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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Missing OH source in a suburban environment near Beijing: observed and modelled OH and $HO_2$ concentrations in summer 2006" *by* K. D. Lu et al.

**Anonymous Referee #3**

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General comments

This manuscript describes comparisons between observed and modeled OH and HO2* concentrations and OH reactivity at Yufa site, south of Beijing, during CAREBeijing2006 field campaign period. The authors found that additional OH production is required at low NO conditions, from a simple budget analysis for OH and from detailed observation-model comparisons. The underestimation of OH concentrations by the base model reached a factor of 2.6 at 0.1 ppb NO. Although the value is lower than that found in PRD and those recently reported in forested sites, this study adds a new and important clue to our knowledge of tropospheric HOx chemistry. The authors suggested several



potential chemical mechanisms that could explain the observations, including generic OH recycling from HO2 (and from RO2 through HO2), and isomerization of peroxy radicals produced from alkenes and aromatics. From a similar analysis for a day with northerly wind, the authors found that the OH reactivity was overpredicted by the model likely because OVOC concentrations are overestimated and, after adjustment of it by introducing a dilution term, that additional HOx production is also necessary under the high-NOx conditions. Basically the subject is appropriate for the journal, and the paper is well organized. However I found several assumptions needing more justification. My major concern is on the concentrations of NO and HCHO used in the analysis. The NO measurement was made at a different building at a different height; if the NO concentration at the HOx instrument is higher by a factor of 2 for example, the main conclusion of this manuscript becomes different. The HCHO concentrations were unmeasured and were simultaneously simulated; from Figures 3 and 4, it seems that >10 ppb of HCHO is likely assumed, whose credibility is not discussed except for an implication that the measured OH reactivity is better explained with that high HCHO concentrations. I am afraid that the OH reactivity might also be well reproduced by assuming unmeasured NMHCs instead of HCHO and other OVOCs. The authors also invoked later the possibility of dilution only for the case of northerly wind, without any justification that it can be neglected for the southerly wind conditions mainly discussed in this manuscript. My request is that the authors take into account the uncertainties in the NO and HCHO concentrations and evaluate the robustness of their conclusions. I suggest that the paper should be published after adding the above analyses and taking into account the following specific comments.

Specific comments:

1. Abstract, page 10881, line 7. Need some explanation of HO2*.

2. Abstract, the authors should mention that the model basically reproduced the observed OH reactivity with calculated OVOCs

3. Page 10883, line 18. Organic nitrates might be involved in SOA formation but it is poorly characterized. Just OVOCs may be enough here.

4. Page 10884, line 14. Change literature Kanaya et al., 2007 to Ren et al. 2003 for NYC.

5. Page 10885, lines 11-12. . . . detailed measurements of OH, HO2 and OH reactivity "in Beijing"

6. Page 10886, lines 7-14. Can we assume that NOx concentrations are not different for the two platforms with different heights? How was the agreement in HONO concentrations measured at the two locations?

7. Page 10886, line 28. Is the flow rate of 1 slm common for the two cells?

8. Page 10887. Can the measurement of OH reactivity be perturbed by reproduction of OH by the HO2 + NO reaction, under high NOx conditions?

9. Page 10888, lines 6-15. Do the authors use downwelling 2-pi sr fractions of actinic flux measurements? How important are the upwelling fractions?

10. Page 10889, lines 3-14. How was the agreement between NOx measurements using the two instruments? Can they give some indication of homogeneity or heterogeneity of the ambient concentrations?

11. Page 10891, line 17. I do not understand 95% percentile of what.

12. Page 10892, line 6. The range of modeled HCHO concentrations should be figured. Its reasonableness should be discussed because of its importance. Can the 24-h lifetime introduced to represent dry deposition be important in determining HCHO concentrations? If so, more discussion is necessary about the uncertainty in the lifetime. Was the 24-h lifetime commonly assumed for the authors' previous study in PRD, for which comparisons are made in this study?

13. Page 10894, line 21. Fig. 3a and b



14. Page 10896, line 19. 7 ppb h-1

15. Page 10900, section 4.1. The authors discuss that only one or two processes were important for initial production of ROx radicals in other cities. I am afraid this is not the case for all cities listed. For Tokyo for example, see Figure 11 of Kanaya et al. (2007) where a wide variety of processes are important for summer.

16. Page 10901, line 14. Figure 7a (remove a space in between)

17. Page 10906, lines 5-8. Although the model's underprediction of OH continues from afternoon to the evening smoothly, the authors propose that the generic OH recycling is only important up to sunset and a different mechanism is necessary for night. I find this might be a weak point of this hypothesis.

18. Page 10907, lines 7-9. The OH underestimation in the late afternoon is not repaired by the LIM mechanism, which is also a weak point of this hypothesis.

19. Page 10909, line 21. What are the important chemical species for the OH reactivity whose concentrations were reduced by introducing the 8-h loss term? Can the authors provide any justification for the shorter lifetime exclusively for the northern wind, especially for products from isoprene chemistry?

20. page 10910, line 2. Remove space

21. Page 10910, lines 2 and 4. Only the average rates of the required source strength are discussed. What is the dependency of the calculated Q(OH) or Q(HO2) on NOx concentrations? The authors compare their own discussion on the OH concentration reproducibility at high NOx with other literatures sometimes on HO2 (not on OH). The imbalances of OH and HO2 can occur differently and thus more careful discussion is necessary. The authors criticize that the HO2 underestimation found at different cities at high NOx can be influenced by artifact by RO2 interference. However, the RO2/HO2 ratio is usually low at high NOx and can be unimportant. 22. Page 10912, lines 6-15. I would suggest shortening this part (e.g., remove literatures) to have a more balanced

conclusion.

23. Table 3. Is acetylene missing from observation?

24. Figure 1 caption, line 2. Maybe Panel (b-d)

25. Figure 2e. Sometimes (e.g., 18 and 27 August) nighttime isoprene concentrations are non-zero. Where are they coming from?

26. Figure 3. The authors should specify which days are included to represent composite diurnal variations of "southerly wind days"

27. Figure 3d. In Figure 1, the modeled OH has a sharp increase in the afternoon on 20 Aug, which is not present in Figure 3d.

28. Figure 4a. The large gap between the green and dotted purple lines is the contribution from HCHO photolysis. The fact that this fraction is not constrained by observation is a weak point of this manuscript and thus the incurred uncertainty should be discussed.

29. Can the authors discuss possible impact of heterogeneous loss of HO2 radicals on the aerosol particles, whose abundance is likely high at the location?

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10879, 2012.