Review of "Influence of Photochemical Loss of VOCs on Understanding Ozone Formation Mechanism"

November 24, 2021

Ma et al. "Influence of Photochemical Loss of VOCs on Understanding Ozone Formation Mechanism" uses measurements in Beijing to demonstrate how failing to account for oxidation of VOCs between the point of emission and measurement can lead to misinterpretation of the dominant chemical regime for ozone production and a misestimate of the rate of ozone production. The authors use measurements of xylene and ethylbenzene to compute the OH exposure since time of emission, assuming that the concentrations of these species between 5 and 6 AM are a good estimate for their concentrations with zero oxidation. They then use that OH exposure along with rate constants for reaction of other VOCs with OH to back out the "photochemical initial concentrations" (PICs) of VOCs. They compare the net ozone production between the measured and PIC VOC concentrations using a box model with the Master Chemical Mechanism and use another box model with the RACM2 mechanism to examine the dominant ozone production chemical regime with these different VOC concentrations. They conclude that using the measured VOC concentrations underestimates the ozone production rates.

The argument that one must consider the effect of photochemical oxidation of VOCs between source and measurement to accurately determine the best approach to reduce ozone exposure is an important one; however, I do not see that this paper adds much to our understanding of this issue, either generally or specific to Beijing. Additionally, elements of the methodology require further explanation or justification. I will discuss these factors in detail below. Taken together, this paper should be reconsidered after major revision.

Major comments

Novelty

My largest concern is that it is not clear what this paper adds to our understanding in regards to the effect of VOC degradation on estimated O_3 production rates. This question has previous been addressed by several papers cited in the introduction to this one (e.g. Shao et al., 2011; Gao et al., 2018) as well as others (e.g. Xie et al., 2008; Shao et al., 2009; Li et al., 2015). Near the end of the introduction, this paper states that "it is unclear how the highly reactive VOCs, which [have] degraded during transport from the source to the receptor site, will affect the instantaneous formation process of O_3." Yet Li et al. (2015) addresses this in Sect. 3.3. of their paper:

> VOC species may experience photochemical losses from emission sources to receptor sites, which are important for ground-level ozone formation. It is very likely that the OFP [ozone formation potential] is underestimated when using only the observed mixing ratio of ambient VOCs at a receptor site. Therefore, the initial mixing ratios of VOCs must be considered if ozone abatement measures are to be implemented.... We calculated the OFP for the initial VOCs (except carbonyls) to avoid misjudging the role of the major VOC species in ozone formation. The OFPs calculated based on the initial mixing ratio of VOC species differed from those based on observations. The OFPs for total NMHCs (excluding isoprene) increased by 16.09% (from 59.60 to 69.18 ppbv O3), 12.06% (from 33.46 to 37.50 ppbv O3), and 3.38% (from 68.89 to 71.22 ppbv O3) after correction for chemical conversion at GC, QZ, and BJ, respectively.... In this region, the OFPs for trans-2-butene, cis-2-butene, cis-2-pentene, and isoprene would be underestimated by up to 40% if chemical losses were neglected.

This analysis by Li et al. (2015) previously showed that not accounting for chemical loss of VOCs will underestimate O_3 production. Replication and confirmation are valuable, but the authors must do a better job placing their paper in the context of earlier work and, especially if replication is the focus, compare their results to previous studies.

Methological concerns

There are several elements of the methodology that I have concerns about. I will order this section from most to least severe.

Choice of initial xylene and ethylbenzene: A key part of this methodology is the use of xylene and ethylbenzene as a chemical clock to compute the integrated OH exposure for all VOCs from emission to measurement. This requires knowing the initial concentrations of xylene and ethylbenzene; for the purposes of this paper, the concentrations between 5 and 6 AM are considered the initial values. This is presumably the last hour before sunrise (and so the last measurement before OH chemistry initiates), but I did not see where the rationale for this selection is given in the paper. The reasoning for that selection should be made clear.

My larger issue with this approach is that it implicitly assumes that the source of xylene and ethylbenzene remains constant throughout the day. This is a risky assumption: shifts in the wind direction or changes in upwind emissions could alter the source emission ratio of xylene to ethylbenzene throughout the day. I did not see anywhere in the paper where the authors carried out a back trajectory or other source area analysis to determine if the assumption of consistent xylene and ethylbenzene sources throughout the day is correct. Without that analysis, we cannot know if the 5-6 AM xylene and ethylbenzene concentrations are a reasonable approximation of the initial concentrations for all airmasses measured throughout the day.

