

***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 #3

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Comment

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

This manuscript describes comparisons between observed and modeled OH and HO₂* concentrations and OH reactivity at Yufa site, south of Beijing, during CAREBeijing2006 field campaign period. The authors found that additional OH production is required at low NO conditions, from a simple budget analysis for OH and from detailed observation model comparisons. The underestimation of OH concentrations by the base model reached a factor of 2.6 at 0.1 ppb NO. Although the value is lower than that found in PRD and those recently reported in forested sites, this study adds a new and important clue to our knowledge of tropospheric HO_x chemistry. The authors suggested several potential chemical mechanisms that could explain the observations, including generic OH recycling from HO₂ (and from RO₂ through HO₂), and isomerization of peroxy radicals produced from alkenes and aromatics. From a similar analysis for a day with northerly wind, the authors found that the OH reactivity was overpredicted by the model likely because OVOC concentrations are overestimated

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and, after adjustment of it by introducing a dilution term, that additional HOx production is also necessary under the high-NOx conditions. Basically the subject is appropriate for the journal, and the paper is well organized. However I found several assumptions needing more justification. My major concern is on the concentrations of NO and HCHO used in the analysis. The NO measurement was made at a different building at a different height; if the NO concentration at the HOx instrument is higher by a factor of 2 for example, the main conclusion of this manuscript becomes different. The HCHO concentrations were unmeasured and were simultaneously simulated; from Figures 3 and 4, it seems that >10 ppb of HCHO is likely assumed, whose credibility is not discussed except for an implication that the measured OH reactivity is better explained with that high HCHO concentrations. I am afraid that the OH reactivity might also be well reproduced by assuming unmeasured NMHCs instead of HCHO and other OVOCs. The authors also invoked later the possibility of dilution only for the case of northerly wind, without any justification that it can be neglected for the southerly wind conditions mainly discussed in this manuscript. My request is that the authors take into account the uncertainties in the NO and HCHO concentrations and evaluate the robustness of their conclusions. I suggest that the paper should be published after adding the above analyses and taking into account the following specific comments.

Response

We acknowledge the concerns of the Referee and will provide a more detailed discussion in the revised manuscript.

1) NO

We have no evidence for significant differences in NO at the two measurement platforms which were only 30 m apart. Under normal conditions we can assume well-mixed air for such spatial scale. A significant difference in NO concentrations would require a nearby source of a small horizontal extension. Such a source would very likely cause transient peaks in the nearby NO measurements. However, such peaks were not observed. Observed O₃ concentrations at both sampling platforms show a

high correlation ($r^2 > 0.9$) and a good agreement within 5% (details see P. 10888 Line 18–25) which gives further support for our assumption of well mixed air. Measurements of submicron aerosols gave no hints for significant local combustion sources that would co-emit NO, except that particles were detected at night probably as part of diesel emissions from a highway at 1.2 km distance east of the Yufa site (Takegawa et al., 2009). We will add this information in Section 2.1

2) HCHO

First, we would like to emphasize that the major result of our paper, a missing OH source in a VOC-rich urban environment, is deduced directly from the comparison of experimentally determined OH production and loss rates (Fig. 3) without need of measured HCHO or OVOC concentration data. Yet, we agree that a plausibility test of the modelled HCHO values is important for the understanding of the HOx simulations.

Concentration of HCHO

The modelled (M0) concentration of HCHO, one of the major calculated OVOCs, is on average 10–15 ppb at daytime. These values are well situated in the range (5–25 ppb) characterized by other ground-based measurements performed in summer at Beijing (Li et al., 2010; Gong et al., 2010). At our site, boundary-layer averaged HCHO concentrations of about 6 ppb were determined remotely by multi-axis differential optical absorption spectroscopy (MaxDOAS) for a few days (Aug 18, 19, 21, 27, 29, 31) (Li et al., 2012). Compared to the reported HCHO measurements, the modelled (M0) concentrations of HCHO appear reasonable for this region and time of the year. This and the mostly good agreement of measured and modelled OH reactivities suggests that the missing OH reactivity was mainly caused by unmeasured OVOCs rather than unmeasured NMHCs. We will add the above information in Section 3.1.

