

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.

Anonymous Referee #2

Received and published: 27 June 2007

General comments

Mills et al have developed and deployed a new low level GC system for the automated measurement of peroxy acetyl nitrate (PAN) in remote locations. There is a visible sparsity of observations of PAN in the polar regions, in particular the Antarctic which is indeed significantly more remote than northern hemispheric polar regions. The instrument has been developed as part of the large UK CHABLIS project at the new CASLab located in the clean zone close to Halley research base in Antarctica. CHABLIS aimed to gather together a solid dataset which will allow us to gain insights into atmospheric

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

chemistry and interactions between the snow/ice and air interface which has been suggested as being significant in the source/sink cycles on many key atmospheric species. One unique aspect of the polar regions is the seasonal solar cycle which may prove very useful in deciphering photochemical driven features and those of long range transport/meteorologically driven events.

The interpretation of the data generated provides us a route into the role of PAN in the overall NO_y budget in this region. Of particular interest is the in situ photochemistry and exactly what drives it, this area has gained considerable interest in recent years following initial work by the likes of Anna Jones who is one of the driving forces behind CHABLIS.

specific comments

The paper provides a detailed description of a nicely thought out instrument, it gives some information on it's overall sensitivity/detection limits which clearly do change over the observing period. Given the extended operational period, the long term stability of the measurement is critical if it is to be assimilated alongside the parallel measurements obtained at the site.

There are a number of questions I have.

P5625, line 23 - What are the effects of the cleanliness of the trap? Could the trap not be heated periodically above the normal desorb temperature which is a common 'conditioning' technique.

What is the stability of the PAN source used for the calibration? The lamp used to photolyse the acetone will have a variation and may suffer a degradation over time. NO calibration gases are often prone to degradation over time. There is no mention of the calibrator being checked against the 4 channel instrument upon its return.

Such performance metrics are vital as the instrument will be working close to its limit for a large proportion of the time

Interactive
Comment

The GC system deployed is probably more than capable of separating other electrophilic species in addition to PAN, ambient halocarbons are commonly observed on such systems especially given the time allowed to perform the analytical separation. Were there any compounds in the ‘separation window’ which could be used for this purpose? Perhaps for the future an improvement would be to spike an internal standard into the sample stream prior to desorbing.

Were measurements of HONO available? There is no mention of these and as I understand it HONO was to be measured during the CHABLIS project. From my recollections, recent research has indicated the importance of snow/ice interactions and HONO production/loss in this sort of environment.

There appears to be measurements made at the site listed in table one which are then ignored for the numerical analysis, for example NO/NO₂ is derived from observed ozone or am I missing something here?

There were good OH/HO₂ measurements made for the shorter intensive period, why have these not been used directly to compare the ‘estimated’ to the real for this admittedly shorted period, it would provide confidence in the methods used. In addition to the OH/HO₂ measurements, surely the FAGE system included a measure of the O₁d photolysis frequency, yet the paper uses the TUV model output for this, I ask why.

Although Jones et al provide a detailed description of the site and the “basic” measurements, it would be good just to identify the techniques used for these supporting measurements (O₃, CO, NMHC, NO_x.)

The trajectory analysis shows information on the source areas of the differing air-masses. Given the three-dimensional nature of the atmosphere I did find it rather surprising that no information on the vertical ‘history’ of the air masses was presented. This would have provided a better picture perhaps of what has occurred during the days leading up to observation. This is a comment stating the higher levels of PAN would be expected to be present in the mid troposphere compared to the marine boundary layer

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

but nothing to support this in the observations.

Scatter plots are a simple very powerful technique to identify patterns and air mass signatures for large datasets such as presented here but they are sadly lacking. There are a number of different relationships which could be examined not just PAN with other compounds but CO vs acetylene is a very useful tracer, as is CO vs Ozone.

Other comments

p5619, line 5 - you state a change in temperature of 30 K changes the dissociation rate by 2 orders of magnitude, please clarify the temperatures used to qualify this statement.

p5620, line 9 - What is the temperature of the heated inlet? This is not stated, although the residence time is noted I would expect that this should not be an issue, the inlet temp should be stated whatever the case.

p5621, line 26 - I notice that a Nafion dryer is used, I'm not aware that this is commonplace with PAN measurements. Is the transfer function of PAN across the Nafion membrane known? Because if it is I've never seen mention of it anywhere.

p5639, Figure 1a - Some items in the figure are labeled but there is no reference to what the label means

This program promises to provide an invaluable dataset which will further our understanding of the gas budget/cycles in this region. Overall the paper is a good piece of work which stands on its own whilst fitting in very nicely into the CHABLIS special issue.

technical corrections

P5618, line 25 - Reference Gaffney et al, is this 1999 or 1992?, the former is stated in the text and the latter is in the reference list p5619, line 22 - delete unnecessary hyphen p5620, line 6 - Reference King, 1989, is this 1989 or 1985?, the former is stated in the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

text and the latter is in the reference list p5621, line 23 - (D in Fig 1) should read (D in Fig 1a) P5622, line 13 - Reference Baker et al, the reference list has Barker, please amend to whichever is correct

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

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper