Atmos. Chem. Phys. Discuss., 13, C2788–C2809, 2013
www.atmos-chem-phys-discuss.net/13/C2788/2013/

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011" *by* J. L. Fry et al.

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Received and published: 25 May 2013

article

Response to reviewer comments on:“Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011"

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25 May 2013

We wish to extend our sincere thanks to the reviewers for the time spent evaluating this manuscript. Thank you for the helpful comments, which we have carefully considered and respond to individually below.

1 Responses to reviewer 1

1.1 Reviewer 1 General comments

This paper reports on organic nitrate measurements in the gas and aerosol phases as part of a summer time study of BVOC photochemistry in a forest site in the Colorado front range. Organic nitrates in the aerosol phase were measured by both the denuder-TD-LIF method, and by AMS, and the two agreed quite well, which is a strength of the paper. The major conclusions of the paper are that nighttime NO3-monoterpene chemistry is a major source of organic nitrate production, and that 6-20% of the organic aerosol mass is organic nitrate. This is high quality data, and one of few such quantitative studies of the organic nitrate production and distribution in both phases. The paper is quite timely given recent studies suggesting the importance of nighttime chemistry in SOA production. The paper is generally well-written. I think it should be published after attention to mostly minor technical issues, which I raise below in the order they appear in the manuscript. However, as discussed below as well, I am concerned about the conclusion that nighttime chemistry is more important than daytime chemistry in producing organic nitrates, because of the value for the effective branching ratio of 2.9%, which quantitatively ties to their conclusions. I think that there is a contradiction in the paper that states that the dominant daytime sinks for OH are MBO and monoterpenes, and yet the average branching ratio is presented to be 2.9%. For MBO, one might reasonably estimate the branching ratio to be 6%, and at least twice that for MTs. Therefore, it does seem likely that there are substantial losses of ANs in the daytime, and the paper should discuss this apparent contradiction, and how the uncertainty in the apparent branching ratio affects their conclusions.

1.1.1 Response to general comments

Both reviewers had the most questions/concerns about the daytime $RO_2 + NO -> RONO_2$ yield determination from comparison of O3 production and alkyl nitrates. It is true that this determination has several caveats that produce uncertainty in the derived 2.9% yield. I have added text to expand on these caveats as described in responses below, and answered specific questions. We stand behind the notion that this analysis is appropriate for this site (explained in responses below), and the field-derived RONO2 yield is therefore an interesting comparison point to previous estimates based on chamber studies. However, since both daytime and nighttime organic nitrate production values are likely underestimates, the uncertainty in the comparison between the two production rates should be noted, and we've reworded to emphasize that the magnitudes are comparable, rather than than nighttime rates exceed daytime.

The fact that we observe a net 2.9% yield of organonitrates, when the dominant measured VOC, MBO, has organic nitrate yield via RO2 + NO after OH oxidation reported in other studies to be about 7% suggests that other (unmeasured) molecules with lower organonitrate yields are contributing to OH loss.

We have added a 2nd calculated daytime organic nitrate production rate to Figure 12 using literature values for the MT and MBO nitrate branching ratios and have added discussion of how a nitrate yield in this range would affect the conclusions about nighttime vs. daytime production of organic nitrates. (Note: in response to Reviewer 1's specific point about yields for monoterpenes possibly being much larger: this new comparison explicitly includes both MBO and MT, but MBO is dominant during the daytime)

1.2 Reviewer 1 Comment #1

Page 8, line 9, you mean NO2 + ANs + PANs?

1.2.1 Response #1-1

No, because the ambient temperature NO2 channel is subtracted from each of these. Added a parenthetical clause stating this.

1.3 Reviewer 1 Comment #2

Page 9, line 3 - You mean limit of detection, not sensitivity.

1.3.1 Response #1-2

Substituted “limit of detection" for “sensitivity".

1.4 Reviewer 1 Comment #3

Page 9, line 10 - how do you determine the filter transmission efficiency for NO3 and N2O5? What is it, and how reproducible is it? Line 12 - this value 12% for both compounds implies that filter losses are either zero, or identical in magnitude and variability, for both NO3 and N2O5. This seems unlikely, and should be discussed in more detail.

