**Atmospheric
Chemistry
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Discussions**

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Comment

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

S. Lou et al.

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Response to Comments by Referee #1

We thank the referee for the valuable and constructive comments. Some issues have also been addressed in other comments (RC, SC). This will be pointed out in our answers by cross-references.

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

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Interactive Discussion

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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

1. 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.'.

Response

We thank the referee for the useful comment. We have expanded Table 1 by adding a new column which indicates the measured species that were used for the calculated reactivities. Following the suggestion by referee #2, we have also added the reactivity measurements in Houston 2000 and 2006 (Mao et al., 2009). Furthermore, we have updated the table by adding new results from Tokyo 2007 (Chatani et al., 2009). The TORCH-1 data (Essex, UK) have been removed from Table 1 as they have been removed in the final version of the quoted literature (Ingham et al., AMT 2009).

Comment

Full Screen / Esc

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2. 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?

Response

This topic is also addressed in questions 3 and 4 by referee #2 who is asking for modelled concentration values of formaldehyde and other OVOCs. The modelled formaldehyde and acetaldehyde concentrations at PRD have high values, the mean daytime values being in the order of 12 ppb and 3.8 ppb, respectively. In-situ measurements of OVOCs were not performed during the campaign, so that a direct comparison of modelled and observed data is not possible. However, the few information that we have available indicates that the aldehyde concentrations are in a plausible range. Meanwhile, remote sensing MAX-DOAS data have been evaluated for formaldehyde, showing average mixing ratios of 11 ± 7 ppb over the height of the boundary layer for 9 days at the measurement site (X. Li, personal communication). Futhermore, a previous study in PRD and near Guangzhou has shown mean values of 10 ppb formaldehyde and 5–6 ppb acetaldehyde (Feng et al, 2005), close to what our model predicts. Corresponding information will be added in the manuscript in section 6.2. For other species, see the answer to question 4 by referee #2.

Comment

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

Response

Yes. The model does reach steady state conditions after 2 days of spin-up, because

no calculated species has a chemical lifetime of greater than one day. The lifetime of all calculated species is limited by the deposition rate for which we assumed a 24h lifetime. See also the answer to comment 5 by referee #2.

Comment

4. 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 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.

Response

This comment is closely linked to comment 1 by referee #2, who points out correctly that the model will significantly overpredict HO2 if the model is constrained by the observed OH, only. We followed the suggestion by referee #2 and have performed another run, in which the model includes additional recycling of peroxy radicals by a new species X as described in Hofzumahaus et al. (2009). Including X ensures that the model reproduces both the observed OH and HO2 reasonably well. If this mechanism is applied, the modelled reactivity becomes larger than in the base case, but somewhat smaller than in the case when only measured OH is used as an additional constraint. In fact, the model with additional recycling by X is mostly in good agreement with the measured kOH. However, the strong overprediction (factor 1.5 - 2) on four days (i.e. 13, 14, 24 and 25 July) remains and must have other reasons. In the revised manuscript, a

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Interactive Discussion

Discussion Paper

discussion of the modelled kOH for the model case with additional radical recycling by X has been added. The corresponding time series of modelled kOH has been included in the revised version of Fig. 4 and is discussed in section 6.3. A new figure (Fig. 9) shows the effect of radical recycling by X on the mean diurnal profile of kOH. In addition, we now discuss possible reasons for the overprediction on particular days. We discuss (1) in more detail the sensitivity to deposition losses on the ground. (2) We have added a discussion of possible OVOC losses on particles and (3) discuss the validity of the implicit model assumption that OVOC concentrations have reached steady state.

Ad (1). Our sensitivity study varies the deposition rate for all species by a factor 0.5 to 2, which covers the range of reported literature values. The maximum assumed deposition rate reduces kOH by only (5-15)% compared to the base case, which cannot explain the overprediction by a factor of 1.5 - 2. In addition, we have modulated the deposition loss by the diurnal variation of the boundary layer height (500–2000 m), derived from MAX-DOAS measurements (Li et al., 2010). Similar small deviations from the base case result are found. We conclude that the treatment of dry deposition in our model contributes only a relatively small error in the modelled OH reactivities and that the uncertainties in the deposition rates cannot explain the discrepancy between measured and modelled reactivities on 13, 14, 24 and 25 July.

