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Atmospheric
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Discussions

Interactive comment on "Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere" *by* K. D. Lu et al.

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Response to Comments by Referee #1

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 an update of the comparison of OH and HO2 observations from the PRIDE-PRD2006 campaign to modeled OH and HO2 concentrations in light of additional analyses of the data and recent laboratory and theoretical results affecting interpretation of the measurements themselves and the mechanisms used to describe the chemistry. The main conclusion of this paper is that OH observed during PRIDE-PRD2006 cannot be modeled at low NO due to yet unknown radical recycling processes. The paper may be publishable after major revisions.

1 Comment

This paper is thorough and well written; however, the paper is unnecessarily long and is for this reason difficult to follow. I suggest the authors aggressively shorten the paper in order to clarify the main points. As a start, Figures 2,3,4,5, 9c,9d,10, 12 and 13 can all be removed without loss to the paper. Figures 8c and 8d should be a single panel. Section 3.1 and 4,3,4 can be cut. Section 4.4 and 4.3.3 can be shortened and merged into 4.3.2.

Response

We thank the referee for taking the time to read the paper. We agree that the paper is relatively long, but in our opinion the paper extent and the number of figures are reasonable and adequate.

(1) First, the paper provides an updated description of the LIF instrument that we used at PRD. Here, Fig. 2 illustrates major features of the setup of the instrument which is technically different from the previously described version in Holland et al. (2003).

(2) Second, the paper demonstrates how the newly discovered interference in HO_2 measurements was implemented in the interpretation of the HOx field data. Here, Fig. 3 provides modelled data in addition to the study by Fuchs et al. (2011) needed to estimate and understand the interference encountered in PRD.

(3) Fig. 4 and 5 are important because they show the original measurements which were not published previously in detail. We think that ACP is the right journal to present

this data to interested readers.

(4) Fig. 9 summarizes the result of our search for possible dependencies of the OH discrepancy on measured parameters. As mentioned in the text, Fig. 9c and 9d serve as examples demonstrating that we did not find a significant dependence on anthropogenic trace gases (e.g., CO, benzene) besides NO.

(5) Fig. 10 is needed to support our statement that the OH discrepancy found at the rural field site in PRD appears to be consistent with results from forest sites published in other papers.

(6) A major part of our work is the study of the HOx sensitivity to newly proposed chemical mechanisms (M3–M6). Fig. 12 is essential, because it shows the results of these model calculations.

(7) A major new result of our paper is the demonstration of a clear NO dependence of the observed-to-modelled OH ratio. Other studies from forest sites did not report such a dependence, probably because of the restricted NO range in (pristine) forests. Fig. 13 is important because it shows for the first time the measured NO dependent trend and illustrates how well the trend can be resolved by different chemical mechanisms.

In conclusion, we think that all figures and the related text are necessary to support our findings and conclusions. We feel encouraged by the other three reviewers who state that the paper is well written and the level of detail is appropriate. In fact, the other reviewers ask for more information instead of deleting any parts (see comments by Ref. #2, #3, #4).

We agree with referee #1 that Fig. 8c and 8d can be merged into a single panel. This has been done in the revised paper. To make the discussion easier to follow, we have rearranged the previous sections 4.3.3, 4.3.4 and 4.4. Section 4.3.2 is now followed by the discussion of heterogeneous uptake of HO_2 (now section 4.3.3) and the OH budget (now section 4.3.4). The material from the previous section 4.3.3 and particular aspects requested by the referees (comments 2 and 6 by referee #1, comment2 by referee #3, comment 1 by referee #4) are now presented in a concluding discussion (now section 4.4).

2 Comment

The introduction of the manuscript offers a nice summary of HOx chemistry, the history of OH LIF measurements, current discrepancies between modeled and measured OH, and the various chemical mechanisms proposed to fix this discrepancy and the experimental section is thorough. However, it should add additional discussion of how the instrument zero is measured and evaluated. Is it possible that there is significant artifact OH during daytime?

