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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elevated levels of OH observed in haze events during wintertime in central Beijing" *by* Eloise J. Slater et al.

Anonymous Referee #2

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This paper focuses on the investigation of the OH, HO2 and RO2 radical chemistry at extremely high NO in Beijing, China. As it was observed by a previous study in the same area (Tan et al., 2018) the current "known" chemistry at high NO cannot reproduce the measured HO2 and RO2 radicals resulting in a large underestimation of the ozone production.

I agree with reviewer one on the possibility of shortening the paper which, at the current status, feels more as a description of the observation (with some model run) but does not really try and push for suggesting possible explanations for the finding or even looking in explanations given in the past (segregation for example or Cl2 chemistry) to check if they would help the situation in this campaign.

General comments

I would suggest trying and making better use of the complex and simple RO2 concentrations. Measurement of RO2 or scarce to start with and here several time the measurement of simple and complex RO2 separately is brought up but then the data is not really used. Even when mentioning that there seems to be a better agreement between the measurement of simple RO2 and model results at high NO (which, by the way, I do not agree with), the discussion stops there and there is no additional use of the data. Why not checking for example if the RO2 measurement is consistent with the VOC load? Does the contribution of simple and complex RO2 changes with time? During the day? From non-haze to haze periods? I think this type of analysis could maybe also help understanding a little bit more where the large discrepancy between measurement and model results arises from. . .

I am missing a small but useful description of all the measurements used within the model and which instrumentation (with accuracy and precision) was used for the different trace gases. It does not have to go too much in details but there is no mentioning of how NO, which is extremely important for the radicals chemistry, was measured. . .or O3 or anything. In addition to this, there is no description of how the OH reactivity was measured and how much of a deviation from the mono-exponential decay could be expected for values of NO reaching up to 250 ppbv. What is the accuracy of the kOH measured at high NO? Could this represent a lower limit? This should be discuss appropriately and it could add an additional explanation of why the model is largely underestimating the RO2 and HO2 concentrations (lack of some primary VOCs).

Specific comments:

Page2 line46: ". . .quality are of serious concern. . ."

Page2 line49: ". . . of the world fastest. . ."

Page2 line51: I would drop the number after the comma and round the percentages

Page2 line 59: NOx, SO2 and VOCs have not been defined

Chapter 2.1 More information on the specific of the campaign site would be beneficial. Was the site on the street? On a platform? On the roof of the building? What was the distance between different instruments? I understand there is a specific paper on the topic but just two lines with a little bit information would suffice.

Chapter 2.2.2 Here as well more details on the sensitivity towards the different RO2 is needed. The different concentrations of RO2 are used later on to justify some of the conclusions on the discrepancies between model and measurements so it is important to mention how well know is the separation in two classes of RO2 and which sensitivity is applied for which classes.

Page8 line212: Is there really no difference between the accuracy of OH, HO2 and RO2 accounting that HO2 requires conversion into OH and RO2 requires a minimum of 2 NO steps?

Page9 line 239: What is the concentration of H2 to 500 ppbv included in the model needed for?

Page 9 line241: What was the time resolution of the GC data?

Page 11 line290: Is the diel variation shown the mean or the median of the data?

Page 11 line300: O3 does not react with high levels of NO but with a high concentration of NO

Page 21 Section 4.1: I assume that here only the results from the model are shown but this is not clear from reading the text.

Page 24 Lines516-521: Has the possibility of segregation of air been investigated and ruled out or why this is mentioned here but there is no discussion on how this could have had an impact on this specific site? It could be worth discussing if this could help bringing measurements and model results in agreement.

Page 24 line539: Assuming that figure 10 is actually figure 11 (where in the caption of

the figure the model line is the red one (?)), I do not agree with the statement in the paper that the model can reproduce the simple RO2 measured for NO above 100 ppbv. Actually, there is overlap between the model and the measured RO2 95th percentile for the complex RO2. In all honesty, I am not sure this plot tells us much as the model equally predicts pretty much zero RO2 expected at NO above 10 ppbv for both type of RO2. Although I agree that the simple RO2 have been studied more carefully, what would be the difference in rate with NO to justify the observed concentration of RO2 or what type of different chemistry for the most complex RO2 would be needed? There is no discussion in this study about it and some suggestions of what is feasible are needed.

Page 27 line 570-573: What would be the concentration of CL2 and/or CINO2 needed to justify such a production of RO2? This could tell us if it could be possible at all.

Page 28 line602-605: I think one needs to be a bit careful here as, as you pointed out, the conditions (NO in particular) are not comparable and this campaign is one extreme case where NO is so large that dominates the losses of HO2 in any case. It is also worth citing the study by (Tan et al., 2020) which came to a similar conclusion for smaller levels of NO.

Section 4.3: Although I agree with reviewer 1 that this session is not really needed as it is descriptive and should be substitute by a better analysis of what could bring measurement and model results in agreement, I think at page 31 line 650 the statement that the model over predict HO2 in non-haze events is wrong. From figure 14 the model clearly under predicts HO2 radical in non-haze events. Same for page 33 line 684 where I do not clearly see a midday peak for NO3-?

Reference

Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Winter-

time photochemistry in Beijing: observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmos. Chem. Phys., 18, 12391-12411, doi:10.5194/acp-18-12391-2018, 2018.

Tan, Z., Hofzumahaus, A., Lu, K., Brown, S. S., Holland, F., Huey, L. G., Kiendler-Scharr, A., Li, X., Liu, X., Ma, N., Min, K.-E., Rohrer, F., Shao, M., Wahner, A., Wang, Y., Wiedensohler, A., Wu, Y., Wu, Z., Zeng, L., Zhang, Y., and Fuchs, H.: No Evidence for a Significant Impact of Heterogeneous Chemistry on Radical Concentrations in the North China Plain in Summer 2014, Environmental Science & Technology, 54, 5973-5979, doi:10.1021/acs.est.0c00525, 2020.

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