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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Radical chemistry at a rural site (Wangdu) in the North China Plain: Observation and model calculations of OH, HO_2 and RO_2 radicals" *by* Zhaofeng Tan et al.

Anonymous Referee #2

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This paper presents measurements of OH, HO_2 and RO_2 radicals using laser-induced fluorescence in a rural site in China together with box model calculations. The authors find that the model predicted radical concentrations are in reasonable agreement with the observations when mixing ratios of NO were greater than 1 ppbv, similar to previous measurements in urban environments. However they find that the model underestimates the observed OH concentrations when mixing ratios of NO were less than 300 pptv. The authors performed some tests to determine whether unknown interferences contributed to the measured OH concentrations, and find that for the limited number of tests performed the measured interference cannot explain the discrepancy between the model predictions and the measurements. Including an unknown species

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that recycles OH equivalent to 100 pptv NO brings the model into better agreement with the measured OH concentrations. The model also underestimates the observed RO_2 concentrations during the morning when NO is high, resulting in the model underestimating the instantaneous rate of ozone production. Increasing the OH reactivity by VOCs to match the observed reactivity improves the agreement of the modeled RO_2 concentrations with the model.

The paper is reasonably written but could use proofreading to improve English grammar and punctuation. The paper would be acceptable for publication in ACP after the authors have addressed the following comments.

1) The authors performed several Interference measurements using an external chemical titration technique. Unfortunately it appears that these interference measurements were not done continuously but were done only on four specific days. However, it is not clear exactly when the tests were done and what the ambient conditions were during each test. Were any tests done when NO was less than 300 pptv, the conditions when the model-measurement discrepancies were the greatest, or was the measured interference similar for all ambient levels of NO? This should be clarified. Adding the times when these tests were done to Figure 3 would provide more information on whether these tests were done under typical ambient conditions for the campaign. Was this interference subtracted from all of the OH measurements?

2) On page 17 the authors state that the measured OH concentrations are approximately 1×10^6 cm^{-3} greater than model predictions during the afternoon when the mixing ratios of NO decrease from 0.3 to 0.1 ppb. This discrepancy appears to be consistent with the average measured interference of 1×10^6 cm^{-3} described on page 14, suggesting that the observed discrepancy with the model could be due to the interference. This possibility should be discussed in more detail.

3) In their measurements of HO_2, the authors varied the added NO to determine the interference from alkene and aromatic peroxy radicals. However, it is unclear to me how

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the authors determined the RO_2 conversion efficiencies described on page 11 unless the absolute conversion efficiency for one of the NO flows was determined through calibrations with known concentrations of peroxy radicals. Did the authors perform RO_2 conversion efficiency calibrations similar to that described in Fuchs et al., 2011? This should be clarified.

4) It is not clear how the authors derive the $RO_2\#$ concentrations and compare it to the model. The measured HO_2* in the RO_x channel reflects the conversion of alkene, aromatic, and other RO_2 radicals to HO_2 in the detection cell with a conversion efficiency dependent on the RO_2 radical as described in Fuchs et al. (2011). Subtracting the HO_2 measured in the HO_2 axis gives $\alpha_{\#}RO_2\#$. Ideally, the authors should compare this measured value which is the result of various conversion efficiencies to the modeled $RO_2\#$, where the individual modeled RO_2 concentrations are scaled by their expected conversion efficiencies, which are not necessarily all 0.8. However, it appears that the authors are scaling the measured $RO_2\#$ by an average conversion efficiency of 0.8 and comparing this value to the modeled concentration of the sum of the interfering RO_2 concentrations. This should be clarified. Have the authors measured the individual RO_2 conversion efficiencies for their instrument?

5) The authors state that the underestimation of the RO_2 concentrations by the model during the high NO conditions in the morning is improved when the OH reactivity of the model is increased, but few details are provided. Similar results were found during CalNex by Griffith et al. (JGR, 2016). How much did the modeled RO_2 increase in this scenario? Perhaps the results of this model run could be added to Figures 5 and 9.

6) Similarly, the authors find that the model underestimates the rate of ozone production under high NO conditions due to the underestimation of RO_2 radicals by the model. Similar results were found during CalNex (Brune et al., Faraday Discuss., 2016, 189, 169; Griffith et al., JGR, 2016). Does the underestimation of RO_2 (and therefore PO_3) depend on the measured OH reactivity? Griffith et al. (2016) found that the underestimation of PO_3 by the model was higher when the OH reactivity from VOCs was the

greatest.

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