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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

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 $1 \times 10^6$ 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 $1 \times 10^6$ 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

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

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greatest.