

## ***Interactive comment on “Importance of biogenic precursors to the budget of organic nitrates during BEARPEX 2009: observations of multifunctional organic nitrates by CIMS and TD-LIF” by M. R. Beaver et al.***

**Anonymous Referee #1**

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This paper reports on measurements of total organic nitrates in a California forest environment, and the role of BVOC chemistry in the production of nitrates likely contributing to that signal. The paper shows that, for this environment, the biogenically-derived nitrates are the major part of the signal, and that of that part, the isoprene nitrates are dominant. This helps answer a major question that was effectively raised by the TD-LIF data from the Berkeley group, showing that organic nitrates can be a significant fraction of odd-nitrogen, and raises questions about the fate of these species, and their atmospheric lifetime, transport, and re-conversion to NO<sub>x</sub>. This paper is well-written,

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and important, and derives from many years of instrument development to enable reliable measurements, and I think should be published after attention to a few, mostly analytical chemistry, details. Because of the difficulty of the measurements, I consider this paper a very significant achievement. A major appeal of the paper, to me, is that it is focused, and succinctly presented. My major concerns are about attribution of MS signals, and uncertainties. For the CIMS instrument, the references cited, and papers cited in those references, indicate that CF<sub>3</sub>O<sup>-</sup> reacts with a wide variety of species, and thus there are potentially a range of interferences. While the uncertainty estimate of +/-40% is reasonable if you know the signal is entirely from a nitrate, the <sup>13</sup>C discussion on page 328 articulates one example case of why this may not be correct. The paper basically indicates that the selectivity in this method derives from the (fact) that organic nitrates are the only species that react with CF<sub>3</sub>O<sup>-</sup> and are odd mass, and thus the only ones that produce adducts with even mass. This requires more discussion. For example, while the literature does imply that this reagent reacts mostly with acidic species, if it is known that it does not react with organic amines, this should be stated. And, if it is believed that there are no other possibilities, this should be stated, ideally with references. Furthermore, the paper should not refer to species as identified, but rather that the identity for any particular m/z is assumed. Just because these masses are observed in laboratory experiments does not mean that the only possible source of the signal at a particular m/z is as you have assumed, right? For example, on page 329, line 15 should say “. . . is assumed to be a sum of these species.” On page 329 line 6 it is stated that the uncertainty for total ANs via the TDLIF method is +/-5%. This is a very impressive number indeed, for measurement of just about any atmospheric species. But in this case, the analytes are adsorptive, and are determined from an essentially doubly indirect method, i.e. from the thermal conversion to NO<sub>2</sub>, and from the difference in signal between two channels. How is this 5% value obtained? In principle, it should be obtained by error propagation based on calibrations from standard addition of actual BVOC nitrates to ambient air. And, is it independent of concentration? Is it independent of the PAN channel concentration and difference between the signals in

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the two channels? This would seem unlikely, and so I think a little more discussion of how uncertainties are derived would be appropriate. More minor issues are listed below, in the order they appear in the manuscript.

1. Page 322, line 14 should probably say "...the lifetime and yields..."
2. Middle paragraph, page 328 - explain how you determine the number of C's in the molecule producing the (m/z - 1) signal, since you don't know what it is.
3. Page 331, line 26 - why not calculate a rate of oxidation-weighted average alpha, given the average BVOC concentration? Or is that how you got 0.15? Specify.
4. Page 333 - I think "alkane nitrates" should be replaced with "alkyl nitrates" throughout.
5. Page 334 - Note that at the end of the day in forest environments (or under cloudy and stable conditions), the BVOC concentrations can be large especially when mixing becomes poor; at such times in the daytime NO<sub>3</sub> reaction with BVOCs can be a significant loss process for NO<sub>3</sub>.
6. Table 1 - Is alpha really 0.0 for MACR?
7. Figure 2 - Can you include a panel for the sum of the CIMS nitrates, to compare with the bottom panel for TDLIF? The existing bottom panel y-axis should start at zero, for ease of comparison with the other panels that do start at zero.

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