

## ***Interactive comment on “Alkyl nitrate production and persistence in the Mexico City Plume” by A. E. Perring et al.***

**A. E. Perring et al.**

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ACPD response to reviewer #1

We thank reviewer #1 for their constructive comments. We describe our detailed responses to scientific comments below.

Comment: Title. The choice of Alkyl nitrate for the title is a bit odd since this usually refers to a specific subset of the compounds you've measured and analyzed

Response: We will amend the title to read “The production and persistence of total RONO<sub>2</sub> in the Mexico City plume.

Comment: Abstract. I don't believe you've demonstrated what is given as main conclu-

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sion #3 “ANs play a comparable role to PNs in the export of NO<sub>y</sub> to the Gulf Region” I don’t see where it is discussed in the main text (except on p. 23766 where it’s stated that PN and AN levels are similar in aged air). It seems that this point would be demonstrated by the area under the curves in Figures 4a and 4b. Despite the fact that ANs and PN converge in this figure at long processing times, the integral over all ages is much longer for PN, which implies to me a substantially greater cumulative role in NO<sub>y</sub> export. Plus, as you point out, the plume measurements were made at fairly low altitude. Presumably whatever fraction of the outflow that is lofted to higher altitudes would have more PN. Finally, any role that ANs play in redistributing reactive nitrogen will depend on the fate of the ANs and to what extent they recycle NO<sub>x</sub>. If they are mainly removed through deposition then there is not a major role for NO<sub>y</sub> redistribution. Either this conclusion needs to be removed or the case needs to be made convincingly in the text.

Response: Figure 4 as described by the reviewer is consistent with our view of the word “comparable.” As the referee has interpreted the word more narrowly to mean a near quantitative equivalence, we will amend the abstract to read “ANs play a significant role in the export of NO<sub>y</sub> from Mexico City to the Gulf Region”. There is no evidence one way or the other that PN would be more important at higher altitudes in the outflow of this or any other urban plume. We are also in complete agreement that the ultimate fate of ANs in terms of permanent removal from the gas phase vs. NO<sub>x</sub> recycling is what will determine their impact on NO<sub>x</sub> redistribution. Their fate, however, is currently one of the major uncertainties in the modeling of ANs and it is our hope that the data presented here will highlight the need for a better understanding of AN loss processes, encourage further laboratory work and offer a first-pass constraint for groups attempting to incorporate them into chemical models.

Comment: 23758, L23-24. I don’t think you really did discuss what is or is not typical about this dataset.

Response: We will modify the sentence “We examine aspects of the chemistry that are

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specific to this plume and discuss features that appear to be more generally applicable to any urban plume” in the revised version of this manuscript.

Comment: 23764, L2-3, please describe by what criteria you consider  $\text{OH} = 3 \times 10^6$  molecules/cm<sup>3</sup> to be “reasonable”

Response: The primary criteria is that a 24 hour average OH of  $3 \times 10^6$  gives chemical ages that are roughly consistent with meteorological transport times. The OH concentration in downtown Mexico City, as reported by Dusanter et al., (ACP, 9, 2009) was  $\sim 7\text{--}8 \times 10^6$  moles/cm<sup>3</sup> at midday. Median values observed aboard the DC8 were  $\sim 8 \times 10^6$  within 100km of the city and  $\sim 4 \times 10^6$  over the Gulf of Mexico (for back trajectories tracing back to the city). 24 hour average OH values are often calculated as between 25% and 33% of noon time peaks. Thus a values of  $3 \times 10^6$  is not inconsistent with the observations. We will add additional explanation of our rationale to the text.

Comment: Please modify Figures 4,5 and 8 to show some measure of the variability in addition to the lines (as you did for Figure 7).

Response: We will modify the figures as requested.

Comment: 23766, L9 “CO, which is a conserved tracer”. Except that it is photochemically produced in addition to directly emitted. Globally this is approximately half the source (according to Duncan et al., 2007), though I expect this to be quite different in the vicinity of Mexico City. Please discuss this point in the text and what effect, if any, you expect it to have on the analysis.

