

***Interactive comment on* “Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO₂ concentrations in summer 2006” by K. D. Lu et al.**

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]K. Lu et al.

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Response to Comments by Referee #2

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We would like to thank the reviewers for their comments and questions which have helped us to improve the manuscript. The reviewer comments are given below together with our responses and changes made to the manuscript.

General comments

The manuscript provides a detailed analysis of the HO_x 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 NO_x. This work provides a very interesting addition to the growing amount of evidence that indicates a problem with our current understanding of HO_x sources in these low NO_x environments. The work presented here provides a detailed analysis of the HO_x and RO_x 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

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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

Comment 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.

Response

The lifetime is treated as in the previous publication by Lu et al. (2012) for PRD. It corresponds to an assumed deposition velocity of 1.2 cm s^{-1} and a well-mixed boundary layer height of about 1 km. The height agrees with measurements of 0.8–1.2 km obtained by a LIDAR instrument at PKU in Beijing (Dr. X. Liu, personal communication). Numerical sensitivity tests show that the assumed deposition lifetime has a relatively small influence on the reactivity of the modelled oxidation products (e.g. OVOCS). As a result, calculated OH and HO₂ concentrations vary by less than 5% and 10%, respectively, if the deposition rate is changed by a factor of two. This result is similar to the findings by Lou et al. (2010) and Lu et al. (2012) for the PRD campaign. We will add this information in the model description (Section 2.2). Furthermore, following the suggestion by Referee 3, we add a new section about *Model uncertainties from unconstrained calculated OVOCS*.

Comment 2

Section 4.3. The $j(\text{O1D})$ 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 $j(\text{O}^1\text{D})$ compared to the observations. This could provide further constraints on the nature of the mechanism of OH regeneration.

Response

The reviewer has raised a good point that we will answer in the revised paper on P.10907 Line 20 as follows: The capability of LIM0 to amplify OH relies on the efficient production of HPALDs and their subsequent photolysis yielding OH radicals. If this mechanism is correct, an improved correlation between modelled OH and $j(\text{O}^1\text{D})$ would be expected for LIM0 compared to the base case. No significant difference in the correlation coefficients is found between M0 ($r^2=0.63$) and M3a ($r^2=0.64$) suggesting that the photolysis of HPALDs was probably not the major missing OH source.

Comment 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.

Response

The interference experiments were performed for the VOCs that contributed mainly to the OH reactivity at PRD and CareBeijing (see our reply to Comment 7 by Referee 1). The experiments and the results are described in detail in the paper by Fuchs et al. (2012) cited on Pg 10909 Line 1 (original manuscript).

Comment 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 HO_x 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

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not have the expected effect would improve the analysis of this very interesting case on August 20th.

Response

Reducing the magnitude of the OH sink does not necessarily lead to an increase in the HO_x concentrations. In our model framework, the NO_x, CO and VOC concentrations are fixed to observed values so that the species subject to dilution are the modelled OVOCs. The reduction of the OH reactivity can be attributed mainly to HCHO (53%), other aldehydes ALD (13%), methylglyoxal MGLY (12%) and the isoprene oxidation products MACR, MVK, CAR4 (11%). Since the photolysis of OVOCs like HCHO or MGLY contributes significantly to the production of HO_x, a decrease of their concentrations reduces both sources and sinks of OH. Furthermore, the reaction of OH with HCHO is HO_x neutral because OH is converted to HO₂. We will extend our discussion to clarify this point.

Technical comments:

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

Corresponding change will be made.

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...”

Corresponding change will be made.

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

We will provide the definitions as requested.

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.

The OH reactivity measurements were tested by Lou et al. (2010) for values in the range 0–190 s⁻¹. We will add a corresponding note on Pg 10888 Line 5 and in Table 1.

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Fuchs, H., Dorn, H.-P., 5 Bachner, M., Bohn, B., Brauers, T., Gomm, S., Hofzumahaus, A., Holland, F., Nehr, S., Rohrer, F., Tillmann, R., and Wahner, A.: Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration, *Atmos. Meas. Tech. Discuss.*, 5, 2077–2110, doi:10.5194/amtd-5-2077-2012, 2012

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.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Haseler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, *Atmos. Chem. Phys.*, 12, 1541–1569, doi:10.5194/acp-12-1541-2012, 2012.

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

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