

## Review of “Radical chemistry at a rural site (Wangdu) in the North China Plain: Observations and model calculations of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals” by Tan et al.

This paper summarizes measurements made in China in 2014 as part of a comprehensive field campaign that included measurements of HOx radicals and many other controlling species and parameters. The observations are analyzed using a 0-dimensional box model with a modified RACM 2 chemical mechanism. Comparison of observations and model results yields specific instances of agreement and some situations of significant disagreement. The authors hypothesize reasons for those differences that could lead to further research on the abundance of HOx radicals and their chemistry in the lower troposphere.

This reviewer believes that this is a fairly well-written and well-organized paper. The logic and presentation were mostly easy to follow, with a couple of minor exceptions. The paper places the current state of the art in HOx measurements in the context of our understanding of tropospheric chemistry for the environmental conditions encountered. There are no suggestions for major changes to the paper by this reviewer, but there are suggestions for changes to grammar, and some questions on the approach and intent of the discussion.

Line 3. Suggest “Observation of radicals by the laser induced fluorescence (LIF technique revealed...”

Lines 7-8. Suggest “...the model can reproduce measured radical concentrations reasonably well during daytime.”

Line 8. Suggest “As in previous...”

Line 14. It is a bit confusing to say the RO<sub>2</sub> is in good agreement, but then to say that RO<sub>2</sub> is underestimated by a large amount in the morning. Suggest changing this text to make the points clearer.

Line 23. Suggest “...has become an issue of great concern for citizens and...”

Line 24. Suggest “...strategies have already been implemented...”

Line 28. Suggest “...air quality has been steadily deteriorating in some locations...”

Line 45. Do the values of 0.8 and 0.4 ppbv refer to average or median values required? If so, state this.

Line 70. Misspelling of “formaldehyde”.

Line 75. Suggest “...calculations compared to results from previous campaigns...”

Line 84. Suggest “...botanical garden...”

Line 85. Suggest “...were growing to within 10 m of the instruments.”

Line 86. Suggest “There was no car or truck traffic in the botanical garden; The closest road was 2 km away.”

Line 88. Suggest removing “from the other containers”

Line 97. Suggest “...monitored by multiple instruments.”

Line 109. Note that peroxy radicals will also shift the NO to NO<sub>2</sub> ratio as the air travels down the sample line.

Line 113. Suggest “...reproducible (10 %) than in previous deployments...”

Table 1. All of the various techniques when multiple instruments were measuring are not given. Suggest making the list complete.

Line 120. This discussion of HONO measurements is good, but given the potential uncertainties in such observations, it might be good to do a more detailed comparison, perhaps including a figure comparing all six measurements.

Line 127. Suggest another phrase rather than “generally reasonable” such as “within quoted errors”.

Line 130. An instrument with higher sensitivity is more sensitive. This is a common confusion. Suggest changing to “are generally better,”

Line 152. Suggest “A 20 m high tower with meteorological instrumentation was set up 15 m south of the containers, where...”

Line 176. Suggest “...similar to instruments from this organization that have been described earlier...”

Line 201. Suggest “...used to detect fluorescence photons...”

Line 214. Suggest “...laser wavelength is tuned off the absorption line.”

Line 219. Suggest “...parameterized using the laser power, and the O<sub>3</sub> and water vapour concentrations.”

Line 220. It says that the correction is small compared to ambient OH, but this depends on the conditions. Near sunrise and sunset (or at night), this could be a large correction.

Line 225. It says that there was no interference from ozonolysis of simple alkenes, but what about larger, more complex alkenes (non-biogenic) that could be present?

Lines 245-246. Suggest “...chemical modulation that was temporarily attached to the OH detection cell during selected periods.”

Line 252. Suggest “...it showed instabilities causing...”

Line 253. Suggest starting a new paragraph on “The two signals...”

Line 257. This reviewer does not like the use of “titration” in this context. The authors can do as they choose, but suggest using “removal” or “conversion” efficiency rather than titration. Also suggest removing both commas on this line.

