

## ***Interactive comment on “Oxidative capacity of the Mexico City atmosphere – Part 1: A radical source perspective” by R. Volkamer et al.***

**R. Volkamer et al.**

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We like to thank the reviewer for the detailed comments.

Detailed response:

C1) Comments HONO as a radical source: HONO that dissociates early in the morning represents OH that got produced by unknown means at night and stored as HONO. Later in the day, the OH from HONO is part of the PSS do-nothing cycle and gives a too high estimate for the production rate of OH. I suggest that new OH from HONO be counted as the dissociation rate minus the production rate. PAN is treated differently than HONO. RO<sub>2</sub> radicals produced from PAN dissociation are (properly) not included as a radical source, presumably because in this urban environment more PAN is formed than dissociates. Reading on I see that this point is raised later in the article on p5388.

Judging from my reading experience, I believe that this point has to be addressed at the point where the rates are tabulated.

R1) We have moved the argument about accounting HONO to the point when rates are discussed. Also, the following text was added in Section 2.2: We choose to account for HONO on an absolute flux basis for two reasons: (1) this definition does justice to the true role of HONO to jump start photochemistry during morning hours; and (2) this definition allows us to quantitatively define the concept of chain length as the amplification of radical source fluxes (this paper) to radical recycling fluxes (part 2, Sheehy et al., 2008). It turns out that an OH radical that is produced in the early morning is re-cycled about 3-4 times before it is removed by radical sink processes. Accounting for HONO on a net-flux basis would not account for this chemical amplification of radical fluxes from HONO. In principle, a similar argument could be made for the radical source from the thermal decomposition of Peroxy Acetyl Nitrate (PAN). We have calculated the radical production from PAN, and find that in this urban environment much more PAN is formed than dissociates, to the point that even accounting for chemical amplification PAN formation is almost exclusively a net radical sink in the near field chemical regime inside the MCMA. We hence have not reflected PAN as a radical source.

C2) Further, I do not understand the basis for the statement that 'if HONO was accounted based on the net-flux the contribution from other sources would be higher'. I agree that the early morning HONO dissociation needs to be included. In the early morning HONO is not in equilibrium and dissociation of HONO formed at night is in excess of HONO production. Is there a counter-argument that this does not give a correct net OH production?

R2) The reviewer misunderstood our statement, which was a simple matter of accounting. Any fixed absolute flux from any given source will have a larger relative share of the overall source flux when the overall source flux is reduced. We have removed the statement as part of moving text into section 2.2, as indeed the statement is trivial.

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C3) Section 2.1 Measurement techniques. The only measurements that are described are from DOAS, PTRMS, and radiometers. But many other species are used to constrain the model and for other purposes. These include OH and HO<sub>2</sub> which are hardly routine. This Section needs introductory text stating that it builds upon the data set collected at CENICA with brief descriptions of instruments and literature references. A Table, including species quantified by DOAS would be a good way of presenting this information. A couple of sentences describing pollutant levels is also needed for those not familiar with CENICA. The diurnal trend of radical production rates and their absolute values would be easier to understand and put into context if more precursor concentrations were given. HCHO and HONO are discussed extensively but there are no numbers for e.g. O<sub>3</sub> and H<sub>2</sub>O concentration.

R3) We have added the following text in the introduction to Section 2: 'An overview of typical pollutant concentrations at the CENICA site is compiled in (Molina et al., 2007); campaign median concentrations were 86 ppb NO<sub>x</sub> during morning rush hour, 20 ppb NO<sub>x</sub> during afternoons, median peak concentrations of 115 ppb O<sub>3</sub>, 0.4 ppt OH, and 40 ppt HO<sub>2</sub> shortly after noon, 120 s<sup>-1</sup> OH-reactivity during morning rush hour. Of the calculated contributions to the OH reactivity, 12% was due to NO<sub>x</sub>, 7% to CO, 4% to HCHO and 72% to VOCs (Shirley et al., 2006). A complete list of measurements used to constrain the MCM model is given in Table 1 of (Sheehy et al., 2008).'

