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The multi-seasonal NO_y budget in coastal Antarctica and its link with surface snow and ice core nitrate: results from the CHABLIS campaign

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Measurements of individual NO_y components were carried out at Halley station in coastal Antarctica. The measurements were made as part of the CHABLIS campaign (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) and cover over half a year, from austral winter 2004 through to austral summer 2005. They are the longest duration and most extensive NO_y budget study carried out to date in polar regions. Results show clear dominance of organic NO_y compounds (PAN and MeONO_2) during the winter months, with low concentrations of inorganic NO_y , but a reversal of this situation towards summer when the balance shifts in favour of inorganic NO_y . Multi-seasonal measurements of surface snow nitrate correlate strongly with inorganic NO_y species. One case study in August suggested that particulate nitrate was the dominant source of nitrate to the snowpack, but this was not the consistent picture throughout the measurement period. An analysis of NO_x production rates showed that emissions of NO_x from the snowpack dominate over gas-phase sources of “new NO_x ”, suggesting that, for certain periods in the past, the flux of NO_x into the boundary layer can be calculated from ice core nitrate data.

1 Introduction

The chemistry of oxidised nitrogen ($\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HONO} + \text{HNO}_3 + \text{p-NO}_3^- + \text{RONO}_2 + \text{PAN} + \text{HNO}_4 + \text{N}_2\text{O}_5 + \text{XONO}_2 + \text{XNO}_2 + \dots$, where p-NO_3^- is particulate nitrate, R is an alkyl group and X is a halogen) in polar regions has received attention over recent years for two primary reasons. Firstly, with the key role of NO_x ($= \text{NO} + \text{NO}_2$) in tropospheric chemistry, sources, concentrations and associated chemistry of NO_x are important to understand and quantify in order to determine its influence on the high latitude boundary layer. Early studies from the Arctic pointed to the dominance of PAN in the NO_y budget (driven predominantly by long-range transport), and explored the role of PAN as an NO_x source (Bottenheim et al., 1993; Solberg

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et al., 1997). More recently, work has shown the surprising source of boundary layer NO_x from nitrate impurities within surface snow (Honrath et al., 1999; Jones et al., 2000; Jones et al., 2001), and that in some polar locations concentrations of NO_x arising from this source are high enough to drive local ozone production (Crawford et al. 2001; Davis et al., 2001; Davis et al., 2004). Furthermore, the snowpack has also been shown to be a source of HONO to the polar boundary layer, driven similarly by photolysis of snowpack N impurities (Zhou et al., 2001; Beine et al., 2002; Dibb et al., 2002).

The second reason for interest relates to ice cores. The deep ice cores that are drilled in polar regions yield a record of changing nitrate through time. Nitrate in ice is easy to measure and there are abundant ice core nitrate data available. Nitrate impurities in ice are driven by deposition of atmospheric NO_y species, and potentially therefore, hold information about concentrations of NO_x in the past and how they have evolved over glacial/interglacial timescales. Our ability to reconstruct past concentrations of NO_x , however, is severely limited by our understanding and knowledge of the present day polar NO_y budget, and we cannot hope to reconstruct past NO_x without knowing how present day NO_x is connected, at minimum, to the depositional sinks for NO_y . Furthermore, we need to understand the depositional processes that generate the record of nitrate in ice. Post-depositional processes are an additional complication, but not one that is addressed in this paper.

The family of NO_y thus comprises a number of components whose concentrations are likely to change throughout the year driven by seasonally-dependent sources and sinks. To probe partitioning within the NO_y family and the relationship to NO_x concentrations, observations of as full a suite of NO_y species as possible is necessary, and measurements should extend over a sufficiently long time period to tease out the major and minor processes at work. Various studies have addressed the budget of NO_y at high latitudes, e.g. in Antarctica at South Pole (Davis et al., 2004, 2005; Huey et al., 2004, Arimoto et al., 2004) and Neumayer (Jones et al., 1999; Jacobi et al., 2000), and in the Arctic at Summit (Honrath et al., 1999; Ford et al., 2002; Dibb et al., 2002;

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Yang et al., 2002) and Ny-Ålesund (Solberg et al., 1997; Beine et al., 2001). As such studies involve by definition a large range of measurements, previous assessments have been conducted with varying degrees of coverage. Furthermore, the majority of these studies have been carried out during summer months with some limited spring-time measurements, but we are unaware of any studies addressing the NO_y budget for other seasons. Our work considers the balance of NO_y components in coastal Antarctica, and explores how this balance changes as the Antarctic seasons progress from winter, through spring and into summer. We also describe seasonality of surface snow nitrate (NO₃⁻) concentrations and look for associations with changing NO_y components through the year.

2 Observations and data averaging

The measurements were made at the British Antarctic Survey research station, Halley, in coastal Antarctica (75°35' S, 26°39' W). The data were collected at the Clean Air Sector Laboratory (CASLab) as part of the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) measurement campaign (see Jones et al., 2007¹). Altogether 11 different NO_y components were measured during the campaign using 8 different methods and techniques (see Table 1).

Instruments measuring the various component species came on line at different times during the year from April onwards, but all species were being measured simultaneously after mid-winter. The data thus allow an assessment of how the NO_y budget varies from mid-winter through spring and into the summer. In recognition of the lower (weekly) sampling frequency for some components (e.g. RONO₂, HNO₃, p-NO₃⁻), measurement intensives were carried out each season whereby sampling for

¹Jones, A. E., Wolff, E. W., Salmon, R. A.: plus 21 co-authors: Chemistry of the Antarctic Boundary Layer and the Interface with Snow: An overview of the CHABLIS campaign, in preparation, 2007.

these species was increased; for 1 week each season they were sampled at daily resolution, and for one day at 6-hourly resolution. Many of the 6-hourly filter/denuder samples were unfortunately below the detection limit, but some higher resolution data (e.g. daily HNO_3) became available as a result. As of January 2005, a GC-MS was measuring speciated alkyl nitrates at Halley, providing significantly higher resolution data (Sturges et al., 2007²). In addition, surface snow was sampled each day from March 2004 onwards, and stored for subsequent analysis for nitrate.

Data in this paper are presented as monthly-averages and standard error of the mean. Full resolution data sets, with details of data validation, are presented in companion papers (Bauguitte et al., 2007³, for NO and NO_2 ; Clemitshaw et al., 2007⁴, for HONO ; Mills et al., 2007⁵, for PAN ; Sturges et al., 2007² for RONO_2). For instruments whose data were collected at high resolution, averages were calculated using all available data and, as data coverage was sufficient, no account was taken for missing data. The filter and denuder data were available as integrated averages for roughly weekly periods. Averages for these species were derived by weighting each filter/denuder sample according to the number of days that the filter/denuder was exposed for. Alkyl nitrate data were derived for most of the year from whole air flask samples; the data are

²Sturges, W. T., Mills, G. P., Worton, D. R., Humphrey, S., Salmon, R. A., Bauguitte, S.J.-B., and Jones, A. E.: Seasonal cycles of several short-lived halocarbons and alkyl nitrates in the Antarctic boundary layer and snowpack interstitial air, in preparation, 2007.

