

## ***Interactive comment on “Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO<sub>2</sub> concentrations in summer 2006” by K. D. Lu et al.***

**Anonymous Referee #1**

Received and published: 13 June 2012

The manuscript describes a detailed analysis of HO<sub>x</sub> photochemistry during the CARE-Beijing2006 campaign. The work focuses on missing source of the OH radical but also contains a thorough analysis of OH reactivity, the OH sink term. The work studies the measured constraints of the RO<sub>x</sub> budget and also investigates different models of HO<sub>x</sub> photochemistry in detail in view of the missing OH source terms. The findings add to the growing evidence of large sources of OH missing from models under low-NO<sub>x</sub> conditions. The work shows that unknown species that convert HO<sub>2</sub> to OH can explain the missing OH source. In contrast to the authors' previous study in the Pearl River Delta (Lu et al. 2012), they conclude that the Leuven isoprene mechanism does reasonably well in explaining the observations. The authors also analyze a high NO<sub>x</sub>

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day with large missing OH sources, which is very interesting. The work adds to the growing number of studies investigating this topic, which is highly relevant. The paper is well written, presents a thorough analysis, is timely, and in the scope of ACPD. I recommend publication after consideration of the following comments.

1. The night of 18-19 is rather interesting. The measured OH is remarkably high, until after midnight, I estimate 3-4E6 (high for nighttime), and isoprene is at ca. 500 ppt. It is remarkable that isoprene can survive at night at these levels of OH as the lifetime should be less than one hour. It appears the model is not even close to reproducing the nighttime OH. Can the authors comment on both what might sustain this OH and how the isoprene levels are being sustained?
2. P. 10891 Line 25. I don't think August 20 looks like particularly good agreement. This day is discussed later in detail, so I would consider removing it from the statement here.
3. Same section (3.1), discussion of HO<sub>2</sub><sup>\*</sup>, HO<sub>2</sub>. It is surprising that a term that, e.g., would affect recycling of HO<sub>2</sub> to OH, as proposed later, would affect only OH but not HO<sub>2</sub>. Can the authors comment on this or refer to the later section, where, I believe, this is discussed in more detail?
4. P. 10892 Line 11-18. Please be more quantitative. How large is the overprediction compared to the contribution from VOCs and OVOCs in the model (and how big are these in the model, respectively), as the numbers should be available from the model. Are any OVOCs (MVK+MACR?) available from GC-FID?
5. P. 10892. Line 28/ P 10893-Line 29: The high NO on August 20 in the afternoon is interesting. It would be very instructive to see the measured/model OH ratio for August 20 compared to other days, and this could be done with figure 9. In my opinion showing the ratio makes it easier to judge the percentage difference than the diurnal cycles.
6. P. 10907 Line 22-24. Except that nighttime measurements are not discussed in

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the mentioned manuscript. Is there any relationship to the night of August 18-19, i.e., possible uncertainties in nighttime OH sources?

7. P. 10908 Line 26 –P. 10909 Line 9 Where any terpenes tested or other alkenes, e.g., butadiene in the mentioned experiments?

Technical comments:

P. 10881 Line 7: It might be confusing to readers to introduce HO<sub>2</sub>\* without definition, but I also admit it might be awkward to define it here.

P. 10883 Line 5: Technically R1, R3, R4 also consist of sequential elementary reactions.

P. 10883 Line 8-10: R6 (1-beta) also is chain terminating.

Section 2.1.1: Please quote the precision of the KOH measurements; you give it for OH and HO<sub>2</sub>\*.

P. 10891 Line 17. The abstract mentions 10-30 s<sup>-1</sup> and here it is quoted as 10-20 s<sup>-1</sup>.

Section 3.1. Which figure are you referring to? If figure 1, please add “M0” to caption as this is not clear.

p. 10896 Line 23, P. 10898, Line 2, please define all acronyms of species.

P. 10897 Line 6-Line19. I think it might be useful to specifically state that RO<sub>2</sub>+RO<sub>2</sub> is not important, if that is correct, to prevent confusion.

P. 10898 Line 12. Is MCMv3.2 not M5?

P. 10903 Line 23-25. How are the HPALD products treated in the M3 models? It would be useful to describe this as it is not clear from the manuscript. Also, the HPALD photolysis rate and OH rate constant have recently been experimentally constrained by the same group, although this might not be relevant (Wolfe et al. 2012).

P. 10910 Line 20: none of “the” recycling

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Figure 1: I believe “b-c” should read “b-d”. Please define the model (M0?).

Figure 6: in c, the lines are very hard to see. Also, please add labels a-c

Figure 7: please define model runs or refer to specific section. I don't see the M0 model or M1,2,3a/b,4 etc. Is there a reason not to use the M0 etc. convention. The pie charts are somewhat randomly distributed. Can they be made a little larger and/or spaced further/more regularly?

References: It appears the page numbers on which references are cited are listed after each reference.

Supplement: P.3 : analysis “was” or “analyses” were ; “measurements”; “available”

Supplement figure S1 Looks very similar to figure 1 manuscript. The caption is slightly different (e.g., M0 is mentioned in supplement, which is helpful) and more days are shown but not the reactivity calculated from measurements. Could this just be included with the main manuscript?

Supplement section 3. “Similarly changes were done for MCMv3.1 and thus updated to be MCMv3.2 (see <http://mcm.leeds.ac.uk/MCM/project.htm#New 3.2>). “ Did you actually use MCMv3.2 or update MCMv3.1 with the two stated mechanistic changes. Please clarify as the MCM v3.2 has a lot more updates than the two mentioned.

Figures S3-S4 Are the significant figures in the legends meaningful?

References:

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 HO<sub>2</sub> 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.

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Wolfe, G.M., Crouse, J.D., Parrish, J., St.Clair, J. Yoon, T.P., Wennberg, P.O., and Keutsch, F.N. : Photolysis and OH reactivity of a Proxy for Isoprene-derived Hydroperoxyenals, *Phys. Chem. Chem. Phys.* 14, 7276–7286, doi:10.1039/c2cp40388a, 2012.

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

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