C4) p 5370 lines 1-4. Not quite a sentence. Missing an 'and'? Also reference to "numerous aromatic species" Not clear what is done. I assume that they contribute lines to wavelength region which you have to work around.

R4) We have information about the DOAS retrievals of aromatic VOCs, and other species, and modified language.

C5) p 5371 lines 8-10 'The above listed wavelength .. reflect smallest uncertainties ..' Meaning?

R5) Clarified

C6) p 5372 line 14 O singlet D 'D' should not be in superscript

R6) Done

C7) p 5373 vertical gradient in NO<sub>3</sub> and scaling I do not understand what was done, even after reading section 3.4. I think you need some explicit equations. What are the concerns behind the scaling procedure?

R7) The formula is now given. Concerns are discussed in the text.

C8) p 5373 line 20-21 'an upper limit for the height of DOAS#1' Poorly worded. I don't know the authors intent but I don't think the upper limit has unit of meters.

R8) The unit for the upper limit is ppt (not meters) as we are scaling a concentration of NO<sub>3</sub>. Wording has changed to avoid the apparent possibility for confusion.

C9) p 5374 line 13 'characteristic VOC split' Meaning?

R9) Reference to Table 1 in Sheehy et al. 2008, where the characteristic VOC split is given, and discussed has been included.

C10) p 5376 line 8 'sensitive feedbacks' The sun goes down and secondary pollutants are advected away. Where are the feedbacks?

R10) One example for such a feedback consists in the fact that secondary pollutants significantly contribute to radical source fluxes, and thus photochemical activity. In turn pollution export slows down photochemistry. Language was modified to make this clearer.

C11) p 5377 line 14 'is high (3.5 - 4.5 ppb/h)' What is the range for?

R11) We now refer to a specific time, and give only one number.

C12) Section 2.3 Source apportionment ... HCHO I don't understand why the contributions of individual VOC classes to HCHO was calculated by setting (all?) other

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VOC classes to zero. This cannot give correct absolute values as an OH radical has to react with something and if you've removed most other alternatives you will overestimate the amount of product from the remaining VOC. Perhaps you can get relative numbers by doing the calculation for all VOC classes then dividing one class by the sum of all classes. Why not simply keep track of the fluxes through individual reactions? The selected procedure needs further explanation and justification. The same considerations apply to calculations in which all but one oxidant is set to zero.

R12) We respectfully disagree. What we did is calculate the HCHO production rate at a fixed (not variable) concentration of oxidants.  $P_{\text{HCHO}}$  can be written as a linear sum of individual source terms for each HCHO source reaction. The rate of HCHO production is something like:  $P_{\text{HCHO}} = \text{OH} \times \sum (k_{i,\text{OH}} \times \text{VOC}_i \times \text{Yield}_{i,\text{OH,HCHO}}) + \text{O}_3 \times \sum (k_{j,\text{O}_3} \times \text{VOC}_j \times \text{Yield}_{j,\text{O}_3,\text{HCHO}})$

The rate of HCHO production from any of the specific source terms will not change, unless the concentration of  $\text{VOC}_i$  or the oxidant is changed. We use our approach only to make relative statements about the rate of HCHO production under typical experimental conditions (described in the text). The reviewer had a point if the concentration of oxidants was kept unconstrained, and did vary as a result of changing VOC sink reactions, but as is described in the text - this is not the case. OH and O<sub>3</sub> are kept constant during all model runs.

C13) Section 2.3 Source apportionment ... HONO I don't know what to make of the first sentence. It implies that the PSS value for HONO is a complicated expression and that you need the whole machinery of MCM to determine it. I recommend that the simple equation for PSS HONO be given. I can't follow the different cases that were considered. The last sentence implies that some calculations were done with the old value of  $J(\text{HONO})$ . Why do calculations with a rate constant that has been superseded by new results? Much later on there is a comparison that shows how changes in  $j(\text{HONO})$  affects results. A Table of calculations would help.

