

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

**Anonymous Referee #1**

Received and published: 3 December 2009

Perring et al. present measurements of organic nitrates (ANs) and other components of NO<sub>y</sub> during the MILAGRO campaign over Mexico City and the Gulf. They apply their data here to examine AN production and chemical impacts in the context of present understanding.

This is an very good paper, a highly interesting analysis, and certainly appropriate to ACP. I recommend it for publication once the following comments are addressed.

Specific comments.

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.

Abstract. I don't believe you've demonstrated what is given as main conclusion #3 –  
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"ANs play a comparable role to PN<sub>s</sub> 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<sub>s</sub> and AN<sub>s</sub> 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 AN<sub>s</sub> and PN<sub>s</sub> converge in this figure at long processing times, the integral over all ages is much larger for PN<sub>s</sub>, 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<sub>s</sub>. Finally, any role that AN<sub>s</sub> play in redistributing reactive nitrogen will depend on the fate of the AN<sub>s</sub> 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.

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

23764, L2-3, please describe by what criteria you consider OH = 3x10<sup>-6</sup> molec/cm<sup>3</sup> to be "reasonable".

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

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.

23766, L18 "Molecules that decay faster than CO are BEING removed by chemistry or deposition" – or not being photochemically produced as quickly?? cf above comment.

23766, L19 "those that decay more slowly are BEING produced in the plume" – more

rapidly than CO<sub>2</sub>?. Also, you could make your argument more clear by adding "since concentrations are decreasing less rapidly than dictated by dilution".

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 by referring the reader to the discussion for Fig 4a.

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

23768, L10, suggest "the IMMEDIATE( or INSTANTANEOUS) oxidation of RHi" or some other way to clarify that you're talking about a single oxidation step for a given hydrocarbon, not following it all the way down the oxidation chain.

Table 1. What about the other OVOCs you mentioned in the Measurements section? They're not used here? Why?

Equation 7. This should be an "approximately equal" sign, not an identity sign. The two are only the same if the C5 ANs lifetime is the same as that for total ANs, which is an approximation. Please state why you think it is a reasonable one.

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

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

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

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

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tion.

Section 4.2, very nice!

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

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.

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 in current models.

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.

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

23760, L5-6 "10 to 1 at 1 atm"; wouldn't this depend on the ambient NO<sub>2</sub> amount?

23760, L15, state supplier of reference gas.

23761, L1-2, a bit confusing where the precision values come from. Are they typical

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observed precision values at those concentrations?

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.

23762, L8 "select points that passed within ~100 miles"; suggest instead "select measured air masses that passed within ~100 miles"

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

23763, L20 "pentyl nitrate", which pentyl nitrate?

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

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" ??

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

23768, L6, delete "which are"

23769, L1. I suggest a sentence first describing what you're about to do.

23769, L10. "bold italics" in Table 1 are hard to distinguish and do not appear to be bold.

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

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23771, L4, some example references would be helpful here.

23771, "cannot bring the calculations and observations into complete agreement", suggest "are unlikely to bring..."

23771, L24, citations for Granite Bay and Houston needed.

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"

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

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