³Bauguitte, S. J.-B., Bloss, W. J., Evans, M. E., Jones, A. E., Lee, J. D., Mills, G.P., Saiz-Lopez, A., Salmon, R. A., Roscoe, H. K., and Wolff, E. W.: An overview of multi-seasonal NO_x measurements during the CHABLIS campaign: Can sources and sinks estimates unravel observed diurnal cycles?, in preparation, 2007.

⁴Clemitshaw, K. C., Ames, D., Fleming, Z., Salmon, R. A., Bauguitte, S. J.-B., and Jones, A. E.: Multi-seasonal measurements of HONO during the CHABLIS campaign in coastal Antarctica, in preparation, 2007.

⁵Mills, G. P., Sturges, W. T., Salmon, R. A., and Bauguitte, S. J.-B.: Seasonal variation of peroxyacetyl nitrate (PAN) in coastal Antarctica measured with a new instrument for the detection of sub-part per trillion mixing ratios of PAN , in preparation, 2007.

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thus spot measurements made on a number of occasions (not always evenly spaced) during each month. To derive a meaningful average, the data were plotted against day of the month, and the slope and intercept used to calculate the mid-month mixing ratio which was then taken as the monthly mean.

3 Results

3.1 Gas-/aerosol-phase measurements

3.1.1 Seasonality of monthly-averaged NO_y species

The variation of monthly-averaged NO_y components throughout the measurement period is shown in Fig. 1. Figure 1a shows the inorganic NO_y species. HONO and HNO_3 showed clear wintertime minima, with mixing ratios around the instrumental detection limit for each species (2 and 1 parts per trillion by volume (pptv) respectively). The mixing ratios increased with the onset of spring, and by December (austral summer) had reached monthly mean mixing ratios of 5.3 pptv for HONO and 5.7 pptv for HNO_3 . By January, the HNO_3 monthly mean mixing ratio was effectively unchanged, at 6.2 pptv, while that for HONO had risen to 10.4 pptv. These observations for gas-phase HNO_3 are consistent with measurements made by nylon filter sampling at Neumayer, both in terms of seasonality (A. Minikin, personal communication) and summertime mixing ratio (Jones et al., 1999; Jacobi et al., 2000). As shown on Fig. 1a, particulate nitrate, p-NO_3^- , was similarly suppressed during the winter months, but displayed a springtime maximum with the monthly mean peaking in October at 4.6 pptv. Over the subsequent months, this value dropped to a monthly mean of 1.8 pptv in January. This seasonality is in line with that measured previously at Halley and at Neumayer (A. Minikin, personal communication). Work by Rankin and Wolff (2003) has shown that at Halley, p-NO_3^- is formed locally by reaction of gaseous HNO_3 with sea salt aerosol; the seasonality of p-NO_3^- is thus a composite of these two annual cycles. Furthermore, the seasonal

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cycle of “total inorganic nitrate” ($TIN = HNO_3 + p\text{-NO}_3^-$) (not shown) shows a characteristic late winter (August–September) peak which has previously been interpreted as sedimentation of polar stratospheric clouds (PSCs) from the stratosphere into the troposphere enhancing tropospheric TIN (Wagenbach et al., 1998; Savarino et al., 2006).

5 Monthly averages of NO and NO₂ for the summer months (November–January) are also shown in Fig. 1a; NO_x is clearly a significant component of summertime NO_y at Halley. Wintertime mixing ratios of NO and NO₂ were below the instrumental detection limit (S. Bauguitte, personal communication); this is consistent with the winter observations of NO made at Neumayer (Weller et al., 2000). Finally, NO₃ measurements
10 were made during the year, but mixing ratios never exceeded the detection limit of 2 pptv. Output from the GEOS-Chem model (Evans and Jacob, 2005), (a global three-dimensional model of tropospheric chemistry, run at a resolution of 4 deg by 5 deg using meteorological input from the NASA Global Modeling and Assimilation Office) suggested that N₂O₅ mixing ratios never exceeded 0.5 pptv during the year (M. Evans,
15 personal communication).

The monthly-averaged data for organic NO_y components are shown in Fig. 1b, plotted on the same scale as Fig. 1a to allow easy comparison. Two things are immediately evident from the plot. Firstly, the organic NO_y components are completely dominated by PAN (peroxyacetyl nitrate) and MeONO₂ (methyl nitrate). For PAN, the highest
20 monthly-averaged mixing ratio observed was in July, reaching 13.7 pptv. Measurements for PAN only began in July so it is not possible to tell from these data whether the annual maximum occurred then or during an earlier month. For MeONO₂, the highest measured monthly average also lay at the start of the data record, with 14.0 pptv measured during April. By July, mixing ratios were still elevated compared with the
25 rest of the year, at 9.5 pptv. For both PAN and MeONO₂, mixing ratios decline toward austral summer, but are still maintained at 7.2 and 5.6 respectively for the month of December. This declining concentration in MeONO₂ throughout winter darkness and into the spring months is in line with recent measurements from South Pole (Beyersdorf et al., 2006). The higher alkyl nitrates exhibit a similar seasonality to that of MeONO₂,

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albeit at lower mixing ratios. They reach monthly averages of 2.5 pptv (ethyl nitrate), 1.4 pptv (i-propyl nitrate) and 0.2 pptv (n-propyl nitrate) during July and drop to around instrumental detection limits during the summer months.

Also striking from Fig. 1 is that the shape of the timeseries of the organic NO_y components are quite different from those of the inorganic ones; rather than wintertime minima increasing with spring/summer, the organics show a maximum in autumn/winter and their mixing ratios decline with the onset of sunlight and the warmer temperatures of the spring and summer. An apparent exception to this is the January mean mixing ratio for PAN, and to a lesser extent, for MeONO_2 both of which are higher than the mean observed during other summertime months. The relatively high January means are driven by two events with exceptionally high PAN and MeONO_2 , and the background mixing ratios are more typically of the order of a few pptv (see Mills et al., 2007⁵ for further details). However, it is interesting to note that mixing ratios of PAN dominate over any other single component during the entire measurement period.

3.1.2 Inorganic vs organic NO_y in winter and summer

The variation of inorganic and organic NO_y components between summer and winter at Halley is presented in Fig. 2. The first month in which all NO_y species were measured is July, and Fig. 2a shows the July averages of all species, as well as the total inorganic and total organic NO_y for this month. The dominance of the organic species is clear, with an integrated mixing ratio of 27.4 pptv, as opposed to the 3.8 pptv of the inorganic species. By December, with significantly higher temperatures and extended daylight hours, the organic NO_y components are considerably reduced, with monthly-averaged mixing ratios of 14.8 pptv. The NO_y budget is now dominated by the inorganic species, whose integrated mixing ratios reach 22.4 pptv.