Validation of adjusted O_3 production: In the conclusion, the authors claim that, "The radical budget analysis illustrated that the O_3 formation processes between the observed and photochemical initial VOCs showed no significant difference, **but the former one underestimated the O_3 production rate obviously**" (emphasis added). While I agree in principle that using the observed VOCs underestimates the O_3 production, it is unclear how well the method presented in this paper corrects for that underestimation, as I saw no comparison against any truth metric for O_3 production.

One method to check the accuracy of the authors' approach would be to use a pair of measurement sites, one upwind and one downwind, with the upwind site measuring O_3 concentration. Combined with a trajectory analysis, one could potentially compute the O_3 production based on the difference in concentrations between the two sites (though mixing may complicate this), and compare that to the modeled O_3 production using observed and PIC VOCs. If an upwind O_3 site is not available, an analysis using $d\mathrm{O_x}/dt$ as in Fig. 5, except with independent constraint on the transport of O_3 (perhaps from a regional model or satellite observations) may be another option.

VOC correction: In Fig. 1, the difference between the observed and "photochemical initial concentration" (PIC) VOCs is zero before 6a and after 7p (19:00). Between 6a and 7p, the offset between the observed and PIC VOC concentrations seems almost (but not quite) constant. What seems particularly odd is how the observed-PIC difference jumps from nothing to essentially its maximum value between 5a and 6a, then likewise drops instantaneously from its maximum value to zero between 7p and 8p. I would expect the transition to be more gradual, with photolysis (and therefore OH concentrations) being less in the hour immediately following sunrise than later in the morning (and vice versa at night). It would be helpful if the authors provided a timeseries (at sub-hourly resolution) of the concentration of xylene and ethylbenzene, their ratio, the OH exposure derived from these quantities, and the solar zenith angle, to demonstrate how the OH exposure correction changes with time of day.

Ozone production and loss metrics: Please discuss for Eq. 3 how alkyl nitrate formation is treated; is $k_{\mathrm{RO_2+NO}}$ the rate constants for only $\mathrm{RO_2} + \mathrm{NO}$ reactions that produce RO and $\mathrm{NO_2}$? If $k_{\mathrm{RO_2+NO}}$ is the rate for all $\mathrm{RO_2} + \mathrm{NO}$ reactions, then the alkyl nitrate branching ratio must be accounted for.

Relately, in Fig. 3, a comparison of panels (c) and (d) appears to indicate that the loss of ozone via reaction of $\mathrm{O^{1D}}$ with H_2O increases when using PIC VOCs rather than measured.

Please elaborate why this is, is this just because there is more O_3 (and so more O^{1D}) in the model with PIC VOCs, and so the rate increases even through the amount of H_2O remains constant? If so, it might help to include a companion figure to Fig. 3 in the supplement that shows $P(O_3)$ and $L(O_3)$ as percentages of O_3 production/loss to help the reader understand the relative change in loss processes as well.

Minor comments

- The argument made in lines 66–71 of the introduction about the different mixing ratios of VOCs at the source vs. measurement site is confusing on a first read because it is not clear that the scenario which applies here is where the source one is attempting to control with policy is significantly upwind of the measurement site. If we were considering a source (e.g. traffic) which is closely clustered around the measurement site, then the VOCs measured at the site will be the correct concentrations to consider for O_3 production.
- It is unclear whether Fig. 1 and (to a lesser extent) Fig. 3 are for one specific day or the entire campaign. For these figures, please specify the time period considered (since Fig. 5 is specific to one day).
- For Fig. 1, specify which series are measurements and which are calculated. (I assume all but the TVOC_PIC series are measurements, but please be explicit.)
- For Fig. 2, define specific times (i.e. "8 AM" or "11 AM to 1 PM") rather than "morning" and "noon" so that we can compare to Fig. 1. Also, line 236 seems to imply that the "noon" points are actually 15:00? That is confusing.
- Please explain in the caption what the percentages in Fig. 4 represent; I only saw a description of the other numbers as production rates in ppb h^{-1}. In general, the discussion of the radical chain on lines 296–309 is pretty dense and difficult to follow, but I cannot give any suggestions to improve it without understanding what all the elements in Fig. 4 are.

Summary

While this paper is a fair study of how one might account for degradation of VOCs between sources and measurements in order to formulate better approaches to controlling O_3 production, there have been a number of earlier studies looking at this problem in Beijing. In my opinion, in order for a revision to be considered for publication, the authors must revise the paper to clarify what new information their work adds compared to the previous studies *or* refocus the paper as a replication study or an update to more recent times. In this second case, the revision should include a thorough comparison with previous studies of this effect in the Beijing area.

References

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