

We thank Referee #1 for the careful reading and helpful review of the manuscript. We have provided responses to each comment below. Review comments are in italics.

General comment #1: 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 CF₃O⁻ 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 13C 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 CF₃O⁻ 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."

In general, the CF₃O⁻ chemistry has been found selective to acidic and multifunctional oxidized organic species. From ambient sampling, we are not aware of any signals attributable to amines, though we have not performed experiments or calculations targeting this class of compounds. A sentence stating more clearly the classes of molecules this chemistry is sensitive to has been added to the experimental section: "In general, this ionization chemistry has been found to be selective for acidic species, peroxides, and multifunctional (hydroxy- and nitrooxy-) molecules (Crouse et al., 2006)." Since the mass spectrometer used here does not have the mass resolution which would enable elemental composition determinations, we have relied on controlled laboratory experiments along with what is known about the measurement site to inform our identifications. To address the reviewer's concern there could be other sources of signal at the m/z analyzed, qualifications about assumed vs identified have been added throughout the text.

General comment #2: 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 NO₂, 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 the two channels? This would seem unlikely, and so I think a little more discussion of how uncertainties are derived would be appropriate.

We thank the reviewer for bringing this to our attention. The 5% number quoted in the text refers to the accuracy of NO₂ detection and we mistakenly neglected to comment on the additional sources of uncertainty for AN detection. We have consistently estimated the total uncertainty in ANs to be 15%, acknowledging the possibility of losses in sampling or other unknown chemical

effects in the conversion to NO₂. We note that additional systematic (as opposed to precision) uncertainty from the subtraction of two channels is of order 1-2%. We have changed the text to the following:

“The sum of total alkyl nitrates, ΣANs, measurement was made by the University of California Berkeley using a thermal dissociation laser induced fluorescence, TD-LIF, instrument similar to that of Day et al. (2002). Briefly, the instrument measures NO₂ by LIF, and thermally dissociates most other constituents of NO_y into NO₂ then measures their contribution by the difference between channels. Specifically, in this instrument ΣANs characteristically dissociate into NO₂ and a companion radical completely at temperatures greater than or equal to 380°C. The difference in the NO₂ signal between ambient air passing through the 380°C oven (ΣANs + ΣPNs + NO₂) and the 200°C oven (ΣPNs + NO₂) is attributed to ΣANs. Measurements in the lab and under field conditions show that HNO₃ is not detected in the □AN channel. The instrument is routinely calibrated using an NO₂ gas standard (4.9 ± 0.2 ppm NO₂ in N₂, Praxair), diluted with zero air, and added to the system at the inlet tip. The accuracy of the NO₂ detection is ±5% due to the uncertainty in the concentration of the diluted calibration standard. The accuracy for the ΣANs measurement also includes terms for the completeness of thermal dissociation and the transmission efficiency through the inlet and is estimated following Day et al. (2002) to be 15%. Measurement comparisons between PTR-MS and TD-LIF of an isoprene nitrate standard show the techniques to be consistent to within 10% (Perring et al., 2009b) and similar accuracy is reported for ΣPNs when compared to various instruments (Wooldridge et al., 2010). The minimum detectable ΣANs signal depends on the concentration of the adjacent channel (NO₂ + ΣPNs) and the associated uncertainties of both channels and is estimated as 63 ppt at 1 ppb of NO₂ + ΣPNs and 20 ppt for 100 ppt of NO₂ + ΣPNs at S/N = 2 on an averaging time of 10 seconds (Day et al., 2002). The TD-LIF ΣANs measurement includes molecules in both the gas and aerosol phase. The sampling frequency for each class of measured NO_y species is 5 Hz and the heated inlets for this instrument were also located on the top level of the North measurement tower.”

Specific comment #1: Page 322, line 14 should probably say “... the lifetime and yields ...”

‘yields’ has been added to this sentence.

Specific comment #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.

One does need to know or assume something about the molecular formula responsible for the interference signal at m/z -1. The only signal discussed here where this correction was applied is affected by the isotopologues of a known, C₅, species (propanone nitrate signal affected by isoprene hydroxyhydroperoxide + isoprene dihydroxyepoxide). For the other even masses, the isotopologues of the m/z-1 signals are too small to contribute to the nitrogen signals.

Specific comment #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.

