

Interactive comment on “Airborne observations of total RONO₂: new constraints on the yield and lifetime of isoprene nitrates” by A. E. Perring et al.

Anonymous Referee #1

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Manuscript Review: ACPD_Perring

This manuscript analyzes measurements of alkyl+multifunctional nitrates from a continental scale research mission, INTEX_NA. The manuscript examines relationships between NMHC, total RONO₂, and formaldehyde to indicate a significant role of organic nitrates in the oxidative chemistry cycle of the lower atmosphere. The manuscript is an interesting analysis of a unique data set and suggests a ubiquitous role for isoprene nitrates throughout the continental boundary layer. I can recommend publication of the manuscript with some modifications. My main recommendation is a more thorough and quantitative treatment of the uncertainties inherent in the analysis, and a clearer treatment of how the data were selected.

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Some more specific comments follow (in somewhat random order):

1) 12318, line 26. I don't recall if the LIF instrument has ever been used to measure isoprene nitrates from chamber studies, but it would be good to reference that if so. It also seems to me that some statement about the response of multifunctional nitrates are equivalent if the thermal degradation characteristics are equivalent (this may not be the case). Also, if the RONO₂ form into a nitrate aerosol phase upon continued oxidation, as has been measured, is the LIF thermal degradation response the same?

2) Methods section: I would like to better understand the uncertainty of the Total AN measurement. There is a lot of scatter in the data that seems to be about +100-150 pptv. Can the authors provide some more quantitative estimate of the uncertainty in the determination, and how it may depend on the magnitude of the NO_y in the other channels? Also, why was it decided to report no ANs from above 4 km?

3) Reference for formaldehyde data? There were 2 measurements of formaldehyde on the aircraft. From the data set, it looks like the URI data are about 35% lower than the NCAR data. Which data set was used? Has there been any resolution to the discrepancy?

4) It is unclear to me how the data were selected into the high isoprene profile. (It is also unclear to me why a vertical profile of these data is relevant, at all.) But if it is, then there should be some clarification how the points are selected. Perhaps a comparison that shows the high isoprene set versus non-high isoprene would be better than high isoprene vs all. Does it make a difference that the isoprene data are collected on a different time base than the CH₂O and AN?

5) The bottom line of the manuscript seems to be that isoprene nitrates are the bulk of the total AN in most of the continental BL (perhaps not in urban centers). If this is the case, then why even make the distinction of 'high isoprene' points vs all points? This distinction disappears in all subsequent analysis (the entire BL data set is used for the analysis).

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6) How does isoprene nitrate formation via NO₃ oxidation factor in to this analysis, if at all? The Horowitz 2007 reference suggests that about 50% of isoprene nitrates may come from this route. Shouldn't this be factored in to the data analysis?

7) Figure 1 shows the relationship on which the estimates are made. I have to wonder about the scatter in this data and what it means to the analysis. I would like to see some error analysis applied to this correlation. Also, what is the relationship of AN to isoprene?

8) Figure 4. While I would not disagree with the conclusion that isoprene nitrates are significant, it seems to me that the role of terpenes is underestimated. There is a high yield of nitrates from terpene oxidation, and only 2 terpenes are reported in the INTEX data. Comparisons of canister data with total terpenes (e.g. from a PTRMS) suggest that the canister data will underestimate total terpenes (esp if not all terpenes are reported). While it may not be possible to quantify the contribution of terpenes, some mention of the uncertainty in this source seems justified.

9) In the calculation of NMHC reactivity and RONO₂ sources, how were the data below detection treated?

10) The lifetime calculation suggests a total oxidative lifetime of about 32 minutes. As noted this depends on the composition of the isoprene nitrates and the individual rates. However, the reaction rate with ozone was suggested by Giacomelli (2005) to be too high in his model, so the true lifetime would more likely be more like the one hour rate from OH oxidation. Also, calculating the total lifetime by using the individual rates reported by Giacomelli results in slightly different lifetimes compared to the weighted average used by the authors. Not sure why this is, but it doesn't make a big difference.

11) Table 1. Patchen et al. 2007 (Int. J. Chem Kinetics) also reported yields of isoprene nitrates (but at reduced pressure). [Direct kinetics study of the product-forming channels of the reaction of isoprene-derived hydroxyperoxy radicals with NO, International Journal of Chemical Kinetics, Volume 39, Issue 6, Date: June 2007, Pages: 353-361]

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12) Can the authors include an analysis of the relationship of IN directly to the precursor, isoprene? I plotted the total AN vs isoprene data and can see something of a relationship between total AN and isoprene, but a large fraction of high AN points at very low levels of isoprene. I could understand the observation of high isoprene and low AN during periods of low photochemical activity, but this doesn't seem to be the case. If lifetimes of AN are really comparable to the parent, then there shouldn't be cases where AN continue to be high when isoprene is low. If the recycling leads to longer lived products measured by the LIF instrument, then the relationship would make more sense. Or, a contrarian view, these high AN are not isoprene nitrates at all. This is just a first impression, and the authors may have considered this in more detail. Some additional comment or analysis of this relationship would be illuminating.

13) Figure 7. Solid line should be labeled 12% BR, 90 min LT (as in caption). Also, shouldn't there be some correction to the yields to account for the fact that really all of the nitrates are not from isoprene?

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