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Pernitric and nitric acid in a coastal Antarctic boundary layer –a winter time study

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It has been mooted that pernitric acid (HO2NO2) might play an important role in low altitude photochemistry of the polar regions. This potential arises from the intrinsic link between PNA and atmospheric NOx and HOx radicals. For example, gas-phase production and destruction reactions are, respectively, sinks and sources of NOx and HOx. Further, like HNO3, PNA can adsorb to ice/snow surfaces, so has the potential to form reservoirs of radicals associated with the condensed phase, either temporary or longer-term. Previous measurements at the South Pole detected significant amounts of boundary layer PNA with a lifetime controlled predominantly by dry deposition and thermal decomposition. No observations at relatively warmer, coastal, Antarctic sites have yet been reported.

As part of a year-round field campaign at the British Antarctic Survey station, Halley, in coastal Antarctica, measurements of PNA and HNO3 were made using a Chemical Ionisation Mass Spectrometer (CIMS). Observations extended from March (austral autumn) through to September (austral spring) with further periods in late spring and summer. Concurrent measurements of NO and NO2 were obtained by a chemiluminescence analyser.

Here we present the winter time observations. Both PNA and HNO3 were present in the winter time boundary layer at Halley. Considerable variability in mixing ratios was evident, between instrumental detection limits and ˜20 pptv, and with the same variability patterns reflected in both PNA and HNO3. The majority of these measurements were made during polar night, so little or no photolysis was active (indeed, [NO] and [NO2] were below detection limit throughout the measurement period). Instead, the variability in PNA and HNO3 appears to have been controlled by transport and physical exchange processes. We explore case studies that suggest higher PNA and HNO3 was associated with air mass transport from the polar plateau and linked to changing temperatures, which in turn would drive air/ice adsorption and desorption processes.

Our data thus suggest that PNA and HNO3 from Plateau snow is feeding into coastal areas under specific environmental conditions. While such events are infrequent at Halley, the process would likely be more important in areas with katabatic outflow. If correct, this would be a new mechanism affecting the nitrogen budget (both air and snow) and radical recycling potential across Antarctica.

Please list some keywords

Pernitric acid, nitric acid, air/snow physical exchange, coastal Antarctica, winter boundary layer

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