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Atmospheric
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Discussions

Interactive comment on “Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget” *by* S. Dusanter et al.

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We are grateful to the first anonymous reviewer for his extensive review and the valuable comments which helped us to improve our manuscript. For clarity, the comments are reproduced below with a bold font, followed by our replies.

Abstract. It is a little confusing saying that the predicted HO2/OH ratios were underestimated. (underestimated by what ? the measurements presumably but this is not explicit). Better to say that the model underestimated the measured ratio HO2/OH ratio – this is clearer.

This has been changed as suggested.

Although there are no measurements in this campaign, it would be worth making the point that OH reactivity measurements in this study would have been useful.
A short section has been added in the revised manuscript to emphasize the value of OH reactivity measurements: “While measurements of OH reactivity performed during the MCMA-2003 field campaign appears to be consistent within 30% with that calculated from the measured pool of VOCs and NO_x (Shirley et al., 2006), such measurements were not performed during MCMA 2006. Potential missing OH reactivity, observed in some environments (Kovacs et al., 2003; Di Carlo et al., 2004; Yoshino et al., 2006; Sinha et al., 2008), cannot be ruled out for the T0 site. It should be noted that measuring the total loss rate of OH during field campaigns is a valuable and important addition to the pool of measurements usually performed to understand atmospheric photochemistry.”

The reference Sheehy et al appears to be missing at the end in the references. Sander and not Sanders page 9830, line 18.
These have been corrected.

It is stated that chemiluminescecne measurements of NO2 are prone to interferences from various NOy. Perhaps be more specific, as there are several ways to convert the NO2, e.g. by photolysis too NO, or by heating with a Mb catalyst to form NO. I assume you were using the latter or are both methods prone to problems in very polluted conditions? Using instead the DOAS with the attendant spatially averaging issues is not ideal.
Local point measurements of NO_2 were performed using a monitor incorporating a Mb catalyst. This detail has been included in the text. To our knowledge, the photolytic converter is more specific to NO_2 and more suitable for polluted environments. How-

ever, photolysis of HONO has been suggested as a potential interference (Clemitshaw, 2004). We agree that using DOAS measurements for local point modeling may lead to substantial errors in the predicted radical concentrations; especially for air masses that are not homogeneous. However, measurements of various chemical species (O_3, HONO, SO_2, toluene) – as well as NO_2 – performed on different spatial scales (section 4.1) suggest that air masses in the MCMA are well mixed at the end of the morning and during the afternoon.

Page 9833 line 20, large fraction of VOCs not measured. Seems a good place to reference some indirect evidence for this, namely missing OH reactivity, thought to be from VOCs, references from the e.g. Brune, Kajii, Heard groups.
See response above.

There is a big discrepancy between predicted and measured glyoxal, which suggests a deviation from photochemical equilibrium. Also heterogeneous loss of glyoxal is mentioned as a possible uncertainty in the model and a reference given. Can some more details be given?
Volkamer et al. (Volkamer et al., 2007) used a box model based on MCM, constrained by measured J-values and concentrations of VOCs and oxidants (OH, O_3) to predict ambient concentrations of glyoxal during an episode as part of the MCMA-2003 campaign. MCM predicted concentrations that were 2-6 times higher than that observed, suggesting missing sinks in the model. The authors suggested that an irreversible uptake onto aerosol surfaces, a reversible partitioning to aerosol liquid water or to oxygenated organic aerosols could account for the missing loss processes. The authors reported that glyoxal uptake onto aerosol surfaces could account for 15% of the SOA formation in MCMA. This missing sink of glyoxal may be linked to an unexpected rapid formation of SOA in MCMA (Volkamer et al., 2006). This has been clarified in the revised manuscript.

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With such a rich chemistry expected in this environment, is the lack of predictive ability for dicarbonyl species the only likely problem? It is likely there are problems predicting many other species.
Concentrations of long lived species that are not constrained in the box model are likely to be overpredicted. This may lead to the prediction of erroneous concentrations of RO_x if the unconstrained species are either important sources or sinks of radicals. Fortunately, a large pool of measurements was performed during MCMA-2006 and RACM was tightly constrained for this study. Except for HNO_3, intermediate species that are not constrained (H_2O_2, OP1, OP2, PAA, ORA1, ORA2, CSL, MACR, UDD, HKET) have a negligible impact on the production and loss rates of RO_x. The radical budget analysis performed in this study indicates that the overestimation of HNO_3 has a minor impact on the initiation (HNO_3 + hv: 4.7%) and termination rates (HNO_3 + OH: 4.1%) of OH. HNO_3 acts as a source and a sink of OH and its impact on the OH concentrations is somewhat buffered. For instance, the total initiation and termination rates for the median campaign measurements (8:40 a.m.-6:40 p.m.) are $8.0\text{x}10^5$ and $1.1\text{x}10^6$ molecule/cm^3/s respectively. A net total loss of OH of $3.0\text{x}10^5$ molecule/cm^3/s is derived for the median campaign measurements. This flux of OH is negligible compared to the radical fluxes displayed in Fig. 8. This has been clarified in the revised manuscript.

