

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

Anonymous Referee #1

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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 con-

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cerned 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. Other issues are as follows:

1. Page 8, line 9, you mean NO₂ + ANs + PANs?
2. Page 9, line 3 - You mean limit of detection, not sensitivity.
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.
4. Lines 15-18: I don't understand comparing the LIF NO₂ with the NO_x box "NO₂", since the NO_x box measures some fraction of NO_z along with NO₂, and so, should not agree at all with the LIF NO₂, unless NO_x/NO_y 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 NO_x box "NO₂" in Figure 4 when you have the LIF data? Or do you?
5. Page 10, line 4 - "used as a measure...".
6. Page 11, lines 14 and 15 - 30% accuracy for what specific determination?
7. Bottom of page 12 - what fraction of the mass is effectively solid? Since this model

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assumes mixing through the organic phase of the particle, this should at least be stated.

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

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

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

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

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

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 night?

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.

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.

16. Page 20, line 13 - "due to high levels...".

17. Page 23, line 12 - overestimates?

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

19. Line 20 - they are not completely distinct!

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

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.

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

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.

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?

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

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

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

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 1979, 2013.

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