Dilution of modelled HCHO and OVOCs

For most of the days (the southerly wind days) aged air pollution was advected by slow, almost stagnant wind from the North China Plain as explained in the original paper on p. 10893 (section 3.1). We assume that under this condition the OVOC concentrations can be represented by modelled quasi steady-state concentrations using a deposition

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lifetime of 24 hours and a spin-up time of 2 days. The steady-state approach can lead to overestimated OVOC concentrations if the OVOCs are formed from fresh emissions and have not reached steady state when they arrive at the measurement site. This condition was most likely fulfilled on the day with northerly wind which brought freshly emitted pollutants at high wind speed from the nearby inner city of Beijing. In fact, the model generates too much OH reactivity on this day compared to the observations. To correct for this bias, we artificially assumed dilution for the model calculated species to match the modelled OH reactivity to the measured k_{OH} . We will explain this more clearly in a new section (*Model uncertainties from unconstrained calculated OVOCs*) and Section 4.3.2.

Impact of HCHO on modelled HOx

The assumed lifetime of atmospheric compounds with respect to deposition and dilution in our model is only relevant for OVOCs, since other trace gases (CO, NO_x, VOCs) are constrained by measurements. The uncertainty of the transport lifetimes has a relatively small impact on the modelled OH, HO₂ and k_{OH} values as we have explained in our answers to the Comments 1 and 4 by Referee 2. In order to address more generally the impact of possible uncertainties of the modelled OVOCs, we have performed an additional sensitivity analysis. The additional model runs were performed constraining the OVOC time series to half and twice the concentration values calculated in the base model run (M0). In case of a variation of HCHO only, the daytime averaged concentrations are about 6 ppb and 24 ppb, respectively, well situated at the lower and upper bounds of the previously reported HCHO concentration range (5–25 ppb) in Beijing (Li et al., 2010; Gong et al., 2010). For these boundary conditions, the modelled OH concentrations prove to be rather insensitive and remain constant within 10%. This low sensitivity can be explained by counteracting effects, i.e. OH production by photolysis of HCHO (HCHO+hv→HO₂, followed by HO₂+NO→OH) is partly compensated by OH loss through the reaction of OH with HCHO. The calculated peroxy radical concentrations are more sensitive and vary by 20–30%, while modelled $k(\text{OH})$ changes by about 20%. Similar results as for HCHO are obtained when all OVOCs (including HCHO) are

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changed by a factor of two. This demonstrates that the OVOC-related model uncertainties are dominated by HCHO. Overall, the simulated diurnal profiles of OH, HO₂^{*}, and k(OH) prove to be quite robust even for large OVOC variations. Thus, the general conclusions obtained from the base model run remain valid, i.e. HO₂^{*} and k(OH) are reasonably well reproduced by the model, while OH is significantly underpredicted in the afternoon. The above sensitivity study will be presented in a new section (*Model uncertainties from unconstrained calculated OVOCs*) in the revised paper, supported by a new figure showing the results of the sensitivity runs. Corresponding tests will be added for the model scenarios M1–M4 in the revised Supplement.

Specific comments:

Comment 1

Abstract, page 10881, line 7. Need some explanation of HO₂^{*}.

Response

We will clarify the meaning of HO₂^{*} (see our answer to the corresponding comment by Referee 1).

Comment 2

Abstract, the authors should mention that the model basically reproduced the observed OH reactivity with calculated OVOCs

Response

We will modify the sentence in P.10881 Line 9 of the abstract as:
...mainly contributed by observed VOCs and their calculated oxidation products.

Comment 3

Page 10883, line 18. Organic nitrates might be involved in SOA formation but it is poorly characterized. Just OVOCs may be enough here.

Response

We agree and will change the text accordingly.

Comment 4

Page 10884, line 14. Change literature Kanaya et al., 2007 to Ren et al. 2003 for NYC.

Response

The text will be changed.

Comment 5

Page 10885, lines 11-12. ... detailed measurements of OH, HO₂ and OH reactivity "in Beijing"

Response

The text will be changed.

Comment 6

Page 10886, lines 7-14. Can we assume that NO_x concentrations are not different for the two platforms with different heights? How was the agreement in HONO concentrations measured at the two locations?

Response

Our arguments for the assumption of well mixed air over these distances is given in our response to the general comment (see above). It is further supported by the comparison of the two sets of HONO measurements at the two locations. The HONO measurements correlated linearly with a slope of 0.85 and a correlation coefficient $r^2 = 0.84$. The two measurements agreed within their accuracies, suggesting homogeneously mixed air.

Comment 7

Page 10886, line 28. Is the flow rate of 1 slm common for the two cells?

