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Atmospheric
Chemistry
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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.

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Response to Comments by Ren, X.

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We would like to thank X. Ren for his comments and questions which have helped us to improve the manuscript. The comments are given below together with our responses and changes made to the manuscript.

General comments

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

Specific comments:

Comment 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 really needed to address these issues.

Comment 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 uncer-

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tainties may this cause in the calculated species, especially OVOCs?

Response to Comment 1+2

We appreciate the comments of X. Ren. First, we like to point out that the major result of our paper, a missing OH source, has been derived from the experimental budget of OH (Fig. 3) without need of measured or modelled concentrations of HCHO and OVOCs. The goal of our paper was not to study OVOCs at Yufa (for which we have no experimental data to compare with), but to explore the capability of models to describe the observed HOx concentrations. Yet, we agree that OVOCs play an important role for HOx in VOC rich environments. We find that OVOCs were both important radical precursors (e.g. by photolysis) and important reactants consuming OH. The effects on the production and loss of OH compensate each other partly, explaining why the influence of uncertainties of the calculated OVOCs on modelled HOx are relatively small. We acknowledge that this subject should be more clearly presented in the revised paper. For that reason, and also in response to similar requests by Referee 2 and 3, we will address the uncertainties in a new section (*Model uncertainties from unconstrained OVOCs (HCHO)*) of the revised paper. Please, see our more detailed response to Referee 2 (Comment 4) and Referee 3 (General Comment). Regarding the spin-up time, this is related to the selection of the lifetime to account for dry deposition losses. The spin-up time was chosen to ensure that calculated long-lived species reach quasi steady-state. We found that an even longer spin-up time was not necessary.

Comment 3

P10882 L18, “These reactions...”.

Response

The text will be changed accordingly.

Comment 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.

Response

The instruments measured only the downwelling part of the actinic flux. The upwelling contribution was neglected because the ground albedo in the UV range is typically small (<10 %), in particular over paved ground and vegetated areas (Feister et al., 1995; McKenzie et al., 1996). We will add a corresponding note on Page 10888, lines 6-15.

Comment 5

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

Response

Will be changed.

Comment 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.

Response

We are aware of the publication by Mao et al. [2012] who reported a factor-of-two OH measurement interference for the Pennstate LIF system with wavelength modulation in a forest with high biogenic VOC emissions. As mentioned in our manuscript, we tested our LIF instrument for interferences by VOCs that contributed mainly to the OH reactivity at Yufa and PRD. During the oxidation of the VOCs in the presence of OH and ozone (at similar concentrations like in Yufa and PRD), we found no indication for an interference that would explain the model-measurement discrepancy for OH in our

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work (see details in Fuchs et al., 2012). We will add the reference to Mao et al. in the revised manuscript.

Comment 7

P10930, Fig.3(c) and (d), there were significant nighttime OH levels (up to a few x10ËĘ6 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 brief discussion would be helpful, although additonal results can be published in a separate paper.

Response

The observed nighttime OH can be explained, if we assume a small additional primary HOx source and at the same time enhanced radical recycling (see our response to Referee 1, Comment 1).

In our interference study (Fuchs et al., 2012) we found indications for an OH artefact in the LIF measurement of about 30–40 % during the photooxidation of MVK (20 ppbv) and toluene (90 ppbv). These values have a large experimental uncertainty and require further experimental investigations. Given the more than an order of magnitude lower concentrations of toluene and MVK in Yufa compared to the simulation study by Fuchs et al., the supposed artefact is not a likely explanation of the nighttime OH in this work.

Reference

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