Atmos. Chem. Phys. Discuss., 11, C3860–C3862, 2011
www.atmos-chem-phys-discuss.net/11/C3860/2011/

Atmospheric Chemistry and Physics 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.

Anonymous Referee #1

Received and published: 24 May 2011

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.

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.

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 evaluatedâĂŤis it possible that there is significant artifact OH during daytime?

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.

The authors should include a line in Figure 8c that includes the best of the available models instead of the reference model. Also the statement that measured and modeled OHJnorm vs. NOx (Figure 8c) agree at high NOx. The fact that the curves cross at $\sim$11 ppb NOx does not indicate model/measurement agreement. It could just be a

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fortuitous crossing of two lines.

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?

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?

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