1.4.1 Response #1-3

The value of 12% uncertainty was to simplify; they are, in fact, slightly different for the 2 channels, and we have updated the text to state these separate uncertainties instead. They arise from different sources of uncertainty, including absorption cross sections, conversion efficiencies, and filter transmission. For example, the NO3 transmission efficiency is 92% compared to 97% for N2O5. The details are provided in the Fuchs

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paper cited at the end of that paragraph.

1.5 Reviewer 1 Comment #4

Lines 15-18: I don't understand comparing the LIF NO2 with the NOx box "NO2", since the NOx box measures some fraction of NOz along with NO2, and so, should not agree at all with the LIF NO2, unless NOx/NOy is very close to 1. This sentence just raises flags to most readers, and you might just want to remove it, or clarify what is really being measured. Why use the NOx box "NO2" in Figure 4 when you have the LIF data? Or do you?

1.5.1 Response #1-4

We used the NOx box rather than TD-LIF NO2 because we have a complete time series of NOx box measured NO2, while the TD-LIF was used for other non-ambient measurements for substantial periods. I've added some text to clarify this to lines 15-18, stating that the TDLIF only has 14 days of ambient data (during which the instruments fell within 8% of each other), while the NOx box has 32 days of data. The figure below, of TD-LIF measured NO2 total NO2 +PNs + ANs vs. NOx box (1 min data) for the 14 days of overlapping measurements, shows that NO2 is a large fraction of (NOz,meas) for most measurements, so this is why this works OK for this site.

1.6 Reviewer 1 Comment #5

Page 10, line 4 - "used as a measure...".

1.6.1 Response #1-5

Thanks!

1.7 Reviewer 1 Comment #6

Page 11, lines 14 and 15 - 30% accuracy for what specific determination?

1.7.1 Response #1-6

The 30% figure refers to the overall calibration error for ammonium nitrate particles and uncertainties in the collection efficiency. So strictly speaking it is relevant to all routinely reported AMS species (ie Org, nitrate, sulfate, ammonium and chloride) where the relative ionization efficiencies are well characterized and or calibrated (for sulfate and ammonium). Text changed to read “is 30% for all AMS species, with better accuracy for ratios due to error cancellation."

1.8 Reviewer 1 Comment #7

Bottom of page 12 - what fraction of the mass is effectively solid? Since this model assumes mixing through the organic phase of the particle, this should at least be stated.

1.8.1 Response #1-7

We have just made the simplified assumption of no solid phase. Added a phrase to the line introducing the partitioning formalism stating this.

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1.9 Reviewer 1 Comment #8

Page 14, line 9 - do you know what fraction is isoprene? Are there any GC measurements?

1.9.1 Response #1-8

Not at this time, but based on a previous work (Kim 2012) we assume the PTR-MS derived “isoprene+MBO" is primarily MBO.

1.10 Reviewer 1 Comment #9

Line 23 - do you mean mobile sources? Saying that might be better than "burning related sources".

1.10.1 Response #1-9

Not necessarily - changed to “fossil fuel and combustion sources" to make the anthropogenic source clearer.

1.11 Reviewer 1 Comment #10

Page 15, line 14 - note that often SO2 peaks do not appear with NOx peaks or the Anth. tracer peaks.

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1.11.1 Response #1-10

Added the sentence: “Also note that SO_2 peaks are often not coincident with NO_2 or Denver/Colorado Springs anthropogenic tracer peaks, suggesting distinct sources. "

1.12 Reviewer 1 Comment #11

Page 16 lines 10-14 - this is an awkward sentence that could be improved.

1.12.1 Response #1-11

Edited to “This makes it far more likely that observed sharp increases in NO_2 arrive with this advected plume, rather than resulting from local soil NO_x production: a buildup of soil NO_x would be diluted out by this drainage flow and cause *decreasing* NO_x."

1.13 Reviewer 1 Comment #12

Line 27 - "though the local winds...".

1.13.1 Response #1-12

Thanks!

1.14 Reviewer 1 Comment #13

Page 17, line 21 - couldn’t the air aloft be more aged? Could you have some production aloft by NO3 + BVOC, but more loss of the products by dry deposition at the surface at

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night?