Line 262. Suggest “...that is measured with no OH scavenger added (S<sub>N2</sub>).”

Line 267. Suggest removing comma.

Line 268. Suggest removing “flow”. Suggest “A flow of 0.02 to 0.2 lpm of a 5 % propane...” Suggest using “lpm” rather than “Liter/min” throughout.

Line 271-272. The issue of mixing reagents into a flow containing HO<sub>x</sub> radicals at ambient pressure has been solved by others, particularly those make CIMS-based HO<sub>x</sub> measurements (e.g. Mauldin et al.).

Line 277. It states that the titration unit caused a 5% difference in OH sensitivity. Was this applied to the data collected while it was present?

Line 282. Suggest removing comma.

Line 286. Suggest removing “cell”.

Line 287. Suggest “...which is comparable to the detection limit.”

Line 294. Suggest "...with an average conversion..."

Line 300. Suggest removing second comma

Line 301. Suggest "At the beginning..."

Line 307. It states that it is assumed that the contribution of  $\text{RO}_2^\#$  scales with added NO. Is this justified by lab studies? How are the correction factors given in lines 309-310 applied? ( $\text{HO}_2 = \text{HO}_2^*/\text{CF}$  ?)

Line 319. Suggest "... these are the dominate  $\text{RO}_2$ ..."

Line 325. Suggest removing comma.

Line 331. Suggest "An average conversion efficiency..."

Line 333. Suggest "Any error in this value adds..."

Lines 334-337. Are the ambient data corrected for the artifacts as described?

Line 344. Suggest stating the reagents used to convert OH to  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  (CO and  $\text{CH}_4$ ?).

Lines 345-346. Suggest "No trends with time for any of the sensitivities were observed."

Lines 349-350. Suggest "...for the  $\text{HO}_2$  cell, 5% and 10% for the high and lower  $\text{HO}_2$  conversion efficiencies, respectively."

Line 358. Based on the discussion, the detection limit at noon is about  $1.5 \times 10^6$ . Is this a systematic or random effect of the solar light leakage? Can the data be corrected for this? Is this included in the overall measurement uncertainties?

Line 363. Do the authors believe that RACM 2 is a suitable mechanism to study detailed  $\text{HO}_x$  radical chemistry? Why not use the explicit MCM mechanism, modified as you did to include updated isoprene chemistry? Perhaps add some discussion as to why the RACM 2 mechanism was selected.

Line 385. Suggest removing "equidistant"

Line 389. When saying that the OH reactivity can "be well explained", suggest adding a quantitative value to the degree of agreement (within 22% or whatever).

Line 394. Suggest replacing "much" with "very".

Line 398. What species are being referred to as "these species"? Suggest a bit more text to make it clear.

Lines 401-402. Suggest "The largest class of  $\text{RO}_2$  radicals that is not included in the ..."

Line 425. Suggest removing comma after "daytime".

Line 447. Suggest "...after harvesting in surrounding..."

Line 452. Suggest "... $\text{NO}_2$  often showed trends similar to CO..."

Line 455. Suggest changing "often" to "sometimes".

Line 456. Suggest changing "nitrogen monoxide" to "nitric oxide".

Line 464. Suggest adding ", respectively" to the end of the sentence. Suggest changing "small" to "low".

Line 465. Suggest changing "raised" to "increased".

Line 467. Suggest "...2 ppbv, leading to enhanced OH production from HONO photolysis." One question: why didn't the peroxy radical concentrations also increase during this time period?

Lines 485-494. It appears to me that the NO<sub>3</sub> interference is sufficient to explain some or all of the nighttime signal observed.

Lines 495-503. Suggest a discussion and perhaps a figure showing the major contributors to the OH reactivity.

Line 509. Suggest chaining “as” to “using”.

Lines 515-516. Suggest rewording this sentence. One suggestion would be to separate the data into two equal groups rather than have this long discussion about why the two groups are not equal in size.

