

Response to Reviewer 1

We thank the reviewer for the helpful comments.

Reviewer 1

P4 line 4: The authors describe how they decide on a cut-off life- time (of 7 hours) to divide the NO_z species between short lived and long lived reactive nitrogen by using estimated NO_x lifetimes determined from satellite observations pre- sented in two cited papers. I realise the details of the estimation are in these papers, however I believe its importance in this manuscript warrants some more discussion here. The authors should explain in more detail how they came to use the 7 hour cut-off.

The cut-off between NO_{SL} and NO_{LL} is reevaluated using the lifetime of NO_x calculated in this paper. Because of this, the choice of 7 hours does not affect the final result. We therefore feel that a detailed analysis of how the 7 hour cut-off was determined is not necessary. We have modified the text to explain how the provisional cutoff was determined and its role in our calculations:

“The division between NO_{SL} and NO_{LL} depends on the lifetime of NO_x. For the initial discussion in this manuscript, we use a provisional lifetime of 7 hours to divide NO_z species between NO_{SL} and NO_{LL}. This cutoff is in the middle of the range of NO_x lifetimes found in plume studies (e.g. Ryerson et al., 1998; Dillon et al., 2003; Alvarado et al., 2010; Valin et al., 2013). The provisional cutoff chosen as a starting point does not affect the final results.”

P5 line 11: Could the authors confirm that this 4th channel on the instrument is the NO₃- species plotted in figure 2 – this wasn't clear to me in the manuscript. Again I realise this measurement is reported in other cited literature, however I feel the aerosol phase measurement does warrant some further discussion. For instance, is it purely and aerosol measurement or could there be some interference from HNO₃?

The NO₃⁻ species plotted in figure 2 was taken from the measurements made by MARGA, and should be specific to only inorganic nitrate. The TD-LIF measurement of organic nitrate is equally sensitive to nitrates in both the gas and particle phases, but the thermal-dissociation oven was set at a temperature where the measurement was not affected by inorganic nitrate. The TD-LIF measurement of organic nitrates in only the particle phase is not used directly in this manuscript, and we have removed the reference to it. We have revised this portion of Section 3 and the caption of Figure 2 to make these points clear:

“NO₂, ΣPNs, and ΣANs were measured via Thermal Dissociation Laser Induced Fluorescence (TD-LIF), as described by Day et al. (2002). Ambient air was drawn into a multipass White cell, where a 532 nm Nd-YAG laser excited the NO₂ molecules, and their fluorescence signal was collected on a photomultiplier tube (Hamamatsu H7421-50). The same instrument was used to measure the sum of peroxy nitrates and the sum of alkyl and multifunctional nitrates by first passing the air through a heated oven, where the organic nitrates dissociated to form NO₂. Organic nitrates present in the particle phase undergo evaporation and thermal dissociation in the heated ovens to form NO₂. The TD-LIF measurement of ΣANs therefore includes alkyl and multifunctional nitrates in both the gas and particle phases, but does not include HNO₃ or particle-phase inorganic nitrate (Day et al., 2002; Rollins et al., 2010).”

“Particle-phase inorganic nitrate (NO₃⁻) was measured using a Monitor for AeRosols and GAses (MARGA) (Allen et al., 2015). Ambient air was drawn through a rotating wet-walled denuder which collected water soluble gas-phase compounds. Particle-phase compounds were captured by a steam-jet aerosol collector downstream of the denuder. Water soluble ions from both phases were then quantified via ion chromatography. This measurement of NO₃⁻ is designed to be specific to inorganic nitrate, and is not affected by ΣANs in the particle phase (Allen et al., 2015).”

“Figure 2. Diurnal cycle of measured reactive nitrogen species during SOAS. Reactive nitrogen species are classified as likely components of NOSL (Fig. 2a), likely components of NOLL (Fig. 2b) or unknown (Fig. 2c). The classification into NOSL and NOLL is based on typical summertime afternoon lifetimes. The measurement of HNO₃ represents nitric acid in the gas phase, while the measurement of NO₃⁻ represents inorganic nitrate in the particle phase. The measurement of ΣANs includes alkyl and multifunctional nitrates in both the gas and particle phase.”

P7 line 24: The authors state that the inferred source of HNO₃ is in-situ chemical production and not long range transport, due to a lack of large NO_x sources near the site and the small variation of the source with wind direction. I am sure this is probably correct however more evidence could be given for this. For instance, in the site description it is stated that the site is 40km SE of Tuscaloosa (population 95000) and 90km SW of Birmingham (population 210000). Do these cities not effect the site at all? Could the authors show a map of the site location with back trajectories to back up their argument?

