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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results" *by* S. Lou et al.

Anonymous Referee #1

Received and published: 2 October 2009

General Comments

This paper presents a very nice OH reactivity dataset from the PRD campaign and through comparison with box model results evaluates the OH sinks in this region. OH reactivity measurements of this kind can provide a means of testing how well the detailed atmospheric chemistry is represented in box models. This paper focuses on how well the model used captures the total OH sinks. The paper presents a good overview of previous OH reactivity data and helps to further understanding of the chemistry in this region. For these reasons I think that the paper should be accepted to ACP after the following specific comments have been addressed.

Specific Comments

The authors present a good review of OH reactivity measurements that have previously been made around the globe and in Table 1, through comparison of these measured reactivities with calculated reactivities, highlight locations where good agreement is obtained and other areas where agreement is not so good. This table has the potential to provide some very useful information to this end; however, it is not clear at the moment whether the calculated reactivities used to determine 'MR' are actually comparable for the different campaigns, as these will be dependent upon the range of co-located ancillary measurements. I think that the table would benefit from an additional column listing the OH sinks (perhaps in lumped form, i.e. VOC, OVOC, etc) that were used in the calculation of 'Kohcalc.'.

Furthermore, the range of co-located measurements will also influence what is used to constrain the box model. In this study, formaldehyde and acetaldehyde were not measured and therefore were not used to constrain the box model. It would be useful to know to what levels these secondary species (and others) built up in the model runs (both when the model was constrained and when it was unconstrained to the OH measurements); are the concentrations realistic for this region?

Page 17046, section 4 Model Calculations, Line 12: Does the model reach steady state conditions after 2 days of spin-up?

Much of the recent literature suggests that there is a large unknown OH source in the presence of high isoprene emissions and, as discussed by the authors, this was seemingly the case during the PRD campaign (Hofzumahaus, 2009). The model run constrained to the OH measurements, therefore, warrants further discussion. The paper would benefit from an additional figure, similar to figure 6 but for the OH constrained model run. The authors touch upon the fact that, when the model is constrained to OH, the OH sinks are over-predicted on several days. Is there a change in the atmospheric composition on these days? Could realistic deposition rates for the secondary polar

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compounds (these exist in the literature for a number of species) bring the measured and modelled reactivities back into agreement? Addressing these queries would enable the reader to better assess the current state of understanding.

Section 3.1 Some technical aspects of the instrument are presented in this section and an instrument paper that is in preparation is referenced; however, if this is not going to be available before this paper is published, further experimental details are necessary here. What is the concentration of OH generated in the flow tube? Do any corrections need to be made for OH-OH self-reaction during the zero-air decays?

Page 17043: Line 2, please comment on the impurities in the synthetic air – how is the synthetic air produced?

Page 17043: Line 17, please comment on potential causes of the non-exponential curvature observed with the faster decays.

Page 17047: A combustion smell has been noted by the authors. Were any combustion type tracer species measured at the site to support this observation?

Technical Corrections

Page 17036, Line 12 change ‘at day’ to ‘during the day’

Page 17038, Line 12 & 13 change ‘from incomplete knowledge of number and abundance of reactive components being present’ to ‘from the incomplete knowledge of the number and abundance of reactive components that are present’

Page 10739, Line 1 suggest ‘A step towards solving this problem was made by the development..’

Page 10739, Line 15 change ‘ allows to quantify the’ to ‘allows quantification of the’

Page 10739, Line 27 remove comma ‘Possible, unidentified’

Page 17040, Line 1 change ‘Such study’ to ‘Such a study’

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Page 17040, Line 7 change ‘Lastly’ to ‘Finally’

Page 17040, Line 7 change ‘This is part of the present paper where OH reactivities from the above mentioned PRD field campaign are presented’ to ‘In this paper OH reactivities from the afore mentioned PRD field campaign are presented’

Page 17040, Line 12 change ‘reactants contributing mostly to’ to reactants that contribute most to’

Page 17040, Line 19 change ‘mid’ to ‘medium’

Page 17041, Line 4 remove ‘showing values’

Page 17041, Line 5 remove ‘r.H.’

Page 17041, Line 8 remove comma ‘At the field site, local’

Page 17041, Line 15 change ‘above ground’ to ‘above the ground’

Page 17041, Line 19 change ‘at 7 m height’ to at a height of 7 m’

Page 17041, Line 21 change ‘Experimentals’ to ‘Experimental’

Page 17041, Line 22 change ‘Measurements’ to Measurement’

Page 17041, Line 23 change ‘as inverse’ to ‘as the inverse’

Page 17042, Line 5 change ‘i.D.’ to ‘I.D.’

