We thank Referee 2 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 2

There seems to be some confusion about whether the ΣPN inlet was at 450K or 473K, both appear at different places. Please clarify.

The inlet was at 473 K. This is now consistent throughout the manuscript and SI.

There is one large question mark that people have about this method, pertaining to the ΣAN measurement, and it would be extremely helpful if this group could explore this issue with some solid work in the laboratory. Nitric acid is the largest NOy compound in well processed air masses in the polluted lower troposphere, often reaching 40 to 60% of total NO*y*, while ΣANs are 5-15% of NOy (depending if one can believe ΣAN measurements). HNO_3 uni-molecular thermal decomposition kinetics have been known for some time [Harrison et al., 1962 and references therein], and indicate that HNO3 will be converted to only a very small extent at the ΣAN conditions, depending on convertor residence time (which needs to be specified in this paper). Indeed one needs a quartz convertor at a higher temperature to convert HNO_3 to NO_2 [Day et al. 2002 , Wild et al., 2014]. However, heterogeneous and catalytic conversion in the presence of VOCs at the lower temperature is a real possibility, indeed the gold and molybdenum NOy catalysts rely on this for conversion of HNO3 to NO_2 at 573 - 598°K. There is a hint of such an effect in the results of Wild et al., [2014] who observed HNO_3 conversion at temperatures as low as 573K in their system. Only a small conversion of such a large NOy component would make a big contribution to ΣAN, and would lend completely unrealistic characteristics to the ΣAN and HNO_3 signals obtained with this method, leading perhaps to one concluding that HNO_3 fluxes were coming out of a forest for example [Farmer and Cohen, 2008]. It is strongly urged that the authors look at HNO_3 in their system, and define its contribution to ΣAN, and possible catalytic and surface effects upon addition of CO and VOCs. This would be a tremendous service to the community

In response to this comment 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.

We agree with the reviewer that detailed, laboratory examination of a potential interference involving HNO_3 when measuring ANs with the TD method would be useful to the community. We note however that doing this with our TD-CRD set-up would not resolve any issues related to measurements made with the TD-LIF method (i.e. by the Berkeley group) as the pressures, residence times etc. in the thermal converter are sometimes completely different, as would be the rate of surface catalysed, (thermal) dissociation of HNO_3 to NO_2. This difference in what we measure to what Wild et al (2014) measure exemplifies this. We are planning to set up a system to measure NO*y* using the TD-CRD method, much as described in the Wild et al paper mentioned in this comment. Among other modifications, this will involve a detailed characterisation of an improved HNO_3 source (with HNO_3 specific detection) and inlet re-design so that we

can sample ambient HNO_3 efficiently into the oven. In short, testing the influence of HNO_3 is not something that can be done (properly) on a short enough time scale to incorporate it into this manuscript.
We also note that, during the PARADE campaign we sampled air though ~10m long, cold, PFA tubes, which were not optimised to sample HNO_3. This poses no problem for non-sticky, non-soluble trace gases like PANs or ANs, but sampling HNO_3 though these inlets is known to be very inefficient. This, combined with the fact that (based on our new lab experiments), we detect "only" 10 % of ambient HNO_3 we do not expect significant amounts of HNO_3 to reach our instrument or to impact severely on our ΣANs measurements.
In summary, our limited laboratory experiments indicate a much lower sensitivity to HNO_3.at the nominal inlet temperature of 723 K than derived by Wild et al (2014). Detailed measurements of the detection of HNO_3 in a NO*y* instrument will be made in this laboratory but are beyond the scope of this study. Text describing the new experiments and indicating the potential role of HNO_3 will be incorporated into the revised manuscript. We also indicate that, in the absence of simultaneous measurements of HNO_3, the ΣAN measurements should be understood as upper limits.

A general comment on ambient measurements with this technique: In principle it is possible to scan convertor temperatures to see if one really is at a 'plateau', which is a necessary (but not entirely sufficient) condition to demonstrate selectivity between the various classes of NOy species. There are some "scans" with laboratory samples that have been reported, but with only the NOy species present. Why not scan in ambient air, especially above 723K, to demonstrate that such a plateau has been reached ?
Yes, there is variability in ambient air, but there are also times when concentrations are stable and such a scan is possible.

Agreed. This we shall do when our NO*y* prototype has been built.

Page 11535, Lines 19 -20. While it is true that the reaction of PAN with OH will not be competitive with thermal decomposition anywhere in the troposphere, photolysis is faster than thermal decomposition above about 7km altitude, give or take, based on average (i.e. Springtime, mid-latitude) conditions.

Agreed. We now restrict our statement to refer to PAN losses in the lowermost troposphere only: "In the lowermost troposphere, other losses of RO_2NO_2 such as photolysis or reaction with OH are vastly reduced in importance compared to thermal decomposition (Talukdar et al., 1995)."

Page 11536. Line 25, the peroxypropionic PAN compound is usually referred to as PPN, and indeed is referred to that way on page 11567 of this paper.

Agreed. We now write: "Recently, PAN and other peroxycarboxylic nitric anhydrides such as MPAN (peroxymethacrylic nitric anhydride) and PPN (peroxypropionic nitric anhydride)……

Page 11537, Line 1. Perhaps the original PAN TD-CIMS reference, Slusher et al., 2004, should be listed here?

Agreed. Slusher et al 2002, have been added to the references.

Page 11537, Lines 9-11. It should be mentioned here that HNO_3 is sometimes 40 -60% of NOy.

At this point in the manuscript, dealing with AN measurements, we would prefer to avoid a lengthy summary of the highly variable contribution of HNO_3 to atmospheric NO*y*. We have added text (section 2) indicating that HNO_3 is a significant contributor to NO*y*.