We believe that this comment (and the similar comment of reviewer 2) results from confusion about what we wrote. For the compounds listed in Table 1, we did use the compound specific

alphas. The 0.15 refers to the formation of nitrates (whether dinitrates or nitrate-retaining products) from the alkyl nitrates. Here, we have assumed an alpha of 0.15 to reflect a mixture of ISOPN and other alkyl nitrates. Our calculation of the AN distribution is not very sensitive to this assumption. Given the confusion, we have amended the text as follows: “The value of alpha for alkyl nitrates (to account for the formation of dinitrates or nitrate retaining oxidation products) is dependent on the distribution of the specific alkyl nitrates present. Here, we have assumed an alpha of 0.15 to reflect a mixture of ISOPN and other alkyl nitrates. Our calculation of the AN distribution is not very sensitive to this assumption.”

Specific comment #4: Page 333 - I think “alkane nitrates” should be replaced with “alkyl nitrates” throughout.

We have changed “alkane nitrates” to “alkyl nitrates” throughout this paragraph.

Specific comment #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 NO₃ reaction with BVOCs can be a significant loss process for NO₃.

The following sentence has been added to the text: “Near the end of the day, as well as during cloudy and stable conditions, reactions with BVOCs and other hydrocarbons can be a significant loss for nitrate radicals (Geyer et al., 2003).”

Specific comment #6: Table 1 - Is alpha really 0.0 for MACR?

We have altered our formulation described in Equation 1 (to include a fraction of peroxy radicals expected to react with NO) to address this point. Crouse et al. (2012) has recently shown the yield of nitrates following addition of OH to MACR is, as expected, about 6%. Because there are two channels in the OH chemistry, the effective yield from reaction of OH with MACR is only ~50% of this value (e.g. 3%). However, Crouse et al. show that for atmospheric conditions like those at BEARPEX ([NO]<1ppb), essentially none of the peroxy radicals formed following addition of OH will react with NO due to fast peroxy radical isomerization reaction. Thus, we expect that the production rate nitrates from MACR will be essentially zero. A citation to the Crouse et al. (2012) paper has been added to the Table 1.

Specific comment #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.

The time series and diurnal average for the CIMS nitrates (grey) have been added on the same panel as the UCB ΣANs (black). The y-axis on the bottom panel has been changed to also start at zero.

We thank Referee #2 for the careful reading and helpful review of the manuscript. We have provided responses to each comment below. Review comments are in italics.

Comment #1: There are several places in the paper, which refer to the CIMS measuring speciated AN. (e.g. page 329, lines 12-15). Whilst the m/z ratios measured for some species can be reasonably assigned to some specific compounds, some can only be assigned to groups (e.g. the sum of hydroxynitrates isomers (ISOPN) and the sum of MVKN and MACRN). I think this needs to be made much clearer upfront and the text modified so as not to be misleading.

It is certainly true that we are not able to identify the specific isomers and so we have added a sentence to the experimental section to address this concern: “Since this technique provides no prior separation step, no isomeric information is determined, and measurements are reported as the sum of the possible isomers (geometric or structural).” However, based on controlled laboratory experiments along with what is known about the measurement site to inform our identifications, we believe we have identified the classes of compounds that give rise to the signals identified. Thus, we have continued to use “speciated”, since we do believe we have assigned molecules (if not specific isomers) responsible for the sum of alkyl nitrates at this site.

Comment #2: What is the impact of the uncertainty in the CIMS data of 40% on the conclusions?

The CIMS uncertainty is primarily the result of the use of calculations to predict sensitivity factors for calibration. These errors can be of either sign, as the dipole moments of the various compounds that give rise to the signals may be either higher or lower than estimated. Thus, given that there are many compounds that contribute significantly to the total nitrate signal it is not necessarily surprising that the mass balance works out as well as it appears to. We believe that the +/-40% uncertainty for an individual class of compounds is not unreasonable.

Comment #3: There should be some discussion in section 3.2 of the effect on the budget calculation of only including the VOCs measured at the site.

The following sentence has been added to the section to highlight the limits of using local VOC measurements: “This type of analysis is limited by using only the VOC measurements at the site. It is possible either these VOC measurements are missing a VOC which is a large local source of nitrates or a VOC that is a large nitrate source upwind is no longer present in the air mass once it reaches the forest and is measured.”

Comment #4: p. 328, l. 1. Need a reference or more details of what is B3LYP/6-31G9(d) level of theory.

We have repeated the Garden et al. (2009) citation here as well. This paper investigated dipole moment calculations using a range of basis sets.

Comment #5: p. 330. The discussion in which the measurements of isoprene nitrates are compared to previous measurements is a bit misleading, since only a limited number of ISOPN

were measured before and thus to compare concentrations with total ISOPN is not comparing like with like.

