

Response to Comments by Referee #1

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We would like to thank the reviewer for careful reading of the manuscript and the constructive 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.

5 **General Comments**

This manuscript describes nighttime observations of OH and HO₂* radicals during PRIDE-PRD 2006 and CAREBEIJING 2006 field campaigns and their comparisons to theoretical model simulation results. While HO₂* was in fair agreement, observed OH levels were significantly larger than simulation. After detailed discussion on the possibility of artifact, the authors suggested possibility
10 that the combination of additional RO_x production and the recycle of OH from RO_x through HO₂ could bring the model simulation in fairly good agreement in OH. For processes, the authors implied that the additional RO_x production would be explained by ozonolysis of unmeasured reactive terpenes at ample amount, or more possibly by the downward mixing of PANs as reservoir of radicals. The topic is well suitable to the scope of the journal. Although large uncertainty needs to be
15 taken into account, the analysis is made on the best knowledge basis, with clear logical flow. Two major comments are that (1) the modeled (and observed, if available) PAN concentrations should be mentioned together with the estimated flux, to convince readers, and that (2) discussion on the resemblance of the night-to-night variations in the observed and modeled radical concentrations should be involved. Overall, I recommend publication after revisions with respect to the points raised above
20 and the following minor comments.

Response

(1) In the revised manuscript, we compare the modeled PAN concentrations together with the estimated flux as suggested. Furthermore, we show measured PAN data for PRD (for Beijing, experimental PAN data were not measured at the field site). In the revised text and revised Fig. 12, we
25 show that the modeled PAN and MPAN concentrations are plausible by comparing with observed

concentrations or previously reported values. For a more detailed answer on this issue, see our answer to comment 14.

(2) In the revised text, we added more discussion on the resemblance of the night-to-night variations in the observed and modeled radical concentrations as suggested. Despite variations in some trace gases from night to night, our main results illustrated by the averaged profiles apply to all nights: (i) much higher observed OH concentrations than expected, with linear regression slopes between modeled and observed OH concentrations smaller than 4% and 8% in PRD and Beijing, respectively, and (ii) a relative good reproduction of the observed HO₂* concentrations by the model. For details, see our answers to comment 5 and comment 9.

Comment 1. Page 31316, line 8. It is better to mention that two separate cells are used for detection of each OH and HO₂*. A single pump draws air from the two cells. Can the back diffusion of NO, added only to the HO₂* cell, to OH cell be a problem, to measure OH and HO₂* simultaneously in such a system, especially when the HO₂*/OH ratio is large (> 1000)?

Response

As suggested by the referee, we have added the following sentence in the experimental description of our LIF instrument: 'The two fluorescence cells to measure the ambient OH and HO₂* radicals were physically separated and each connected by a 3 m long vacuum line to a low-pressure pump'.

Comment 2. Page 31318, line 11. How did the authors estimate concentrations of C₂ species at BG site, as listed in Table 1?

Response

The following explanation has been included in the revised manuscript: 'A few gas canister samples were taken during the campaign and analyzed by gas chromatography (GC) in order to determine concentrations of C₂ species, while C₃–C₁₂ NMHCs were measured and identified by an automated online gas-chromatography flame ionization detector (GC-FID) system (Wang et al., 2008)'.

Comment 3. Page 31319, Section 2.2. It is unclear if the model simulation was made for individual nights and then averaged to obtain the shown average time series (Figure 3 etc) or if only one model night with average concentrations of ancillary species was simulated. In the latter case, the titration relationship between O₃ and NO will not be adequately represented in the model.

Response

In this work, the model simulation was made for individual nights and then averaged to obtain the shown average time series. To clarify this point, we added a description in section 2.2 as '...The model runs are constrained by the measured time-series of O₃, HONO, NO, NO₂, CO, VOCs, photolysis frequencies, water vapor, ambient temperature and pressure for each individual night, and assumed deposition loss ...'.

Comment 4. Page 31319, lines 16-17. List date of the seven and nine days specifically.

Response

Seven nights in PRD: Jul 9-10, 12-13, 19-20, 20-21, 21-22, 23-24, 24-25; Nine nights in Beijing: Aug 18-19, 19-20, 20-21, 21-22, 22-23, 23-24, 26-27, 29-30, 30-31 We added these information
65 accordingly.

Comment 5. Page 31320, lines 16-17. Did the big differences in the CO and isoprene concentrations from night to night have correlation with radical concentrations, and indicate potentially important parent RO₂ that have been recycled to OH?

Response

70 As proposed by the reviewer, we have analyzed the correlations between observed OH and HO₂* radicals with the CO and isoprene concentrations. We found that the corresponding correlation coefficients (r^2) are small and do not provide a useful hint to the chemical reason for the unexplained high OH concentrations.

| | $r^2(\text{CO,OH})$ | $r^2(\text{CO,HO}_2^*)$ | $r^2(\text{ISO,OH})$ | $r^2(\text{ISO,HO}_2^*)$ |
|---------|---------------------|-------------------------|----------------------|--------------------------|
| PRD | 0.070 | 0.066 | 0.062 | 0.340 |
| Beijing | 4×10^{-6} | 0.036 | 0.190 | 0.371 |

75 We added the table and this information to the revised manuscript.

Comment 6. Page 31321, line 16. What was the estimated average concentration level of HCHO? Was the 24-h lifetime regarding deposition important?

Response

80 The averaged concentration level of HCHO was 10 – 12 ppb for PRD and 9 – 11 ppb for Beijing without significant variations. Though the assumed deposition lifetime has a significant influence on the modelled HCHO and OVOC concentrations, it has a relatively small impact on the simulated results of OH, HO₂* and OH reactivity, as already discussed in detail by Lou et al. (2010); Lu et al. (2012, 2013). A corresponding note has been added in the revised manuscript.

Comment 7. Page 31322, line 21. It is unclear what are meant by "large oxidation rates of the
85 sum of reactive trace gases."

Response

We revised the sentence to be "...with equally large oxidation rates of trace gases reacting with OH".

Comment 8. Page 31323, line 3. Was the contribution of the O₃+NO reaction included in the
90 nighttime O₃ turnover rate?

Response

The reviewer has made a good point. We would like to highlight that OH played an unexpectedly large role for nighttime chemistry. What we have shown in the original figure is not consistent (we compare apples with oranges): (i) the turnover rate of OH contains the reactions of OH with
95 'everything', i.e. VOCs (measured + unmeasured), OVOCs (unmeasured), CO (measured), NO + NO₂ (measured). (ii) the turnover rate of NO₃ contains the reactions of NO₃ with VOCs (measured) and OVOCs (modelled), and (iii) the turnover rate of O₃ contains the reactions of ozone with alkenes

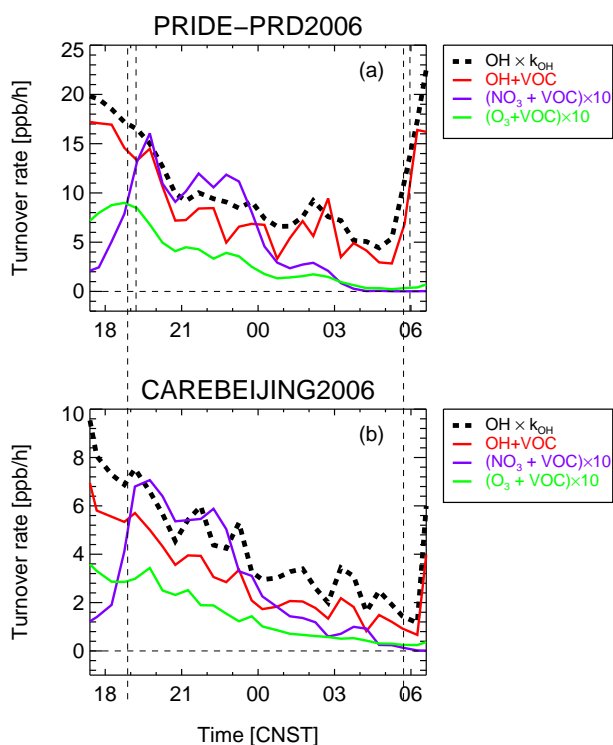


Fig. 5 Nighttime oxidation rates of VOCs (=observed HCs + modelled OVOCs) for their reaction with OH, NO₃ and O₃ during PRIDE-PRD2006 and CAREBEIJING. The VOC oxidation rate for OH was estimated as the difference of the measured total OH reaction rate ($k_{OH} \times [OH]$, black dashed line) and the calculated reaction rates of OH with CO and NO_x. The reaction rates of NO₃ and O₃ are taken from the base model and use modelled NO₃ and measured O₃ concentrations, respectively. The vertical dashed lines denote the sunset and sunrise.

(measured) and OVOCs (modelled). To clarify this, in the revised manuscript, (a) we discuss and keep the total OH turnover rate in the original Fig. 5 as it is, but (b) compare the relative role of OH, NO₃, and O₃ as oxidants for VOCs, only (see revised Fig. 5).

Comment 9. Section 4.1. Only average levels of the observed and modeled radical concentrations are compared. It is recommended to include correlation analysis between them, representing features of night-to-night variations.

Response

We performed a correlation analysis between observed and modelled radical concentrations for each night as suggested. We find similar results for each night. The squared correlation coefficients between observed and modeled OH radicals were lower than 0.07 for each night in both campaigns. The slopes of the linear regression between modelled and observed OH radicals was between 0.1 % to 4 % for individual nights in PRD and between 0.1 % to 8 % in Beijing. These correlations agree well with the behaviour of the averaged data of observation and modelling. This correlation analysis of night-to-night is added in the beginning of Section 4.1.

Comment 10. Page 31326, line 9. Can the artefact from Criegee intermediate for example be common for LIF and CIMS instruments and thus be overlooked during the intercomparison studies?

Response

115 We think that the referee refers to page 31325, line 25–29. The artefact from Criegee intermediate is not common for LIF and CIMS instruments since their zero point determination methods were different. The zero point of LIF OH measurements were often determined by spectral modulation while the CIMS instrument were determined by chemical modulations (e.g. adding OH scavengers like propane). As discussed in Mao et al. (2012), the artefact from Criegee intermediate can be
120 significant for LIF OH measurements if determined with spectral modulation method while removed with chemical modulation method. Mao et al. (2012) referred their chemical modulation method to the CIMS OH measurements. We added a short note "The CIMS technique discriminates between OH and Criegee radicals by chemical modulation and its OH data are therefore expected to be free from interferences by Criegee radicals. Thus, the small offset in the regression between LIF and
125 CIMS indicates that the LIF measurements were likely not subject to an artefact as it is discussed by (Mao et al., 2012)." on this point in the revised text after the sentence "The data showed an OH calibration difference of a factor of 1.4, which could be explained by the calibration uncertainties of LIF (20 %) and CIMS (38 %). Only a very small, insignificant offset of $(0.04 \pm 0.03) \times 10^6 \text{ cm}^{-3}$ was found in the linear regression of the two instruments."

130 **Comment 11.** Page 31328, line 18. comparison (not intercomparison)

Response Revised accordingly.

Comment 12. Page 31330, lines 5-8. Do we expect large differences in the simulated NO₃ concentration levels in the two model runs, as suspected from the large difference in OLNN and OLND? If yes, why was it?

135 **Response**

The simulated NO₃ concentration levels in the two model runs (M0 and M0+X+p_{OH}) were almost identical. The large difference of OLNN and OLND was caused by the additionally introduced RO₂ loss channel – RO₂ + X → HO₂ in the model run (M0+X+p_{OH}). OLNN and OLND are products of NO₃ oxidation processes. They have no feedback influence on the NO₃ budget. We
140 further explained this in the revised text as "Nevertheless, the introduced additional pathways in M0+X+p_{OH} that changes the ROx budget significantly do not show a impact on the NO₃ budget since the simulated NO₃ concentration in the two model runs (M0 and M0+X+p_{OH}) were almost identical."

Comment 13. Page 31332, line 25. 10**6 (not 10**-6)

145 **Response** Revised accordingly.

Comment 14. Section 4.4.2. Can the authors evaluate simulated PAN concentrations, through comparison to observations if available, or to the levels typically present in the nighttime boundary layer? Can the PAN entrainment from the top boundary of the upper layer be also important, to

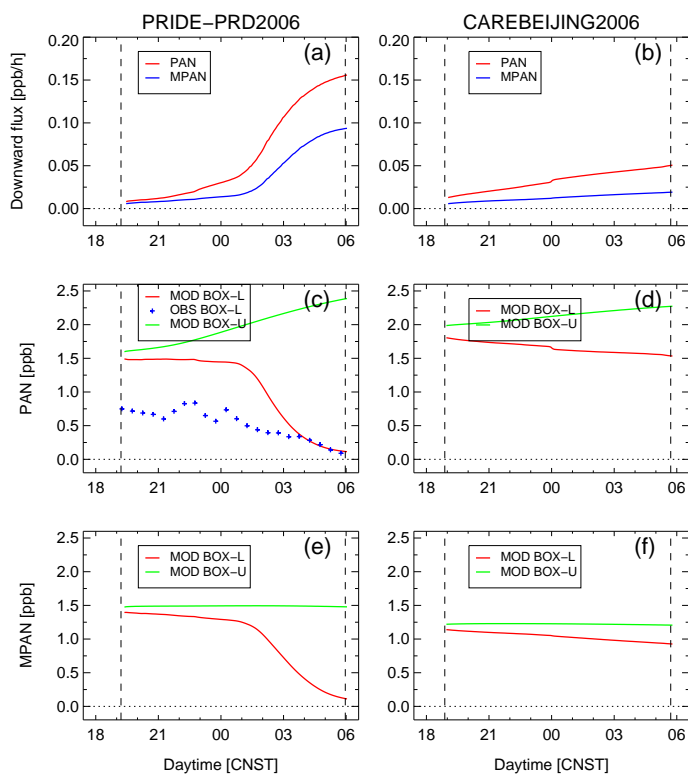


Fig. 12 Estimated fluxes of PAN and MPAN transported downward from the residual layer to the stable surface layer during PRIDE-PRD2006 (a) and CAREBEIJING2006 (b). In the lower layer, the transported compounds decompose thermally and produce peroxy radicals at a rate approximately equal to the downward fluxes. The observed (if available) and modelled PAN and MPAN concentrations are shown in (c)-(f).

increase the flux to the lower layer?

