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Discussions

Interactive comment on "Nighttime observation and chemistry of HO_x in the Pearl River Delta and Beijing in summer 2006" *by* K. D. Lu et al.

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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.

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, HO_2 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 NO_3 turnover rates were calculated by multiplying the modeled NO_3 with the NO_3 reactivity from the observed VOCs and modeled OVOCs. We scaled up the NO_3 and O_3 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 $\mathrm{ppb\,h^{-1}}$. The turnover rate of 5-10 $\mathrm{ppb\,h^{-1}}$ is sustained by an additional efficient recycling ($RO_2 \rightarrow HO_2 \rightarrow$ 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 ($RO_2 \rightarrow HO_2 \rightarrow$ 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 NO_3 oxidations

since the O_3 and NO_3 were high therein. For the period close to sunrise, when the additional ROx production can not be driven by O_3 and NO_3 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

Faloona, I., Tan, D., Brune, W., Hurst, J., Barket, D., Couch, T. L., Shepson, P., Apel, E., Riemer, D., Thornberry, T., Carroll, M. A., Sillman, S., Keeler, G. J., Sagady, J., Hooper, D., and Paterson, K.: Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, J. Geophys. Res., 106, 24 315–24 333, 2001.

Sillman, S., Carroll, M. A., Thornberry, T., Lamb, B. K., Westberg, H., Brune, W. H., Faloona, I., Tan, D., Shepson, P. B., Sumner, A. L., Hastie, D. R., Mihele, C. M., Apel, E. C., Riemer, D. D., and Zika, R. G.: Loss of isoprene and sources of nighttime OH radicals at a rural site in the United States: Results from photochemical models, J. Geophys. Res., 107, –, 2002.