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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 #3

Received and published: 7 June 2011

This paper presents an update of the analysis of OH and HO₂ measurements from 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 an analysis of several recently proposed chemical mechanisms for HO_x 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

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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) The authors find that although several proposed mechanisms for HO_x 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.

2) 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?

3) 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 measure-

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ments should be included.

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

ACPD

11, C4523–C4525, 2011

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