We retain this discussion as we feel it is relevant to highlight how limited measurements of isoprene hydroxynitrates are. However, we do acknowledge the reviewers point and have added the following to the last sentence of this paragraph: “Our measurements are generally much higher than observed at either the Michigan or Tennessee sites, which can likely be explained by differences in location, season, oxidative environment, and measurement methods (individual isomers vs. the sum of the isomers).”

Comment #6: p. 331. l. 26-27. This sentence about assuming an alpha value of 0.15 is confusing. What exactly was this alpha value assumed? From Table 1, can the reader take this to be for the formation of secondary AN from primary AN?

We believe that this comment (and the similar comment of reviewer 1) results from confusion about what we wrote. For the compounds listed in Table 1, we did use the compound specific alphas. The 0.15 refers to the formation of nitrates (whether dinitrates or nitrate-retaining products) from the alkyl nitrates. Here, we have assumed an alpha of 0.15 to reflect a mixture of ISOPN and other alkyl nitrates. Our calculation of the AN distribution is not very sensitive to this assumption. Given the confusion, we have amended the text as follows: “The value of alpha for alkyl nitrates (to account for the formation of dinitrates or nitrate retaining oxidation products) is dependent on the distribution of the specific alkyl nitrates present. Here, we have assumed an alpha of 0.15 to reflect a mixture of ISOPN and other alkyl nitrates. Our calculation of the AN distribution is not very sensitive to this assumption.”

Comment #7: p. 332. L. 4. Where does this value of 41% come from. Table 1 gives a value of 36% for isoprene.

This was a typo. The table lists 36% for isoprene, not 41%. We have corrected this.

Comment #8: p. 334, l. 18. The fact that monoterpene emissions are temperature dependent means that they “can” be emitted at night (not “are”).

This sentence has been changed to read: “These monoterpenes are generally modeled as temperature dependent emissions, and can be emitted at night when NO₃ chemistry is important”.

Comment #9: p. 334, l. 26. Suggest this sentence is part of the previous paragraph and the new paragraph is started by the next sentence.

We have merged these two paragraphs.

Comment #10: p. 335, l. 15. Please provide a reference/comment as to why the CIMS only measures the gas phase.

Past ambient measurements using the CIT CIMS instruments suggest that the residence time and temperatures in the inlet are not conducive to the evaporation of condensed phase species. Particles which stick to the walls of the instrument likely just add to the frequently determined background signals (where we use a denuder to remove compounds from ambient air). As an example, during flights through biomass burning plumes (during MILAGRO and ARCTAS) the CIMS measures little nitric acid, despite high ammonia and aerosol nitrate signals (i.e. no evaporation of the nitrate aerosol). [Crouse, J.D., personal communication].

Comment #11: Table 2. and Figures 3 and 4. Figure 3 captions refers to Table 2 for the organic nitrate species observed by the CIMS and yet that table only gives m/z, with no explanation. Only becomes clear later in the text. The letters in the last column of Table 2 needed to be referenced to Figure 4 as they are meaningless.

A reference to Fig. 4 has been added to the caption for Table 2.

Comment #12: Figure 5. It would be interesting to see other m/z ratios (structures given in Figure 4) plotted in Figure 5.

The other m/z are now included in Figure 5.

References added:

Crouse, J. D., Knap, H. C., Ornsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: On the Atmospheric Fate of Methacrolein: 1. Peroxy Radical Isomerization Following Addition of OH and O₂, *Journal of Physical Chemistry A*, doi:10.1021/jp211560u, 2012.

Geyer, A., Alicke, B., Ackermann, R., Martinez, M., Harder, H., Brune, W., di Carlo, P., Williams, E., Jobson, T., Hall, S., Shetter, R., and Stutz, J.: Direct observations of daytime NO₃: Implications for urban boundary layer chemistry, *Journal of Geophysical Research - Atmospheres*, 108, doi:10.1029/2002jd002967, 2003.

Wooldridge, P. J., Perring, A. E., Bertram, T. H., Flocke, F. M., Roberts, J. M., Singh, H. B., G., H. L., Thornton, J. A., Wolfe, G. M., Murphy, J. G., Fry, J. L., Rollins, A. W., LaFranchi, B. W., and Cohen, R. C.: Total Peroxy Nitrates (SigmaPNs) in the atmosphere: the Thermal Dissociation - Laser Induced Fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements, *Atmospheric Measurement Techniques*, 3, 593–607, doi: 10.5194/amt-3-593-2010, 2010.