

Interactive comment on “Wintertime photochemistry in Beijing: Observations of RO_x radical concentrations in the North China Plain during the BEST-ONE campaign” by Zhaofeng Tan et al.

Anonymous Referee #1

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This paper presents measurements of OH, HO₂ and RO₂ radicals during the winter (January – March) at a suburban site near Beijing. The measurements are separated according to three different chemical groups based on measured total OH reactivity, CO, and PM_{2.5}, and were classified as “background,” “clean,” and “polluted.” The radical concentrations were modeled using a 0D model based on the RACM2 condensed chemical mechanism constrained by the measured concentrations of NO_x, VOCs, and others. The authors find that overall, the model can reproduce the observed OH to within 30%, with photolysis of HONO being the dominant OH source. However, the

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agreement is better during “clean” episodes compared to “polluted” episodes, with the model underestimating the observed OH by a factor of 1.8 on “polluted” days. Similar to OH, the model is able to reproduce the observed HO₂ and RO₂ concentrations during “clean” episodes, but underestimates the observed HO₂ and RO₂ concentrations by a factor of 5 during “polluted” episodes, implying that the model is underestimating the instantaneous rate of ozone production during these periods.

Because the model was able to reproduce the observed OH reactivity, the authors conclude that the underestimation of HO₂ and RO₂ concentrations by the model is not due to unmeasured VOCs, but rather due to a missing primary source of peroxy radicals. Using a steady-state approach, the authors calculate a missing peroxy radical source rate of approximately 5 ppb/hour during “polluted” episodes. However, while addition of a generic peroxy radical source would improve the agreement between the model and the measured peroxy radical concentrations, addition of this source would increase the modeled OH concentrations by a factor of 5 greater than the measured concentrations, suggesting a significant missing OH sink, in contrast to the agreement of the measured and modeled OH reactivity. Overall, the authors find that the measured OH concentrations during this winter study were significantly greater than predicted by global models, suggesting that winter photochemistry in the region may be significantly greater than previously believed.

The paper addresses an important topic relevant to ACP. I recommend publication after the authors have addressed the following comments.

1) The authors conduct several chemical modulation tests to measure interferences using an “improved” chemical modulation reactor (CMR). Unfortunately there are limited details on the design of the CMR and how it was improved over the previous version. The paper would benefit from an expanded discussion of the CMR, including a schematic diagram, which could be included in a supplement.

2) The chemical modulation experiments should have allowed a direct measurement

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of the ozone interference that is subtracted from the wavelength modulation signal (equation 2). Did the chemical modulation experiments confirm the correction for the ozone interference?

3) For the regression of the chemical modulation measurements versus the wavelength modulation measurements (Figure 2), the authors should clarify the regression method. They should use a bivariate regression weighted by the measurement precision of both OH chem and OH wave.

4) The description of the RO₂ measurements appears to be incomplete, as the addition of NO and CO would result in the measurement of both RO₂ + HO₂ + OH (RO_x as described in Fuchs et al., 2008). Measurements with CO addition only result in detection of HO_x (OH + HO₂) only. To obtain measurements of RO₂ only, the measured HO_x concentrations must be subtracted from the measured RO_x concentrations. Based on the description in Tan et al. (2017), it appears that the HO_x measurements from the other two axis are used to obtain the RO₂ concentrations from the RO_x measurements, but this should be clarified in this paper.

5) Related to this, it is not clear that the uncertainty for the RO₂ measurements listed in Table 2 reflect the fact that the HO_x measurements are subtracted from the RO_x measurements. Fuchs et al. (2008) estimates the accuracy of the RO₂ measurements to be approximately 20%. This should be clarified. In addition, the authors state that the measurement accuracies reflect both the “the uncertainty of the calibration source (10%, 1σ) and the 1σ standard deviation of the variability of individual calibration sensitivities” (page 4). However the accuracies of the OH and HO₂ measurements in Table 2 appear to only reflect the standard deviation of the variability of the individual calibration sensitivities, and do not appear to include the uncertainty associated with the calibration source. This should be clarified.

6) The authors should also provide an estimate of the model uncertainty.

7) Figure 7 could be improved to better show the model/measurement agree-

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ment/disagreement. Instead of separating the plots with measurements on one side and modeling on the other, I would suggest separating them by episode (background, clean, polluted), and then showing the model results and the measurements on the same plot, including the measurement and model variability, similar to that done in Tan et al. (2017).

8) While the measured/modeled ratios illustrated in Figure 11 suggest that the increase in the modeled underestimation of HO₂ as a function of NO is similar to that observed previously (page 12), the HO₂ measurements in some of the previous studies mentioned may have suffered from the RO₂ interference discussed on page 3, resulting in reported HO₂ measurements that may be greater than the actual HO₂ concentrations. This potential interference would enhance the model-measurement discrepancies reported in these studies. This should be clarified in the discussion on page 12 of the manuscript.

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