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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 #2

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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

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HO_2/OH ratio (constrained by NO_x and VOCs), the modeled HO_2 will increase accordingly. Therefore a new HO_x 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 HO_x 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 HO_x level does not change much (although the HO_2/OH cycling makes a big change).

$$\frac{\text{HO}_2}{\text{OH}} = \frac{k_{\text{OH}}}{k_{\text{HO}_2+\text{NO}}[\text{NO}]} \quad (1)$$

2. Temperature difference between ambient and flow tube. Since the authors use the flow tube temperature (313K) to calculate $k_{\text{OH}}^{\text{model}}$ and $k_{\text{OH}}^{\text{cal}}$, 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 HO_x data.

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.

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).

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)?

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

7. According to Sadanaga et al.[2004], the photolysis of HCHO by 266nm laser may produce a few ppts of HO₂ in the flow tube. Some discussion of possible interference for the measurement will be necessary.

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].

References

Hofzumahaus, A., et al. (2009), Amplified Trace Gas Removal in the Troposphere, *Science*, 324(5935), 1702-1704.

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Sadanaga, Y., A. Yoshino, K. Watanabe, A. Yoshioka, Y. Wakazono, Y. Kanaya, and Y. Kajii (2004), Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique, *Rev. Sci. Instrum.*, 75(8), 2648-2655.

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