1.14.1 Response #1-13

Since most of the time the aging increase corresponds roughly to the actual time elapsed, we think this renders the "downward mixing of more aged air" explanation unlikely. This certainly doesn't rule it out, but our sense is that it would be unlikely for more aged air aloft + deposition at the surface to balance to coincidentally work out to be exactly the same timescale. We also note, however, that on those some occasions when the photochemical age measure increases more rapidly, it is likely due to exactly what you describe. I've tried to reword these sentences to clarify this.

1.15 Reviewer 1 Comment #14

Equation 4 - again, you should note that it is possible that the lifetime of some of the MT-nitrates could be fairly short, and losses could be important.

1.15.1 Response #1-14

We think these deposition lifetimes are of order several hours, and therefore not likely to influence the results dramatically. However, we acknowledge that this is not included in our estimate, so have added to the end of the paragraph after this equation: “A further assumption is that ΣANs losses are small on the six-hour timescale of the correlation plot. This latter assumption introduces some uncertainty to this estimate: especially if monoterpene nitrate products are multi-functional, losses could be substantial and depress the apparent yield."

1.16 Reviewer 1 Comment #15

Page 19, line 19 - but you have calculated F sub N, as discussed on page 30, so, you have a good handle on it. A simple box model run would answer some of these questions. Perhaps it is beyond the scope of this paper, but it would be interesting and useful to produce a simulated plot of O3 vs ANs.

1.16.1 Response #1-15

Agreed on both counts - this would be an interesting follow-up but is beyond the scope of this paper.

1.17 Reviewer 1 Comment #16&17

Page 20, line 13 - "due to high levels...". Page 23, line 12 - overestimates?

1.17.1 Response #1-16&17

Thanks!

1.18 Reviewer 1 Comment #18

Page 24, line 13 - explain that that compound is produced from oxidation of glycolaldehye.

1.18.1 Response #1-18

Done

1.19 Reviewer 1 Comment #19

Line 20 - they are not completely distinct!

1.19.1 Response #1-19

Changed to "predicted to include distinct structures,"

1.20 Reviewer 1 Comment #20

Page 24, line 24 - is it a null hypothesis?

1.20.1 Response #1-20

I called it “null" since what we show is that this explanation is insufficient to explain the variation we see. But I don’t think naming it thus clarifies anything, so I just removed “null hypothesis".

1.21 Reviewer 1 Comment #21

Page 25, line 6 - do you think you should be accounting for condensed phase hydrolysis of the ANs? At least the discussion should mention this possibility. The discussion at the bottom of the page should also mention the possibility of condensed phase chemistry of the nitrates.

1.21.1 Response #1-21

Added text at bottom of page: “After condensation, these organic nitrates may also continue to evolve via condensed-phase reactions, resulting in a different aerosol composition than dictated by the initial condensing species. Such potential continuing transformations are not treated in this simple thermodynamic model."

1.22 Reviewer 1 Comment #22

Page 29, line 4 - "markedly good agreement" is subjective, and not necessary - the plot speaks for itself.

1.22.1 Response #1-22

edited to omit subjective statement.

1.23 Reviewer 1 Comment #23

Page 30, line 6 - you should note that if you used an estimate of the branching ratio based on measurements for these or structurally similar compounds, you would get a quite different result.

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1.23.1 Response #1-23

Added another daytime organonitrate source estimate based on literature MBO yield of 7% and MT of 23% to show this comparison directly in Figure 12, and added discussion in text.

1.24 Reviewer 1 Comment #24

Page 32, line 21 - but you should again note that you are comparing concentrations in a very shallow surface layer at night with a likely considerably deeper layer during daytime, so the total boundary layer integrated mass amounts might be closer?

1.24.1 Response #1-24

Added “total mass" to the discussion of this boundary layer issue - I think this paragraph addresses the reviewer concern by explicitly citing the boundary layer heights from radiosonde measurements and stating that the total daytime integral is likely to be higher unless NOx and BVOC are diminished above the NBL.

1.25 Reviewer 1 Comment #25

Figure 5 - do you understand why the early morning rise of ANs is very fast, but slows very considerable by 8-9am.

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1.25.1 Response #1-25

One can see in Figure 3 that ozone also rises rapidly during this period, so I would guess the same pattern would be found in OH concentrations - perhaps due to the local topography and tree cover, photochemistry “turns on" quite rapidly at this site.