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R13) A clearer distinction is now made between the three model runs, and additional sensitivity studies that were carried out for each of the model scenarios.

C14) Section 3.1 OH-equivalent RO<sub>x</sub> radical production rates Conversion of primary radical production to OH equivalents can be made more understandable by explicitly stating the alternate pathways (or classes of pathways). The fraction of HO<sub>2</sub> and RO<sub>2</sub> radicals that do not form OH should be an interesting parameter. There are alternate ways of providing the total radical production rate. I'm interested in learning why the authors choose OH equivalents.

R14) The formula for calculation of OH-equivalent radical production is now given in this manuscript. For the formulas to calculate gamma values, the reader is referred to specific equations in Sheehy et al., 2008. We have chosen to express all radical sources in terms of OH-equivalents because OH is the primary oxidant of interest when studying oxidative capacity. Also, our decision to express all sources also as OH-equivalent sources was motivated by the fact that the 'chain length' of radical cycling via the radical chain OH->RO<sub>2</sub>->RO->HO<sub>2</sub>->OH (part 2 of this sequence) is only a well defined quantity if there is only one source to the cycle. Multiple sources will necessarily make the value of the chain length dependent on the perspective that is taken on the cycle. We have decided to look at the radical chain from the perspective of the OH radical. A common terminology between both parts of this paper sequence was considered prudent. The reviewer is referred to part 2 for further information on radical termination reactions and further information on chain length.

C15) P 5381 line 5 and 8 peroxy mis-spelled

R15) corrected

C16) p 5391 discussion of effect of NO<sub>3</sub> on RO<sub>2</sub> to OH conversions There is a need here for explicit reactions.

R16) Explicit reactions are now included

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C17) p 5381 last paragraph Comparison between Mexico City and Houston Ozone concentrations are not all that different. As to more abundant NO<sub>3</sub>-sink reactions in Mexico City, do you mean NO + NO<sub>3</sub>?

R17) We agree that Houston and Mexico City have similar VOC reactivities. To our knowledge the NO<sub>3</sub> + furanone reaction has not been found relevant to affect the NO<sub>3</sub> lifetime. This may partly be due to the fact that furanone chemistry is not explicitly represented in atmospheric models that use lumped chemical codes.

C18) Line 18, which follows the statement about more abundant NO<sub>3</sub> sink reactions, starts a discussion of VOCs which are not important sinks of NO<sub>3</sub> accounting 'for about 7% of the daytime NO<sub>3</sub> sink reactions. The juxtaposition of these 2 sentences sets up a contradiction. At the very least, the sentence on line 18 starting with "In contrast ...' should start a new paragraph.

R18) 7% of the NO<sub>3</sub> fate may not appear much. However, at 100 ppb O<sub>3</sub> and 10 ppb NO<sub>2</sub>, the NO<sub>3</sub> production rate is about 1.3 10<sup>7</sup> molec/cm<sup>3</sup>, and the overall flux through NO<sub>3</sub> + VOC reactions is on the order of 10<sup>6</sup> molec/cm<sup>3</sup>/sec. An according calculation has been added to illustrate this point.

C19) Section 3.4 Comparison of measured and calculated HONO. PSS HONO is slightly more than half at 7:00, if I'm reading Table 1 correctly. The dark HONO production is arrived at to get the measured HONO averaged from 8:00 pm to 4:00 am. I don't understand how the comparisons in Figure 4 can constitute evidence for low OH or high j(HONO) given the large adjustments.

R19) By 9am the HONO lifetime is only on the order of 30-40mins; essentially all HONO at 9am has not been produced at night. This is also reflected by the fact that the dark HONO production accounts for <10% of the OH production from HONO at 9am. Scaling of dark HONO is admittedly uncertain, but it does not make a significant contribution at 9am. Further, by 9am the two DOAS measurements of HONO agree well, albeit take over light paths that point in opposite direction and have mean heights

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of 16m and 70m. This indicates that vertical mixing is strong enough by that time to reduce vertical gradients to levels that no longer limit our conclusions.