Response

Each measurement cell has its own inlet with an orifice diameter of 0.4 mm. The flow through each inlet is 1 slm. We will clarify this point in the experimental description.

Comment 8

Page 10887. Can the measurement of OH reactivity be perturbed by reproduction of OH by the HO₂ + NO reaction, under high NO_x conditions?

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Response

In the early morning at high NO, the OH decays were influenced by OH recycling from HO₂+NO. In this case, biexponential fits were applied to determine k_{OH} . Details of this approach are given by Lou et al. (2010).

Comment 9

Page 10888, lines 6-15. Do the authors use downwelling 2-pi sr fractions of actinic flux measurements? How important are the upwelling fractions?

Response

The instruments measured only the downwelling part of the actinic flux. The upwelling contribution was neglected because the ground albedo in the UV range is typically small (<10%), in particular over paved ground and vegetated areas (Feister et al., 1995; McKenzie et al., 1996). We will add a corresponding note on Page 10888, lines 6-15.

Comment 10

Page 10889, lines 3-14. How was the agreement between NO_x measurements using the two instruments? Can they give some indication of homogeneity or heterogeneity of the ambient concentrations?

Response

The measurements of the two NO_x instruments agreed within their accuracies and showed a high correlation for both NO and NO₂. The two instruments were deployed at the same location, providing no indication of local NO gradients.

Comment 11

Page 10891, line 17. I do not understand 95% percentile of what.

Response

We will remove the remark since it is confusing and not relevant for the understanding of paper.

Comment 12

Page 10892, line 6. The range of modeled HCHO concentrations should be figured. Its reasonableness should be discussed because of its importance. Can the 24-h lifetime introduced to represent dry deposition be important in determining HCHO concentrations? If so, more discussion is necessary about the uncertainty in the lifetime. Was the 24-h lifetime commonly assumed for the authors' previous study in PRD, for which comparisons are made in this study?

Response

Please see our response to the general comment above and to Comments 1 and 4 by Referee 2.

Comment 13

Page 10894, line 21. Fig. 3a and b

Response

We will change the text accordingly.

Comment 14

Page 10896, line 19. 7 ppb h-1

Response

We will change the text accordingly.

Comment 15

Page 10900, section 4.1. The authors discuss that only one or two processes were important for initial production of ROx radicals in other cities. I am afraid this is not the case for all cities listed. For Tokyo for example, see Figure 11 of Kanaya et al. (2007) where a wide variety of processes are important for summer.

Response

We agree and will change the text.

Comment 16

Page 10901, line 14. Figure 7a (remove a space in between)

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We will change the text accordingly.

Comment 17

Page 10906, lines 5-8. Although the model's underprediction of OH continues from afternoon to the evening smoothly, the authors propose that the generic OH recycling is only important up to sunset and a different mechanism is necessary for night. I find this might be a weak point of this hypothesis.

Response

We apologize for not being clear enough in our statement. Our point is that we cannot explain the nighttime values by assumed additional recycling alone. In fact, we need additional recycling plus an additional primary source of HO_x to describe the HO_x observations after sunset. See our response to Referee 1 (Comment 1).

Comment 18

Page 10907, lines 7-9. The OH underestimation in the late afternoon is not repaired by the LIM mechanism, which is also a weak point of this hypothesis.

Response

The LIM mechanism by Peeters and Mueller (2010) is only consistent with our daytime observations of OH at Yufa if we account for conservative model error estimates. The highly efficient OH regeneration by isomerization of the isoprene peroxy radicals in the LIM mechanism is, however, in conflict with a laboratory study by Crouse et al. (2011), who derived a much slower isomerization rate. Thus, it is indeed unlikely that LIM represents the missing OH source.

Comment 19

Page 10909, line 21. What are the important chemical species for the OH reactivity whose concentrations were reduced by introducing the 8-h loss term? Can the authors provide any justification for the shorter lifetime exclusively for the northern wind, especially for products from isoprene chemistry?

Response

The chemical species are HCHO, ALD, MGLY and OISO (=MACR+MVK+CAR4) which

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contributed 53%, 13%, 12% and 11% to the reduction of k_{OH} , respectively. Our rationale to use a shorter lifetime for Aug 20 is explained in our answer to the general comment above.

Comment 20

page 10910, line 2. Remove space

Response

We will change the text accordingly.

