Comment on acp-2021-814

Anonymous Referee #2

Referee comment on "Influence of photochemical loss of volatile organic compounds on understanding ozone formation mechanism" by Wei Ma et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-814-RC2, 2021

This manuscript uses a chemical box model approach to calculate VOC and NOx loss rates, radical chemistry and ozone production rates when constrained with pollutant concentrations in a suburb of Beijing, China. Overall, I recommend revisions of the modelling approach. Below are my specific comments:

Line 41. Reference for Seinfeld is missing Pandis author.

Line 108. To compare the model vs measurements, it is advised to look at slope, intercept and not just correlation coefficient.

Line 143. The hydrocarbon ratio photochemical clock concept works well when you have an isolated source that co-emits the hydrocarbons and a receptor site with no emissions in between. If there are different sources in between and also mixing of airmasses into the plume with different photochemical ages then it complicates the concept and rationale. The use of an early morning time to define the aromatic ratio is also not explained well. The early morning measurements likely reflect the concentration of local emissions under a shallow inversion layer. If the emissions are uniformly distributed across region then this might be the best time to estimate the emission ratio for xylene to ethylbenzene. The assumption that the emission source remains constant over the region is questionable. It might be helpful to look at gridded regional air quality emissions over the region and plot the emission ratio to see if it is relatively uniform spatially.

Line 146-148. The mean daytime OH used for the calculation was 4.3E6 molec/cm3. Please state that the measured aromatic ratio was also a mean value for the same

daytime period used to calculate the OH.

Line 156. I agree that the biogneic isoprene emission is not co-located with the aromatic emission sources and this complicates the ratio method. Can the authors look at regional model emissions for isoprene to see if the isoprene sources are local near the site or whether they are closer to the aromatic sources? A possible assumption is that the production and loss of isoprene balance along the transport and concentration of isoprene remain constant in the trajectory from the aromatic source region to the site. Again, regional air quality model results would be able to show what the distributiion of isoprene looks like around the site.

Line 195. I would recommend "grouped into lumped species" instead of parcels.

Line 198. Five minutes is enough time for the radicals to reach steady-state but not the NOx and OVOCs. For example, PAN has a long lifetime and would not reach steady state in 5 min. Given that the intent is to "correct" the VOCs to an initial condition and you expect an ~ 2hr photochemical time then an equivalent time to run the model might be best approach and would give time for OVOCs to spin up to more reasonable mixing ratios.

One major concern that I have in the photochemical initiation of VOCs is that the authors are not considering the correction needed for NOx as it also reacts in the trajectory reaching the site. The VOCs and NOx can be emitted by common combustion processes, particularly in an urban area. The authors also note they follow the same diurnal profile as VOCs. The lifetime of NOx is comparable to some VOCs so why not correct the NOx as well? Other studies have done this and in fact the NOx/NOy is an alternative ratio in the photochemical clock method (Hayes et al., 2013).

Line 206. If I understand ths section, the observed ozone max was 119 ppbv and the modeled max was 70 ppbv. This seems like a large difference. If this can be explained by the mixing and transport of ozone from regional scale then maybe it might be best to constrain the ozone to the observed value each hour. For diagnosing the chemistry pathways (Figure 3,4), this ensures the ozone is at a reasonble level for calculating the alkene ozonolysis and O1D+H2O reaction rate.

Line 267. The daytime average P(O3) is calculated at 3 ppbv/hr higher than with using measured VOCs. The authors appear to extrapolate to a 24-hr average by multiplying by 24 hr to get 36 ppbv/hr higher than with the measured VOCs. The nighttime P(O3) averages could be different than daytime averages, so it would be preferred to state what the daytime average difference is between corrected and measured VOC approaches.

Line 354. I think the discussion of the diurnal profile and the different chemical and transport processes should include the mixing of the stable noctural surface layer in the

mid-morning. As the sun heats the surface, there is significant mixing of surface layer with air above in the residual atmospheric layer which is likely composed air from the prior day mixed boundary layer and then transported to the site overnight. This residual air likely contains hydrocarbons and ozone from different sources and at different photochemical ages. The ozone increase around 9-10am is often associated with this vertical mixing. The ozone mixing down to surface is photochemically produced but from a different region from previous days (unless the region is influenced by a lake/land breeze where recirculation of the same air mass can occur.

Line 370. The authors state that "The radical budget analysis illustrated that the O3 formation processes between the observed and photochemical initial VOCs showed no significant difference." The title of the manuscript implies that the initial photochemical loss of VOCs does have an impact on the ozone formation mechanism. It seems that the ozone production rates are sensitive to the corrected VOC loss (and likely corrected NOx loss as well). Maybe an improved title could be "Influence of Photochemical Loss of VOCs and NOx on Ozone Formation Rates and Diagnosed Ozone Production Sensitivity in Beijing, China"

Figure S5 shows some days with large model over-predictions. Can the authors explain what factors are contributing to the model over-predictions?

Overall, I really like Figures 3, 4 and 5. My recommendation would be to include a NOx correction, as well as the VOC correction, and to consider a longer model time so that the OVOCs reach closer to their typical ambient concentrations. Of particular interest would be the aromatic and monoterpene oxidation products as the precursor aromatic and monoterpene have an intermediate lifetime (several hours) and their OVOCs are not typically measured. The figures are of very good quality. The paper needs some improvements for English language.

Reference

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglück, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corri[1]gan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreis[1]berg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Of[1]fenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol com[1]position and sources in Pasadena, California during the 2010 CalNex campaign, J. Geophys. Res.-Atmos., 118, 9233–9257, doi:10.1002/jgrd.50530, 2013.