

We thank Referee 1 for these constructive and helpful comments. Our replies (in blue/red) to each comment (in black) are listed below. Red text indicates changes to the manuscript.

Referee 1
<i>General Comments</i>
1. Previous TD-CRDS instruments should be discussed and similarities/differences discussed more fully (Paul et al., 2009; Paul and Osthoff 2010; Thaler et al., 2011; Mielke and Osthoff 2012). The recent development of multiple CIMS approaches to measuring the major components of total ANs (e.g., Beaver et al., 2012) should be mentioned.
The most relevant TD-CRDS instruments are those of Paul et al, (2009, 2010) who used this method to detect ANs and PNs. These publications are now mentioned in the introduction and also in various places in the manuscript in which we compare the observations made during laboratory characterisation. The Thaler et al. 2011 reference is already cited where we discuss CINO ₂ detection. The work by Beaver et al. 2012 on speciated, biogenic ANs is now mentioned in the introduction.
2. The paper should explain the motivation for lasers at two different wavelengths and address any additional complexity associated with this choice?
Two lasers were used to get more light into the cavities. We have added text to section 2 to explain this. “The use of two lasers rather than one increases the light intensity at the detector and thus improves signal-to-noise, but brings with it the added complexity of needing to measure two-laser spectra (see below) and using two different NO ₂ absorption cross sections.”
3. The paper should explain the choice of operating pressure, since that affects the TD signals and is presumably a parameter that could be optimized to improve specificity of the measurements.
Operating pressures of slightly sub-ambient (800 mbar) were chosen to enable accurate pressure regulation without significant reduction of overall concentration in the cavity. The instrument described here was not set up for operation at much lower pressures but we indicate in the conclusions / outlook section that future developments will include systematic investigations to define the “best” pressure.
4. The authors are correct that pyrolysis of O ₃ was not important for Day et al. (2002) since the residence time in that instrument was short. In Lee et al. (2014), the authors demonstrated that at long enough residence time, pyrolysis of O ₃ becomes sufficient to become a positive interference in the total ANs channel. Where does the TD-CRDS fall in these two regimes? Also, was pyrolysis of O ₃ tested at all or just calculated? The negative ANs in the field might be an indicator of an O ₃ effect.
Reviewer 2 made a similar comment and we have reassessed the role of O ₃ pyrolysis. We have conducted experiments and modelled the results to examine the effect of O(³ P) reactions with NO ₂ . Section 2.1.6 dealing with this has been re-written and the ΣANs dataset corrected accordingly (See also reply to reviewer 2).
5. The authors demonstrated that the temperatures selected fully decompose total PNs and total ANs and the temperature selected for total PNs does not decompose any total ANs. Were any experiments conducted to determine if any HNO ₃ is decomposing at the temperature selected for total ANs?
In response to a similar comment by referee 2 we have performed a limited set of experiments to see whether we detect HNO ₃ as NO ₂ when sampling via the TD 723 K inlet. A description of the experiments and the conclusion (at RH 40 % we detect HNO ₃ at ~ 10 % efficiency when added directly to the front of the oven without additional inlet

