Reply to comments on "Total peroxy nitrates (ΣPNs) in the atmosphere: the thermal dissociation-laser induced fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements" by P. J. Wooldridge et al.

We thank the referees for the positive assessment and helpful comments. We have addressed them as detailed below.

Anonymous Referee #1:
This paper presents an update on the TD-LIF technique for measuring total peroxy nitrates, including an analysis of potential interferences and techniques to reduce these interferences. A summary of the measurement campaigns as well as a summary of comparisons with speciated measurements are also presented. In addition to providing an update on the status of this instrument, the general agreement between the TD-LIF results and the speciated measurements suggest that there are not significant concentrations of unmeasured PAN-type compounds in the atmosphere. The paper is well written and suitable for publication in AMT. I recommend publication after the authors have addressed the following minor comments:

In general, this paper demonstrates that the TD-LIF technique is capable of accurately measuring total peroxy nitrates with minimal interferences under most atmospheric conditions. However, production of NO_x by peroxy radicals and ozone reacting with NO, as well as production of PANs from the reaction of peroxy radicals with NO_2 can interfere with this technique under high NO_x conditions. This paper provides a detailed analysis of these interferences, and describes modifications to the instrument inlet to minimize these interferences. It appears that the interference is only significant for inlet configurations B and C under high NO_x conditions, and may explain the poor agreement between the TD-LIF measurements and the speciated PAN measurements during INTEX B and PIE where the instrument used inlet C. The paper would benefit from some additional details on the levels of NO_x observed during these measurements in comparison with the other measurements where the agreement between the TD-LIF measurements and the speciated measurements was better. A column in Table 1 or 2 that included the range of NO_x values observed and the percent correction associated with these NO_x levels would help to identify these episodes.
Answer:
The NO_2 levels as a fraction of the measured NO_2+PNs signals are presented graphically as the histograms in Figure 8. A column will be added to Table 2 with the minimum, median, and maximum NO_2 levels for each dataset.

Anonymous Referee #1:
It is clear that the inlet A configuration, where the drop in pressure occurs prior to thermal dissociation is the most appropriate for a wide range of conditions, including high NO_x conditions, as the interferences are minimal in this configuration. However, it appears that the inlet C configuration will still be used for remote locations. Obviously there are advantages and disadvantages to using the inlet A configuration under all conditions, and the paper briefly mentions that there are trade-offs in sensitivity, power consumption, size, and interferences for each configuration, but does not provide de-tails for each inlet configuration. A brief discussion of the disadvantages of using inlet A would help in the justification for using inlet C for remote locations.
Answer:
Will add a note explaining that configuration C (pressure reduction at the LIF cell) is necessary when the jet expansion is employed to achieve a gain of ten or higher in sensitivity.

Anonymous Referee #2:
The authors present an overview of total peroxy nitrates ΣPNs measurements taken by thermal dissociation laser induced fluorescence (TD LIF). The instruments inlet configuration and possible

interferences from recombination and oxidation of peroxy radicals during high NOx conditions is discussed in detail. Furthermore, 11 deployments with inter-comparison possibility to speciated PAN measurements between 2000 and 2007 under various NOx levels are reported. The authors find agreement between ΣPNs and speciated PANs within 10 % and conclude that this argues against the existence of unmeasured PAN-like substances. The paper offers a comprehensive inter-comparison between the TD-LIF measured ΣPNs and speciated PANs, it is clearly written and after some corrections should be published in AMT.

Major comments
The only 'major' comments concern details on the regression method and the conclusion drawn from the variety of inter-comparisons.
The presented inter-comparison relies on the regression between ΣPNs and concurring measurements of speciated PANs. Some additional information would increase the confidence in the obtained regression slopes. The authors apply a regression model that takes uncertainties in both variables into account. The given uncertainties for x and y will be critical for the regression analysis. On page 3068, line 27 the authors give the uncertainties used for the regression (basically 15 % for both the PNs and the speciated PANs). Within the discussion of the individual employments the authors give somewhat different estimates (for example: page 3069, line 16: 15 %; page 3072, line 5: 13 % for ΣPNs). If the combined uncertainty was estimated for each employment individually, I suggest that a) these uncertainties should be given in the text (and Table 2) for each campaign separately and b) they should be used separately in the regression model. The same (individual uncertainty estimates by employment) should be done for the speciated PAN measurements. Furthermore, the authors don't give the uncertainties that are connected to the regression slopes. It would be beneficial if those uncertainties could be included in Table 2 to indicate if the slope is significantly different from 1 or not.
Answer:
For uniformity 15% will be used throughout for ΣPNs. The weighting for the individual sums will be added as a column in Table 2, along with the other regression outputs.

