

***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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Response to Comments by Referee #1

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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 describes a detailed analysis of HOx 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 ROx budget and also investigates different models of HOx 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-NOx conditions. The work shows that unknown species that convert HO₂ 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 NOx 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

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recommend publication after consideration of the following comments.

Comment 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?

Response

The high nighttime OH concentrations are indeed interesting and will be analyzed in a forthcoming publication (Lu et al., in preparation). In short, we can state that the observed OH concentrations decreased after sunset from $4 \times 10^6 \text{ cm}^{-3}$ to $2 \times 10^6 \text{ cm}^{-3}$ (running average) until after midnight of Aug 18-19. This is very much larger than the model calculated concentrations. The observed nighttime values can be described, if a small, additional primary ROx radical source of less or equal 1 ppb/h is assumed plus additional recycling by X equivalent to 1 ppb NO. The nature of the required OH source at night is an open question as it is for the day. We will add a corresponding remark to the discussion in Section 4.3.1 where the nighttime radical source has already been mentioned (original manuscript, p.10906 lines 5–8).

Nighttime isoprene can have different sources. Isoprene may be advected as the left-over of biogenic daytime emission and may also come from weak nocturnal emissions which enter a shallow atmospheric boundary layer at night. Examples of weak sources are traffic emissions in urban areas (e.g., Lee et al., 2006; Liu et al., 2008) and biogenic emissions under dark conditions (Shao et al., 2001). It is interesting to note that isoprene showed a general decrease after sunset which is consistent with an oxidative removal by an OH concentration of about $1 \times 10^6 \text{ cm}^{-3}$. Such an OH estimate, however, has a large uncertainty in an urban environment, because it neglects the influence of transport and possible emission of isoprene in a shallow nocturnal boundary-layer.

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Comment 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.

Response

We thank the referee for pointing out an error in our manuscript. Figure 1 shows apparent disagreement between modelled and measured OH in the afternoon on Aug 20. It is caused by a large peak in the modelled OH profile resulting from invalid NO data that erroneously entered the model calculation. In the revised paper we have removed the invalid input data from the model and corrected Figure 1 accordingly.

Comment 3

Same section (3.1) , discussion of HO₂^{*}, HO₂. It is surprising that a term that, e.g., would affect recycling of HO₂ to OH, as proposed later, would affect only OH but not HO₂. Can the authors comment on this or refer to the later section, where, I believe, this is discussed in more detail?

Response

This effect is explained in the discussion of the original paper in Sect. 4.3.1. In the revised version of the paper, the following comment will be added in Section 3.1 (p.10892, line 2): "The robust agreement of measured and modelled HO₂ which contrasts the behaviour of OH is discussed in Sect. 4.3.1."

Comment 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?

Response

The OH reactivity on Aug 29 is overpredicted by the model by about a factor of 2.5 with contributions of 40 % from measured compounds and 60 % from modelled OVOCs. The overprediction seems to come entirely from the modelled OVOCs. Unfortunately,

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these cannot be compared to observations due to the lack of OVOC measurements in the campaign. We add this information in the revised text.

Comment 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/modell 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.

Response

We will add two new panels to Figure 9 (Figure 10 in revised manuscript) which show the diurnal variation and NO dependence of the measured-to-modelled OH ratio, respectively. The NO dependence of the OH ratio on days with southerly winds is shown for comparison.

Comment 6

P. 10907 Line 22-24. Except that nighttime measurements are not discussed in the mentioned manuscript. Is there any relationship to the night of August 18-19, i.e., possible uncertainties in nighttime OH sources?

Response

The good agreement of modelled and measured OH during the HOxComp field campaign stated in Elshorbany et al. (2012) and Kanaya et al. (2012) refers to daytime values. We will add a corresponding note in the revised paper. We further note that the nighttime OH measurements during HOxComp were generally below $1 \times 10^6 \text{ cm}^{-3}$. There was good agreement for our LIF instrument, the CIMS instrument, and the model at night. The mentioned papers give no clue to explain the unusually large nighttime measurements of OH by our instrument in Beijing.

Comment 7

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

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Response

We tested different VOCs including isoprene, MVK, MACR, t-butene, benzene, toluene, p-xylene, and mesitylene. Terpenes or butadiene were not tested. We will explicitly mention the list of tested VOCs in the revised paper.

Technical comments:

P. 10881 Line 7: It might be confusing to readers to introduce HO₂ without definition, but I also admit it might be awkward to define it here.*

We will change the sentence to: "Observed daily concentration maxima were in the range of $(4 - 17) \times 10^6 \text{ cm}^{-3}$ for OH and $(2 - 24) \times 10^8 \text{ cm}^{-3}$ for HO₂ (including an estimated interference of 25 % from RO₂).".