P8 line 6: Again could transport be considered as a missing source of HNO₃ (see

comment above).

We find no evidence that these cities impact the inferred production rate. We have added an additional paragraph to section 4.1 to explain our reasoning:

“Since the calculation of the inferred production rate considers only the hour-to-hour change in nitric acid and not its gross concentration, the inferred production rate is not affected by distant nitric acid sources. We find very small (less than 15%) variation in the concentration of NO_x with wind direction and no correlation of the inferred production rate around noon with sulfate (a power plant tracer) or benzene (an urban tracer). As the transport time from these sources to the CTR site is significantly greater than 1 hour, this result is not surprising.”

P12 lines 4 – 8: I am a bit confused by this statement. Surely it is obvious that NO SL will contain the ‘reactive’ component of ANs and NO LL the unreactive component. What do the authors actually mean by reactive and unreactive components? Could some quantitative measure be put on this and hence what are the type of ANs that make up the two classes?

The relationship between concentration and production of ΣANs (Fig. 6) found here indicates that there is a portion of ΣANs that has a lifetime under 2 hours and a portion that has a significantly longer lifetime, although we cannot determine it precisely. Previous work suggests that small, monofunctional nitrates have atmospheric lifetime of days to weeks, making them likely to be the unreactive component of ΣANs . We have added the following text to page 10 to clarify this point:

“This background is likely composed of small monofunctional alkyl nitrates, since these compounds typically have lifetimes of days or weeks in the summertime troposphere (e.g. Clemitshaw et al., 1997).”

“This reactive component is likely composed of larger, multi- functional nitrates that can be lost rapidly by oxidation, deposition, or hydrolysis (Lee et al., 2014; Nguyen et al., 2015; Darer et al., 2011).”

We have also revised the statement on page 12 to read:

“We interpret the y-intercept in the correlation between ΣAN production and concentration (Fig. 6) to represent a 40 ppt background of unreactive ΣANs , likely composed of small monofunctional nitrates. We treat all ΣANs greater than this constant background as short-lived.”

P13 lines 13 – 15: A statement is made here about both daytime and nighttime chemistry needing to be understood to properly understand the transport and distribution of NO_x, however the analysis concentrates on the daytime chemistry. I feel the conclusions are therefore slightly misleading, unless some nighttime analysis is added to the manuscript.

Our intention with this statement was explain that, when considering the distribution and transportation of NO_x across a region, applying the noontime lifetime of NO_x is not sufficient. We have revised the statement as follows:

“To fully understand the transport and distribution of NO_x across a region the daytime chemistry of NO_x discussed here must be combined with additional analyses of the nighttime chemistry of NO_x and NO_y (e.g. Brown et al., 2009; Crowley et al., 2011; Ayres et al., 2015).”

P13 lines 24 – 25: could a statement be made in the conclusions about how this analysis compares to a more ‘classical’ analysis of NO_x / total NO_y (without taking the NO_y speciation into account)? This would help cement the importance of the work.

We do not believe that a calculation of the NO_x lifetime using the NO_x/NO_y ratio is applicable here. Previous analyses doing this have all been in the outflow of a clearly defined plume, which is not the case here. We have added a sentence here explaining this:

“More quantitative calculations of the NO_x lifetime using the ratio of NO_{SL} to NO_{LL} or NO_x to NO_y have been developed for analyses of plumes (e.g. Kleinman et al., 2000; Ryerson et al., 2003) but are not adaptable to this data set.”

Minor comments / corrections: P3 line 20: It is strange that this is labelled R2b even though it appears first. Should this be re-numbered R2a?

While we appreciate that it is unusual for R2b to appear before R2a, most descriptions of the RO₂ + NO reaction (e.g. Perring et al, 2013, Finlayson-Pitts and Pitts, 1999) refer to the channel that forms alkyl nitrates as the ‘b’ reaction. We have kept this reaction labeled R2b in order to be consistent with these analyses.

P11 line 16: should ‘NO SL’ actually be ‘NO_x’?

We have revised the sentence to read:

“At the same time, deposition and the rapid conversion of reactive multifunctional nitrates to nitric acid means that the formation of Σ ANs leads to the significant removal of NO_x , and therefore NO_x , from the atmosphere.”

At numerous points throughout the manuscript HNO_3 and nitric acid are used. The authors should pick one and stick to it throughout.

We have chosen to use ‘nitric acid’ throughout the manuscript, except in a few cases where we feel using the chemical formula is more appropriate.

Figure 3: It maybe of interest to show the O_3 average profile as well.

We have added the diurnal profile of ozone to Figure 3.