Page 17042, Line 6 change ‘In the PRD campaign, temperatures’ to ‘During the PRD campaign, the temperature’

Page 17042, Line 8 change ‘an aircond-‘ to ‘an air-cond-‘

Page 17042, Line 23 change ‘mode in a’ to ‘mode by a’

Page 17047, Line 2 change ‘like’ to ‘such as’

Page 17047, Line4 change ‘boundary layer and were reduced by’ to ‘boundary layer at

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night and were depleted by'

Page 17047, Line 6 remove 'it is'

Page 17047, Line 14 remove comma after 'nearby'

Page 17047, Line 16 change 'July, smell' to 'July, a smell'

Page 17047, Line 18 change 'starting rain' to 'the onset of rain'

Page 17047, Line 18 change 'The rain fall in the wake of typhoon Kaemi continued on the next day and kept the reactivity on a level of 20 s-1' to 'The rainfall in the wake of typhoon Kaemi continued throughout 26 July and the reactivity remained at $\sim$ 20 s-1'

Page 17047, Line 26 change 'when combustion smell' to 'when the combustion smell'

Page 17047, Line29 change 'pointing to missing reactivity in the set of trace gas measurements' to 'suggesting an additional missing reactivity'

Page 17048, Line 9 change 'Apparently, isoprene was the' to 'Isoprene was seemingly the'

Page 17048, Line 10 change 'during daytime' to 'during the daytime'

Page 17048, Line10 change 'contribution up' to 'contribution of up'

Page 17048, Line 12 change 'were dominating' to 'were dominant'

Page 17048, Line 15 change full stop to question mark.

Page 17048, Line 20 change 'sources, or to unmeasured chemical' to 'sources directly, or to unmeasured secondary chemical'

Page 17048, Lines 23 & 24 change 'In order to estimate the possible contribution of unmeasured, secondary pollutants to the missing OH reactivity, a photochemical box model (RACM) was applied' to 'In order to estimate the possible contribution of unmeasured secondary pollutants to the missing OH reactivity a photochemical box

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model (RACM) was used'

Page 17048, Line25 add table 2 ref 'measured trace gases (table 2)'

Page 17049, Line 1 change 'a similar' to 'a similarly'

Page 17049, Line13 change '2001), highest' to '2001), the highest'

Page 17049, Line19 change 'typ.' to 'typically'

Page 17051, Line 5 change 'including various' to 'in a variety of'

Page 17051, Line 11 change 'OVOCs did account for' to 'OVOCs accounted for'

Page 17051, Line 14 change 'could explain' to 'explained'

Page 17051, Line 16 change 'At wintertime, hydrocarbons did account for' to 'During the wintertime, hydrocarbons accounted for'

Page 17051, Line 18 change 'cate much smaller photochemical activity and less production of oxygenated VOCs in winter' to 'cate a much lower photochemical activity and lower OVOC production in the winter'

Page 17051, Line 20 change 'at' to 'during the'

Page 17051, Line 20 change ', analyzing the' to ', who analyzed the'

Page 17051, Line 23 change 'contributing' to 'which contributed'

Page 17051, Line 23 change 'of' to 'to'

Page 17051, Line 28 change 'were' to 'have been'

Page 17052, Line 1 change 'at' to 'on'

Page 17052, Line 3 change 'was' to 'were'

Page 17052, Line 15 change 'when combustion' to 'when a combustion'

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Page 17052, Line 20 change ‘all’ to ‘none’

Page 17052, Line 21 delete ‘not’

Page 17052, Line 24 change ‘at’ to ‘during the’

Page 17052, Line 24 change ‘Apparently, the’ to ‘The’

Page 17052, Line 28 change full stop to a question mark

Page 17054, Line 14 change ‘as inverse chemical’ to ‘as the inverse of chemical’

Page 17054, Line 16 change ‘was’ to ‘were’

Page 17054, Line 23 change ‘places’ to ‘locations’

Page 17054, Line 25 remove comma

Page 17055, Line 18 change ‘at’ to ‘during the’

Page 17055, Line 18 change ‘important role of OVOCs was’ to ‘importance of OVOCs has’

Page 17055, Line 19 change ‘studies, analyzing’ to ‘studies, which have analyzed’

Page 17055, Line 23 change ‘but’ to’yet’

Fig. 2 Line 4 change ‘BILIS’ to ‘Bilis’

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17035, 2009.