Page 9845, line 2, does Mao et al 2009 cover discussion of OH reactivity measurements? If so, explicitly say so.
The following sentences have been added at the end of the paragraph: “Note that in the latter study, this imbalance was derived from measurements of both total OH reactivity and absolute OH concentrations, which allows a direct quantification of the total flux of OH reactions in the field.”

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Page 9851, line 8. the incomplete mixing between HO2 and NO (an anthropoenic emission) is analogous to a hypothesis put forward from the Suriname GABRIEL campaign, which suggested OH and isoprene (a biogenic emission) were not mixed properly either, as the new OH source necessary being postulated (Lelieveld et al, Nature 2008) to bring modelled and measured OH into agreement then gave the models problems in calculating isoprene. Perhaps discuss this link between the two studies.

Kinetic parameters of gas-phase chemical reactions are commonly determined using experimental setup designed to investigate the chemical reactions into well mixed mediums. A common assumption of atmospheric models is to consider that our atmosphere is also well mixed and that chemical reactions will behave as that observed during laboratory studies. However, areas close to emission sources of trace gases are likely inhomogeneous and the use of kinetic parameters derived for homogeneous mediums may lead to an incorrect description of the kinetic processes occurring in the real atmosphere. Butler et al. (Butler et al., 2008) proposed that segregation between OH and isoprene may be part of the disagreement observed between measured and model-predicted concentrations of OH for the GABRIEL field campaign. In this study, we investigate a similar concept, suggesting that the HO_2 + NO reaction rate is overestimated by the model due to segregation between the reactants as multiple sources of trace gases likely lead to inhomogeneities in urban environments. This has been clarified in the revised manuscript.

Page 9854. Line 18. A further investigation is mentioned – is this via a paper in preparation?

The imbalance observed between loss and production rates of HONO in this study suggest a source of HONO that is not included in our model. A study is in progress to investigate the budget of HONO during the MCMA-2006 field campaign, using

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measured J(HONO), [OH] and [NO]. The primary goal of this study is to determine the strength of an additional source necessary to explain the concentrations observed during the day as well as its origin. This paper is in preparation for future submission.

Page 9855. It is likely that the electronically excited NO2 plus water vapour reaction being a source of OH is erroneous. There is a new paper in Science (Carr et al. 2009) which throws doubt on this new source of OH, in agreement with measurements by Crowley's group in Mainz, and also by Christa Fittschen in Lille. It is worth leaving the section in though as the conclusion is that this source of OH is not important, even using the initial results (Li et al., 2008). However, it should be pointed out that there are new results (see above) which cast doubt on this source of OH.
We added the following sentences in the manuscript: "It is worth noting that this new source of OH is still questionable. A previous study using a pulsed-laser-excitation/resonance fluorescence technique reported that the reactive quenching of NO_2* by water was negligible under tropospheric conditions and that OH was produced by a 2-photon absorption sequence leading to the production of excited atoms of oxygen (O^1D) that then react with water to produce OH (Crowley and Carl, 1997). These authors derived a rate constant for R10b of approximately $1.2x10^{-14}$ cm^3/molecule/s that is 10 times slower than that derived in the study of Li et al. (Li et al., 2008). In addition, a recent study using a laser-induced fluorescence technique to detect OH also report an OH yield for R10b that is 17 times lower than that observed by Li et al. (2008). In this paper, we demonstrate that if this new source of OH radicals occurs in the troposphere, its contribution to the total rate of OH initiation is negligible in the MCMA."

References. Sheehy et al 2008 is not on the list. Fig 1, 2, 3 need to be bigger, hard to see when I printed out (OK on screen is blown up). Figure 8. Can you

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split up the OH loss as well to RO2?
These changes have been incorporated in the revised manuscript.

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