1.26 Reviewer 1 Comment #26

The inset in the bottom panel of figure 7 is too small to be readable; can you make a separate plot?

1.26.1 Response #1-26

Done.

1.27 Reviewer 1 Comment #27

Figure 8: identify the blue and orange boxes in the figure caption.

1.27.1 Response #1-27

Added color labels to caption.

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2 Responses to reviewer 2

2.1 Reviewer 2 Comment #1

Justification that requirements for relating ANs to O3 are satisfied?

2.1.1 Response #2-1

Please see “Response to general comments" above, and response #2-3 below.

2.2 Reviewer 2 Comment #2

Evolving plume means that the organic nitrate/Ox correlation isn’t necessarily reflective of the local VOCs because OH might be much lower at the site than upstream in the city. Much like the ratio reported in previous publications about Blodgett is low even though the local source molecules should have high nitrate yields.

2.2.1 Response #2-2

We find evidence that the observed morning increase in alkyl nitrates is local photochemistry and not transport, described in section 3.1.3., and given the site’s location and distance from urban sources, we believe the dominant morning OH chemistry to be reaction with MBO (and its products) and not upwind VOCs.

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2.3 Reviewer 2 Comment #3

Along similar lines, on p1997, line 14-15: couldn't this 2.9% apparent yield also be seen if a) the upwind source molecules had low nitrate yields b) there was loss of ANs during transport or c) there was a lot of secondary Ox producers with organic nitrate yields of 0 (i.e. CO and CH2O). For point b, you say that you have chosen the time of day to minimize this but it still could be a significant effect on this slope. Is there any way to look at the relative abundances of transported vs locally produced nitrates? For point c, you have measurements for CO and CH2O right? Can you calculate the OH reactivity to them as compared to MBO and monoterpenes to determine how much of the local Ox production is even expected have an alternative nitrate channel? I think you need to either expand this section to attempt to quantify how much of this 2.9% is driven by local chemistry vs. transport from Denver or abbreviate this section and say simply that this relationship indicates that local daytime production of organic nitrates is small. The latter option may require significant changes elsewhere but as written this treatment is oversimplified and the main interesting results are really driven by the nighttime chemistry so it might be worthwhile to refocus a bit.

2.3.1 Response #2-3

We believe we are mostly sampling local photochemical production of RONO2 from RO2+NO from the dominant local forest "R" of MBO. This is based on (1) the light and variable daytime winds (Fig. 3, typical wind speeds of 3 m/s (6 mph or 11 kph)), (2) our distance into the forest and the spatial expanse around the site with similar BVOC emissions (Fig. 2), such that most transport to the site would contain similar VOC mix. Of course we cannot completely rule out any transport contribution, both in terms of altering the BVOC mix and potentially incorporating losses of ANs. I've added some text to alert readers to this caveat. To address your point c: I calculated the lifetime of OH with MBO (3 ppb), CO (100 ppb) and CH2O (1 ppb) at the measured representative concentrations at BEACHON shown in the parentheses, using IUPAC rate constants. tau = 1/k[MBO] = 0.2 s, while tau = 1/k[CO] = 4.0 s and tau = 1/k[HCHO]= 4.7 s, so much of the daytime reactivity of OH will go via MBO. Of course, since so much initial reaction goes to MBO, its products will also be abundant at this site. OH reaction with first generation oxidation products of MBO might be an OH sink with lower organonitrate yield than MBO itself.

2.4 Reviewer 2 Comment #4

Section 3.4, similar issues to those outlined above. By assuming that the 2.9% number is reflective of local organic nitrate formation you may be underestimating local nitrate production. If you calculated an expected branching ratio, how different would it be from 2.9%?

2.4.1 Response #2-4

Using our measured VOC mix, most reactivity during the day goes to MBO, so the expected branching ratio would be $\approx$ 7%. I've added a piece to the conclusion comparing daytime and nighttime nitrate production using one of those chamber results rather than our field result, to assess how different the overall conclusion would be with someone else's measurement of (MBO-only) nitrate yield, and discussed the fact that our lower yield is likely evidence of the presence of other “R" with zero or lower organonitrate yields.

