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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "Seasonal variation of peroxyacetylnitrate (PAN) in coastal Antarctica measured with a new instrument for the detection of sub-part pertrillion mixing ratios of PAN" *by* G. P. Mills et al.

**G. P. Mills et al.**

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We would like to thank the referee for the constructive and helpful comments and suggestions for the improvement of the manuscript.

Long term stability of instrument and Calibration source:

As the reviewer suggests, halocarbons such as CCl4 would be a very good measure of instrument sensitivity and stability over the long term. Our chromatograms of air (but not the calibrations) do indeed have several other peaks earlier in the chromatogram, and the largest (and nearly last eluting) of which (peak X) is quite likely to be CCl4.

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However the halocarbons elute much more rapidly than PAN on the MXT-200 column, where they are not fully resolved and the baseline is poor. The peak area for peak X, however, shows a very similar pattern of longer term variation to the calibration derived sensitivity of the GC, suggesting that it is the GC that has changed and that large calibration output variations are unlikely to have occurred. The peak X area also shows most of the shorter-term variations seen in the calibrations as well. However there are two issues. 1) The relative magnitudes of the short-term variations in PAN and peak X are not constant. This may be due to different sensitivities to trap conditions, variation in the calibration output or variations in peak X area caused by co-elutants and other non-fully resolved components. 2) In the last few months, the trend in the ratio of peak X area to calibration sensitivity drifts upwards and by the end of the campaign is 10 % higher than at the start. This again could be due to a decrease in the calibration unit output efficiency, but could also be due to a real increase in Peak X area.

We have appended a time series of the calibration sensitivity and Peak X area to figure 2 and have added text discussing the stability of the calibration source in the above terms.

Changes in the Penray lamp output are unlikely to have an effect on calibration output unless they are large since the excess acetone and quite long residence time in the photolysis cell of approximately 3 minutes will mean that NOx availability is easily the limiting factor in PAN production in the system. While we did minimise the acetone usage, enough acetone was available that even with NO flows of over 5ml min-1 the PAN output as measured by the GC was observed to be linear. This would mean that for the lower NO flow used during the campaign, the lamp output could decrease significantly and still photolyse enough acetone to allow complete conversion.

The Calibration unit used in this study was also deployed during the PAN Intercomparison Exercise in Boulder in July 2005 shortly after its return from Antarctica, where it gave results that were in agreement with those obtained with other calibration sources, suggesting that the PAN production efficiency had not changed much since the unit

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was deployed in Antarctica. As part of PIE, the NO standard was re-analysed by Eric Williams and found to be approximately 2% lower than the pre-campaign certification level.This work is as yet unpublished.

Sensitivity corrections:

Simple linear interpolation between calibrations was used as the only sensitivity correction in this study. Variations in sensitivity between the calibrations will have an impact on the precision of the measurements and are discussed below.

Precision estimate:

Precision is a measure of how closely two measurements agree. In the short term this could be termed reproducibility and will not involve drifts in instrument sensitivity, but in the longer term any changes in instrument sensitivity not accounted for will, as indicated by the referee, affect this comparison. Both are precision, but the timescale is important to note. The precision estimate we state does not include any error due to long-term variation or drift in the calibration source which would affect the comparison of seasonal data. We have amended the text to clarify our definition and to comment on the possibility of a long-term drift suggested by peak X . The short term precision quoted is slightly smaller than the variation of Peak X between calibrations, but given the large uncertainties associated with our measurement of Peak X we feel that our estimation based on the PAN peaks is an accurate representation of between calibration variation.

Absence of PAN -CO relationship:

CO-PAN relationships are based on the assumption that the higher CO is an indicator of enhanced levels of precursor materials such as hydrocarbons, oxygenates and NOx. This is entirely reasonable in most areas of the world. In this study, CO changes throughout most of the measurement period are the gradual seasonal change, with acute changes of only 1-2 ppbv observed on a background of 45 -55 ppbv. This sug-

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gests that transport of air containing enhanced PAN precursors co-emitted with CO does not typically occur. We do not find this surprising given the extreme remoteness of Halley from areas impacted by large sporadic CO sources. The lack of CO variation indicates well mixed, aged air with background levels of species in most cases, and thus, we believe, implies than the PAN that we see has been made under background CO conditions.

Data analysis:

The referee suggests more detailed analyses and interpretation of the data using scatter plots and trajectory analyses to identify and look at differences between airmasses, in particular the single period where pan and a significant change in CO correlate. This 3-5 day period where CO, alkenes and PAN are all elevated is the only time in 7 months that such an event occurs and has trajectories low over the south Atlantic. We could speculate if it is mildly polluted/processed air that has had some recent oceanic influence, and also if the PAN is from oceanic source or not but that is all, we have no other tracers with which to test any hypotheses, since acetylene/CO shows only a gentle seasonal drift throughout winter and early spring and acetylene is at or below detection limit most of the time in the summer. The particular event stands out only in the magnitude of the CO change and apparent oceanic impact as evidenced by the very high alkenes, and that this trajectory source was the only one in January that came from as far north as it did. In comparison with other times of the year, the trajectory does not stand out as unusual in latitudinal extent. The addition of figures describing this event in more detail would increase the paper length with no real increase in understanding of PAN sources or chemistry since the changes in CO, PAN, ozone and alkenes are readily seen in fig 3 and there are increases in CO, PAN and alkenes in summer (though not together) that come from trajectories of all types (low and high as well as from higher latitudes) and do not show a clear pattern . For example several CO increases in summer are associated with the whole range of trajectory types and as stated above, there are no other useful tracers with which to classify or differentiate these events for comparison. We therefore feel we have analysed the data as far as we think is justifiable.

Specific comments: Title: While this study is not a complete year, we do not describe it as an annual cycle and since the paper does describe measurements in 3 Antarctic seasons showing a possible variation of PAN over those 3 seasons, albeit tentatively, we think that the title is not inappropriate.

Peltier: full details of the devices and the voltages used are now included in the revised manuscript

Nafion Dryer losses: We have measured the calibrator output both with and without a nafion dryer in place and observed no detectable difference. We have used nafion dryers for the measurement of C1-C7 organic nitrates using GC-MS for several years with no observed problems of losses or memory effects.

Humidity effect: The nafion dryer used in this study used molecular sieves rather than counter-purge gas, which is inherently less effective method anyway, achieving higher final dewpoints for the dried gas, and the molecular sieves effectiveness would likely change with use. On occasion when the molecular sieves were changed, small differences in baseline noise and instrument sensitivity were observed. These sensitivity changes were small compared to the effect of trap temperature.

Technical corrections: Table 1: has been removed and the information is included and expanded slightly in the experimental section.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 5617, 2007.

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