methylglyoxal as a ROx source. If this figure is limited to observed oVOC, this should be stated clearly in the caption and probably discussed in the text, since there are likely even more oVOC than those observed by the PTRMS.

L687: Does the blue line use the “minimum” oVOCs contribution? If so, I think there should also be a dashed blue line for the maximum case, or just eliminate the dashed red line. As it stands, it is not clear what the blue line should be compared to.

### Technical Comments

L34: “comparable to”

L49: replace “hydroxide” with “hydrogen oxide”

L51: Recommend replacing “Photodegradable species...including” with “Photolysis of” and deleting “via photolysis reactions.”

L139: PTR-ToF-MS

L202: “radicals”

L207: space after period

L270: delete “basically”

L271: “species and calculated photolysis frequencies derived from observed actinic flux.”

L361: Start a new paragraph.

L424: Availability of model code?

L543: Qu reference missing information.

L661: What is shading in Fig. 1?

L667: ozonolysis is in this figure but never mentioned in the paper

Supplement, L57: Define ChL here.

Table S1: 4<sup>th</sup> column is a mixing ratio, not concentration. Also you may wish to include measurement uncertainty here (your choice).