Response

In the experimental part (Sect. 2.2) we state that "the laser is tuned periodically on- and off-resonance to distinguish the OH fluorescence signal from non-resonant laser excited background signals (Hofzumahaus et al., 1996). The amount of detected OH fluorescence integrated over successive laser pulses can be converted into an ambient radical concentration, of which the required sensitivity is determined by calibration". Here, the OH fluorescence is spectroscopically determined as the difference between the on- and off-resonance measurements (for better understanding, we will add this sentence to the revised paper). The fluorescence signal is then converted to ambient OH concentrations by means of a calibration factor. As explained in the paper, we routinely correct the measurement for a small amount of artifical OH signal which originates from laser photolysis of sampled ambient ozone. As pointed out in our response to comment 1 by referee #2, this interference contribution was small at PRD (within the limit-of-detection of our instrument).

Our LIF technique has been compared several times with OH measurements by laser long-path absorption spectroscopy (DOAS) as an independent absolute method. These tests have shown agreement within the combined measurement errors and gave

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no evidence for unexplained interferences (POPCORN: Hofzumahaus et al., 1998; SAPHIR: Schlosser et al., 2006; HOxComp: Schlosser et al., 2009). It should be noted, however, that these tests were made at VOC reactivities which are at least a factor of two smaller than in PRD. In order to cover also PRD-like conditions, we have recently performed new intercomparisons in VOC and isoprene rich air in our simulation chamber SAPHIR. The preliminary analysis shows no indication of a significant interference that could explain the OH discrepancy observed at PRD. We will add a corresponding note in the final discussion. See also our response to the related comment 2 by referee #3.

3 Comment

Section 4 suggests that the PRD analysis will be compared to other sites where OH and HO2 measurements have been made. The authors point out that the PRD HOx measurements are highest ever reported. Previous measurements are again mentioned in section 4.2 to state that OH model/measurement discrepancies were also observed at all other sites noting that this is true regardless of the model employed, the unique VOC mixture characterizing the site, and the variable magnitude of the RO2 interference to HO2 measurements. The authors plot PRD OHobs/mod verses NO and isoprene showing the PRD data fit the across site trend; this is unfortunately the extent of the comparative analysis. The authors present considerable evidence that suggests that it is the ratio of reaction of RO2 with HO2 (or some surrogate related to isoprene) to the reaction of RO2 with NO that is most relevant. However they seem reluctant to directly make a plot of obs/model as a function of this ratio. Some explanation of this reluctance should appear in the text.

Response

As explained in our response to comment 1 (above), a major new finding from PRD is a continuous NO dependent trend of the observed-to-modelled OH ratio over a broad range of NO. Fig. 13 shows the trend for the different model scenarios (M0–M7). Unlike the established models M1 (RACM-MIM-GK) and M7 (MCM), the mechanisms M1–M6 contain additional recycling reactions that convert peroxy radicals to OH in competition with the known reactions of peroxy radicals with NO. The plot proposed by the referee (i.e. OHobs/mod versus the ratio of the reaction rate of RO_2 and NO to RO_2 and HO_2 is only meaningful for mechanisms M3 and M6, where reactions of RO_2 with HO_2 are assumed to generate additional OH. Not surprisingly, the corresponding plots look qualitatively similar to Fig. 13, because the ratio of the RO_2 reaction rates (with/without NO) correlates directly with NO. For the other mechanisms, where different OH recycling mechanisms are proposed (e.g. reaction of HO_2+Y in M2, or isomerization of RO2 in M5), other model-specific ratios would need to be defined on the x-axis and would require different plots. In order to avoid too many new figures, we prefer to keep Fig. 13 which allows to present the NO dependence for all model runs in a unified plot.

4 Comment

The authors should include a line in Figure 8c that includes the best of the available models instead of the reference model.

Response

Following the first comment of the reviewer (above), we have merged Fig. 8c and 8d into one panel. Adding more model curves would overload the figure panel. Therefore, we now present the requested lines in a separate figure in the supplement of the revised paper.

5 Comment

Also the statement that measured and modeled OHJnorm vs. NOx (Figure 8c) agree at high NOx. The fact that the curves cross at 11 ppb NOx does not indicate model/measurement agreement. It could just be a fortuitous crossing of two lines.

Response

The reviewer has raised a good point. Although the sets of measured and modelled data points overlap at 10–20 ppb NOx, the averaged data seem to indicate different trends of the measured and modelled OH as a function of NOx. Unfortunately, we have no data to follow the trends at even higher NOx. We can extrapolate the model curve, but have no OH observations for comparison. In the revised paper, we will add a corresponding statement in the description of Fig. 8c and point out that we have no observations to draw conclusions about the model measurement agreement above 20 ppb NOx (see also our response to comment 6 by referee #2).

