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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 #4

We would like to thank the reviewers for their comments and questions which have helped to improve the manuscript. The reviewer comments are given below together with our responses and changes made to the manuscript.

General Comments

This paper is a more detailed follow up from the Hofzumahaus et al paper published in Science in 2009. It is very much in scope for ACP and demonstrates clearly that under low NOx conditions in this environment, our current understanding of sources of the OH radical are lacking. Since the 2009 paper, the Julich group has discovered an interference in HO2 measurements, which comes from the decomposition of RO2 radicals derived from certain VOCs, in particular alkene and aromatic species. The effect of this is that the true HO2 concentration is lower than that measured, and the authors have attempted to allow for this by combining fractional sensitivities towards certain RO2 species producing a HO2 signal measured in the laboratory with a box model which calculates the distribution of RO2 species. There are two main impacts of this. The first is that it is not necessary now to invoke both a RO2+X = HO2 and HO2+ X = OH step to bring the field measurements of OH and HO2 into line with experiments (although this could still be an explanation), rather a single step HO2+Y = OH could bring into agreement field measurements and model calculations within the combined uncertainties of model and measurements. Secondly, as the true HO2 is lower, the HO2+NO source of OH is lower than before, and the missing sink of OH becomes a larger fraction of the total production rate of OH, which is measured via k'(OH) x [OH], determined using the LIF OH instrument and the OH reactivity instrument.

The authors have also shown using a variety of models, with different mechanisms, the impact of including new chemistry that has been suggested over the last couple of years, for example the Peeters mechanism for decomposition of isoprene related RO2 radicals in to HO2 and also products which generate further HOx radicals (e.g. multifunctional carbonyls), the Paulot mechanism for reaction of isoprene related epoxide species generating HOx, and also reactions of RO2 with HO2 which can regenerate HOx radicals rather than acting as a termination step. It is shown that although some of these have a significant impact (e.g. Peeters), others do not, but that there is still an unknown source of OH from HO2+Y (or RO2+X = HO2 and HO2+X = OH). There are however, large uncertainties still in these mechanisms, with many rate parameters and yields unmeasured and an important conclusion is that further laboratory work is needed urgently to confirm. The absence of OVOC measurements in this study is a gap

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that needs filling for future campaigns in this type of environment, and these species represent large sinks for OH and candidate sources for some of the unexplained chemistry. It might have been nice to have had some discussion on exactly what X or Y are, but it would be speculative at this point, but maybe some candidates could be ruled out?

The paper also contains a nice synthesis of work done in similar environments, either in urban centres or in regions impacted by high isoprene concentrations at low NOx. It seems that although the mechanisms to explain the behaviour are unknown, there is at least consistent behaviour now observed between several groups. This is important as the OH and HO2 measurements are very difficult. The authors have collected together a significant body of previous work for comparison. It seems that the unexplained behaviour in tropical forests, north American forests and this urbanised region in southern China may all have the same origins, although the NO concentration here, even at its lowest, is still significantly higher than in Amazonia or SE Asia tropical forests, and so the importance of RO2+HO2 reactions compared with RO2 or HO2 with NO is diminished. In a later update posted by the authors, the MCM v3.2 is used rather than MCM v3.1 to compare the relative sensitivities for specific RO2 compared with HO2 - and there is better agreement. This provides a good validation of certain aspects of the update of the MCM. Also, the authors show that using RACM-MIM-GK, which has a lumped scheme for much of the chemistry, gave similar results to the MCMc3.1, and so any discrepancies with the field measurements is probably not due to lumping aspects of the RO2 chemistry.

Another interesting result is that the OH concentration normalised for J(O1D) does not show a strong dependence on NO, in contrast to previous studies, and in contrast to the model predictions. I recommend publication in ACP. The paper is very well presented with very few technical errors, and the results are highly significant. There are a few further specific points below.

Response

We agree with the referee that there is still another unknown source of OH besides the mechanisms that we have tested in the model scenarios M3–M6. It is true that without new laboratory studies, a discussion of the identity of X or Y is speculative. However, as suggested, we can rule out some possibilities, for example the reactions of HO_2 with halogen oxides (BrO, IO) or heterogeneous reactions of HO_2 on particle surfaces. Referee #3 has also raised the question about the identity of X or Y. See our detailed answer to his/her comment 1.

1 Comment

The night-time measurements are potentially very interesting given the significant OH and HO2 that has been observed. Although a future paper is planned on the origins of the nighttime HOx, given that the data are displayed in this paper, some discussion, albeit brief, of the major conclusions at night would round the paper off.

Response

We will add the following remark in the final discussion of the paper.

It is interesting that the unknown recycling mechanism (M1, M2) is also a requirement to explain the nighttime measurements of OH and HO_2^*, which had mean values of $2 \times 10^6\,\mathrm{cm}^{-3}$ and $2 \times 10^8\,\mathrm{cm}^{-3}$, respectively. The base model (M0) can explain HO_2^* from ozonolysis, but strongly underestimates the measured OH levels. In order to explain both OH and HO_2^* at night, an additional recycling process like at daytime is needed and a small additional primary source of OH which would be neglegible during daytime. Details of this analysis will be presented elsewhere.

2 Comment

What is a heavy-duty car? Does this mean lorries? The NO profile is unusual, being pretty high in the mornings (many ppbs) yet going down to 0.2 ppb in the afternoons. This ban in the afternoon certain types of traffic could be a unique feature which has allowed the conclusions from this study to be drawn.

Response

We have meant diesel-powered trucks. Please see our corresponding answer to referee #2 (comment 3).

3 Comment

Page 11341. Line 20, M5 is the Peeters mechanism, M4 is the Paulot mechanism and so do not concern peroxy-peroxy reactions? , or did (M3-M6) refer to the radical sink reactions? Perhaps some rewording to make this sentence clearer.

Response

The sentence in the original paper is not correct. The main difference is that M1 and M2 apply reactions with unknown species (X, Y), whereas M3-M6 use reactions of chemically specified components that have been discovered or proposed. We have rephrased the text as follows.

One concept introduces generic reactions with unknown species driving additional radical recycling (M1, M2). The other concept (M3–M6) relies on the implementation of newly discovered or proposed specific reactions that reproduce OH from peroxy radicals.

4 Comment

Page 11344, line 27, "ratio" not "ration".

Response

Has been corrected.

5 Comment

Figure 13. Although the NO2 concentration is quite high (up to 40 ppb fig 5, which presumably corresponds to the right hand pie-chart in fig 13), the loss of OH by reaction with NO2 (which is in the "other" slice of the pie-charts) seems quite small?

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Response

The pie charts show the organic composition of the total VOC reactitivty and do not contain a contribution of NOx. We will rephrase the text for better understanding.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11311, 2011.