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

We agree and will change the sentence to: "Reactions R1 and R3–R7 are overall reactions each comprising a set of elementary radical reactions."

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

We will change the sentence to: "The radicals are finally destroyed by chain-termination reactions with NO₂ (R10), recombination reactions of peroxy radicals (R11, R12), and the reaction channel leading to organic nitrate formation in reaction R6."

Section 2.1.1: Please quote the precision of the k_{OH} measurements; you give it for OH and HO₂.*

We will add: "The precision of the derived k_{OH} values is 4–10 % at integration times of 1–3 min."

P. 10891 Line 17. The abstract mentions 10–30 s⁻¹ and here it is quoted as 10–20 s⁻¹.

The values in P. 10891 Line 17 will be changed to 10–30 s⁻¹.

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

Figure 1 contains results from the base model (M0). We will change the figure caption accordingly.

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

We will add the definitions for the mentioned RACM species: GLY (glyoxal), MGLY (methylglyoxal and other α -carbonyl aldehydes), and DCB (unsaturated dicarbonyls).

P. 10897 Line 6-Line19. I think it might be useful to specifically state that RO₂+RO₂ is not important, if that is correct, to prevent confusion.

The reviewer is right. In order to avoid confusion, we will replace "RO_x + RO_x" by "RO_x + HO_x". The sentence now reads: "For southerly wind days at noontime, there was a change of the dominating L(RO_X) channel from RO_x + NO_x to RO_x + HO_x reactions."

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

We will change the sentence to: "Only a few percent difference is found between the results of the base model (M0) and RACM-MIM-GK, and between MCMv3.1 and MCMv3.2 (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).

The implementation of the Leuven Isoprene Mechanism (LIM0) into our base model (M0) is explained in detail by Lu et al. (2012). We will refer to this paper and modify the text as follows:

Another scenario, M3a, incorporates the theoretical Leuven Isoprene Mechanism (LIM0) by Peeters and Müller (2010) assuming fast isomerization and decomposition

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of isoprene peroxy radicals (ISOP). The isomerization can proceed by intramolecular 1,5-H- or 1,6-H-shifts and yield OH or HO₂, respectively.

ISOP → 0.9 OH + 0.9 HCHO + 0.3 MACR + 0.6 MVK

ISOP → 0.9 HO₂ + 0.6 HPALD1 + 0.3 HPALD2

Among these two reactions, the 1,6-H-shift is predicted to be the dominating path. The resulting HPALDs (isoprene hydroperoxy aldehydes) are further assumed to undergo OH neutral reactions, or to produce photochemically up to three additional OH radicals (Peeters and Müller, 2010).

HPALD1,2 + OH → OH

HPALD1,2 + hν → m OH + HO₂ + OVOCs (m ≤ 3)

Rate constants for these reactions and the yields of OVOCs (hydroxyacetone, glycolaldehyde, methylglyoxal, glyoxal, HCHO) from HPALD photolysis have been taken from the mechanism in the global model of Peeters and Müller (2010). The implementation into our base model (M0) is explained in detail in Lu et al. (2012)."

We will also add the following comment on P. 10903 line 23–25: "A new laboratory study confirms that the photolysis frequency of HPALDs is as fast as estimated in LIMO (Wolfe et al. 2012), while the isomerization by the 1,6H-shift is most likely a factor of 50 slower than theoretically predicted (Crouse et al. 2011). Therefore, an additional scenario M3b with a factor of 50 reduced reaction rate was also tested."

P. 10910 Line 20: none of "the" recycling

Corresponding change will be made.

Figure 1: I believe "b-c" should read "b-d". Please define the modell (M0?).

Corresponding changes will be made.

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

Corresponding changes will be made.

Figure 7: please define modell runs or refer to specific section. I don't see the M0

modell 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?

We will change the figure legend and use M0, M1, etc. for the different model runs. We will distribute the pie charts evenly along the x-axis for better readability.

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

This is ACPD style. The numbers are interactive links representing the page numbers where the reference has been cited in the paper. You may click back and forth between the citation in the text and the reference list (does not work in the printer-friendly version).

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

Will be corrected.

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?

In Figure S1, we show for completeness all our measured HO_x data (from Aug and Sep 2006). However, other measurements (e.g., NO, NO₂, CO) needed to calculate OH reactivities or to perform model calculations were finished on 31 August 2006 and are therefore not available for September 2006.

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#New3.2>). “ 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.

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We used MCMv3.2. We will clarify the text.

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

No. The regression lines (and regression parameters) only serve the purpose to show that the different models agree very well with each other when they are applied to the conditions of our field campaign. We will reduce the number of displayed digits.

Reference

Crouse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 13, 13607–13613, doi:10.1039/c1cp21330j, 2011.

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