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

Anonymous Referee #2

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This paper describes measurements of gas and aerosol-phase nitrate species during the BEACHON campaign of 2011. The authors find a low average alkyl nitrate yield during the daytime and a peak in aerosol organic nitrate at night. They use a simple partitioning model to show that thermodynamic partitioning cannot fully explain the relationship between aerosol and gas-phase nitrates and infer that nighttime nitrates (resulting from interactions between NO3 and monoterpenes) must have an increased number of functional groups as compared to the daytime nitrates.

This paper is generally well written and certainly of interest to the readership of ACP and should be published after the authors consider the following comments:

1. Justification that requirements for relating ANs to O3 are satisfied? 2. Evolving plume means that the organic nitrate/Ox correlation isn't necessarily reflective of the

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Interactive Discussion

Discussion Paper

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. 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. 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%? 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. 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. 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?

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.

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