

Interactive comment on “Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO₂ concentrations in summer 2006” by K. D. Lu et al.

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Review of Atmos. Chem. Phys. Manuscript (#acp-12-10878-2012) “Missing OH source in a suburban environment near Beijing : observed and modelled OH and HO₂ concentrations in summer 2006” by K. Lu et al.

General comments

This paper reports HO_x and OH reactivity measurements at a suburban site in Beijing, China. Observationally constrained box models were used to simulate the photochemistry and reproduce HO_x observations in this urban-influenced environment. OH budget analysis shows that under low NO_x conditions (typically in the afternoon),

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there was a significant missing OH source (~10-20 ppb/hr). With an additional HO₂ to OH recycling processing without involvement of NO, the model was able to reproduce the observed HO_x and OH reactivity. If recycling of OH from isoprene perxy radicals as proposed by Lelieveld et al. [2008] and Petters and Muller [2010] is included in the model, the model still under-predicted observed OH by ~40% under low NO conditions, indicating the large uncertainties in the OH recycling from isoprene radicals and further laboratory studies are needed. Radical budget analysis shows that besides the photolysis of ozone and HONO, the photolysis of OVOCs (mainly HCHO and dicarbonyls—although not measured (see comments below)) accounts for about half of the radical production. In general the paper is well written and reports important results. I support its publication in ACP after revision and ask the authors to address the following special comments in their revision.

Special Comments

1. One major shortcoming of this study is that no measurements of OVOCs (surprisingly including formaldehyde) were made, and thus modeled OVOCs have to be used in the analysis. Because the photolysis of OVOCs accounts for about half of the radical production, any significant errors in the modeled OVOCs can cause bias in the model OH, HO₂, and OH reactivity and thus potentially weaken some of the conclusions (e.g., the significant contribution of OVOC photolysis to radical production). I wonder if the authors can at least compare the model calculated species (e.g., formaldehyde or other photochemically important species) levels with the smae measurements at a similar location in Beijing in other times or in other locations under similar chemical and physical conditions. This will ensure that the levels of modeled species are not too far off from the actual valves. Also since different mechanisms were used, were the calculated species (especially HCHO and dicarbonyls) in the different mechanisms about the same? Because of the importance of the calculated species in both radical budget and OH reactivity (i.e., the measured species only account for about half of the measured OH reactivity and the rest from calculated species), more discussion is

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really needed to address these issues.

2. L10891 top, I noticed that in the model, a 24-hour lifetime was set for all modeled species (including OVOCs) to account for dry deposition losses. Why 24 hours and not for example 12 hours or 48 hours? How would this set lifetime affect the modeled OVOC levels? Also a 2-day spin-up was conducted for the model calculations. Does that mean the calculation results after a 2-day integration period were used for the concentrations of modeled species? Was this 2-day spin-up enough (or not too short but not too long for both short-lived and long-lived calculated species)? How much uncertainties may this cause in the calculated species, especially OVOCs?

3. P10882 L18, "These reactions...".

4. P10890, Section 2.1.2: was any upwelling radiation measured? If not, was a surface albedo considered in the photolysis frequencies calculation? The surface albedo can contribute ~5-15% more radiation of the downwelling radiation, depending on the kind of surface.

5. P10890 L14, not sure what (G; 2003) and (K; 2006) means. Shouldn't they be (2003) and (2006) instead?

6. P10908 bottom and P10909 top, in the discussion of OH interference, a recent ACPD paper (Mao et al., 2012 - probably published at about the same time when this paper was submitted) should be cited. Mao et al. [2012] found that in an environment influenced by biogenic emissions, the measured OH levels using a chemical removal method (C3F6) are only about half of those using traditional wavelength modulation. Is it possible that the FAGE system used in this study suffered similar interferences? Further discussion is needed.

7. P10930, Fig.3(c) and (d), there were significant nighttime OH levels (up to a few $\times 10^6$ cm⁻³), which are much larger than the model calculations. What are the possible sources for these levels of nighttime OH? Could any interference play a role here? A

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brief discussion would be helpful, although additional results can be published in a separate paper.

References: Mao, J., Ren, X., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and the atmospheric oxidation in a California forest, *Atmos. Chem. Phys. Discuss.*, 12, 6715-6744, 2012.

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