

Interactive comment on “Temporal variability, sources, and sinks of C₁-C₅ alkyl nitrates in Coastal New England” by R. S. Russo et al.

Anonymous Referee #1

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General comments.

The authors present some beautiful alkyl nitrate measurements spanning several years in New Hampshire. They are to be commended for the effort involved in collecting these data.

The paper is well-written and the analysis is interesting. It is appropriate to ACP and should be published after the following (generally minor) revisions are complete.

Specific comments.

The deposition analysis for MeONO₂ assumes a constant concentration with height in the NBL. But on these calm nights while MeONO₂ is depositing there must be a vertical gradient in concentration. How would this calculation depend on the measurement

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height?

Do you see similar behavior indicating dry deposition for the other ANs? Is there any reason to expect MeONO₂ to behave differently than these?

How would these dry deposition losses affect your sequential reaction analysis (Section 5)?

Ocean source/sink analysis (section 4.2). "These results suggest that the New England coastal waters were undersaturated in 2-PrONO₂ and 2-BuONO₂ and that MeONO₂ was near equilibrium with respect to the overlying atmosphere". Why do these results suggest that? To infer that you need to know the sign of the quantity (C_g/H - C_l) [Liss & Slater, 1974]. You have what you need to calculate this and tell us for sure whether the flux is going in or out of the ocean. (Calculating the actual flux is a bit more complicated b/c you need to calculate the transfer resistance). I don't know if H values are known for all the ANs but you could estimate based on MeONO₂.

Abstract is very wordy and I recommend shortening. A point of the abstract is to extract the key elements for those who are scanning (most readers, probably). If it's too verbose you're defeating the purpose.

Introduction. Somewhere, please talk about how the compounds you're measuring compare to the total organic nitrates (i.e., including hydroxy-nitrates and other multifunctional nitrates). Some other groups use the same terminology you're using (sigma(RONO₂)) to refer to the sum of all organic nitrates, not just the C1-C5 alkyl nitrates, and readers may be confused by this.

Sections 2.1-2.3 – many experimental details are given here. In the interest of readability consider just putting the basics here (e.g., in-situ GC-FID-ECD, canisters, etc) and move the nitty gritty details to Supplemental Information for those who are interested.

Section 2.3.2 – were tests done to verify compound stability in the canisters over this long storage time (1-3 months)?

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Section 2.4 – again, consider just stating the key finding ("good agreement") and moving the intercomparison details and figure to supplemental.

Section 3.1 and elsewhere. Laundry lists of numeric values in the text are tiresome. Recommend discussing the implications and interpretation, and refer the reader to the table for the actual numbers and SDs.

p. 23381, L1. From Fig. 4, the MeONO₂ and EtONO₂ seasonality seems to become more pronounced in 2006-7. Is that the case and is it real?

p. 23381, L3. I don't think you've told us yet what the lifetimes are.

p. 23381, L20-end. Differing seasonal lags would be one way to look at causes of seasonality. Do you see any lag between the different RONO₂ compounds reflecting differing photochemical lifetimes? One example of this type of analysis is Goldstein et al., JGR, 100, 21023-21033, 1995.

p. 23383, L18. I believe ozone deposition occurs mainly via stomatal uptake (i.e. controlled by stomatal conductance), and possibly reaction with biogenic hydrocarbons, and not so much by solubility-controlled deposition to surfaces. So this comparison seems inappropriate.

p. 23384. Comment on why the NO_y behavior is so different for the two highlighted nights in Fig 6?

p. 23385. SE's in table 3 for V_d seem small. Are they the standard error for the regression? if so this generally underestimates the true uncertainty. Better to use a bootstrap or jackknife approach.

Table 4. I suggest presenting information in Table 4 in a more communication-friendly plot form. Perhaps a wind-rose plot showing colors for different concentration means?

p. 23388, L18-20. Also depends on differing amounts of the various NMHCs.

p. 23389, L10. What different sources? Please discuss somewhere the differing an-

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thropogenic sources of the NMHC precursors for the nitrates you're looking at.

p. 23391, R7. Assumes dominant fate of RO₂ is reaction with NO, i.e. high-NO_x conditions. Should be mentioned and stated why this is an appropriate assumption.

p. 23394, L1 "significant amount" – give fraction

p.23394, L18-end. This argument doesn't seem to make sense and I recommend deleting the last 4 sentences of the section. The shorter lifetime should already be reflected in lower mean and background concentrations.

A couple other questions about the sequential reaction analysis: Are the denominators (ie. NMHC concentration) always above LOD? How well-defined are the RONO₂ + OH rate constants?

Technical comments.

p. 23377, L25 "an EVACUATED two-liter..."

p. 23387, L17. Which mixing ratios are you referring to? All alkyl nitrates?

p. 2388, L2-3. Rephrase, it's not a new discovery that the industrialized NE is a source of NMHCs.

p. 23388, L13 "their major source" – unclear whether "their" is referring to PrONO₂ and BuONO₂ or to sigma(RONO₂)

p. 23388, L22. "to be undersaturated IN THE SURFACE OCEAN"

Please increase font size on Figures 3-10

Fig 10, symbols and labels are too small and hard to see.

Fig 10, color schemes seem unnecessarily complicated and confusing. Why not have just three colored lines which are the same in every panel and for both the abscissa and ordinate: RONO₂/RH = 0, seasonal background, and seasonal mean.

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