

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

Anonymous Referee #1

Received and published: 7 June 2007

Review of "Oxidative capacity of the Mexico City atmosphere - Part 1: A radical source perspective by R. Volkamer, P.H. Sheehy, L.T. Molina, and M.J. Molina for ACPD

This is one of the few articles that I've seen that focuses on radical production rates which are a very important component of urban photochemistry. The comparison of radical production rates and HONO in different areas is a strong point. Importance (or lack there of) of second generation oxidation products is a unique finding. Discussion on the numerical requirements for characterizing daytime HONO sources is well done. Implications for Mexico City Air quality is important and thought provoking.

As indicated by my comments I found many aspects of this manuscript hard to follow. Part of the problem may be that missing material is contained in a yet to be published

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companion paper. Part of the problem is that the sections and subsections are missing clear introductions as to what is being done and what the concerns are. At various points in the paper cases and sub-cases are defined, not be used until later on. I could not keep these cases straight. A lot of attention is paid to NO₃ which is interesting in comparison to other areas but has a limited effect on radical production rates. In contrast, 27% of daytime radical production is due to secondary OVOCs other than HCHO, but there is almost no detail on these compounds. My questions include some aspects of the calculations. I don't know why source attribution for VOC classes and oxidants was done by setting all but one VOC class or oxidant equal to zero. I don't know whether this procedure is proper. I would like to be convinced that the contribution of HONO to radical production couldn't be handled as a net flux.

In summary this is an ambitious and important article. It is also an article that is not clearly presented and may have methodological flaws (which probably don't compromise the major conclusions). I would like to see a much clearer version make its way into ACP.

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. RO₂ 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. 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

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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?

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 HO₂ 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. O₃ and H₂O concentration.

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.

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

p 5372 line 14 O singlet D "D" should not be in superscript

p 5373 vertical gradient in NO₃ 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?

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.

p 5374 line 13 "characteristic VOC split" Meaning?

p 5376 line 8 "sensitive feedbacks" The sun goes down and secondary pollutants are

advected away. Where are the feedbacks?

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

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 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.

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.

Section 3.1 OH-equivalent ROx 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 HO₂ and RO₂ 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.

P 5381 line 5 and 8 peroxy mis-spelled

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p 5391 discussion of effect of NO₃ on RO₂ to OH conversions There is a need here for explicit reactions.

p 5381 last paragraph Comparison between Mexico City and Houston Ozone concentrations are not all that different. As to more abundant NO₃-sink reactions in Mexico City, do you mean NO + NO₃? Line 18, which follows the statement about more abundant NO₃ sink reactions, starts a discussion of VOCs which are not important sinks of NO₃ accounting "for about 7% of the daytime NO₃ 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.

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. 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. An additional point of confusion is the identity of NO₃ sources in the model that are not PSS or dark.

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.

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?

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.

Table 1. What do italic numbers mean? Why is there a range for HONO PSS?

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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.

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?

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

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