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Pernitric acid in a coastal Antarctic boundary layer – a wintertime study

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INTRODUCTION

1) Pernitric acid (PNA, i.e. HO_2NO_2)

PNA couples HOx and NOx chemistry through its production and loss reactions:

$HO_2 + NO_2 + M \leftrightarrow HO_2NO_2 + M$
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ **or** $OH + NO_3$
$HO_2NO_2 + OH \rightarrow H_2O + NO_2 + O_2$

Further, PNA can strongly adsorb to ice/snow surfaces, so has the potential to act as NOx/HOx reservoirs, either short or longer-term.

$HO_2NO_2 \rightarrow$ deposition

The only previous measurements in Antarctica were at South Pole during the summer. Then, significant amounts of boundary layer PNA were detected (<5 to 54 pptv, mean 25 pptv), with lifetime controlled predominantly by dry deposition and thermal decomposition (Slusher et al., 2002). No wintertime observations have previously been made.

2) Measurement Location and Instrumentation

PNA was measured during the 2007 overwinter campaign at the British Antarctic Survey station, Halley, in coastal Antarctica (see Fig. 1).

Observations were made at the Clean Air Sector Laboratory (CASLab) (Fig. 2) using a Chemical ionisation Mass Spectrometer (CIMS) using the SF_6 technique described by Slusher et al. (2001).

The CIMS concurrently measured nitric acid (HNO_3) and measurements of NO and NO_2 were obtained by a chemiluminescence analyser.

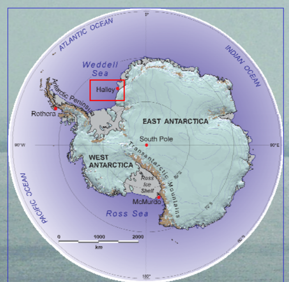


Fig. 1 Map of Antarctica

Fig. 2 The Clean Air Sector Laboratory (CASLab)

RESULTS

3) Overall dataset

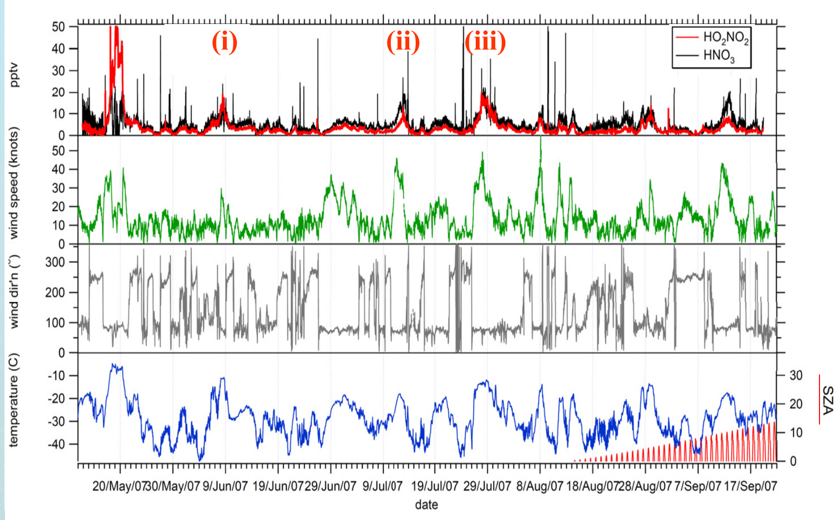


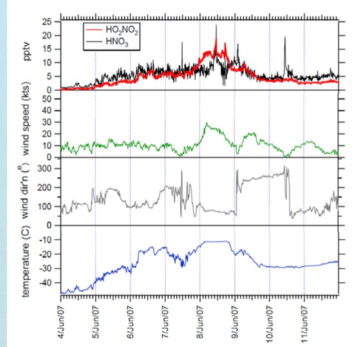
Fig. 3 HO_2NO_2 and HNO_3 measurements during the 2007 Antarctic winter. Spikes are from contamination, but included as contrast to natural atmospheric variability. Also shown are local environmental parameters.