6 Comment

Section 4.3.2 describes improvements in modeled OH with M3-M7. With all mechanisms, even the higher HOx yield variants M5b and M6b, there is still a sizable underestimate in modeled OH; with M5 and M6, HO2* observation are overestimated. In this section, the authors have provided a description of Figure 12 but no discussion of it. What do these modeling results teach us about PRD photochemistry specifically and HOx recycling mechanisms in general?

Response

We have revised our discussion as follows (see also our answers to comment 1 and 6).

Among the tested mechanisms, the additional recycling of OH from isoprene peroxy radicals in scenarios M5b and M6b offers the largest potential to brigde the gap between modelled (M0) and measured OH at low NO. Considering an estimated accuracy for OH(obs)/OH(mod) of 45 %, calculated by error propagation of the corresponding experimental and model uncertainties, the remaining discrepancy of a factor of two at NO $<$ 0.2 ppb is still significant. Apparently, the additional OH production in M5b or M6b is not efficient enough to explain the high OH concentrations at low NO. This may be due to uncertainties of the postulated mechanisms or to the relatively small amount of isoprene peroxy radicals which contribute only about 16 % of the modelled RO_2 radicals (cf., Table S8 in the supplement). A new laboratory study by Crounse et al. (2011) suggests that HPALD formation in the LIM0 mechanism is slower and the

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resulting OH recycling less efficient than originally proposed. Thus, besides OH recycling from isoprene peroxy radicals, another unidentified OH source must have been present at PRD. Apparently, the unknown OH source at PRD is not solely connected to isoprene and may be possibly related to other VOCs. Further laboratory studies are urgently needed to resolve this open question.

The overprediction of HO_2^* is still within the model error of 40 %. Nevertheless, it could also be an indication that a sink process for peroxy radicals is missing in the model. In a similar case, Whalley et al. (2011) report an overprediction of HO_2 when they implement additional OH recycling in their model to explain OH observations in Borneo. They suppose that the mismatch between modelled and measured HO_2 points to a yet unknown additional HO_2 loss mechanism. A possible HO_2 sink, which is not included in our model runs (M0–M7), is heterogeneous loss on particles which was however negligible at PRD (see corresponding discussion in section 4.3.4 in the original paper). Thus, we have no firm indication of an unknown HO_2 sink at PRD.

7 Comment

Section 4.3.3 provides a good example of why the paper needs to be shortened. The section includes a redundant description of the model results. I see no new information in Figure 13. Why include a breakdown of the speciated VOC reactivity if the implications are not discussed?

Response

With respect to the value of Fig. 13, see our response to comments 1 and 3 (above). A major difference between our study at PRD and other studies in forested environments is the concentration range of NO and VOCs that can be investigated. At PRD, the total VOC reactivity was rather constant during daytime, while NO showed a variation over more than two orders of magnitude (Fig. 13). Contrary, the field studies in Amazonia and Borneo were characterized by a very small NO concentration, but much higher variability of isoprene compared to PRD. Thus, our study explores a different chemical regime which is characterized in Fig. 13 by the NO dependence and the corresponding VOC reactivities. We have added the following text in the final discussion of the revised paper.

The observed NO dependence of the measured-to-modelled OH ratio (M0) is a new result that could be obtained at PRD due to the large variability of anthropogenic pollution in a rural area. Other studies at forest sites did not report such a NO dependence, probably because of the restricted NO range in (pristine) forests like in Amazonia (Lelieveld et al., 2008) or Borneo (Whalley et al., 2011). In fact, the NO concentrations there were generally smaller than the lowest NO values found at PRD. Contrary, the forest sites exhibited a large variability of (biogenic) VOCs, whereas the total VOC reactivity at PRD was rather constant ($20\,s^{-1}$) during daytime with a moderate increase of isoprene by a factor of 1.6 from high (7 ppb) to low (0.08 ppb) values of NO (see reactivity data in Fig. 13).

Additional References

Crounse et al., Peroxy radical isomerization in the oxidation of isoprene, Phys. Chem. Chem. Phys., DOI:10.1039/c1cp21330j, 2011.

Hofzumahaus et al., Intercomparison of Tropospheric OH Measurements by Different Laser Techniques during the POPCORN Campaign 1994, J. Atmos. Chem. 31, 227-246, 1998.

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