

Interactive comment on “Seasonal variation of peroxyacetyl nitrate (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 #1

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Mills et al. present continuous measurements of peroxyacetyl nitrate (PAN) at Halley during the CHABLIS campaign. The measurements were made by a custom-built gas chromatography/electron capture detection (GC/ECD) instrument, and covered winter, spring, and summer seasons of 2004/2005. In general, the manuscript is well organized and clearly written. The authors present a significantly new and very interesting dataset of PAN in coastal Antarctica, where previous measurements are very sparse. An insightful interpretation of these data would certainly lead to valuable enhancement of the understanding of the roles of PAN in NO_y budget, tropospheric photochemistry,

and air-snow interaction in this region. The main body of the manuscript contains instrumentation and its validation, and presentation and interpretation of PAN data with ancillary parameters. Although the paper is a nice piece of work, I have a couple of concerns that are listed below in detail.

General comments:

Instrument performance:

My concern lies in long-term stability of the instrument sensitivity/precision during such a long period. The authors generally describe their instrument performance very well (as illustrated in Figure 2). Although they mention precision based on relatively short-term measurements, this seems repeatability/reproducibility. Detailed information about long-term stability of sensitivity and precision is lacking. In addition to low detection limits, this point is an important part in the present paper since the authors discuss much about seasonal variations of PAN. In deed, achieving long-term stability is technically not easy especially in measurements at such a challenging site, and the authors note that temperature changes affected the instrument sensitivity. However, since the authors mention that they made calibration every 2 days (Page 5626), they can show these results, add some explanation about sensitivity correction (if any), and demonstrate its robustness. This would provide their data quality with more strength. Also, I would like to see halocarbons data (if available), which were potentially co-eluted with PAN in similar systems used here, as they sometimes can be used as internal standards to check long-term stability of the instrument.

In Page 5625, precision is estimated. Does this include stability of PAN photo-source? It seems to me that stability of a photolytic calibration source is worse than that of ECD detection. What about temperature effect on stability of a pen ray intensity.

Data interpretation:

As the authors discuss, seasonal cycles of PAN are not apparent. This suggests that

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the background-levels of PAN are nearly zero, and occasional transport of PAN and/or other more local impacts dominates its variability. I would not be surprised at the absence of ozone-CO (and hence ozone-PAN) correlation, since natural sources for ozone are more intense, in relative, in the southern hemisphere than in northern hemisphere, especially around Antarctica regions. However, the lack of PAN-CO correlation would be rather surprising. The authors' explanations that local influences such as temperature during transport and/or snow pack chemistry are one of potential ones, but short-term PAN-CO relationship could be worth more careful investigation. This can be made by exploring some case studies for January events and by adding/improving figures. This exercise would significantly improve their interpretation and benefit the present paper. For example, as the authors already describe, positive PAN-CO correlation was observed in the end of January (Page 5632, line 5-11). Not only illustration of overall dataset like Figure 3, adding more expanded figures like Figure 7 for multi-species (ozone and CO + PAN and sum of C2-C5 NMHCs) during the period, when correlative behavior was observed, would potentially provide more useful information. Back trajectories for each day during the event can be included (as are mentioned in text). Scatter plots of PAN-CO, PAN-NMHCs, and ethene or propene-CO can be examined in terms of air mass types (or potential source regions). These features can be compared to data in other period when correlation was not observed.

Specific comments:

Title: The authors' measurements did not cover a full year, and continuous PAN data do not show clear season-dependent variations. I would suggest to modify the title to "Continuous measurements of peroxyacetylnitrate (PAN) in coastal Antarctica measured with a new instrument for the detection of sub-part per trillion mixing ratios" or the other one appropriately.

Introduction: Roberts (1990) paper is a nice reference to be put here.

Experimental: A triple-stage cascade peltier cooler used for a sample trap needs make

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and model names.

The authors use a long Nafion dryer to remove water vapor from sample air. I do not think this is common deployment for PAN measurements. How about possibility of PAN loss? What about the range of humidity of ambient air in Antarctica during the campaign? I would like to see some explanation of sensitivity dependence on humidity with a Nafion dryer.

Technical corrections:

Table 1: I do not think this table necessary, since Jones et al. paper has the same table, and the authors do not describe it in the text. I would suggest removing this table, and adding brief explanation of measurements of ozone, CO, NMHCs, and NO_x discussed in the paper.

Figure 1: Explanation of F, G, and H should be included in the caption.

Page 5625: Fig. 4 would be Fig. 2c; propyl nitrate... should be Propyl nitrate...

Page 5626: Table 1 should be Table 2

Acknowledgements: B. Bandy is acknowledged, but he seems a co-author. In that case this should be removed.

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

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