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Atmospheric
Chemistry
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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 #3

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 presents an update of the analysis of OH and HO2 measurements from

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the Pearl River Delta in China originally published by Hofzumahaus et al. (2009). The paper includes a reevaluation of the HO2 data in light of the recently discovered interference in the reported HO2 measurements by RO2 radicals derived from alkenes and aromatics (Fuchs et al., 2011), as well as and analysis of several recently proposed chemical mechanisms for HOx radical recycling in the isoprene oxidation mechanism. The authors find that even when the interference in their HO2 measurements from select RO2 radicals is taken into account, the base model is still unable to reproduce the observed OH concentrations, although the agreement with the modeled and measured HO2* is reasonable. As a result, the main conclusions of Hofzumahaus et al. are unchanged - that there is a significant source of OH radicals missing from current atmospheric chemistry models. The paper is well written and suitable for publication in ACP. I have a few comments that the authors may wish to consider in their revision of the manuscript.

1 Comment

The authors find that although several proposed mechanisms for HOx radical recycling improves the agreement between the modeled and observed OH concentrations, their originally proposed empirical mechanism (HO2/RO2+X → OH) is the only mechanism that is able to fully reproduce the NO dependence of the observations. However there is little discussion about potential identity of the missing species (X and Y). Is it possible that the missing species is an oxidation product in the model, perhaps a product of isoprene oxidation? Although a detailed analysis is beyond the scope of this paper, it would benefit with an expanded discussion of the potential identity of X/Y.

Response

An expanded discussion of the potential identity of X/Y has also been suggested by referee #4 (general comment). We will add the following discussion to the revised manuscript (Sect. 4.3.1):

The proposed reactions with X or Y are the two most simple generic mechanisms that

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allow to reproduce the observed OH and HO_2^* concentrations. The reactions could either be real and involve an unidentified compound, or represent the overall effect of a more complex mechanism. Besides reactions of HO_2 with organic species, which are investigated in the next section, one could think of HO_2 reactions with halogen oxides (YO = BrO or IO). The influence of these species on atmospheric HO_x has been demonstrated for clean marine air (Read et al., 2008; Kanaya et al., 2007; Bloss et al., 2005). For example, mean concentrations of 2.5 ppt BrO and 1.5 ppt IO observed at Cape Verde were found to enhance daytime OH by 5–12 % through the reactions HO_2 + YO → HOY + O_2 followed by HOY + hν → OH + Y (Read et al., 2008). The largest reported halogen oxide concentrations in the troposphere, 200 ppt BrO above the Dead Sea (Tas et al., 2005) and 20 ppt IO over sea-ice surfaces in coastal Antarctica (Saiz-Lopez et al., 2008) have HO_2 reactivities which correspond to 0.5 ppb and 0.2 ppb of NO, respectively. These values are too small compared to the required reactivities of X (equivalent of $\sim$ 0.8 ppb NO) or Y (equivalent of $\sim$ 5 ppb NO) displayed in Fig.11. Since no particular halogen sources were noted in PRD and as the required halogen oxide concentrations exceed all tropospheric observations, halogen oxide reactions are an unlikely the missing OH source. Another speculative mechanism resembling HO_2 + Y → OH would be surface catalyzed conversion of HO_2 to OH on aerosols. This mechanism, however, can be excluded due to the limitation in the HO_2 uptake as discussed in Section 4.3.4 (original paper).

The question about the potential role of (isoprene) oxidation products for OH recycling has also been raised by referee #1 (comment 6). See our corresponding answer to referee #1.

2 Comment

Another possible explanation for the extremely high OH concentration is an unknown interference with the LIF measurement. Although the recent intercomparison of OH instruments (Schlosser et al., ACP, 2009) gives confidence in the accuracy of the OH measurements, there still may be an unknown interference in this unique and highly reactive VOC environment. Did the authors perform any additional tests (external OH titration with perfluoropropylene for example - Brune et al., OH and HO2 Measurements in Blodgett Forest, CA during BEARPEX 2009, American Geophysical Union Fall Meeting 2010, 13-17 December, San Francisco, California, USA, 2010) to insure that the measurements were free from interferences?

Response

We have performed new OH intercomparisons at PRD-like conditions in the atmosphere simulation chamber in Juelich showing no indications of an artifact that might explain the high daytime OH concentrations. See our corresponding answer to Referee #1, comment 2. We have not yet tested the chemical modulation technique deployed by Brune et al. which offers an interesting option to identify possible interferences, in particular when no reference method (DOAS) is simultaneously available. More field and laboratory tests are definitely needed to investigate possible interferences in high VOC environments.

3 Comment

The paper would benefit from a brief summary of the agreement between the measured and modeled total OH reactivity as discussed in Lou et al. Does the agreement between the measured and modeled OH and HO2 in the morning correspond to periods when the modeled total OH reactivity agrees well with the measured total OH reactivity? A more detailed comparison of agreement in light of the reactivity measurements should be included.

Response

There is general good agreement (within 20 %) of the measured and modelled OH reactivity for both the lumped (RACM-MIM-GK, M0) and detailed (MCMv3.1, M7) models throughout daytime, independent of the model-measurement agreement for OH and HO_2. We have added a corresponding remark in Section 3.2 of the revised manuscript.

We find neither a significant correlation of the measured-to-modelled OH ratio with the measured or modelled total OH reactivity, nor with the reactivity of VOCs. We add a corresponding comment in Section 4.3.3 of the revised paper.

Additional References

Bloss et al., Impact of halogen monoxide chemistry upon boundary layer OH and HO_2 concentrations at a coastal site, Geophys. Res. Lett. 32, L06814, DOI:10.1029/2004GL022084, 2005.

Kanaya et al., Chemistry of OH and HO_2 radicals observed at Rishiri Island, Japan, in September 2003: Missing daytime sink of HO_2 and positive nighttime correlations with monoterpenes, J. Geophys. Res. 112, D11308, doi=10.1029/2006JD007987, 2007.

Read et al., Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature 453, 1232-123, 2008.

Saiz-Lopez et al., On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O_3, HO_x, NO_x and the Hg lifetime, Atmos. Chem. Phys. 8, 887–900, 2005.

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