

“The critical role of oxygenated volatile organic compounds (OVOCs) in shaping photochemical O₃ chemistry and control strategy in a subtropical coastal environment” presents a comprehensive and well written box modelling study of the drivers of photochemical O₃ formation at a subtropical coastal region in South China, particularly highlighting the importance of including a detailed representation of oxygenated VOCs (OVOCs) in the modelling study. An OVOC sensitivity study is presented, including model results with and without detailed OVOC inclusion, relevant to the broader photochemical O₃ production community. I would recommend this manuscript for publication, provided a few further questions are addressed.

Main comment/suggestion:

The authors present two case studies: Box modelling with and without the inclusion of OVOCs, and the impact this has on modelling photochemical O₃ production. However, in reality, it is more typical for studies to include a subset of OVOCs (though not 63, as is the case in your study), since many of these species can be measured using GC techniques alone. It would be interesting to know how good a job your box modelling does if just a “common” subset of OVOCs is incorporated (e.g. acetone, methanol, acetaldehyde). Does this subset sufficiently describe the ozone production regime? Or is it necessary to include a much more comprehensive suite of OVOCs to fully describe the chemistry? It would be worth taking a look at some literature to see which OVOCs are typically included in modelling studies for this analysis. Some examples: Whalley et al., 2018, Whalley et al., 2021, Nelson et al., 2021. In the absence of re-running the model using a hybrid between no OVOCs and 63 OVOCs, perhaps the authors already have enough information from their current model study to comment on which OVOCs are particularly important to include?

Additional comments:

Line 95 – Is it correct to say that summer is Sept 4 – Oct 12, autumn is Oct 13 – Dec 1, and winter is Dec 2 – Dec 20 in this region? This is quite a short timeframe to cover these seasons. How representative do you feel these windows are of the “summer”, “autumn”, and “winter” in South China?

Line 135 – We “attempted” to assign signals based on likely contributors, and that your quantification of OVOCs is semi-quantitative for uncalibrated species, is an honest and fair account of what you have done here. Whilst I completely understand that this must be the case due to instrument limitations, some readers may feel a little mis-sold up to this point, as the abstract implies that we are to expect 63 explicitly measured and quantified OVOCs. Perhaps you could be more upfront in the abstract on what you have

done to describe the OVOCs, as this is a major component of your study. Even if you just said “X quantified and Y semi-quantified OVOC species”, rather than 63 quantified (abstract – line 22).

Line 160 – I was struggling to follow exactly what you’ve done here. “VOC species from daytime canister samples were linearly interpolated to hourly resolution for the model input”. Is this just the VOCs measured using the GC-MS/FID/ECD? I assume the PTR measurements are online? Please be clear on the time resolution of the measurement of both things. How often were canister samples taken? Is interpolating the data to hourly resolution appropriate for this measurement resolution?

225 – A lot of effort has been put into speciating the OVOCs, but what about the biogenic species? The authors state there were measurements made of 2 biogenic species – isoprene, and monoterpenes. However, there are only 3 monoterpenes in the MCM (the pinenes and limonene), and they later describe their monoterpene measurement as the pinenes only. As these are highly reactive species, it is important to discuss how your assignment of the total monoterpene measurement to (what I assume is 50:50?) a- and b- pinene. There are also many monoterpene species not included in the MCM, some with faster reaction rates than these species. I understand the need for your assumption to be made, but please acknowledge the potential implications this has in the text.

300 – Just to reiterate my early point, the authors say your measurements are high-resolution here, but the resolution needs to be stated more explicitly earlier in the text.

344 - More discussion of the implications of BVOCs in your model here – again, worth pointing out that this result is based on the monoterpenes being split between the pinenes only.

397 – The authors say that including the OVOCs means that observed O₃ was successfully reproduced. Are the observed and model concentrations identical? I would expect some impact from transportation to play a role here, since not all the observed O₃ can be expected to be photochemically produced in situ. Please discuss.

Line 444 – “our results highlight that many other OVOCs,...,remain overlooked”, and line 451 “key OVOC species such as methanol, acetaldehyde, and acetone,..., were underestimated”. These key OVOCs are more typically incorporated into box modelling studies in the literature, as they can be measured using GC techniques (see my main suggestion earlier in this review).

Line 494 – When you vary the VOCs and NO_x for the isopleth analysis, do you also vary OVOCs? The difficulty here is that some of your OVOCs will be formed photochemically, and some from primary sources, meaning the two will not necessarily ever decrease or increase uniformly. Do you also reduce biogenic species, or just anthropogenic? How do you navigate this issue to make the isopleth findings relevant from a policy perspective?

References:

Whalley et al (2018): Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project (ClearfLo), *Atmos. Chem. Phys.*, 18, 2547–2571, <https://doi.org/10.5194/acp-18-2547-2018>, 2018.

Whalley et al (2021).: Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NO_x in Beijing, *Atmos. Chem. Phys.*, 21, 2125–2147, <https://doi.org/10.5194/acp-21-2125-2021>, 2021.

Nelson et al. (2021): In situ ozone production is highly sensitive to volatile organic compounds in Delhi, India, *Atmos. Chem. Phys.*, 21, 13609–13630, <https://doi.org/10.5194/acp-21-13609-2021>, 2021.