Anonymous Referee #2:
Coming back to the final conclusion of the paper that the presented measurements argue against the existence of unmeasured PAN-like substances. It seems to me that this conclusion cannot be drawn under high NOx conditions. As discussed by the authors the setting of the critical orifice at position B and C is not free of interferences under high NOx. From Fig 8 I take that the only employments that were dominated by high NOx were TexAQS and PIE. For both campaigns a ΣPNs correction depending on NO, NO2 and O3 was performed. However, for PIE the unmeasured PANs fraction remained much larger than 10 % while it was about 10 % for TexAQS. This does not give a conclusive picture. As stated by the authors this measurement setup is not recommended for such conditions. I would thus suggest that the authors add to the conclusions that under high NOx conditions the presence of larger fractions of unmeasured PANs cannot be ruled out from the current observations.
Answer:
We believe we have presented a convincing case that the PIE ambient data comparison at high NO_x is dominated by interferences and should thus be ignored. We concur with the reviewer that the TexAQS comparison is at about 10%. Since we make the relatively weak claim that unusual PNs are less than 10% of the total we think the observations do support that claim.

Anonymous Referee #2:
Minor comments
p 3073, l 23f: It would be helpful if the authors could give the typical range of observed BVOCs during BEARPEX-2007. If BVOCs were low it cannot be argued against the existence of unspeciated PANs from BVOC.
Answer:

will add to section describing the BEARPEX data:
"Bouvier-Brown, et al. [2009] provides details of the large concentrations of monoterpenes (daytime average of 722 pptv), methylbutenol (459 pptv), isoprene (132 pptv), and other BVOCs during this experiment. LaFranchi, et al. [2009] demonstrated that oxidation of biogenic volatile organic compounds plays a significant role in the PANs budget at this site."

and to references:
Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., de Gouw, J. A., In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9, 5505-5518, 2009.

Anonymous Referee #2:
The labels for individual campaigns in Table 1, 2 and Figure 7, 8 do not agree all the time (for example INTEX-NA in Fig.8, but INTEX-A in Tab. 2, or 4 different sub-periods of INTEX-B in Fig.8, but only 3 in Tab. 2). I suggest to harmonise the labels and also the displayed cases between Fig. 8 and Tab. 2. Currently Fig. 8 shows 12 scatter plots, but Tab. 2 lists 14 regression results. That's somewhat confusing.
Answer:
Will change INTEX-A to INTEX-NA throughout.
About the 12 plots vs. 14 regressions: for most of the datasets only the principal species PAN, PPN and sometimes MPAN are available individually, but the ARCTAS data set had additional minor species available. In addition, we make the point that pernitric acid (HO_2NO_2) is detected in the ΣPNs category. The effects of including or omitting these species are illustrated by the two additional ARCTAS regression results, but the differences are too small to make the scatter plots significantly different in appearance. We will add text to remind the reader what we have done.

Anonymous Referee #2:
Furthermore, I suggest to restructure and complement Tab. 2. Currently it is difficult to extract the estimated slopes and correlations from the table. It would be easier if slope and regression get their own columns. As mentioned above, the slope should be complemented by its uncertainty. In addition, the intercept (and its uncertainty) of the regression should be given as well. This might be skipped if it is never significantly different from zero, which then needs to be mentioned in the text. If different uncertain-ties were estimated for different campaigns (see above) these should also be added to the table.
Answer:
The additional columns have been included in Table 2.

Anonymous Referee #2:
Figure 8: The current figure is too small. Furthermore, the axes and the figure caption are missing units. In addition, it would be useful to show the one to one line in addition to the regression line (if that is what we see right now).
Answer:
Figure 8 is intended to provide a compact view of all the datasets without devoting space to a full-sized scatter plot for each. We felt this would complement the Table 2 results without excessive duplication.
Will change the caption from "Speciated ΣPANs vs. TD-LIF ΣPNs ppbv scatterplots and ΣPNs fraction of ΣPNs+NO_2 histograms." to "Speciated ΣPANs (ppbv) vs. TD-LIF ΣPNs (ppbv) scatterplots with fitted lines. Below each are histograms of the ΣPNs fraction of the ΣPNs+NO_2 sums."

We agree that 1:1 lines are useful on larger plots, but feel that they would add clutter to plots of this size.

Anonymous Referee #2:
Figure 10: The figure caption is a little to Spartan. Please indicate which campaign these time series are taken from.
Answer:
will change from “30 June-1 July 2005 ambient sampling period.” to “PAN Intercomparison Exercise ambient sampling period: 30 June-1 July 2005, Boulder, Colorado.”

Anonymous Referee #2:
Technical corrections
p 3058, l 29: "Bowman et al. complemented ...", year of publication missing
Answer:
will change to "Bowman et al. [2003] complemented ..."