Page 11540, Lines 23. From the conditions mentioned here, it would appear that the residence times of air with the heated zones were on the order of 0.2 to 0.4 sec, is that

correct? What residence times were used for the model calculations?
As the gas exiting the oven does not heat instantaneously upon entering the oven and does not cool instantaneously to room temperature upon exiting it we used position (i.e. time) dependent temperatures in the simulations (see text on page 11549, Lines 8-11) and not a fixed oven-residence-time. We have added a Figure in the SI (4) to show this. The text on page 11549 now reads: The simulations were initialised with position dependent temperature gradients in the oven and subsequent piping and cavities (see Fig. SI 4), which were derived by inserting a thermocouple……..
Page 11541. Line 14. This text says i-butyl nitrate, which is CH3CH(CH3)CH2ONO2, and the Figure caption says 2-butyl nitrate, which is CH3CH(ONO2)CH2CH3. Which is it?
It was iso-butyl nitrate. All reference to 2-butyl nitrate has been removed. Likewise, the one mention of isopropyl nitrate has been replaced by 2-propyl nitrate.
Page 11542. Lines 9-22. Ideally, one can predict the behavior of a given $–NO_2$ containing compound based on O-N bond dissociation energies; peroxynitrates have been reviewed by Kirchner et al., [1999] and tend to range from 20 to 27 Kcal/mole; $RO-NO_2$ bonds tend to be on the order of 38 to 41 Kcal/mole [see for example Roberts 1990]; nitric acid has a $HO-NO_2$ bond strength of 47-49 Kcal/mole. The behavior of these compounds in the quartz convertors follows these trends, implying that the quartz surfaces are "inert", at least under the laboratory conditions used here. This simple picture needs to be tested under real world conditions , to see if there is catalytic behavior due to the presence of other species, O_3 , VOCs etc.
Agreed. We shall do these "real world" tests with the upcoming NO*y* instrument. Text has been added to section 2 (principal of operation) to highlight the fact that the potential detection of HNO_3 means that our ambient ΣANs mixing ratios may be regarded as upper limits.
Page 11545. Line 17. Should read "and its concentration was.."
Correction made.
Page 11546. Pyrolysis of O_3. Not sure what to make of this section, Lee et al., [2014] found that this did have an effect, even at 380°C. Why the difference?
We are most grateful for this comment, which has unveiled a faulty assumption in our analysis, namely that the reaction of $O(^3P)$ (from O_3 pyrolysis) with NO_2 was insignificant. This assumption had been based on initial calculations of $O(^3P)$ concentrations using an incorrect (too low) rate constant for the thermal decomposition of O_3. We have now conducted some new experiments and done some simulations using new rate constants for the thermal decomposition of O_3 (k_d) at temperatures relevant for these experiments *(Peukert, S. L., Sivaramakrishnan, R., and Michael, J. V., J. Phys. Chem. A, 117, 3729-3738, 2013.)* This section has been re-written and the correction procedure described in detail along with indicative corrections for the PARADE campaign. The ΣANs dataset has been modified and the few negative values previously obtained are now positive !
Page 11547. 473 K Inlet. The photolytic PAN source is typically run with a considerable excess of acetone. Does this have any effect on the chemistry?
We have used both the PAN-tridecane diffusion source and the photochemical source of PAN. The simulations do equally well with both datasets, indicating that the large amount of acetone has no apparent effect.
Page 11549. Lines 11-14. I would be interested to see what the temperature profiles look like. The related issue is what residence times were associated with the convertors and do they make sense given the chemical simulations ?
The temperature profiles are now included as supplementary information (SI 4).

Page 11555, Line 12. This should read 10ppbNO, not NO_2.

Correction made.

Page 11561, Line 27, Should read 893mb for consistency.

Correction made.

Page 11562, Line 6. The phrase “1 sigma precision increases for integration times up to 40s” is a bit confusing. One gets the point when looking at the graph, but really 1 sigma decreases, which corresponds to increased precision, or maybe a more appropriate word would be “better” precision.

We have replaced “increased” with “improved”

Page 11565, TD-CRDS vs. CLD. Can the authors comment on how the results of Reed et al. 2015 might impact the inter comparisons?

Reed et al. 2015 suggest that PAN or other thermally instable NO*y* species may positively bias NO_2 measured in low NO*x* environments by chemiluminescence devices (CLD) with “blue-light” converters (of NO_2 to detectable NO). In PARADE, the CLD measured less than the CRD at all concentrations (slope less than unity and negative intercept) as shown already in Figure 16. In this intercomparison we therefore have no evidence for a positive bias in the CLD dataset. Reed also indicate that the size of such effects will be instrument specific, so that their results are in any case not necessarily transferable to the CLD used here.

Page 11567. MPN should be MPAN for consistency.

Correction made.

Page 11568. Conclusions and Outlook. I guess I want to make one more pitch for looking at the behavior of HNO_3 in these systems, especially under conditions of high CO and VOCs. For the good of the community, someone needs to do this.

For this manuscript we have done tests in synthetic air at ambient RH. More detailed examination of the HNO_3 impact will be conducted in a new apparatus that is presently being constructed to detect NOy. See reply to same comment above.

Page 11578. The Yin-Nan, L. reference is wrong, Yin-Nan is actually his given name, same with Xian-Lang, so this reference should read: Lee, Y.-N., Zhou, X.-L., and Hallock, K.

Correction made.

Page 11596. The caption for Figure 18 should have the details about the red and green points in the ΣANs panel. Typo on Line 4, “when sampling from the...”. Was it a 450K or 473K inlet?

Correction made.

Supplement. Figure SI 1, this says 450K, is that correct?

No, 473 is correct. Correction made.