- PNA is present in the wintertime boundary layer at Halley!
- Considerable variability is evident, with mixing ratios varying between instrumental detection limits and ~20 pptv;
- Generally, the same variability patterns reflected in HNO_3 mixing ratios;
- The majority of these measurements were made during polar night, so little or no sunlight, as shown by SZA trace;
- No in situ production of HO_2NO_2, or loss via photolysis or OH are possible. ([NO] and [NO_2] were below detection limit throughout). [PNA] must be controlled by transport and physical exchange processes;
- At first glance, higher mixing ratios of both HO_2NO_2 and HNO_3 associated with strong winds and warmer temperatures (*but see next panel*);
- 3 case studies during polar night examined in more detail with air parcel history explored using Hysplit trajectory model (Draxler and Rolf, 2003)

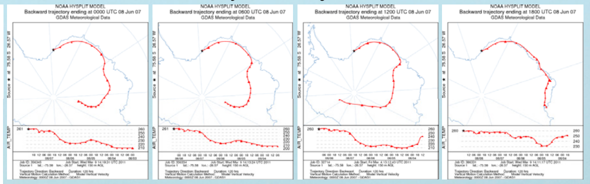
References:
Draxler, R.R. and Rolph, G.D., 2003. NOAA Air Resources Laboratory, Silver Spring, MD.; Li et al., JGR (101), 6795, 1996; Slusher et al., GRL (28), 3875, 2001; Slusher et al., GRL (29), doi:10.1029/2002GL015703, 2002

CASE STUDIES

Case (i)

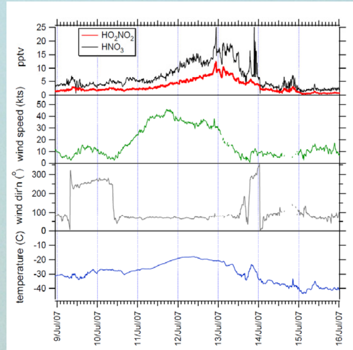


5-day back trajectories

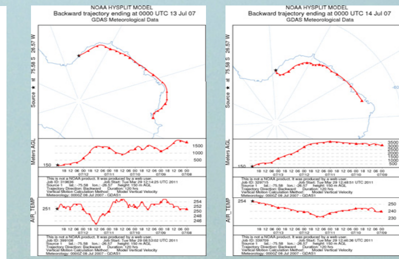


During higher PNA at Halley: i) winds and temps at Halley were increased; ii) air arrived from plateau region with history of low temperatures.

Case (ii)



5-day back trajectories



Note different scales!

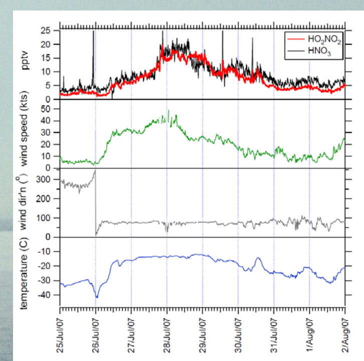
Path above model ground level

Air temperature history

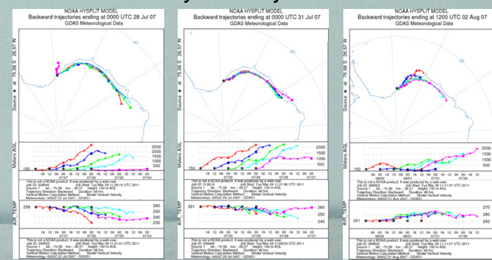
higher PNA at Halley | lower PNA at Halley → ***WHY..??***

Due to... Different length of fetch..? Different altitude history..? Different temperature history..? Different wind speeds at Halley..? – *work in progress!!*

Case (iii)



2-day back trajectories



*Gives broad view...*Evolution of higher PNA at Halley clearly linked to air mass origin; highest concentrations associated with highest altitude and lowest temperatures in preceding 2 days – also highest winds and higher temps at Halley.

CONCEPTUAL MODEL....

All case studies shown here imply a link between enhanced coastal PNA and air transport from the Antarctic Plateau. But air temperatures at the coast increase with increasing PNA which is counter-intuitive given that a major loss of PNA is thermal decomposition.

However, we know that PNA can adsorb onto ice surfaces and desorb as temperatures rise (Li et al., 1996); thermal desorption from the snowpack would thus be associated with increasing temperatures. Our data suggest that PNA from Plateau snow is feeding into coastal areas under specific environmental conditions.

While such events are infrequent at Halley, the process would be more important in areas with katabatic outflow. If correct, this would be a new mechanism affecting the nitrogen budget (both air and snow) across Antarctica.

British Antarctic Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL