Response to Comments by Referee #1

K. Lu et al.
yhzhang@pku.edu.cn & a.hofzumahaus@fz-juelich.de

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.

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 that the combination of additional ROx production and the recycle of OH from ROx through HO2 could bring the model simulation in fairly good agreement in OH. For processes, the authors implied that the additional ROx 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 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 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 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 HO\textsubscript{2} 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 HO\textsubscript{2}* . A single pump draws air from the two cells. Can the back diffusion of NO, added only to the HO\textsubscript{2}* cell, to OH cell be a problem, to measure OH and HO\textsubscript{2}* simultaneously in such a system, especially when the HO\textsubscript{2}*/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 HO\textsubscript{2} 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 C\textsubscript{2} 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 C\textsubscript{2} species, while C\textsubscript{3}–C\textsubscript{12} 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 O\textsubscript{3} 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 O\textsubscript{3}, HONO, NO, NO\textsubscript{2}, 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

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

As proposed by the reviewer, we have analyzed the correlations between observed OH and HO\textsubscript{2} 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.

<table>
<thead>
<tr>
<th></th>
<th>$r^2$(CO,OH)</th>
<th>$r^2$(CO,HO\textsubscript{2})</th>
<th>$r^2$(ISO,OH)</th>
<th>$r^2$(ISO,HO\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRD</td>
<td>0.070</td>
<td>0.066</td>
<td>0.062</td>
<td>0.340</td>
</tr>
<tr>
<td>Beijing</td>
<td>4×10\textsuperscript{-6}</td>
<td>0.036</td>
<td>0.190</td>
<td>0.371</td>
</tr>
</tbody>
</table>

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

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, HO\textsubscript{2} 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 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 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 "everything", i.e. VOCs (measured + unmeasured), OVOCs (unmeasured), CO (measured), NO + NO\textsubscript{2} (measured). (ii) the turnover rate of NO\textsubscript{3} contains the reactions of NO\textsubscript{3} with VOCs (measured) and OVOCs (modelled), and (iii) the turnover rate of O\textsubscript{3} contains the reactions of ozone with alkenes...
Fig. 5 Nighttime oxidation rates of VOCs (=observed HCs + modelled OVOCs) for their reaction with OH, NO\textsubscript{3} and O\textsubscript{3} during PRIDE-PRD2006 and CAREBEIJING. The VOC oxidation rate for OH was estimated as the difference of the measured total OH reaction rate (k\textsubscript{OH} \times [OH], black dashed line) and the calculated reaction rates of OH with CO and NO\textsubscript{x}. The reaction rates of NO\textsubscript{3} and O\textsubscript{3} are taken from the base model and use modelled NO\textsubscript{3} and measured O\textsubscript{3} 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, NO\textsubscript{3}, and O\textsubscript{3} 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 intercompaison studies?

Response

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 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 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 \(0.04 \pm 0.03\) \(10^6 \text{ cm}^{-3}\) was found in the linear regression of the two instruments.”.

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?

Response

The simulated NO3 concentration levels in the two model runs (M0 and M0+X+pOH) were almost identical. The large difference of OLNN and OLND was caused by the additionally introduced RO2 loss channel – RO2 + X → H2O in the model run (M0+X+pOH). OLNN and OLND are products of NO3 oxidation processes. They have no feedback influence on the NO3 budget. We further explained this in the revised text as "Nevertheless, the introduced additional pathways in M0+X+pOH 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+pOH) were almost identical.”.

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

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?

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 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 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 Kz depend on z? The value for the 50-m altitude level was used?

**Response**

Yes, we considered the z dependence of Kz 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 HO2 + Y → 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 RO2 + X → HO2 + X → 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 RO2 + X → HO2 + X → 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 HO2 + Y → 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 a intrinsic feature of the chemistry in the troposphere.
References

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K.,
Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified Trace Gas Removal in

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C., Fuchs, H., Häselker, R., Kita, K.,
OH reactivities in the Pearl River Delta China in summer 2006: measurement and model results, Atmos.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häselker, R., Hu, M., Kita, K.,
A.: Observation and modelling of OH and HO\textsubscript{2} concentrations in the Pearl River Delta 2006: a missing OH
source in a VOC rich atmosphere, Atmos. Chem. Phys., 12, 1057–1080, doi:10.5194/acp-13-1057-2013,
2013.

Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H., Paulot, F., Beaver,
M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W.,

Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., Hubler, G., Kuster, W. C.,
McKeen, S. A., Ryerson, T. B., Trainer, M., Williams, E. J., Fehsenfeld, F. C., Bertman, S. B., Nouaime, G.,
Seaver, C., Grodzinsky, G., Rodgers, M., and Young, V. L.: Measurements of PAN, PPN, and MPAN made
during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: Implications for regional
ozone production from biogenic hydrocarbons, Journal of Geophysical Research-Atmospheres, 103, 22473–
22490, roberts, JM Williams, J Baumann, K Buhr, MP Goldan, PD Holloway, J Hubler, G Kuster, WC
McKeen, SA Ryerson, TB Trainer, M Williams, EJ Fehsenfeld, FC Bertman, SB Nouaime, G Seaver, C
Grodzinsky, G Rodgers, M Young, VL, 1998.

Wang, B., Shao, M., Roberts, J. M., Yang, G., Yang, F., Hu, M., Zeng, L. M., Zhang, Y. H., and Zhang, J. B.: Ground-based on-line measurements of peroxyacetyl nitrate (PAN) and peroxypropiony nitrate (PPN) in the
Response to Comments by Referee #2

K. Lu et al.
yhzhang@pku.edu.cn & a.hofzumahaus@fz-juelich.de

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.

**General Comments**

This paper describes nighttime measurements of OH at two locations in China during 2006 that both showed concentrations much larger than predicted by standard models. If correct, these observations suggest shortcomings in current models of HOx chemistry, and further suggest that nighttime oxidation rates by OH can be much larger than previously thought. Derived oxidation rates are much larger than those of the conventional nighttime oxidants, O3 and NO3.

The authors discuss three different mechanisms that could explain the observations. These include as yet unknown HOx recycling reactions, similar to that used to explain large daytime concentrations of HOx from the same campaigns; a source of HOx from nighttime ozonolysis reactions of highly reactive biogenic VOCs; and transport of radical reservoirs from a layer aloft to the surface. None of the three mechanisms satisfactorily explain the magnitude or time dependences of the observations, but they do suggest useful tests that can be applied in future investigations, especially with regard to the measurements of nighttime vertical gradients.

The major weakness of the analysis, and one that is adequately acknowledged and addressed in the paper, is that the observations could arise from measurement artifacts in the OH instrument. A recent paper from Mao et al. (2012) shows that a different OH zeroing scheme applied to the Penn State OH LIF instrument largely resolved recently observed model to measurement discrepancies, including nighttime observations from the recent literature. The authors of the current paper allow for the possibility that their instrument could be subject to similar interferences during the specific measurements in China in 2006, while arguing that their recent work suggests that such artifacts are unlikely. Because they have directly addressed this issue and argued at least plausibly (if not fully
convincingly) for the validity of their nighttime data, I find the paper suitable for publication. The suggestions for additional work to determine the source of the observed nighttime OH, including further work on measurement artifacts, will serve as a useful reference for future investigations. The authors should address the specific comments below prior to publication.

Specific Comments:

Comment 1. Page 319, section 2.2: Why use a RACM scheme for a zero D model rather than a more detailed scheme like the MCM? Is there a use for the lumped model when it is compared to MCM anyway later in the paper?

Response

RACM-MIM-GK and MCM represent state-of-the-art chemical mechanisms which - as we show in our paper - yield very similar model results for OH, HO₂ and kOH for the conditions in PRD and Beijing. Both mechanisms include an explicit description of inorganic atmospheric chemistry, but differ in details of the organic chemistry. The differences in the OH model results between both mechanisms are completely negligible compared to the discrepancy between modelled and measured OH. This demonstrates that something fundamental is missing in the current understanding of nighttime chemistry independent of the used mechanism. Our analysis of hypothetical processes that may possibly explain the OH discrepancy does not require the level of detail provided by MCM. In fact, we would not have gained more insight, if we had done the sensitivity tests with MCM rather than with RACM. Since RACM is numerically faster und easier to handle for sensitivity tests and radical budget calculations, we preferred to use RACM. The comparison of results of MCM and RACM in Fig. 3 just served as a confirmation that lumping of VOC chemistry in RACM is not the reason for the large underestimation of the OH observations at night.

Comment 2. Page 319, Figures 1 and 2: Headings are missing in these figures. Presumably the right column is PRD and the left is Beijing?

Response

We added headings in the revised figure 1 and 2. The left columns refer to PRD and the right columns to Beijing.

Comment 3. Page 322, lines 1-5: The modeled NO₃ seems too high for periods in which the NO is large (e.g., >10 ppbv after midnight in Figure 1 at PRD). Is this a consequence of averaging some nights with lower NO and non-zero NO₃ together with others that have higher NO and zero NO₃? Or does the model take diurnal average values of the inputs? If the former, could such a model non-linearity have any influence on the OH model to measurement comparison?

Response

We ran the model with observed values night by night and then calculated mean nighttime variations by averaging over different nights. As correctly explained by the referee, this can lead to high values of mean NO₃ concentrations together with high values of mean NO concentrations. To make this point clear, we will explain this result in the revised paper. Averaging of the measured
and modelled nocturnal variations of OH has no influence for the interpretation of the OH model-to-measurement comparison since we always observed much higher OH concentrations than modeled. The major features of the observed and modeled OH concentrations in all nights are therefore well represented by the averaged profiles. See also our answers to the related comments 5 and 9 of referee 1.

**Comment 4.** Page 322-323, section 3.3: The observations imply large nighttime oxidation rates. Later in the manuscript, however, the authors argue that the high OH may be confined to a shallow layer. The section requires caveats that the nighttime OH oxidation could not represent a quarter of total oxidation if there were strong gradients at night but not during day.

**Response**

We introduced an additional caveat - "As a result, nocturnal OH would be responsible for about a quarter of the total trace gas oxidation by OH integrated over 24 h for the air masses characterized at the measurement sites. It should be noted that the observed high nighttime OH may be confined to a shallow layer near the surface where the measurements took place (see section 4.4.2). Thus, the general relevance of nighttime compared to daytime oxidation by OH in the lower troposphere cannot be derived from our data."

**Comment 5.** Page 322, lines 25-27 and description of figure 5: How are the NO3 turnover rates calculated? Is this modeled NO3 multiplied by an NO3 reactivity from the VOC measurements, or is it the NO3 production rate? If the latter, how does this compare to the simpler calculation represented by the former. Also, in Figure 5, suggest showing the NO3 and O3 turnover rates on separate scales, or at least multiplied by a factor of 10, so that they are visible. The average values given in the text hide some of the detail of the time dependence, which is not easy for the reader to see in this figure.

**Response**

The NO₃ turnover rates were calculated by multiplying the modeled NO₃ with the NO₃ reactivity from the observed VOCs and modeled OVOCs. We scaled up the NO₃ and O₃ turnover rates by factor of 10 as suggested. See also our answers to comment 8 of referee 1.

**Comment 6.** Page 323, introduction to section 4: The introduction to this section, and the presentation of the literature in Table 2, gives the impression to the reader that large nighttime OH and model to measurement discrepancies are well accepted. This is not the case, as the later discussion in this section shows. The first four references in Table 2, were they to be corrected by the more recent findings from the same group (see Mao et al, 2012), would not produce large model to measurement discrepancies. Thus, the observations from the studies in China in 2006 are more unusual than implied by this discussion. Strongly suggest rewording this section so that it leads with the results of Mao et al. and does not present high nighttime OH as an accepted finding.

**Response**

As Mao et al. 2012 discussed in their text, the interference is likely dependent on the specific...
instrumental design, and as it may vary with the VOC mix, and therefore it is not clear about how to transfer the results from the study of Mao et al. (2012) to other field campaigns (e.g., PROPHET) or other LIF instruments. The first paragraph of section 4.1 is a short summary of what has been published in literature, without further interpretation. In the second paragraph we have provided a detailed discussion about the possible OH measurement artefact according to Mao et al. (2012). We consider our short review of the previous nighttime OH studies as balanced. Just to further stress the possible measurement artefact, we added a footnote to the measurement campaigns performed by the Pennstate instrument in revised table 2 as "These observed OH concentrations may have suffered from a significant measurement artefact as indicated by Mao et al. (2012)".

Comment 7. Page 326, lines 12-13: The nighttime isoprene decays at the PROPHET site is controversial, and likely due to transport, not chemistry. See Sillman et al, JGR, 107, 4043 (2002). The concluding statement of this paragraph is likely more correct than the introductory statement. Suggest omitting chemical arguments regarding isoprene at night.

Response
In the conclusion part of Sillman et al, JGR, 107, 4043 (2002), the authors pointed out "Nighttime loss of isoprene is attributed to three factors: chemical reaction with OH, vertical diffusion, and advection from Lake Michigan. Model results suggest that the observed loss of isoprene can be explained primarily by vertical diffusion. Nighttime OH has a smaller impact on isoprene than would be inferred from its measured concentration because high nighttime OH is likely to be confined to a shallow surface layer." We modified the text on Page 326, lines 19-21 as follows:

"Besides its chemical removal by OH, isoprene is also subject to transport for which we have insufficient knowledge with respect to the spatial/vertical isoprene distribution around the measurement sites. As diagnosed by Sillman et al. (2002) for the Michigan forested areas, the nighttime loss of isoprene can be attributed to three factors: chemical reaction with OH, vertical diffusion, and advection. In their model results, the observed loss of isoprene was mainly caused by the vertical diffusions. Nevertheless, Sillman et al. (2002) also pointed out that in a shallow layer near the surface, the chemical reaction with OH might be important as diagnosed by Faloona et al. (2001) for the same campaign."

Comment 8. Page 328, lines 14-16: Would these imbalances be sufficient to sustain turnover rates of 5-10 ppbv hr-1, as shown in Figure 5? The argument would imply a PAN + HO2NO2 loss rate of similar magnitude, further implying a very large reservoir of these compounds. Realistic?

Response
As discussed later in Section 4.4.2, the imbalance between RCO$_3$ radical and PANs may contribute an additional RO$_X$ primary production rate up to 0.25 ppbh$^{-1}$. The turnover rate of 5-10 ppbh$^{-1}$ is sustained by an additional efficient recycling (RO$_2$→HO$_2$→OH) and a small additional ROX production process as stated in our conclusion part. Therefore, we do not mean a significant loss rate of PAN + HO2NO2.
Comment 9. Page 334-335, end of section 4.4.2. Although the argument is interesting and certainly consistent with the model of Geyer and Stutz, it produces a large flux of radicals late at night, when they are less needed to resolve the model to measurement discrepancy? The cited flux of 0.25 ppbv hr⁻¹ at PRD occurs at sunrise, rather than sunset, when it is quite small. The authors should comment on this aspect of the proposed radical source.

Response

As shown by Fig. 3, we observed much higher than expected OH concentrations from sunset to sunrise. With model sensitivity studies, we deduced that the unexpected high nighttime OH concentrations shall be sustained by an additional efficient recycling (RO₂→HO₂→OH) and a small additional ROx production. For the period of sunset where the highest nighttime OH normally appeared, such small additional ROx production may be contributed by unrecognized ozonolysis processes or NO₃ oxidations since the O₃ and NO₃ were high therein. For the period close to sunrise, when the additional ROx production can not be driven by O₃ and NO₃ anymore, the vertical transport of reservoir species like PANs may then take over the sustain the nighttime oxidation for the very last step at night.

As suggested, we added a comment to our proposed radical source at the end of section 4.4.2 in the revised text as the followings:

Thus, future field campaigns studying the nighttime chemistry would greatly benefit from additional measurement of vertical profiles of key species such as NO as well as of flux and micrometeorological measurements at different heights. The downward transport of PAN and its analogs would be especially important as an additional ROx radical source when the near surface NO concentration becomes high.

Technical corrections

Page 314, line 8: comma after radicals
Page 314, line 26, comma after "involvement of NO"
Page 316, line 11, "electronic" rather than "electronical"
Page 329, line 24: "relatively"
Page 336, line 6: "well" not needed or awkward. "Easily" would be better if the adverb is needed

Response Revised accordingly.
References
