**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.

S. Lou et al.

a.hofzumahaus@fz-juelich.de

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Response to Comments by Referee #2

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

Comment

This paper provides a valuable dataset of OH reactivity measurement during PRIDE-PRD2006 field campaign. To my knowledge, this is the first OH reactivity measurement

ever made in China, and it will certainly improve our understanding of the photochemistry and air quality in China. This paper also investigates the possible reasons for missing OH reactivity from the secondary products in the box model. I would recommend this paper gets published in ACP after the following issues are addressed:

1. Model constrained by measured OH seems problematic to me. The modeled OH is about a factor of 3–5 less than the measured OH at low NO levels [Hofzumahaus et al., 2009]. If the model is constrained by the measured OH, in order to maintain HO_2/OH ratio (constrained by NOx and VOCs), the modeled HO_2 will increase accordingly. Therefore a new HOx steady state is reached in the box model and a larger OH sink is found (Green line in Figure 3), possibly due to the elevated HO_2. However, the modeled HO_2 without constraining OH is in good agreement with the measured HO_2 [Hofzumahaus et al., 2009]. According to Equation (1), HO_2 will be largely overestimated in this case. Therefore it is not suitable for solely constraining measured OH (without constraining measured HO_2) in the box model, because it will change HOx level and may not reflect the real state of the atmosphere. On the other hand, if the box model introduces a new species(X), as described in Hofzumahaus et al. [2009], a good mod/obs agreement will be achieved for both OH and HO_2. It will be interesting to see how much modeled OH reactivity there is with this new species. My guess is that the new modeled OH reactivity might be close to the base model run, as total HOx level does not change much (although the HO_2/OH cycling makes a big change). HO_2/OH = kOH / (kHO_2+NO[NO]) (1)

Response

We agree with that comment. Constraining the model by OH produces far too high HO_2 concentrations, which has implications for the photochemical production of OVOCs. If we run the model with the new species X as described in Hofzumahaus et al. (2009), the model reproduces OH and HO_2 reasonably well. If this mechanism is applied in the present work, 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. The model with additional recycling by X is generally closer to the observations than the model constrained by OH, only. However, overprediction of the observed reactivity on certain days (13, 14, 24 and 25 July) remains in both model cases. The reason is likely due to a shift in wind direction on these particular days, bringing fresh isoprene emissions which are not photochemically aged as implicitly assumed in the model (see detailed answer to question 4 by referee #1). If we exclude the data from these four days, we find that the observed and modelled reactivities agree on average within 20% for the other days. A discussion of the model calculated kOH for the model case with additional radical recycling by X has been added in the manuscript. 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.

Comment

2. Temperature difference between ambient and flow tube. Since the authors use the flow tube temperature (313K) to calculate kmodel OH and kcal OH, some discussions would be needed to examine the difference with ambient temperature for these calculations. After all, the readers would really want to know the OH reactivity in the ambient air. This difference could be very small, but it is important to use ambient OH reactivity to interpret ambient HOx data.

Response

The effect is indeed small. The temperature in the flow tube was slightly higher than ambient temperature, causing a negative bias in the measured kOH of up to 6 % compared to the ambient reactivity. The effect is caused by a reduced number density of the reactants in the flow tube by -0.3%/K according to the ideal gas law and by a kinetic temperature dependence of about -0.2%/K. The latter effect has been estimated by the model and is caused by the zero or negative activation energies of the major OH reactants (e.g., CO, NO_2, HCHO, MVK, MACR, alkenes, aromatics etc.). A corresponding

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description of the temperature influence has been added in the experimental section 3.1.

Comment

3. According to Fig 6, the contribution from HCHO is comparable to Isoprene. Regarding the factor of 10 differences in their reaction coefficients with OH, a large amount of HCHO is expected in the model. Please specify the HCHO concentration in the box model.

Response

The concentration of formaldehyde was in the order of 12 ppb. This value is in a range that can be expected at PRD (see answer to question 2 by referee #1).

Comment

4. If OISO contribute even more than Isoprene in OH reactivity, as shown in Fig 6, please specify what species in the model that makes such an important contribution. Is it MVK or MACR? As MVK and MACR both have much slower reaction rates with OH than Isoprene, it would require a significant amount of MVK and MACR to do so (much more than Isoprene).

Response

The major modelled oxygenated VOCs (OVOCs) have mean daytime concentrations of about 12 ppb HCHO, 3.8 ppb ALD, 1.1 ppb MVK, 0.6 ppbMACR, 0.9 ppb CAR4, and 0.44 ppb hydroxy hydroperoxide (ISHP, from isoprene). These compounds sum up to about 70% of the OVOC reactivity, while the remainder comes from small contributions of other model species. MVK, MACR, CAR4 and ISHP are the major OISO species, summing up to about 77% of the OISO reactivity. Concentration values of the major OVOC species are now given in the text in section 6.2.

Comment

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5. Page 10746, Line 11, "The model was operated in a time-dependent mode with 5 min time resolution and 2 days spin-up time." This is not very clear to me. Is there a 5-min dataset generated from measurements from different time resolutions and all interpolated to 5-min? During the model run, all the measurements (except OH) in Table 2 are kept constant in each five minutes and the rest of modeled species from last five minutes are used as initial condition for next time step(5min)?

Response

Yes. We have added the following explanation in the model description (section 4): The model was operated in a time-dependent mode with 5-min time resolution. First, a 5-min dataset was generated by interpolation from measurements which had different time resolutions. During the model run, all measured input data were kept constant in each five minute interval and the calculated species concentrations were used as initial condition for the next 5-min time step. Each model run started with 2 days spin-up time to reach steady-state conditions for long-lived species. Additional loss by deposition with a corresponding lifetime of 24 h for calculated species was assumed to avoid build-up of unrealistic amounts of secondary products.

Comment

6. How much OH is initially generated in the flow tube?

Response

The photolytically generated initial OH concentrations were less than 5×10^9 molecules per cm^3 during the field campaign. See also the answer to question 5 by referee #1.

Comment

7. According to Sadanaga et al.[2004], the photolysis of HCHO by 266nm laser may produce a few ppts of HO$_2$ in the flow tube. Some discussion of possible interference for the measurement will be necessary.

Response

Sadanaga et al. (2004) noted that HO$_2$ can be produced by 266 nm laser photolysis of ambient formaldehyde. In our case, the pulse energy of the photolysis laser is similar to the one used by Sadanaga et al., but we use a 3 times larger beam diameter. Thus, our laser pulse energy density (mJ/cm^2) is an order of magnitude smaller than in the case of Sadanaga et al. The laser generated HO$_2$ concentration in our instrument is calculated to be 4×10^6 molecules per cm^3 at 20 ppb HCHO and 10 mJ laser energy. This radical concentration is an upper limit, as tropospheric HCHO mixing ratios were less than 20 ppb at PRD. Given an initial HO$_2$ to OH ratio in the order of 10^{-3} in our instrument, the interference from conversion of laser generated HO$_2$ to OH by atmospheric NO is negligible. A discussion of this potential interference has been added to the experimental section 3.1.

Comment

8. More OH reactivity measurements should be included in Table 1, such as the measurements in Houston in 2000 and in 2006, which can be found in Mao et al. [2009].

Response

We thank the referee for pointing out this reference. We have included the corresponding data in Table 1. See also our answer to comment 1 by referee #1.

References

Hofzumahaus et al., Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702–1704, 2009.

Mao et al., Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmos. Environ., doi:10.1016/j.atmosenv.2009.01.013, 2009.

Sadanaga et al., Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique, Rev. Sci. Instrum., 75, 2648–2655, 2004.

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