Figure 4 provides evidence for an additional HONO sink: the model predicted HONO is too high; increasing JHONO appears to have the correct time dependence to resolve this persistent mismatch over the entire morning, i.e., as long as HONO is high enough that conclusions are not yet limited by measurement precision (panel c and d).

Our data does not allow unambiguous conclusions about 'low OH', because vertical gradients matter more in the early morning. However, neither DOAS#1, nor DOAS#2 shows any change in the rate of HONO production around 5am. This is different for the model predicted HONO production rate based on the measured OH, where the HONO production rate increases by a factor of 3-4 from before to shortly after 5am. The effect is significantly reduced if the model is constrained based on a lower limit OH concentration.

The text has been modified to reflect better the key points of this argument.

C20) Lines 21-25. Two sentences are contradictory. 1) Dark sources are important only before 8:00 am. 2) After 8:00 am PSS and dark sources can account for essentially all HONO.

R20) This is no contradiction. Dark sources still account for a small portion of the HONO after 8am. Wording has been clarified.

C21) An additional point of confusion is the identity of NO<sub>3</sub> sources in the model that are not PSS or dark.

R21) We do not identify NO<sub>3</sub> sources in the model that are not PSS or dark. It is not clear to us where the confusion is.

C22) Section 3.5 Source apportionment of HCHO Explanation need for "Subtracting an appropriately scaled tracer for HCHO emissions" I'm not sure what 'background HCHO' represents and from this paper do not know how significant it is.

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R22) 'background' HCHO (which is essentially the residual HCHO that is not accounted well by the tracer approach, and a small portion of the measured HCHO. We now give the relevant equations from Garcia et al. 2006. The reviewer is referred to that work for further details on the analysis.

C23) P 5391 line 6 "is about 5 times higher compared to the alkene abundance" I don't understand. Is this referring to other cities? Should '3-6% ppbC' be 3-6% per ppbC?

R23) We indeed mean to say ppbC. The point is that about 30% of the radical sources can either directly or indirectly be linked with alkenes, while they only account for 3-6% of VOC on a ppbC basis. We have modified the text to highlight this important result. The indirect role of alkenes only becomes apparent due to the detailed source apportionment of other radical sources.

C24) P 5391 line 11 'O3/alkene reactions are the predominate source for OH radicals at night' I thought a source of OH sufficient to explain the observed OH had not been identified.

R24) Indeed our MCM model does better than other models to reproduce nighttime OH. See Figure 3 in Sheehy et al., 2008, and the related discussion for a more information. The issue of nighttime OH is still a subject of ongoing debate. However; at least in our mind; it is not a question of whether nighttime OH is real or not, but more a question of how much of it there is.

C25) Table 1. What do italic numbers mean? Why is there a range for HONO PSS? What is the "other" source for HONO? All but 2 columns add up to a number that is slightly different from 100%, persuadably due to round off. The two exceptions add up to 97.1 and 97.9% which is more than can be explained by round off.

R25) We have updated Table 1. We now give more detail, and the balance adds up within 0.5%. The legend now explains what italic numbers mean. The range of PSS-

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HONO reflects calculations based on measured OH, or the lower limit OH (within measurement uncertainty). Other HONO sources include photoinduced HONO formation, which we demonstrate makes a small contribution in the MCMA based on (Stemmler et al. 2006), also due to the abundance of other sources, e.g. OVOC photolysis.

C26) Figure 4 Captions '(a) OH ... (d) jHONO' are confusing. I don't have a reasonable alternative. By the time I got to this figure I forgot what the lower limit of OH was about. I don't understand last line of caption. I assume that the calculated results in Fig. 4 include the dark source. Why isn't this dark source a radical source if it yields HONO that dissociates?

R26) We have revised the text of Caption 4 to improve its readability.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 5365, 2007.

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