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3.1.3 Comparison with NO_y and budget measurements from other Antarctic sites

Previous studies with simultaneous measurements of a range of NO_y components have been carried out at two other Antarctic stations, the German research station, Neumayer (70°37' S, 8°22' W), another coastal site in the Weddell Sea sector of Antarctica, and the American Amundsen-Scott station at the South Pole. At Neumayer, studies were carried out in 1997 and 1999 with measurements extending from late January through to early March. The South Pole measurements were made during December 2003. A comparison between the monthly mean Neumayer (February), South Pole (December) and Halley (January) data is given in Table 2. The Halley data are of a similar order to those from Neumayer in all species measured at both stations. This suggests that, at least in this sector of coastal Antarctica, there is some representative boundary layer chemical composition. In contrast, those from South Pole show large differences for certain species measured, in particular NO, NO₂ and HNO₃. These data highlight the large differences in the boundary layer chemistry between coastal and inland, plateau, sites.

Direct measurements of NO_y were made at Neumayer during a full year in 1999, using a CO/gold catalyst combination to reduce NO_y components to NO, followed by NO detection using a chemiluminescence detector (Weller et al., 2002). Although no direct assessment of NO_y was made at Halley, it is possible to integrate the individual NO_y component measurements to derive an approximation which can then be compared with the Neumayer data. Various provisos must be borne in mind: i) The Neumayer convertor is assumed not to convert particulate NO₃⁻ given its operating temperature so p-NO₃⁻ is not included in the Halley integrated NO_y; ii) the NO_y convertor does not reduce all species with 100% efficiency, so some will be underestimated; iii) it is likely that not all NO_y components are included in the Halley data coverage – for example, neither HNO₄ (important at South Pole) nor halogen nitrates (which other results from CHABLIS suggest may be present in non-insignificant amounts) were measured. Figure 3 shows the comparison between the directly measured Neumayer NO_y and the

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integrated Halley NO_y . During both the winter and the summertime, the integrated NO_y is of a similar order to the measured NO_y . This suggests that the Halley data capture the dominant NO_y components.

3.2 Linking boundary layer and snowpack measurements

5 3.2.1 Year-round NO_y and surface snow nitrate

The concentration of nitrate in surface snow is determined by the combination of input and loss terms. Loss of nitrate is driven both by physical (volatilisation) and photochemical processes. At very low accumulation sites such as those of central Antarctica, physical loss processes are believed to be predominantly responsible for the very large nitrate losses observed there (Röthlisberger et al., 2000). The incorporation of impurities into snow can occur at various heights within the troposphere. For example, snow forms either by condensation of water vapour or by riming (Pruppacher and Klett, 1978). Both processes require nuclei which can be provided, among other candidates, by minerals such as nitrate aerosols. As snow crystals grow, additional molecules can be incorporated by adsorption onto the surface. At tropospheric temperatures, even in polar regions, the surface of snow crystals is disordered (e.g. Petrenko and Withworth, 1999) to the extent that the surface layer is commonly referred to as the quasi-liquid layer (QLL). Uptake of trace gases commonly approximate to gas/liquid interactions, and can be described by the Henry's Law coefficient, K_H . Thus, as snow falls, it can scrub the atmosphere, both through adsorption of gases and scavenging of aerosols, thereby collecting additional impurities which can contribute to nitrate measured in surface snow. Uptake of impurities may continue once the snow has reached the Earth's surface as long as crystal surfaces remain exposed to ambient air.

The suite of measurements gathered during CHABLIS allows us to investigate possible links between changes in boundary layer concentration of individual NO_y components and changes in the concentration of surface snow nitrate. If the surface snow nitrate inventory is driven by uptake within the boundary layer, some association be-

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tween snow nitrate and the NO_y component source gas might be expected. However, if nitrate becomes incorporated into snow as it forms aloft and while it falls to the ground, associations between surface snow nitrate and boundary layer NO_y components are likely to be less apparent.

5 Of the inorganic NO_y species measured during the CHABLIS campaign, the highly acid gas, HNO_3 , with a Henry's Law coefficient of the order 10^5 M/atm (e.g. Brimblecombe and Clegg, 1989; Lelieveld and Crutzen, 1991), is the most likely to be taken up onto the snow surface (Huthwelker et al., 2006). For HONO, K_H is considerably lower, of the order 5×10^1 M/atm (e.g. Park and Lee, 1988; Becker et al., 1996), so uptake will
10 be less than for HNO_3 but could nonetheless be significant. Particulate nitrate, p-NO_3^- can be scrubbed from the atmosphere by falling snow, or deposit directly to the surface of the snowpack, so again, is a likely candidate as a snowpack nitrate source. NO and NO_2 on the other hand, with their relatively low solubility are not likely to be direct sources of snowpack nitrate. Henry's Law coefficients for PAN and the alkyl nitrates are
15 only an order of magnitude smaller than for HONO (Kames and Schurath, 1992, 1995), so some uptake for these molecules by snow crystals might be expected depending on their concentrations.

Figure 4a shows the sum of $\text{HONO} + \text{HNO}_3 + \text{p-NO}_3^-$, and the sum of $\text{PAN} + \text{MeONO}_2$, plotted together with daily surface snow nitrate concentrations. It is clear
20 that the seasonality of surface snow nitrate closely matches that of the inorganic components, with winter minima increasing through spring to summer maxima. There is no equivalent association between surface snow nitrate and the organic NO_y components. Even if individual organic NO_y species were considered, their winter maxima, shown in Fig. 1b) clearly does not match the surface snow seasonality. If there is a
25 direct role for organic NO_y components to contribute to surface snow nitrate, then that role is significantly smaller than that of the inorganic components. Figure 4b shows in more detail the variation throughout the year of the inorganic components and surface snow nitrate: HNO_3 is clearly the most closely correlated with nitrate in surface snow. We return to the reasons for this in the Discussion.

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3.2.2 The August surface snow nitrate “event”

A useful way to probe deeper into potential sources of snowpack nitrate is to consider case studies. Figure 5 shows the time period in August 2004 when surface snow nitrate concentrations became significantly elevated for a number of days. The surface snow sample collected on 15 August had a background concentration of nitrate of roughly 50 ppb; on 16 August, the sample collected had a concentration of over 200 ppb. These high concentrations were maintained through until the end of August. By 30 August, concentrations of nitrate had fallen to roughly 80 ppb, and following a short data gap, by 2 September, concentrations had returned to background.

Having assessed that the most likely contributors to surface snow nitrate are the inorganic NO_y components, Fig. 5 also shows the coincident measurements for HONO, HNO_3 and p-NO_3^- at their maximum resolution. Mixing ratios of HONO are generally constant across this time period, varying little around a background of ~ 1 ppbv. Some increase is measured from 7 September onwards, but this occurs after the surface snow nitrate event has occurred. HNO_3 , being measured using weekly denuder sampling, is not available at such high resolution as the HONO data, but nonetheless it is clear from the figure that there is also little variation in HNO_3 during this time period. Mixing ratios are relatively constant at about 1 ppbv. Particulate nitrate concentrations, however, show considerable variability. Again, the data are only available as weekly averages, so the variation from day to day can only be surmised. However an interesting picture emerges when considering these data together with occurrences of snowfall.