tubing) will be added to the paper. This is substantially less than the ~ 70 % efficiency observed by Wild et al. (2014) at the same nominal oven temperature. The efficiency of detection of HNO ₃ as a function of temperature is presented as an additional plot in the supplementary info
6. It seems likely that a fuller suite of PNs were measured by TD-CIMS? A direct comparison of totals or scaling of the PAN by the measured ratios would seem a better approach.
Masses corresponding to other PNs ($m/z = 71, 73, 75, 85$ and 87) were monitored during this campaign but were uncalibrated. Assuming the same sensitivity for all PNs detected we can show that non-PAN PNs were ~ 20 % of the total amount. We now write: In addition to PAN, the TD-CIMS monitored 5 masses corresponding to other PNs. These masses have not been calibrated, though by assuming the same detection efficiency as PAN, we can show that PNs other than PAN represented ~ 20 % of all PNs, consistent with the value above. A more detailed analysis of the TD-CIMS dataset during PARADE will be presented in a future publication.
7. The interpolation necessary to measure total ANs can be affected by atmospheric variation on the measurement time scale. Perhaps a strategy for assessing maximum variability in the underlying NO ₂ or SPNs would be useful?
Yes. This is necessary when analysing the data in detail and will be dealt with when we publish the full dataset of ANs and PNs from this campaign.
8. Some additional comments on the transmission of sticky molecules from the inlet through the sampling system would be useful. Would isoprene hydroxynitrates, ClNO ₂ or HNO ₃ reach the heater without losses?
In response to questions raised by reviewer 2 concerning (unwanted) detection of HNO ₃ in the TD-723 cavity, we have added text in section 2 to mention that sticky HNO₃ is not expected to be detected quantitatively. We now also mention that large hydroxynitrates may also be lost in the inlet. We expect ClNO₂ to be transmitted with close to 100 % efficiency.
<i>Specific Comments</i>
1. Page 11534, line 17 – “nutrient” should be “nutrients”
Correction made.
2. Page 11535, line 17 – For upper tropospheric measurements of HO ₂ NO ₂ and CH ₃ O ₂ NO ₂ , other references are missing, including Murphy et al., 2004, Kim et al., 2007, and Nault et al., 2015.
References added.
3. Page 11535, line 19-20 – The authors are correct that near the surface of the planet, thermal decomposition is the most important loss rate; however, at higher altitudes, photolysis and reactions with OH dominate
We agree. We now write: “In the lowermost troposphere, other losses of RO₂NO₂ such as photolysis or reaction with OH are vastly reduced in importance compared to thermal decomposition.”
4. Page 11537, line 19-20 – Please define delta and be consistent with its use throughout the entire paper.
Δ has been removed throughout.
5. Page 11540, lines 7-8 – Any experiments to determine if multifunctional nitrates are filtered out as well?
No. We have not tested the transmission of multifunctional nitrates. We now mention in section 2 that we assume that all organic nitrates (but not HNO₃) are transmitted with

100 % efficiency.
6. Page 11563, lines 24-26: Where does correction factor maximum uncertainty of 30% come from?
This is a conservative estimate, which we now state. A more rigorous assessment would require that we had done the tests for all possible PN sub-types.
7. Page 11564, lines 20-21: can you state what the certain conditions are?
Certainly. We now write: As we indicate later, reliable AN measurements can only be made under certain conditions (low PAN variability and $[\text{NO}_2] < \sim 5$ ppbv).
8. Figure 6 caption – how much O ₃ was present during the experiments?
O ₃ mixing ratios added. The Caption now reads: NO ₂ formation in the reaction of O ₃ (25, 48 or 80 ppbv) with NO in the inlet (in this case at ambient temperature), and reference cavity (at 308 K) and connecting tubing.
9. Page 11586, Figure 8: If poor fit is caused by problem with PAN mixing ratio during experiment, why not repeat experiment?
This was not necessary as variation in PAN can be accounted for as shown in Figure 10. This is already stated in the Caption to Figure 8.
10. Page 11588, Figure 10: Figure legend is too small.
Corrected
11. Page 11591, Figure 13: Figure legend is too small.
Corrected
12. Figure 18 caption – what are the green points? May also want to reconsider colors and descriptions for colors since the reader may think any black data points are uncorrected data, including for NO ₂ , which the reader could interpret to mean the NO ₂ measurements would need corrections.
Caption modified and now reads: “Time series of PARADE data over a 5 day period. <i>Upper panel:</i> NO ₂ mixing ratios measured in the reference cavity along with NO measured by the CLD. <i>Central panel:</i> TD cavity measurements when sampling from the 723 K inlet. Black data points are uncorrected (raw data). The green data points were obtained by directly subtracting the NO ₂ mixing ratios measured when sampling from the 473 K inlet from that when sampling from the 723 K inlet. The red data points include the corrections described in the text. <i>Lower panel:</i> Uncorrected (black) and corrected (red) ΣPNs measurements.”