

We thank the anonymous referees for their comments. We have addressed the comments individually below.

Responses to Anonymous Referee #1

It is often unclear whether “HNO₃” refers to “HNO₃(gas)” or “HNO₃(particle)” or “HNO₃(gas+particle). Please clarify throughout the manuscript. For example, I am assuming that the comparison of the concentration of organic nitrates vs nitric acid considers both gaseous and particulate forms of both species. However, this should be clarified, and if it does not, then it would seem appropriate to also consider gas-particle partitioning of both species.

We have added clarification in Section 3. In the manuscript we note that particulate NO₃⁻ is a small contribution to the total HNO₃ (see Fig. 2 in the discussion paper). We have also added the following to the end of Section 3:

In the remainder of the manuscript HNO₃ will refer to the sum of gas phase HNO₃ and particulate NO₃⁻ unless stated otherwise.

As is noted, BVOC concentrations, and thus organic nitrate concentrations, are altitude dependent, even within the boundary layer. Therefore, please state (at the end of section 2) the altitude range of the measurements averaged for the analysis in the manuscript. The reader could infer from later discussion that the measurements were from 500-1500 m agl, but this is not clear. What was the variance in the sum(ANs) within this altitude range? This variance could impact the discussion in section 3.

At the beginning of Section 3 we have stated that we are only using boundary layer measurements and that the boundary layer was 1.5 to 3.4 km a.g.l. (pg 208, line 7). ΣANs ranged from below our limit of detection to > 300 ppt. As we noted in Section 3, in 90% of the data the concentration of ΣANs is less than that of HNO₃, while the production rate of ΣANs (with a dilution correction that is likely an upper limit) is greater than that of HNO₃ in over 50% of the data. Therefore, we believe it is appropriate to use the median values for the discussion. To make this more clear, we have modified the beginning of Section 3 to read:

The boundary layer heights determined by this method (~ 1.5–2.4 km a.g.l.) are consistent with boundary layer heights measured over Northern Saskatchewan in July 2002 (Shashkov et al., 2007). The minimum altitude of sampling was just under 500 m. We see no evidence of a significant vertical gradient in the contribution of ΣANs to NO_y, and thus believe the use of median values to be appropriate.

When discussing Table A2 in the text, it might be useful to include the names of the sensitivity studies (as shown in the table) in parentheses in the text. This should make it easier to follow when comparing to Table A2.

Done.

Pg. 226, lines 11-12: Since experimental evidence of organic nitrate hydrolysis leading to HNO₃ production was only inferred, not observed, it might be more appropriate to state that “This study suggests that particulate organic nitrates...”.

We have changed the line in question to read: *We also provide evidence which suggests that...*

Technical Corrections: For references to the relative yields of various isoprene nitrates, see Table 2 in Pratt et al. (2012, ACP) for corrections to Lockwood et al. (2010).

These numbers have been updated.

Pg. 224, lines 8-9: VOC reactivity with respect to what oxidant(s)? Please clarify.

VOC reactivity with respect to OH. This has been clarified in the text.

Additional technical corrections raised by Reviewer 1 have been fixed.

Responses to Anonymous Referee #2

I do have one suggestion for how to improve the manuscript. At the start of Section 5, the authors state "Using the ARCTAS data we are unable to constrain the exact PANs lifetime since to do so would require knowledge of the photochemical age of the airmass..." The sections that follow present a credible calculation, and furthermore, the authors test their results against uncertainties in the assumptions. This is a real strength of this work. However, I am left wondering if some of the results are influenced by the differences in photochemical age of the air parcels. For example, in Figure 5(a), evidence is shown for an additional HNO₃ source when the HNO₃:NO₂ ratio is high but OH is low. An alternate explanation is that photochemically aged airmasses tend to have low NO_x, high HNO₃ and high PANs, where as airmasses recently influenced by NO emissions have relatively low HNO₃ and low PANs. Is it possible to segregate the data set based on an indicator of aging, such as altitude or acetone:monoterpene, and then check if the relationships presented in Fig. 5 still hold for both recently influenced and aged airmasses?

Our interpretation of Fig. 5 is based on the fact that if HNO₃ is in steady-state then the HNO₃ to NO₂ ratio must be proportional to OH. The alternative explanation proposed by the reviewer would require HNO₃ to be out of steady-state. Given its short lifetime with respect to deposition (on the order of half a day), the long daylight hours, and the relatively homogeneous area over which these measurements were made, this seems unlikely. Furthermore, we see that the HNO₃ to NO₂ ratio is higher than expected only when ΣANs are high and that when ΣANs are low the ratio is similar to expected. This discrepancy in the HNO₃ to NO₂ ratio between high and low ΣANs is most prominent at the lowest NO_x concentrations making it unlikely that recent NO emissions are playing a roll.

We do not believe that the acetone to monoterpene ratio is a good indicator of photochemical age given the extremely long lifetime of acetone. Other indicators such as the ratio of MVK or MACR to isoprene also are unhelpful since Σ ANs, MACR, and MVK are all products of isoprene oxidation with fairly short lifetimes.

We do note that the highest discrepancy between the HNO_3 to NO_2 ratio and the expectations occur when monoterpenes are the highest (and thus likely more particulate Σ ANs), whereas isoprene does not exhibit as clear a trend.

Does excluding airmasses with greater than 200 pptv NO_x help restrict the analysis to airmasses of a certain photochemical age where the steady-state assumptions are representative?

We choose a cutoff of 200 pptv to ensure that we are only sampling remote airmasses with minimal biomass burning influences. Biomass burning, which is prevalent over the Canadian boreal forest in July, would introduce different photochemistry. Unlike in an urban environment, in this remote environment the low NO_x concentration restriction does not necessarily indicate high photochemical age due to the small NO_x sources present in this remote region.

These are potential suggestions for how to address this, but the main issue is that it would be useful for the authors to address the issue of photochemical age again in the Implications.

We have modified the beginning of Section 5.4.2 to address this issue:

It is unlikely that variations in photochemical age are the dominant factor explaining the observed behavior of the HNO_3 to NO_2 ratio (Fig. 5a). The largest deviation in the expected behavior of the HNO_3 to NO_2 ratio as a function of NO_x occurs at the lowest NO_x concentrations – airmasses which are likely to be more aged than those with higher NO_x concentrations. However, the deviation only occurs in those airmasses with a substantial concentration of both Σ ANs (Fig. 5a) and monoterpenes (not shown) and thus likely higher aerosol phase organic nitrates. Other than NO_x concentration, other available chemical tracers for defining age with time zero at biogenic emissions were found to be unsuitable because of their direct correlations with Σ ANs or because their sources were not unique.

The technical correction has been fixed.