At Halley, meteorological observations are made every 3 h. They include information on periods of snowfall – whether it is snowing at the time and whether it has snowed in the previous 3 h. These snowfall observations are represented as red dots in Fig. 5, and they show that the sudden increase in surface snow nitrate concentrations that occurred between sampling on 14 and 15 August was the result of fallen snow: on 14 August, surface snow was sampled at 11:00, with nitrate concentration of around 50 ppb; by the time the sample of surface snow was collected, at 15:00 on 15 August,

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nitrate concentrations had risen to over 200 ppb. Snowfall was reported at 09:00 on 15 August. As discussed above, the newly fallen snow could have brought impurities to the snow surface from sources at various heights. However, on this occasion, the measurements are consistent with scrubbing of particulate nitrate in the lowermost layer of the atmosphere. During the sampling period from 10 August to 17 August, the concentration of $p\text{-NO}_3^-$ is significantly elevated above prior weekly sampling periods. As the data are integrated measurements they are intrinsically smoothed and there will have been periods during the sampling period when the $p\text{-NO}_3^-$ mixing ratios were further elevated. It is quite consistent that falling snow would have incorporated particles in the boundary layer and deposited them to the snow surface. Over the following days, there is further variability in surface snow nitrate concentrations which could have been caused by a number of factors: the subsequent snowfall could have deposited snow with a different impurity loading; post-depositional losses could have released some nitrate to the atmosphere; or simply heterogeneity in the surface layer could result in different samples having different concentrations. The progressive decrease in surface snow nitrate from 27 August, which resulted in concentrations returning to background on 2 September, appear to have been driven by the recorded snowfalls. At this time, particulate nitrate mixing ratios were also at background values suggesting that there was little boundary layer $p\text{-NO}_3^-$ available to be scrubbed from the atmosphere. Although $p\text{-NO}_3^-$ was again elevated after 2 September, there was no snowfall to deposit any aerosol to the snow surface.

Previous analyses of surface snow nitrate and ground level aerosol, even sampled at daily resolution did not find the two to be consistently highly correlated (Wolff et al., 1998). This suggests that impurities in surface snow can be determined by factors other than the ground level aerosol composition (as discussed above). Indeed, a limited number of profiling measurements subsequently showed that aerosol composition varied quite markedly with height, and that air masses aloft (~200 m above the ground) could have an aerosol loading quite different to that measured on the ground (Rankin and Wolff, 2002). However, for the event described here, at least, it appears that the

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source of surface snow nitrate was wet deposition and scrubbing, and the data are consistent with the nitrate source being $p\text{-NO}_3^-$ within the boundary layer.

4 Boundary layer trace gas versus snowpack sources of NO_x

A key question among polar atmospheric chemists concerns the role of polar snowpacks as a source of trace gases to the overlying boundary layer. For those studying nitrogen chemistry, the interest lies in understanding the budget of NO_x ; we know that NO_x is photochemically produced (Honrath et al., 1999; Jones et al., 2000) and then released (Jones et al., 2001; Wolff et al., 2002) from the snowpack, but the relative contribution compare to NO_x production from trace gases in the background atmosphere has not yet been assessed. The data gathered during CHABLIS allow us to constrain the dominant NO_x production mechanisms, and by comparing these calculated production rates, to assess the relative importance of sources of boundary layer NO_x , both in the air and from the snowpack. This approach also provides insight into which gas-phase species are dominating NO_x production within the boundary layer.

4.1 Methodology

We selected two 24-h periods, one in summer and one in spring, within which to calculate diurnally-averaged NO_x (as either NO or NO_2) production. The periods selected were 18 January 2005 and from noon of 28 September 2004 through to noon of 29 September 2004. The former period was the first day in the summer season when high-resolution alkyl nitrate data were available to compliment the other high-resolution datasets. This was also a time when an NO_y intensive was carried out, so that daily HNO_3 measurements are available. During the latter period, an NO_y measurement intensive was also conducted, giving, in addition, alkyl nitrate measurements every 6 h – the highest resolution alkyl nitrate data available for the spring period.

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4.1.1 Deriving gas-phase data

NO_x production rates were calculated every 3 h during these diurnal periods, giving 8 data points from which daily means could be calculated. Where possible (e.g. for HONO, PAN, summertime methyl and ethyl nitrates), input data were taken from an hourly data merger carried out for all the CHABLIS data and the few missing data points were derived by linear interpolation. For the 6-hourly springtime methyl and ethyl nitrate mixing ratios, it was by default necessary to interpolate to achieve data at a 3-h frequency. These data were thus point-averages rather than hourly-averages, but as mixing ratios did not vary rapidly over the day, the uncertainty introduced by this approach is limited. For HNO₃, sampled over a longer timeframe, it was necessary to reconstruct higher resolution data. Summertime HNO₃ was measured as a 24-h-mean centred around 23:59 on both 17 January and 18 January. These two data points were averaged to derive a daily mean for 18 January. The diurnal variation was reconstructed by comparing with 6-hourly resolution HNO₃ data measured previously at Neumayer station (Jones et al., 1999). There, a diurnal cycle with amplitude 7.5 pptv was measured, centred around noon. This amplitude was applied to the 18 January mean to give a reasonable diurnal cycle. For the 28/29 September HNO₃, the 6-hourly-resolution data were below the detection limit, so the daily mean for 27 September and 29 September were averaged to give a mean for the calculation period. This mean was only 0.96 pptv, and, being so low, it was taken to be constant over the 24-h period of interest. Finally, several measured NO_y species did not exceed 2 pptv throughout the year (e.g. NO₃ and the higher alkyl nitrates), and they were ignored for this calculation. Similarly, output from the GEOS-Chem model suggested that HNO₄ also remained well below this threshold throughout the year (M. Evans, personal communication) so no account for HNO₄ was taken here.

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4.1.2 Gas-phase kinetic data

Gas-phase reaction rates were taken from Atkinson et al. (2004, 2006) and photolysis rates for each 3-h period were calculated using the on-line version of the radiative transfer model TUV (Madronich and Flocke, 1998). For these calculations, input parameters included the total ozone column measured at Halley for these days, and an albedo of 0.9. Clear sky conditions were assumed, so photolysis rates will be overestimated, but the relative effect on all species will be comparable. In addition, OH concentrations were necessary for some kinetic calculations. On 18 January 2005, OH was measured by the FAGE (Fluorescence Assay by Gas Expansion) instrument (Bloss et al., 2007). These data were included in the CHABLIS data merger, so that mean hourly OH concentrations were available for this period. No OH measurements were available for September, so OH was derived indirectly. Bloss et al. (2007) calculated a mid-month OH throughout the CHABLIS measurement period based on varying $jO(^1D)$ (from the TUV model). To derive a daily mean OH for 28/29 September, we averaged the mid-month values for September and October, and found that $(28/29 \text{ September})_{\text{calculated}} = 0.561$ (15 January) $_{\text{calculated}}$. A diurnally-varying OH for 28/29 September was calculated from $0.561 \cdot \text{each 3-hourly measured January OH}$. Temperature data were taken from measured values. For PAN thermal decomposition, the upper limit was calculated according to $-d[\text{PAN}]/dt = k[\text{PAN}]$.

