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Atmospheric
Chemistry
and Physics
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.

Halocarbons and Calibration source stability:

Our chromatograms do show several additional peaks which elute much earlier than PAN, one of which, peak X, may be CCl4. These additional peaks do not appear in calibrations. We have appended a timeseries of PAN calibration sensitivity and peak X area to figure 2. This figure shows that the calibration sensitivity and peak X area

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follow a very similar pattern even on a short timescale- suggesting that it is the GC that is changing sensitivity and not the calibration source. The relationship is not perfect and there are both differences in the relative magnitudes of the short term variations of peak X and PAN and a 10% drift in the mean ratio of the calibration sensitivity and peak X area over the course of the campaign. These effects could be due to differences in the relative sensitivity of PAN and peak X to trapping conditions, changes in the calibration output or real changes in peak X area or possible co-elutants. In the revised manuscript, we 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.

Whilst the calibration unit used in this study was not reanalysed on the 4 channel NOxy instrument upon its return to the UK (the NOxy was not available) it was 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 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.

The suggestion by the referee of spiking the samples (and perhaps the calibration output) with a stable reference compound as an additional stability check is appreciated and we will attempt some form of this in the future.

Effect of trap cleanliness:

The sample trap adsorbent area is very small and it is possible that in periods where there have been high levels of involatile species, the efficiency of trapping the more volatile compounds could have been affected. The trap was heated to 70 C for 1 minute (we were limited to quite low temperatures by the insulation material used on the trap) after each injection to try and reduce any such effects. This effect is likely to be less important than the of temperature variation.

HONO chemistry:

HONO was measured throughout CHABLIS and is discussed in the Jones et al paper in this special issue. HONO plays a significant role in the snowpack recycling of NOx and thus perhaps the atmospheric NOx levels in the Boundary layer above the snow. There is however a pronounced difference in the trends of PAN and snowpack HONO, suggesting that NOx from the snowpack HONO is not significantly affecting the observed PAN. In our calculations we make the implicit assumption that there is enough NOx for all peroxyacetyl radicals to react without hindrance, so sporadic snowpack NOx sources would not change our conclusions (sources of the PA radical or PAN itself, however, would).

Table 1 information:

Table 1 has been removed and slightly expanded details are now included in the experimental section. NOx was included in table 1 because it was used in figure 7 and used to show PAN can be an important NOx source. NO/NO2 is indeed derived from TUV calculated photolysis rates and ozone since, at the time of writing, validated NOx data is not available except for January and February. TUV was used throughout the measurement period since the spectral radiometer at Halley suffered damage during a spring storm and thus there was no data until spares arrived in summer. It was used for all calculations, even in summer when spectral radiometer data were indeed available, purely for consistency, as was the scaled HO2/OH data. The scaling of the HO2/OH

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data is the same relationship as that employed by Bloss et al. in their paper (Bloss et al. acpd 2007) (that we omitted to mention in the paper) which was based on fitting observed OH/HO2 data to measured JO1d. Since the other assumptions and influences on sources/sinks for PAN (such as acetaldehyde or other peroxyacetyl radical sources and temperature) are likely to be much bigger sources of error in the calculations we do not think the extra detail adds anything or affects our conclusions.

Vertical aspect of trajectories:

Figure 6 has been modified to show the vertical history of the trajectories and has been coloured to make the visualisation easier. It also has additional data for the last half of January which was inexplicably missing from the original. It now shows that trajectories from oceanic regions are typically low level and those from the continent are by necessity higher. The changes still illustrate the absence of any distinct relationship between back trajectory history and PAN mixing ratios.

Mid -tropospheric PAN levels:

Our statement regarding mid-tropospheric PAN levels is too simple and the reality is less certain. In our experience of several aircraft campaigns in the remote Atlantic around the Azores, PAN is almost always lower in the warm boundary layer than the colder air above. Roberts et al (JGR 2004) have seen similar patterns in the pacific as have Kotchenruther et al (jgr 2001). However, the variability of PAN observed at all altitudes is typically greater than the differences in mean or median PAN between altitudes We have added text and references to the revised manuscript to reflect this lesser degree of certainty and included the two references above.

Air mass signatures:

It is almost impossible to identify airmass types by tracer signatures with the data available. The tracer suggested, the acetylene/CO ratio, shows a smooth, gradual decline throughout the winter and early spring with no large deviations. During October and beyond, the acetylene drops below detection limit for most of the time. Scatter plots involving CO are also not very useful since short-term CO changes were very small (less than 1-2 ppbv on a background of 45-55 ppbv) for almost the entire measurement period. During January when the largest CO changes occurred, many hydrocarbons were at or below detection limit and there is simply no correlation between ozone, total alkanes nor the available NOx data and CO. What this suggests is that the air arriving at Halley is typically well-mixed, processed air containing background levels of CO and other species, and that transport of polluted air is a rare event. Given the very small number of occasions where CO deviates noticeably from its seasonal trend and the absence of other useful distinctive tracer information we believe we have interpreted the data as much as we sensibly can.

Temperature of heated inlet: The Inlet was not heated. This has been corrected in the revised manuscript.

Nafion dryer:

The referee is correct that dryers are rarely used in PAN measurements since, unlike our pre-concentrator method, there is usually no need to remove water from the sample. To our knowledge there are no reports of studies of PAN transfer through nafion. We have sampled the calibration unit output alone and through the dryer on several occasions, with no observable difference, which we do state in the paper. We have also used counter-purge nafion dryers for several years for the measurement of C1-C7 organic nitrates using GC-MS with no problems of losses.

PAN decomposition rates:

We have changed the statement about 30 K change to “...change in temperature from 300 K to 270 K changes the calculated rate of dissociation..."

Figure labels: Now include missing items in caption

Technical corrections:

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Reference years corrected.

New References: J M. Roberts, et al. Measurement of peroxycarboxylic nitric anhydrides (PANs) during the ITCT 2K2 aircraft intensive experiment, J. Geophys. Res., VOL. 109, D23S21, doi:10.1029/2004JD004960, 2004

R.A. Kotchenruther et al.,Observations of ozone and related species in the northeast Pacific during the PHOBEA campaigns 2. airborne observations., J. Geophys. Res., 106(D17), 20,507-20,508, 2001.

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