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2.5 Reviewer 2 Comment #5

P2009, probably should at least mention the range of organic nitrate yields reported for monoterpenes other than b-pinene. If there is a reason to expect that most of the MT is b-pinene state that as well. At the bottom of the page you state that both production rates are likely underestimates but I don't think that's warranted for the nighttime given the range of possible NO3 product yields you could have chosen or for the daytime given that you have assumed 2.9% to be reflective of local production based on a correlation with Ox that is not proven to be reflective of local chemistry.

2.5.1 Response #2-5

Added a reference and listed some organic nitrate yields from NO3 + BVOC for other monoterpenes on p. 2009. I still believe that on the balance we're likely underestimating both daytime and nighttime nitrate production, for the reasons stated in the paragraphs at the top of p. 2010. I agree with you that given the uncertainties, the quantitative comparison of daytime and nighttime production of organic nitrates is uncertain. I've added some text to hedge on that direct comparison a bit, by including discussion of what this would look like if we used a daytime RO2+NO organic nitrate yield from the chamber studies rather than our in situ data.

2.6 Reviewer 2 Comment #6

P2010, isn't your assertion that losses will be worse for daytime RONO2 in direct contrast to your earlier finding that nighttime RONO2 must be more highly functionalized than expected for 1st generation products.

2.6.1 Response #2-6

Daytime organonitrates derived from methyl butenol will be already triply functionalized at the first generation of OH oxidation, and have only a 5-carbon backbone, while nighttime monoterpene nitrates will have 2 oxidized functional groups initially on a C10 backbone. So, MBO nitrates will have a larger oxidized group to carbon ratio, which I'm assuming is related to deposition rates. Of course, we speculate that these molecules must be oxidized further, and it's unclear how many generations of oxidation must elapse before their hydroscopicity will overtake MBO nitrates.

2.7 Reviewer 2 Comment #7

Figure 6: this doesn't really look like a very convincing correlation. Can you give confidence limits? Also, could you use the larger PNs+ANs dataset for this correlation assuming some baseline PNs or a max value given the (likely hot) local temperature?

2.7.1 Response #2-7

Unfortunately, we can't really assume PNs are negligible - it actually wasn't all that hot, and we observe them to also have an appreciable diurnal cycle (Fig. 5). So we're stuck with this data set. I re-did the regression calculation and put the confidence limits on the plot to help. In the process I discovered an error in the confidence limits reported in the paper and updated it.

2.8 Reviewer 2 Minor comments

More minor comments include: 1. p1981, line 20: Nitrogen oxides don’t really control the branching ratios of products. Suggest replacing branching ratios and say instead that they “control the relative abundance of oxidized VOC’s such as: : :” 2. p1982, line 2: unclear what you mean by the “RO and RONO2 channel”. RO can be produced in both the nitrate and non-nitrate channel. Suggest omitting the RO. 3. p1983, line 10: does the TD-LIF technique really measure NOy? Seems like you are missing an NO measurement? Also, for similar reasons, you probably shouldn’t refer to the Berkeley TD-LIF NOy instrument. Berkeley TD-LIF should be sufficient. 4. P1998, line 13: “detectable due high levels”!”detectable due to high levels” 5. P2000, line 10-11: Sentence that starts “For the average: : :” is incomplete 6. P2001, line 12: the model overestimates NO3 not underestimates correct? If the observed is 5ppt and modeled is 18ppt as stated. 7. P2002, line 9: change “observed” to “predicted” or “modeled” unless these were actually observed by the PTRMS 8. P2004: seems like the short section on this page should be either 3.2.3 b or 3.2.4 but not 3.2.4 b. Also it seems like maybe this paragraph is more related to 3.2.2? 9. Figure 7: It is hard to see the difference between the blue and aqua. Also the inset as shown is too small to be informative.

2.8.1 Response #2-minors

1. Reworded. 2. Reworded. 3. True, we are not measuring *all* NO_y species. Reworded. 4. Fixed- thanks! 5. Reworded. 6. Yes, thank you. Fixed. 7. Substituted “predicted" 8. Changed section headers to omit a/b 9. Expanded the inset, this will also help the blue/aqua distinction, which is only relevant during that two-day period.

Thank you!

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NO2TDLIF-NOx-compare.pdf

Fig. 1. TD-LIF measured NOy vs NO2, both correlated against NOx box measured NO2.

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