4.1.3 Calculating snowpack NO_x emissions

The rates with which NO_x was emitted from the snowpack during the periods of interest were calculated in line with previous work by Wolff et al. (2002). In brief, spectral irradiance at 3-h intervals was calculated using the TUV model. These were converted to actinic flux as a function of depth according to output from a model designed to simulate light propagation through snow (Grenfell, 1991). The actinic fluxes were then convoluted with the absorption cross-sections and the quantum yield to give J values. In this case, temperature-dependent quantum yields were used (Chu and Anastasio,

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2003) which were not available at the time of the Wolff et al., 2002 work. A temperature of -4°C was taken for 18 January, and of -20°C for 28/29 September. These were chosen by assuming that the top few cms of snow saw an average of the near surface (1 m) air temperature for the preceding 1–2 days. Finally, the nitrate concentration in snow was derived using the average of the 0 cm, 5 cm and 10 cm snow nitrate concentration from the snowpit dug nearest to the date in question. This gave 73 ng/g for September and 157 ng/g for January.

4.2 Outcome

The results for the gas-phase production rates are given in Table 3a. It is immediately evident that the contribution from HONO photolysis completely dominates NO_x production for both periods, with rates of $6.20\text{E}+05$ and $4.80\text{E}+04$ molecs $\text{cm}^{-3} \text{s}^{-1}$ for January and September respectively. This is no great surprise, given the very short lifetime of HONO to photolysis, and reflects a recycling of NO_x through HONO (via $\text{NO} + \text{OH} \rightarrow \text{HONO}$) rather than a pure source of NO_x . Indeed, NO_x , although generally defined as $\text{NO} + \text{NO}_2$, is sometimes expanded to include HONO as well. However, as discussed earlier, HONO also has a source from snowpack photochemistry (Zhou et al., 2001; Beine et al., 2002; Dibb et al., 2002) so as well as facilitating recycling, boundary layer HONO that has been released from the snowpack can act as a source of atmospheric NO_x . With our data it is not possible to determine how much of the NO_x produced by HONO photolysis (or reaction with OH) is “new” and how much is merely recycled. From the longer-lived “reservoir” species, the dominant mechanism for NO_x production in January is thermal decomposition of PAN with contributions from photolysis of the other reservoir species of roughly similar orders of magnitude. In late September, with lower temperatures, thermal decomposition of PAN is less important, as is photolysis of HNO_3 , reflecting its lower background mixing ratio at this time of the year. Instead, other than the HONO source, NO_x production from gas-phase reactions is governed predominantly by photolysis of PAN and methyl nitrate.

The diurnally-averaged rates of NO_x emission from the surface snowpack are given

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in Table 3b. For 28/29 September, an emission rate of $1.22\text{E}+06$ molecs $\text{cm}^{-2} \text{s}^{-1}$ is calculated, with almost all production in about 6 h around midday. For 18 January, a daily averaged emission rate of $1.92\text{E}+08$ molecs $\text{cm}^{-2} \text{s}^{-1}$ is calculated, spread a little more evenly throughout the day (midday value being roughly a factor 10 higher than the midnight value).

In order to compare with the gas-phase NO_x sources, we need to convert the snow-pack emissions to units of $\text{molec s cm}^{-3} \text{s}^{-1}$. To do this, we need to make certain assumptions about the height of the boundary layer into which these emissions can be assumed to be well-mixed. Defining the boundary-layer height over coastal Antarctica is not straightforward (Anderson and Neff, 2007⁶). Acoustic radar measurements made at Halley (Anderson, 2003) indicate a significantly varying upper boundary, with varying degrees of definition from day to day. However, for the purposes of this analysis it is reasonable to assume that on the periods in question, it lay somewhere between 100 m and 500 m above the snowpack surface. Figure 6 shows the gas-phase rate of NO_x production presented in Table 3a. It also shows the integrated rate of NO_x production from the reservoir species $\text{PAN} + \text{HNO}_3 + \text{MeONO}_2 + \text{EtONO}_2$ the role of HONO being ignored for the moment because of the recycling arguments outlined above. The figure also indicates the equivalent emission of NO_x from snow for various BL heights; 1000 m, 100 m, and 10 m. This representation shows immediately that even if the boundary layer stretched to 1000 m height, production of NO_x would be dominated by emission from the snowpack. This source of NO_x thus far outweighs any of the gas-phase production mechanisms.

4.3 Uncertainties

Of course there are important assumptions and uncertainties within the approach of this analysis. For instance, we have focussed on only two 24-h periods, and measure-

⁶Anderson, P. S. and Neff, W. D.: Boundary layer physics over snow and ice, in preparation, 2007.

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ments on other days will have a different distribution of NO_y components. For example, on 28 January, daily averaged PAN mixing ratios reached 29.8 pptv. Using these higher mixing ratios in this calculation would have increased the NO_x contribution from PAN by a factor 6.5. However, although this would have increased the dominance of PAN as a gas-phase source of NO_x , the combined contribution from reservoir species would still not have exceeded calculated NO_x emissions from the snowpack, even for a BL height of 1000 m. Similarly, HONO measurements at high latitudes are often difficult to reconcile, through numerical model calculations, with measured HO_x and NO_x (e.g. Chen et al., 2004; Bloss et al., 2007). At South Pole, as shown in Table 2, two different HONO measurement techniques recorded HONO values that differed by roughly a factor 6. We could reduce the HONO data here without any influence on our conclusions. We have also made noticeable assumptions in the way we reconstructed diurnally-varying cycles of HNO_3 and September OH. Again, though, the uncertainty here will not affect the overall conclusion. For the derivation of snow NO_x emissions, the biggest uncertainty lies in how to scale the combination of e-folding depth for actinic flux, quantum yield and proportion released so as to match measurements. With the newer quantum yields (Chu and Anastasio, 2003) used here, the modelled values given in Wolff et al. (2002) would be reduced by a factor of 2; this would mean that they would have been lower by this factor than the values measured on one day for the NO_x flux at that site. If real, this discrepancy is most likely caused by us using too low a value for the effective e-folding depth for actinic flux (Warren et al., 2006). We have therefore taken values midway between the calculated values and those implied by using the Neumayer data to “calibrate” our model. The values we use should therefore be assumed to have an uncertainty of $\pm 50\%$, as shown in Table 3b. A further choice in the analysis was whether to use surface snow nitrate concentrations or those from snowpits. Had we used surface snow values on the actual day in question, the calculated emissions would have been similar to within about 10%.