Line 522. The median measure-model difference discussed is of the order of the various artifacts and interferences. Have the data been corrected for all of them before doing this comparison? If so, suggest stating this somewhere.

Line 523. It is not clear what is meant by “At the same time”. Suggest rewording to make this clearer.

Line 551. Suggest changing “taking” to “using”.

Line 563. Is there any evidence of organic nitrites contributing to the enhancement of peroxy radicals in the morning? Photolysis of such species, if they exist, could contribute to the difference seen.

Line 592. It states that the production rate of RO<sub>2</sub> could be underestimated, but one should also consider that the loss rate of RO<sub>2</sub> could be overestimated somehow.

Line 594. It states that VOC concentrations are scaled to match measurements. Which measurements? Are they the VOCs or k<sub>OH</sub>?

Line 598. Suggest “...predict RO<sub>2</sub> at night...”

Line 599. Suggest “...caused by values near the limit of detection...”

Line 600. Suggest “...concentrations that are used as constraints.” A thought on nighttime chemistry: if there is NO<sub>3</sub> present, then the NO concentration should be very small unless the NO<sub>3</sub> production rate is very large. This is because of the rapid reaction between NO and NO<sub>3</sub>. This could help with the modeling of nighttime chemistry.

Line 606. Suggest “...ppbv when other conditions controlling OH are constant.”

Line 607. Suggest “Figure 9 shows the dependence of the measured and modelled radicals concentrations on the NO mixing ratio.”

Line 612. Suggest replacing “with” with “at”

Line 619. Suggest “OH behavior similar to that shown in...”

Line 628. Suggest replacing “when” with “as”.

Line 629. Suggest “At 3 ppbv NO, the modelled RO<sub>2</sub> concentration is less than  $1 \times 10^8 \text{ cm}^{-3}$ , whereas the median measured RO<sub>2</sub> is  $3.5 \times 10^8 \text{ cm}^{-3}$ .”

Line 631. Suggest “...than the model values...”

Line 644. Suggest removing comma.

Line 660. Suggest “...allow the calculation of net ozone...”

Line 665 and 668. Often P(O<sub>3</sub>) refers to gross ozone production and P(O<sub>3</sub>)-L(O<sub>3</sub>) is the net. Suggest perhaps indicating by using P(O<sub>3</sub>)<sub>net</sub>.

Line 692. Suggest “Cl radicals may...”

Line 693. Suggest “...with a maximum...”

Line 710. It is good to see meteorology mentioned as important to observed O<sub>3</sub> concentrations. This is likely very important in determining the diurnal cycle of ozone. Suggest changing text to “...by the increase of the boundary layer depth.”

Line 730. Suggest removing first comma.

Line 738. Suggest “...and HCHO concentrations as well as...”

Lines 758-769. Suggest including Ye et al in the discussion of HONO budgets.

Line 770. Suggest giving an example of a reaction of OH with VOCs that do not lead to peroxy radicals.

Lines 787-788. Suggest adding the word “each” before “account” since it appears that NO reactions with each of the species accounts for 26% of the conversion (total of about 50%).

Line 824. Suggest “...applying a laser induced fluorescence...”

Line 832. Yes, the interference would be minor compared to the daytime maximum, but it could be very important at sunrise and sunset.

Line 834. Suggest “setup” rather than “set-up”.

Line 842 and 846. Suggest “As” in place of “Like”.

Line 860. Suggest “...but caused by values of the modelled HO<sub>2</sub> that are too low...”

References. The papers on HO<sub>x</sub> measurements are very Euro-centric. Suggest adding some papers from US HO<sub>x</sub> measurement groups.

Figure 1. The colors for S<sub>N2</sub> and S<sub>OH</sub> are very similar. Suggest changing one of them to a very different color.

Figures 3 and 4. Suggest changing x-axis title to “Date (local)”.

Figures 3, 4, 5, 6, 8, and 10. Is the gray period meant to signify nighttime? If so, the authors should check this carefully. It appears that there are photolysis processes (such as O<sub>3</sub>) that occur after sunset (see Figure 10).