Response: The global source of CO is produced chemically on vary different spatial scales than in this plume. Photochemical production of CO within this plume is a small effect compared to dilution. During 40 hours of aging at an OH concentration of  $3 \times 10^6$  moles/cm<sup>3</sup>, we calculate that  $\sim 2.6$ ppb of CO would be produced from methane oxidation and 3-4 ppb from formaldehyde, acetone and ethane (using concentrations of each observed in/near Mexico City). Oxidation of larger hydrocarbons is likely to con-

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tribute primarily through production of H<sub>2</sub>CO, which we account for above. In contrast to these slow production rates, CO decreases from 600 ppb at 0-5 hrs of photochemical age to 480ppb at about 10 hours age, and is mixing into a background of 132 ppb. CO produced from methane, ethane, acetone and formaldehyde over 40 hours of photochemical aging is only <2% of the total decrease observed. We will add a brief discussion explaining why one can neglect CO production in the analysis.

Comment: 23766, L18 “Molecules that decay faster than CO are BEING removed by chemistry or deposition” - or not being photochemically produced as quickly??

Response: see response to above comment.

Comment: 23766, L19 “those that decay more slowly are BEING produced in the plume” – more rapidly than CO?? Also, you could make your argument more clear by adding “since concentrations are decreasing less rapidly than dictated by dilution”

Response: We will amend the revised manuscript as suggested.

Comment: 23767, L2-3 “they too continue to be produced as the plume ages” but you might mention that most production appears to be in the near field. Also, I suggest briefly explaining the pattern for PNs, even if only referring the reader to the discussion for Fig. 4a.

Response: In section 4.2 of the revised manuscript, we will highlight the fact that most of the ANs production occurs in the near-field of Mexico City and briefly revisit the pattern of PNs as discussed above with respect to figure 4 and figure 5b.

Comment: 23767, L9-10 “as long as losses of both are slow relative to production”. This point needs some discussion and justification as it underpins all of the analyses that follow.

Response: We discuss this more extensively in section 4.2 and will refer the reader to that section for additional details. In addition, we will add detail to section 4.2 to describe calculations we have performed using rate constants from the MCM to esti-

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mate instantaneous production and loss rates for ANs and O<sub>3</sub> at longer chemical ages so the reader is more equipped to determine when our assumptions about production exceeding loss might break down.

Comment: 23768, L10, suggest “the IMMEDIATE (or INSTANTANEOUS) oxidation of RHI” or some other way to clarify that you are talking about a single oxidation step for a given hydrocarbon, not following it all the way down the oxidation chain.

Response: We will amend the manuscript as suggested.

Comment: Table 1. What about the other OVOCs you mention in the Measurements section? They’re not used here? Why?

Response: We thank the reviewer for noting our omission and we will add MEK, methanol, ethanol and acetone to our PO<sub>3</sub> calculation in Table 1 in the revised manuscript.

Comment: Equation 7. This should be an “approximately equal” sign, not an identity sign. The two are only the same if the C<sub>5</sub> ANs lifetime is the same as that for total ANs, which is an approximation. Please state why you think it is a reasonable one.

Response: We will change the equals sign to an approximately equals sign. We will also add a few sentences to this paragraph alerting the reader to the fact that, similar to the Ox vs. ANs analysis, we have made the assumption that the loss rates of C<sub>1</sub>-C<sub>5</sub> ANs and sigma(ANs) are slow relative to their production. In addition we will clearly state the lifetimes of the C<sub>1</sub>-C<sub>5</sub> nitrates (which are fairly well constrained based on prior lab and field measurements) and give estimates for the lifetimes of some more functionalized nitrates for comparison.

Comment: 23770, L10-14. This is a nice corroboration. Perhaps discuss the consistency a bit more? 27% vs. 10% implies 2.7 times more ANs present than expected; 17 versus 60 implies a production rate of 3.5 times higher than expected right?