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5 Discussion

There are two main questions which the work presented here can go some way to address. The first is, what are the main net sources of NO_y to the coastal Antarctic boundary layer. We have evidence for the late winter stratospheric source seen also at other coastal stations. Long-range transport of PAN and alkyl nitrates plays a role in delivering NO_y to Antarctica. The overall budget and distribution of NO_y species between the boundary layer and the snowpack, however, is made complicated by the recycling mechanisms in operation. For example, we show here a strong correlation between BL HNO_3 and surface snow nitrate. Assuming that this correlation is real, the question then arises – which could be driving which? Some help is provided by a recent study from Savarino et al. (2006), who report measurements of TIN made at the French coastal Antarctic station, Dumont D'Urville. They interpret the seasonality based on isotopic analyses of both ^{15}N and ^{18}O . As mentioned above, they attribute the late winter (August–September) peak to PSC sedimentation from the stratosphere, in line with previous observations from Halley and Neumayer (Wagenbach et al., 1998). A second, major, late spring (November–December) peak is attributed to re-emission of both NO_x and HNO_3 from the snow on the polar plateau, which is then transported to the coastal regions. Their work supports the notion of recycling of N-species between the air and the snow which one would then expect to see evidence for in correlations, such as shown in Fig. 4b. Support for the idea of plateau air delivering enhanced NO_y to the coastal regions is also given in the work of Weller et al. (2002). They reported year-round measurements of NO_y made at Neumayer station and demonstrated that, between March and May, air masses with elevated NO_y had originated in the free troposphere over the plateau. Unfortunately, we have no budget data during the equivalent months. The Antarctic NO_y system is complex with significant overlaps between net sources of NO_y , and NO_y species that are merely recycled. The next stage, to try to elucidate further the driving mechanisms, is a full three-dimensional model assessment. Such a study goes beyond the scope of this paper, but the data included here

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can provide constraints.

The second question concerns understanding sources of BL NO_x , and what the present day atmosphere/cryosphere can tell us about the atmosphere of the past. Ice core records suggest that during glacial times, nitrate is bound up within the cryosphere by higher levels of impurities such as dust (Röthlisberger et al., 2000). Emission rates for NO_x out of the snowpack would thus be different from those of today. However, during past interglacials, snowpack nitrate should be equally available for photolysis and consequent NO_x emission. Interestingly, there are times, even within an interglacial, when the concentration of nitrate deposited to ice in at least parts of Antarctica has fluctuated (Röthlisberger et al., 2000), raising questions regarding the response by NO_x emissions. Our work shows that, of the major NO_x production routes, emissions from the snowpack dominate to a considerable extent over gas-phase sources under the interglacial conditions that we experience today. For past interglacial periods, therefore, all other things being equal (e.g. snow accumulation rate, boundary layer height, NO_x destruction mechanisms (see Bauguitte et al., 2007³ for a full analysis)) changing cryospheric nitrate suggests a changing NO_x flux, with significant impacts on boundary layer composition. This response would be amplified by enhanced HONO snowpack emissions, with a consequent additional NO_x source. As has been shown by the field measurements over South Pole, under conditions of elevated NO , the influence is seen in radical cycling, with shifts in the HO_x budget towards OH, as well as in boundary layer ozone production.

6 Summary and conclusions

We report here the longest-duration assessment of the NO_y budget in Antarctica carried out to date. The data show that during the winter months, organic NO_y components dominate the budget, but that their importance diminished with the move towards the summer, when inorganic NO_y compounds become predominant. PAN, however, has the highest mixing ratio of any NO_y component throughout the period of measurements.

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By comparing daily measurements of surface snow nitrate a strong association with inorganic NO_y species is apparent, that is completely lacking when compared with organic NO_y components. This suggests either that the snowpack is an important source for inorganic NO_y, or that inorganic NO_y components are depositing to the snowpack to ultimately build up the nitrate record through the cryosphere. One case study supported wet deposition from boundary layer nitrate aerosol, but this was not a consistent picture throughout the measurement period, suggesting other mechanisms, e.g. incorporation aloft, must be playing a role.

Photochemical release of NO_x from the snowpack appears to be an extremely important source of NO_x to the coastal Antarctic boundary layer, and dominates over any single gas-phase production mechanism (as well as the integrated source from the longer-lived reservoir species). HONO is also a key producer of NO_x, but it is not possible to deduce how much arises from recycling within the boundary layer, and how much of the HONO also has a source within the snowpack and is therefore generating “new NO_x”.

Our work suggests that, for some periods in the past, we should now be able to derive a direct flux of NO_x to the BL using ice core nitrate data. A secondary source of NO_x, via snowpack production of HONO and subsequent photolysis or reaction with OH, would further enhance this amount.

We cannot yet say definitively where the nitrate in surface snow originates. Certainly emissions of NO_x from snow will include a significant component of recycled NO_x, and will not solely be a net source. However, knowing that the emissions of NO_x from snowpack nitrate will dominate over gas-phase NO_x sources during interglacials helps us a significant way towards assessing how BL NO_x may have changed in the past.

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Table 1. Details of techniques used to measure NO_y components during CHABLIS.

Molecule	Technique	Detection Limit	Normal sampling resolution	Data capture
NO	Chemiluminescence	1.5 pptv	1 min	July onwards
NO ₂	Chemiluminescence	5.0 pptv	1 min	July onwards
HONO	Colorimetry	2 pptv	15 min	May onwards
HNO ₃	Denuder + IC	< 1 pptv	daily/weekly	April onwards
p-NO ₃ ⁻	Filter + IC	< 1 pptv	daily/weekly	April onwards
PAN	GC-ECD	< 1 pptv	30 min	July onwards
NO ₃	BL-DOAS	2 pptv	10 min	February onwards
MeONO ₂	Flasks + GC-MS	< 1 pptv	weekly	April onwards
EtONO ₂	Flasks + GC-MS	< 1 pptv	weekly	April onwards
i-PrONO ₂	Flasks + GC-MS	< 1 pptv	weekly	April onwards
n-PrONO ₂	Flasks + GC-MS	< 1 pptv	weekly	April onwards
speciated RONO ₂	in situ GC-MS	< 1 pptv	hourly	January 2005 onwards
snow NO ₃ ⁻	IC	< 1 ppb	daily	March onwards

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Table 2. Comparison of measurements of NO_y component species made at Antarctic sites. (Neumayer 1997 data from Jones et al., 1999; Neumayer 1999 data from Jacobi et al., 2000; South Pole data from Davis et al., 2004, 2005; Huey et al., 2004, Arimoto et al., 2004). CIMS = Chemical Ionisation Mass Spectrometer ; MC = Mist Chamber. * These data are revised estimates of 1997 measurements following a re-calibration that showed the original data were overestimated by a factor 3 (Weller et al., 2002).

Species	Halley (January 2005)	Neumayer February 1997	Neumayer February 1999	South Pole December 2003
NO	7.1±0.5	3±5	1.2±2.2	143+128
NO ₂	2.2±0.7		3.2±3.7	
HONO	10.4±0.1			5.3±2.5 -LIF 30±4 -MC 39±1
HO ₂ NO ₂				86±78 CIMS 23±5 -MC
HNO ₃	6.2±0.5	5±2	4.0±2.0	
p-NO ₃ ⁻	1.7±0.3	4±3	4.2±2.4	
PAN	11.4±0.4		13.1±7.3	15.5±4.3
MeONO ₂	7.2±0.6	10±2*	9.5±1.4	
EtONO ₂	1.5±0.2	3±1*	2.3±0.5	
1-PrONO ₂	0.2±0.1		1.1±0.8	
2-PrONO ₂	0.8±0.1		1.2±0.5	

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Table 3a. 24-h average NO_x production rates calculated from various mechanisms for 18 January 2005 and 28/29 September 2004.