150 **Response**

In PRD where the PAN measurements were available, we added a brief description about the PAN measurements as "In PRD, PAN measurements were performed with an on-line gas chromatography equipped with an electron capture detector (GC-ECD) technique (Wang et al., 2010). The accuracy of the PAN measurement is estimated to be 25% by convoluting the errors of the photochemical
155 PAN standard, variability of the calibration results, inlet and column thermal losses, etc." in the experimental section.

In the revised paper, we have added simulated PAN and MPAN concentrations in Fig. 12.

The modelled concentrations of the RACM-species PAN (= PAN and other higher saturated PANs) in the lower layer in PRD are comparable to measured values and show a similar temporal variation
160 throughout the night. The simulated MPAN concentration level is also plausible as judged by the observed PAN to MPAN ratio (e.g. 6 to 10) reported for biogenically dominated air masses (Roberts et al., 1998). The role of entrainment of PAN from the top boundary of the upper layer is difficult to estimate without more detailed information about the nocturnal structure of the lower troposphere

at the measurement sites. Such information is not available. Nevertheless, our analysis demonstrates that vertical transport is a possible candidate to explain at least part of the enhanced radical concentrations near the ground. We further included those explanation into our revised text.

Comment 15. Section 4.4.2. Does K_z depend on z ? The value for the 50-m altitude level was used?

Response

Yes, we considered the z dependence of K_z according to eqn. 6 (Page 31334) in the paper. We used the value for the 50-m altitude level. We noted this explicitly in the revised text.

Comment 16. Page 31334, line 8. How was the nocturnal temperature lapse rate used?

Response

The observed temperature is used as model boundary conditions for the lower box that represents the nocturnal boundary layer. The temperature at 500 m height is calculated by the observed surface temperature and the determined nocturnal temperature lapse rate. The temperature at 500 m height is further used as model boundary conditions for the upper box that represents the nocturnal residual layer. We noted this explicitly in the revised text.

Comment 17. Page 31334. Can the dry deposition of the radicals on the ground be effective?

Response

Dry deposition of HOx radicals has a negligible influence on the HOx concentrations at our measurement height, since the transport time (~ 0.5 h) by eddy diffusion is much larger than the chemical lifetime (< 50 ms) of the radicals.

Comment 18. In Lu et al. (2012) and (2013) for daytime analysis for PRIDE-PRD and CARE-BEIJING, the authors discussed that the importance of the RO₂-to-HO₂ conversion was reduced, after considering RO₂ artefact in the HO₂* measurement. On the other hand, the manuscript indicated that the RO₂-to-HO₂ and HO₂-to-OH conversion was required in the nighttime similarly to the daytime. Are they consistent to each other?

Response

In Lu et al. (2012) and (2013), we found that the generic reaction like $\text{HO}_2 + \text{Y} \rightarrow \text{OH}$ is also possible after considering RO₂ artefact in the HO₂* measurement. But we also pointed out that after considering RO₂ artefact in the HO₂* measurement, the generic reactions $\text{RO}_2 + \text{X} \rightarrow \text{HO}_2 + \text{X} \rightarrow \text{OH}$ which we originally proposed (Hofzumahaus et al., 2009) is still plausible. Both the two different reaction mechanisms we deduced mean that there is an unrecognized OH regeneration mechanism in the VOC rich atmosphere. In the present manuscript, we incorporated the generic reactions $\text{RO}_2 + \text{X} \rightarrow \text{HO}_2 + \text{X} \rightarrow \text{OH}$ for the nighttime study since the X reactant is considered to be constant and its concentration was derived in corresponding daytime studies (Lu et al., 2012; 2013). We have not incorporated the other reaction $\text{HO}_2 + \text{Y} \rightarrow \text{OH}$ since the reactant Y is considered to be variable. Nevertheless, the major point we want to convey is that unrecognized OH regeneration mechanism must be presented in both daytime and nighttime, and therefore, that kind of unrecognized reaction

mechanism is most likely to be an intrinsic feature of the chemistry in the troposphere.

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