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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 #1

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The manuscript reports HOx measurements and model comparison for the Wangdu region in China. The model is able to reproduce the daytime radical observations with two notable exceptions: OH concentrations are under-predicted at NO concentrations less than 300 pptv and RO2 radicals are under-predicted at high NOx concentrations which has implications for estimations of ozone production rates. The paper is well written and presents a balanced discussion of the findings in the context of previous results and is suitable for publication in Atmospheric Chemistry and Physics. I have a few comments below which should be addressed before final publications to strengthen the overall conclusions.

Interferences in the OH detection, OH chemical modulation tests: Was the propane

concentration varied in the field? From lines 265 – 267 it is unclear if the variable titration efficiency is a laboratory result or field observation. If it was the latter, how was titration efficiency determined in the field? Were laboratory tests conducted to ensure no internal removal of OH in the cell (line 273)? Figure 2: What do the dashed lines correspond to? It is difficult to assess from this figure if there is any diurnal variation in the magnitude of the interference signal? Could the authors comment on any variation observed, e.g. as a function of atmospheric composition? Is this possible unknown interference signal of sufficient magnitude to account for the modelled measured OH discrepancy at [NO] < 300pptv (line 479)?

Possible RO2 interference: Fuchs et al. (Review of Scientific Instruments, 2008) report a possible interference in the RO2 instrument from pernitric acid and methyl peroxy nitrate which have the potential to thermally decompose in ROx system and be detected as HO2 and CH3O2. Could the authors comment on the impact this interference may have for these field conditions, particularly under the high NOx conditions experienced in the morning? Could this interference explain the model measured discrepancy in RO2 at this time? What is the impact of this interference on the ozone production rate calculated from the measured HO2 and RO2 concentrations?

Model measurement comparison of RO2: The manuscript focusses on the differences observed between measured and modelled RO2 in the morning, but in figure 5 the model under-predicts RO2 and RO2# until ∼16:00. Some comments should be provided on this under-prediction; the under-prediction in OH reactivity cannot account for this under-prediction beyond 10am. Please extend this commentary to lines 849 in the Conclusion also. Owing to the strong coupling between RO2, HO2 and OH (highlighted in figure 11), how does the model under-prediction of total RO2 impact the model's ability to predict OH and HO2? Could the model be scaled to reproduce [RO2] and then the performance of the model to predict OH and HO2 re-assessed? There are inconsistencies in the modelled and measured radical ratios (and OH reactivity) that warrant further investigation. Section 3.6 would benefit from a more detailed discussion of the

modelled RO2 species – what are the other RO2# species in figure 8? Please define 'MO2' in this figure caption.

Minor comments:

Line 331: Do the RO2# concentrations determined in the HO2 and RO2 cell agree?

Line 358: Please give the typical solar background at noon. Was it necessary to shade the cells?

Line 527: 'HO2 concentrations are well reproduced by the model during the daytime'. From figure 5 it looks like the model has a tendency to over-predict [HO2] in the afternoon. Could this over-prediction be masking the full magnitude of the model underprediction of OH at this time (as HO2 is a strong secondary source of OH)?

Line 593-594: 'scaling VOC concentrations to match measurements..' which VOC species were scaled? Does the VOC species chosen influence the modelled [RO2]?

Line 595 ' can be partly closed..' and also, line 701 'rate better agrees..' please provide the percentage change.

Line 720 – 723: This statement seems to be at odds with the model-measurement comparison presented in this manuscript which shows good agreement between modelled and measured HO2 in the morning but a modelled measurement discrepancy for RO2. Calculating ozone production from an RO2 concentration estimated from HO2 could mask a high morning ozone production rate.

Line 769: There is no experimental evidence that HONO formed from the reaction of HO2.H2O + NO2, as postulated by Li et al., (2014), occurs and so shouldn't be speculated on here.

Line 770: Could an example of OH+hydrocarbon which does not form HO2 or RO2 be provided here.

Line 848: Please provide the equivalent NO required in the previous campaigns for

comparison.

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