Gas-phase NO _x production mechanism	NO _x production rate (molec _s cm ⁻³ s ⁻¹)	
	mid-January	end-September
HONO + hν → OH + NO	6.20E+05	4.80E+04
HNO ₃ + hν → OH + NO ₂	7.60E+01	2.57E+00
PAN + hν → CH ₃ C(O)OO + NO ₂	6.48E+01	3.24E+01
CH ₃ C(O) + O ₂ + NO ₂		
MeONO ₂ + hν → CH ₃ O + NO ₂	7.26E+01	2.01E+01
EtONO ₂ + hν → C ₂ H ₅ O + NO ₂	3.41E+01	4.71E+00
HONO + OH → H ₂ O + NO ₂	4.42E+02	9.88E+01
PAN + M → CH ₃ C(O)OO + NO ₂	1.22E+02	4.74E+00

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Table 3b. As for Table 3a, but now the rate of NO_x emission from the snowpack into the overlying boundary layer.

NO _x production mechanism	NO _x emission rate (molecs cm ⁻² s ⁻¹)	
	mid-January	end-September
Snowpack emission of NO _x	1.92E+08 +/-50%	1.22 E+07 +/-50%

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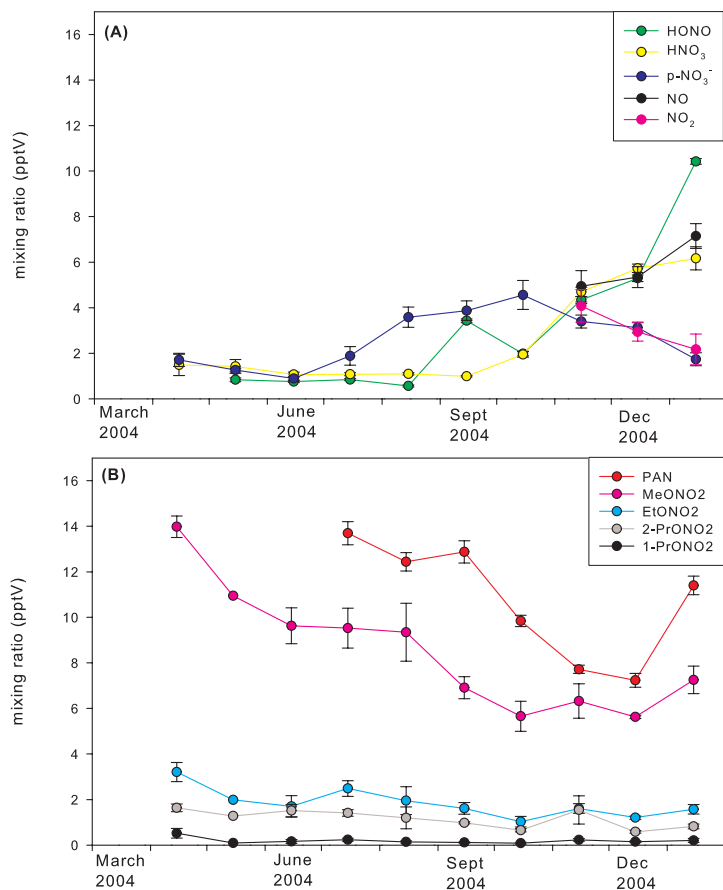


Fig. 1. (a) Variation in monthly-averaged inorganic NO_y components during the measurement period. (b) as for (a), but now showing organic components. Data are plotted on the same scale to allow direct comparison.

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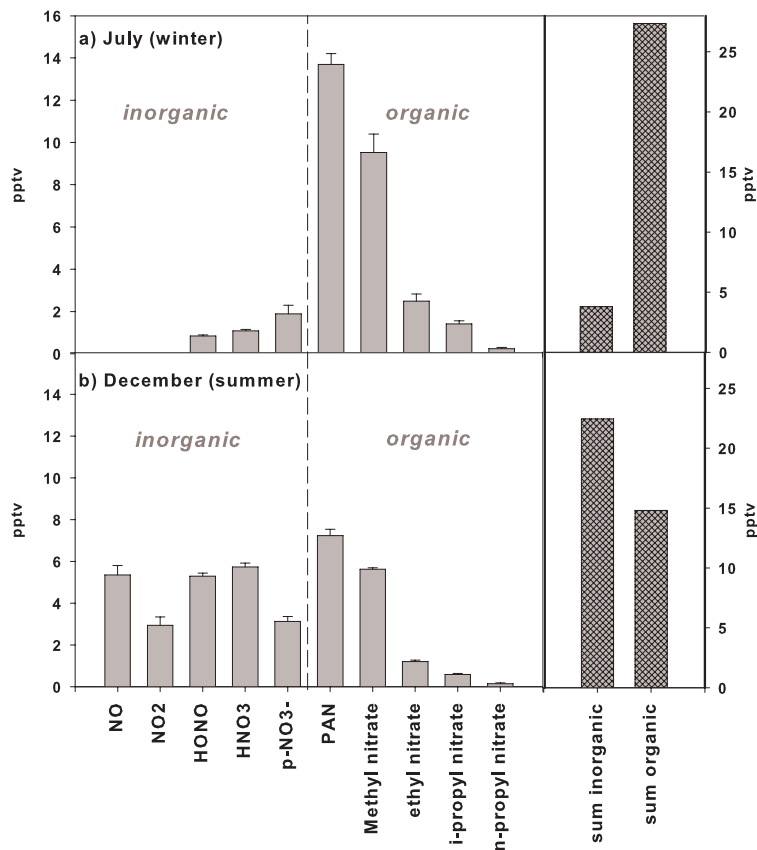


Fig. 2. Monthly-averaged inorganic and organic NO_y components during **(a)** the winter (July) and **(b)** the summer (December). Each plot also shows the sum of the organic and inorganic components to highlight which dominates in the respective seasons.

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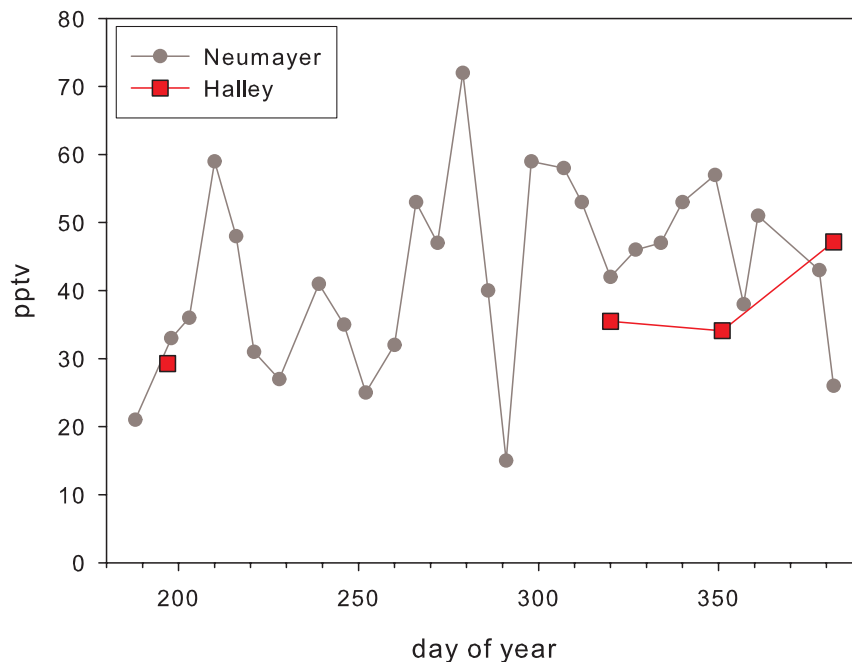


Fig. 3. A comparison of NO_y measured directly at Neumayer station and integrated NO_y species from Halley. As the NO_y measurement is not considered to include particulate nitrate, this component is excluded from the Halley integrated NO_y. The Neumayer data were taken from Weller et al. (2002).

