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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO_2 concentrations in summer 2006" *by* K. D. Lu et al.

Anonymous Referee #2

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The manuscript provides a detailed analysis of the HOx photochemistry observed in a region of China with characteristic air masses showing both anthropogenic and biogenic influences, during the CAREBeijing2006 study. The analysis is thorough and well structured, with a focus on the topical subject of missing OH sources identified in regions of high VOC loadings and low NOx. This work provides a very interesting addition to the growing amount of evidence that indicates a problem with our current understanding of HOx sources in these low NOx environments. The work presented here provides a detailed analysis of the HOx and ROx budgets, and tests current mechanisms against an extensive measurement suite, including direct observations of OH reactivity. The authors find that current chemistry schemes underestimate the observed

OH concentrations by as much as a factor of 2.6, and that this discrepancy correlates with NO concentration. The model: measurement differences can however be resolved with either the inclusion of an unidentified species to convert HO2 → OH, as postulated by Hofzumahaus et al. 2009, or with the inclusion of the theoretical Leuven isoprene mechanism (LIM) proposed by Peeters et al. 2010.

This paper is well written and provides a very detailed analysis of a highly relevant topic. The paper is certainly within the scope of ACP, and I would recommend publication after the authors have addressed the minor comments below.

Minor comments

1- Pg 10891 Line 1. "A 24 h lifetime was introduced for all modeled species to account for dry deposition losses." The author should comment on why 24 hours was chosen, citing any supporting literature, and what implications this value has on the conclusions of the paper.

2- Section 4.3. The j(O1D) dependence of OH described in section 3.4 is not revisited when the different OH recycling schemes are used in the model. As the LIM mechanism involves the photolysis of the HPALD to yield OH it would be interesting to see if its inclusion improves the correlation between the calculated OH and j(O1D) compared to the observations. This could provide further constraints on the nature of the mechanism of OH regeneration.

3- Pages 10908-10909. The interference experiments described here are highly relevant and important to the subject. These experiments require a more detailed description. In particular the nature of the interference seen for MVK and toluene as this could have implications for other compounds not studied in the chamber. If this work is to be described in detail elsewhere it should at least be mentioned that the analysis of these experiments is in preparation.

4- Pg 10909 lines 22-25. One would expect that reducing the magnitude of the OH

sink within a model calculation would lead to an increase in the HOx concentration. However, in simulations both with and without the added dilution, OH and HO2* concentrations are underestimated by a factor of 2. An explanation of why this dilution term did not have the expected effect would improve the analysis of this very interesting case on August 20th.

Technical comments

Page 10882 line 18 – "these reaction involve CO..." should read "These reactions involve CO..."

Page 10885 line 11 – "CAREBeijing2006 was the first study that included also detailed measurements of..." Should read "CAREBeijing2006 was the first study that also included detailed measurements of..."

Page 10896 line 23 and Page 10898 line 2 – The model acronym species names should be defined.

Table 1 – The upper limit of detection for the kOH observations should also be quoted, i.e. the limit at which rapid OH loss results in insufficient OH signal for a decay to be fit.

References

Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. c., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li. X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., and Zhang, Y. H.: Amplified trace gas removal in the troposphere, Science, 324, 1702-1704, 2009.

Peeters, J. and Muller, J.-F.: HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: Experimental evidence and global impact, Phys. Chem. Chem. Phys., 12, 14227-14235, 2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10879, 2012.