

Interactive comment on “Summertime photochemistry during CAREBeijing-2007: RO_x budgets and O₃ formation” by Z. Liu et al.

Anonymous Referee #2

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This paper presents a detailed model study of photochemistry in Beijing during the summer of 2007. The authors present a number of potentially important findings regarding the role of oxygenated and aromatic VOC in the formation of peroxy radicals and ozone. Without doubt, there are few studies in that region, so it could be an interesting addition to the literature. I have however several major concerns about the methodology and I think there are some serious flaws in the study, which I outline below; therefore I do not recommend publication at the present moment.

Major Issues:

- the use of a 1-D model in this context is highly problematic. The authors say that the model was constrained to the observations, which were presumably made at ground level. What happens to the unmeasured species, which are calculated by the model?

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I would assume they can be transported upwards or downwards along the model column. How this can bias the calculations and the conclusions of the paper is unclear. If the precursors and the sinks of RO_x can be transported along the model column, this should have a significant impact on the calculated RO_x levels. As there is no way to check the correctness of the RO_x calculation (see below) the use of a 1-D model introduces a major uncertainty in the whole analysis.

- RO_x were not measured, so the only way to assess how good the model calculation is, would be to see how well SAPRC performed in other studies. However, it appears that the authors have modified the aromatics scheme, making it difficult to compare the reliability of their mechanism with that of SAPRC. In any case, this question is not addressed at all, nor the uncertainty of the model discussed in any way. Since a major part of the paper consists in using calculated RO_x, this is a major deficiency.

- a significant part of the paper is dedicated to HO₂ interaction with aerosol. First, aerosol measurements are not mentioned, so it is not clear where the surface area is coming from. Second, the reason given for the choice of gamma (page 4685) does not make any sense.

- a potentially important finding is the role of HONO. It appears that the model generates HONO based on a "fake" reaction converting NO₂. This is not, per se, a problem but several things should be discussed: 1) how good was the HONO measurement 2) has this source any relation with laboratory or field studies of heterogenous formation of HONO 3) is this source consistent with the aerosol measurements (if any) and the total nitrogen data? The only comment on the reliability of HONO measurements is on page 4691, where the authors make the bold statement that because the HONO concentrations are so much higher than in other places the instrument uncertainty are likely lower (!) I don't think the authors can draw the conclusion that HONO plays such a major role under these conditions, based on unfounded estimates and assumptions for its measurement and formation process. The authors state that HONO is an ozone loss term in the sense that consumes NO₂; however, it is also a source in the sense

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that produces NO which forms NO₂. Has this feedback being considered?

- I think there is a serious methodological mistake in sections 3.2 and 3.4. The authors use the model to calculate ozone production and then change the model parameters to observe the sensitivity of ozone production. Given that the model is constrained to ozone and NO_x observations, it does not make sense to use it to calculate the formation of ozone. What the authors are doing in this case is equivalent to use the answer to obtain a question which is already known; only a model unconstrained to ozone may be used to calculate ozone formation and loss. This, without considering the complications introduced by the use of a constrained 1-D model. Also, I would be extremely careful in drawing conclusions on the VOC-limited or NO_x-limited regime, based on the correlation of the model results with some empirical diagnostic equations. First of all, it defies the purpose of using a model. Second, it is, at best, highly uncertain, and, at worst, a wild guess. In any case the reliability of these equations should be debated thoroughly.

Minor Issues:

- in sec. 2.1, three instruments to measure VOC are mentioned, although the authors don't say which species the GC/MS/FID measured. Were C₂ VOC measured? and CH₄? Which oVOC?

- the authors say that the model was run with a 1 min timestep. Since the VOC measurements have a 30 min frequency, the authors should say whether they were interpolated to 1 min and if so how and how it could impact the results.

- how are the production/loss rates calculated? are these reaction rates (eg, $k[\text{HO}_2][\text{NO}]$) or pseudo-first order rates (eg, $k[\text{NO}]$)? it is very different.

- section 3.1.2: the last paragraph is not clear: either it is stating the obvious or it does not make any sense.

- the style and quality of the paper is mixed, with some parts in decent english and

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some in really bad english.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4679, 2012.

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