Response: The reviewer is correct that the ratio of C<sub>1</sub>-C<sub>5</sub> nitrates to total(ANs) implies

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the rate of ANs formation is 2.7x higher than expected. We calculate that a slope of 17 implies a nitrate formation branching ratio of 10.5% ( $2/(17+2)$ ) while a slope of 60 implies a branching ratio of 3.2% so that the Ox/ANs correlation implies that the rate of ANs production is 3.3x higher than expected. In the revised manuscript we will briefly outline these calculations and more explicitly state how they corroborate each other.

Comment: The discrepancy between observed and expected ANs could be either larger or smaller than you're describing if either Ox or AN losses are important

Response: It is our opinion that the production of both Ox and ANs in the near field of the city so far exceed even the highest possible estimates of chemical loss rates that the potential impacts of loss are minimal. We will add text to the revised manuscript stating this and placing bounds on the magnitudes of the loss processes.

Comment: 23770, L18-21, yes, but wouldn't NO titration be much more pronounced near-source at T1 than in the air masses you are sampling.

Response: Yes, NO titration would be more pronounced within Mexico City than in lofted airmasses as sampled by the DC8. We were attempting to calculate an upper limit of the effect of NO<sub>3</sub> chemistry and so neglected NO effects. We will add to the revised manuscript comments that clarify that we believe NO<sub>3</sub> chemistry is less important than this upper limit .

Comment: 23773, L24-28, it's not clear to me what you're doing here. Please clarify the description.

Response: We will add the text and representative calculations presented in the supplement to this reply to clarify the analysis.

Comment: Figure 7, why use different variability metrics (IQR vs sigma) for the different quantities? You should probably also define IQR somewhere in the caption.

Response: We have changed all instances of IQR to sigma and state in the captions what we mean by that measure.

Comment: 23775, somewhere please define HO<sub>x</sub> and state briefly why you consider RO<sub>2</sub>+RO<sub>2</sub> and RO<sub>2</sub>+NO→RONO<sub>2</sub> (but not RH+OH) as HO<sub>x</sub> losses since this may not be obvious to all readers.

Response: We will define HO<sub>x</sub> on line 21 of p. 23775 as the sum of OH, HO<sub>2</sub> and RO<sub>2</sub> and we will add a sentence at the top of page 23776 before the statement of the L(HO<sub>x</sub>) equation to clarify why we consider the production of HNO<sub>3</sub>, ANs and peroxides to be HO<sub>x</sub> losses while OH+RH is not.

Comment: Figure 8 is very nice. Perhaps there are two points that could be made here. The first is the effect of AN formation on PO<sub>3</sub>, which is what you've shown. The second is the likely model error in PO<sub>3</sub> due to ANs, which is not shown. Models that I know of do not neglect ANs but their treatment of them is probably not very good. What about adding another line to each panel in Figure 8 showing the PO<sub>3</sub> you'd predict using the info in Table 1, which is a reasonable reflection of what might be in a detailed chemical model? Then you could use Fig. 8 to show both the total effect of ANs on PO<sub>3</sub> and the extent to which that effect is not reflected in current understanding and current models.

Response: We thank the reviewer for their constructive suggestion and will add the recommended data to the figure in the revised manuscript.

Comment: Technical comments: Throughout, please be specific whether referring to Ox vs. ANs measured or calculated slope, concentration ratio or production ratio. There are several spots that are lazy in terminology (e.g. just "Ox vs. ANs" or "Ox/ANs" or "ratio") and it's not clear what you mean. There are also some places where you say "correlation when "slope" is meant.

Response: We will review our usage of this terminology and edit the revised manuscript to clarify the exact quantities or slopes we intend to discuss.

Comment: 23759, L10 "each class of compounds"; awkward, how about "each compound class"

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Response: We will edit as suggested.

Comment: 23760, L5-6 “10 to 1 at 1atm”; wouldn’t this depend on the ambient NO<sub>2</sub> amount?

