Atmospheric Measurement Techniques Discussions

Interactive comment 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.

Anonymous Referee #2

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General

The authors present an overview of total peroxy nitrates $\sum PNs$ 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 $\sum PNs$ 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 $\sum PNs$ 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 $\sum PNs$ 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 $\sum PNs$ 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 $\sum PNs$). 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.

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 $\sum PNs$ 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.

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.

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.

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 uncertainties were estimated for different campaigns (see above) these should also be added to the table.

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).

Figure 10: The figure caption is a little to Spartan. Please indicate which campaign these time series are taken from.

Technical corrections

p 3058, l 29: "Bowman et al. complemented ...", year of publication missing