Ad (2). In principle, heterogenous loss of OVOC species on particles (not included in the model) could have played a pronounced role on 24 and 25 July, when the atmospheric aerosol load was a factor of 2–3 higher than on the other days of the campaign. Loss of a carbonyl compound on particles has been reported in case of glyoxal (Volkamer et al., 2007; Liggio et al., 2005; Kroll et al. 2005). Glyoxal, however, contributes only about 2 % of the total gas-phase reactivity in the present model. In order to compensate the overprediction, heterogeneous uptake would be required for formaldehyde, acetaldeyhde, MVK and MACR etc. which together contribute the major OVOC reactivity in the present work. These carbonyl compounds are known to have low physical

Interactive Comment

Full Screen / Esc

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Interactive Discussion

Discussion Paper

solubilities (Sander et al., 2006; Iraci et al., 1999). Reactive uptake might play a role for acidic solutions, but published results remain controversial for latter conditions (e.g., Noziere et al., 2006; Jang et al., 2005; Kroll et al., 2005). Since the enhanced aerosol load on 24 and 25 July contained a large fraction of soot in PRD (Garland et al., 2008), reactive uptake is not a likely explanation for the smaller than expected OVOC reactivity on these particular two days. It would also not explain the discrepancy between modelled and measured kOH on the other two days (13–14 July), which did not exhibit elevated aerosol concentrations.

Ad (3). There was a marked difference in the meteorological conditions on the four days when kOH is overpredicted by the model. During most of the campaign, wind came from the south and southeast at slow wind speeds. On 13–14 July and 24–25 July, local wind slowed down to almost zero and turned into opposite direction, coming then from the north. These episodes are associated with the highest isoprene concentrations during the campaign. The elevated isoprene concentrations and the very low wind speed point to the influence of a strong local isoprene source at close distance north of the field site. This is plausible, since there were trees in the direct neighborhood north of the measurement building, whereas a drinking water reservoir with a fetch of about 1 km was located in the southern direction. It is likely that freshly emitted isoprene from the local source (north) was not significantly photochemically aged when it reached the sampling point of the kOH instrument, but was mostly photochemically degraded downwind of the measurement site. The model, however, builds up isoprene oxidation products during daytime until the products reach steady state within few hours, a condition which was likely not fulfilled at the measurement site on 13–14 July and 24–25 July. In contrast, on the other days with continuously prevailing southern wind, primary VOCs were most likely photochemically aged when they reached Backgarden, as implicitly assumed by the model. If we exclude the data from 13–14 July and 24–25 July, we find that the observed and modelled reactivities agree on average within 20% for the other days.

Interactive Comment

Full Screen / Esc

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Interactive Discussion

Discussion Paper

Comment

5. 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?

Response

The photolytically generated initial OH concentrations were less than 5×10^9 molecules per cm^3 during the field campaign. The self-reaction (OH+OH) contributes a reactivity of <0.04 s^{-1} which can be neglected even in zero-decay measurements. A corresponding remark and additional technical information has been added in the experimental section of the revised manuscript. See also the answers to the comments by referee #2 (question 2, 6, 7) and to the comments by referee #3 and V. Sinha.

Comment

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

Response

We used pressurized synthetic air (99.999%) from gas cylinders which had been delivered by Messer Griesheim (Austria). GC analysis has shown a small contamination of a few ppb of alkanes, whereas NOx is not detectable (< 20 ppt). The total estimated reactivity of the gaseous contaminants is 0.05 s^{-1}. A corresponding remark has been added in the experimental section.

Comment

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

Response

The curvature is found to be independent of the chemical conditions. It partly comes from the rise of the OH fluorescence signal, when OH propagates initially into the LIF detection cell after the laser flash. Furthermore, the curvature may be influenced by non-homogeneous spatial distribution of OH in the flow tube near the inlet nozzle which deflects some of the photolysis laser radiation. A corresponding remark has been added to the experimental section.

Comment

8. 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?

Response

Besides personal observations (smell, smoke), measurements of aerosols gave a clear indication of combustion for exactly this time period. Garland et al. (2008) reported a marked increase of the aerosol load and a distinct change in aerosol properties (indicating smouldering fires) for the days on which kOH values were scattered and reached the highest values during the campaign. A corresponding remark has been added in section 5.1.

Comment

9. Technical Corrections

Response

We have performed all technical corrections as suggested by referee #1.

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