Response: Because the signal at both frequencies is due to NO<sub>2</sub> the ratio does not depend on absolute NO<sub>2</sub>. We will change the phrasing describing the off-resonance position from “background” to “off-resonance” to clarify this point.

Comment: 23760, L15, state supplier of reference gas.

Response: Our reference gas is supplied by PraxAir and we will add this information to the revised text.

Comment: 23761, L1-2, a bit confusing where precision values come from. Are they typical observed precision values at those concentrations?

Response: The stated precision values come from typical observed instrument sensitivities (determined by laser power and alignment) and counting statistics where the noise in a measurement is given by the square root of the observed counts. We will clarify the origin of these values in the revised manuscript.

Comment: 23761, L16, specify whether UNH HNO<sub>3</sub> measurement is gas-phase, particle-phase or both. Which measurement are you using in the analysis, the TD-LIF HNO<sub>3</sub> or the UNH HNO<sub>3</sub>? It’s not clear.

Response: The UNH measurement is the sum of gas- and particle-phase HNO<sub>3</sub> and we will add this statement to the text. In this analysis we use the UNH HNO<sub>3</sub> measurements and we will clarify this fact in the revised text.

Comment: 23762, L8 “select points that passed within 100 miles”; suggest instead “select measured air masses that passed within ~100 miles”

Response: We will amend the text to read as suggested.

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Comment: Throughout, sometimes you say 2-butyl nitrate, sometimes butyl, sometimes n-butyl nitrate. Please just use 2-butyl nitrate.

Response: We will use 2-butyl nitrate consistently throughout the manuscript.

Comment: 23763, L20 “pentyl nitrate”, which pentyl nitrate?

Response: Both 2- and 3-pentyl nitrate were assessed and we will state this in the text.

Comment: 23764, L2, “diurnal” can mean daytime only. Suggest “diel” or “24-hour” if that is your intent.

Response: We do intend “diurnal” to mean daytime only and we will clarify this in the revised text. The chemistry is expected to shut down at night and in later discussions we state explicitly that the “clock” refers specifically to hours of daytime aging.

Comment: 23764, L18, suggest “between the calculated age FOR THESE POINTS and the distance” 23765, L2, suggest “For example, the AVERAGE MEASURED wind velocity” 23766, L13-14, “Xinitial is the MEAN observed concentration. . . Xbackground is the MEAN observed concentration”??

Response: We will edit as suggested.

Comment: 23766, L22 and 28 “dilution rate of NO<sub>y</sub> to CO” and “Toward the end of the plume” are both awkward; suggest rephrasing.

Response: We will rephrase in the revised manuscript.

Comment: 23768, L6, delete “which are”

Response: We will edit as suggested.

Comment: 23769, L1. I suggest a sentence first describing what you are about to do. 23769, L10. “bold italics” in Table 1 are hard to distinguish and do not appear to be bold

Response: We will add the suggested introductory sentence and change the text in

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Table 1.

Comment: 23770, L4, “a large component of di-nitrate formation”, explain that a di-nitrate would count twice in the TD-LIF.

Response: We will add this explanation to the text.

Comment: 23771, L4, some example references would be helpful here

Response: We will add a few representative references for aromatic oxidation experiments.

Comment: 23771, “cannot bring the calculations and observations into complete agreement”, suggest “are unlikely to bring. . .”

Response: We will edit as suggested.

Comment: 23771, L24, citations for Granite Bay and Houston are needed.

Response: We will add citations for those two field studies.

Comment: 23772, L28, suggest “possible candidates” instead of “quantities” 23774, L20, suggest “by ASSUMING conservation of radicals” 23775, Equation 9, clarify O<sub>3</sub> photolysis is channel giving O(1D). 23775, L10, “an effective branching ratio FROM THE OBSERVATIONS”

Response: We will edit as suggested.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/9/C11759/2010/acpd-9-C11759-2010-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23755, 2009.

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9, C11759–C11768,  
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