Comment 21

Page 10910, lines 2 and 4. Only the average rates of the required source strength are discussed. What is the dependency of the calculated $Q(OH)$ or $Q(HO_2)$ on NO_x concentrations? The authors compare their own discussion on the OH concentration reproducibility at high NO_x with other literatures sometimes on HO_2 (not on OH). The imbalances of OH and HO_2 can occur differently and thus more careful discussion is necessary. The authors criticize that the HO_2 underestimation found at different cities at high NO_x can be influenced by artifact by RO_2 interference. However, the RO_2/HO_2 ratio is usually low at high NO_x and can be unimportant.

Response

The calculated $Q(OH)$ and $Q(HO_2)$ show no dependence on NO_x concentrations. Both of them show similar diurnal variations with a broad peak during 09:00 – 13:00. We will include this information in the corresponding discussion.

It is difficult to judge to what extent HO_2 data from other LIF instruments might be influenced by interferences due to RO_2 . The possible artefact depends on the specific instrumental design, the RO_2/HO_2 ratio of the sampled air and the speciation of RO_2 . In general, the RO_2/HO_2 ratio approaches unity at high NO_x conditions, whereas it can be larger or equal to unity at low NO_x conditions (Mihelcic et al., 2003). The RO_2 speciation depends on the corresponding VOC mixture and photochemical conditions, which may be different for each study. The major uncertainty comes from the unknown cross-sensitivity to RO_2 for the reported field campaigns. To indicate this uncertainty,

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we will modify line 16–17 on Page 10910 as follows:

...Part of this underestimation might be caused by a recently discovered measurement interference resulting from a partially conversion of RO₂ to HO₂ in LIF instruments (Fuchs et al., 2011). The contribution of such an artefact is instrument-specific and, due to lack of quantification, uncertain for the reported field campaigns.

Comment 22

Page 10912, lines 6-15. I would suggest shortening this part (e.g., remove literatures) to have a more balanced conclusion.

Response

We will change the text accordingly.

Comment 23

Table 3. Is acetylene missing from observation?

Response

Yes, we do not have acetylene measurements.

Comment 24

Figure 1 caption, line 2. Maybe Panel (b-d)

Response

We will change the text accordingly.

Comment 25

Figure 2e. Sometimes (e.g., 18 and 27 August) nighttime isoprene concentrations are non-zero. Where are they coming from?

Response

At Yufa, the dominant daytime isoprene emission source is some distance away from the observation site. During nighttime, the Yufa site may receive isoprene through transportation from source regions as leftover of daytime emissions, or possibly from nighttime emission sources. See our response to Comment 1 of Referee 1.

Comment 26

Figure 3. The authors should specify which days are included to represent composite diurnal variations of "southerly wind days"

Response

The southerly wind days in Fig. 3 are a subset of days (19, 23, 27 and 31 August) for which all required measurements are simultaneously available over complete diurnal cycles. We will add this information in the text and figure caption.

Comment 27

Figure 3d. In Figure 1, the modeled OH has a sharp increase in the afternoon on 20 Aug, which is not present in Figure3d.

Response

Figure 1 contains an error which we will correct in the revised paper. See our response to Referee 1, Comment 2.

Comment 28

Figure 4a. The large gap between the green and dotted purple lines is the contribution from HCHO photolysis. The fact that this fraction is not constrained by observation is a weak point of this manuscript and thus the incurred uncertainty should be discussed.

Response

We acknowledge that this point needs to be discussed. See our response to the general comments above.

Comment 29

Can the authors discuss possible impact of heterogeneous loss of HO₂ radicals on the aerosol particles, whose abundance is likely high at the location?

Response

The aerosol concentrations and surface-area densities in Beijing were similar high as in PRD. Accordingly, as reported by Lu et al. (2012), a considerable HO₂ reduction in the order of 50% can be expected by heterogeneous HO₂ loss, if an uptake coefficient of 0.5 is assumed. The aerosols at Yufa were mainly composed of soot and organic material (Garland et al., 2009), for which uptake coefficients of less

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than 0.1 are likely (Thornton and Abbatt, 2005; Bedjanian et al., 2005; Taketani et al., 2009, 2010). Based on the latter values, the possible HO₂ reduction is smaller than 20%. A hypothetical HO₂ to OH recycling process aided by a heterogeneous aerosol process appears therefore to be an unlikely explanation for the missing OH source. We will add this text to the discussion on page 10908 of the original manuscript.

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