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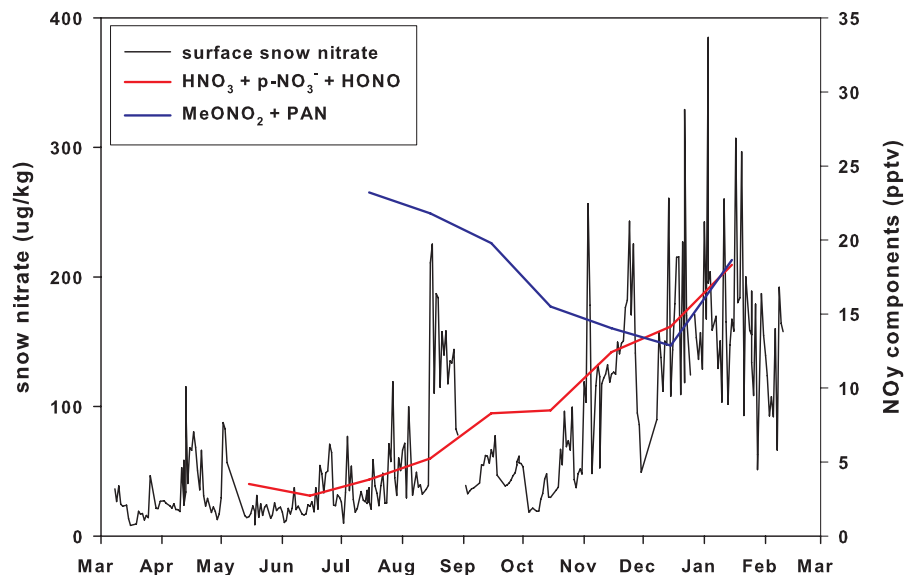


Fig. 4a. Daily surface snow nitrate plotted against the sum ($\text{HNO}_3 + \text{p-NO}_3^- + \text{HONO}$) and the sum ($\text{PAN} + \text{MeONO}_2$).

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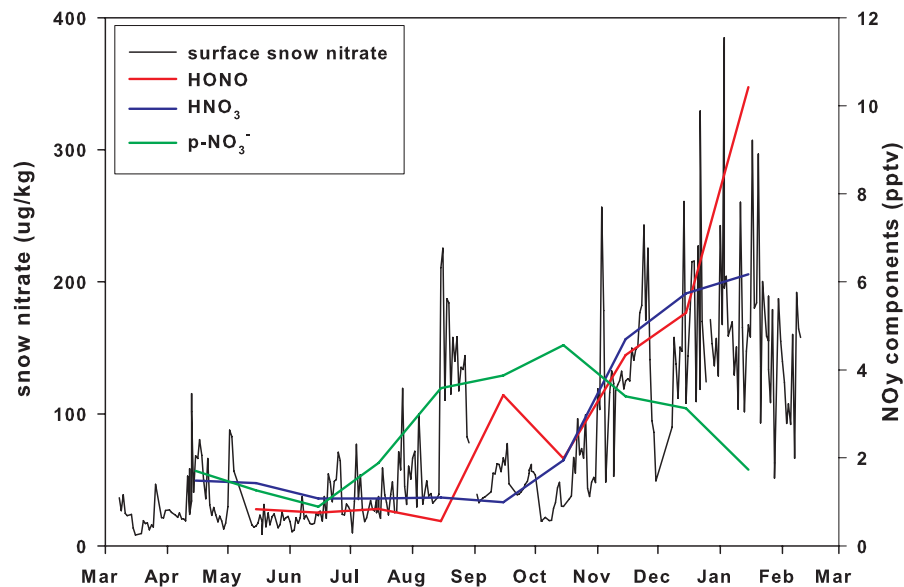


Fig. 4b. Daily surface snow nitrate plotted against individual inorganic NO_y components.

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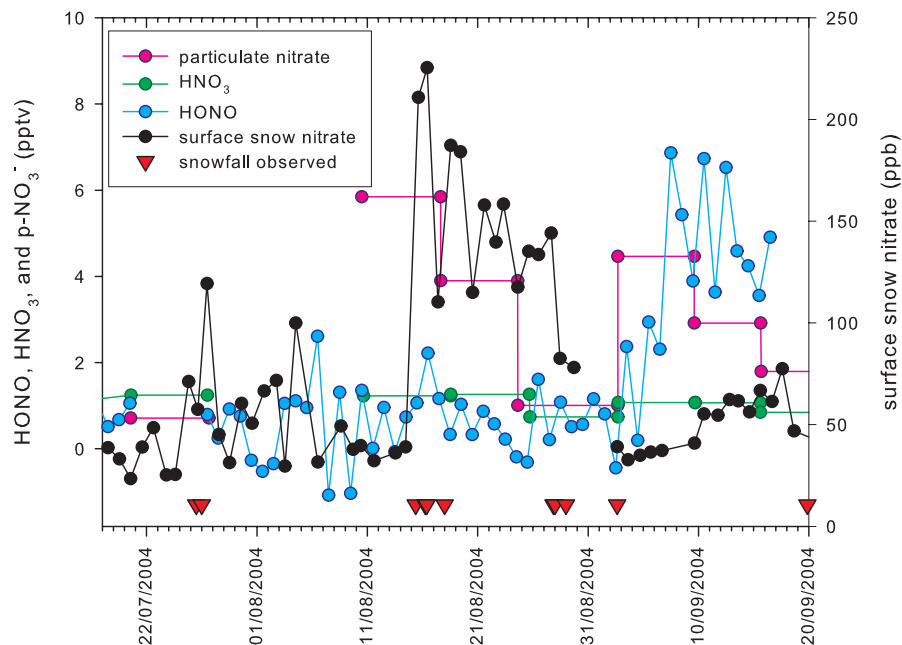


Fig. 5. The period in August when surface snow nitrate concentrations increased markedly. Coincident data shown include HONO, HNO₃, p-NO₃⁻. Also shown are snowfall observations which indicate either whether it was snowing at that time or whether it had snowed during the previous 3 h.

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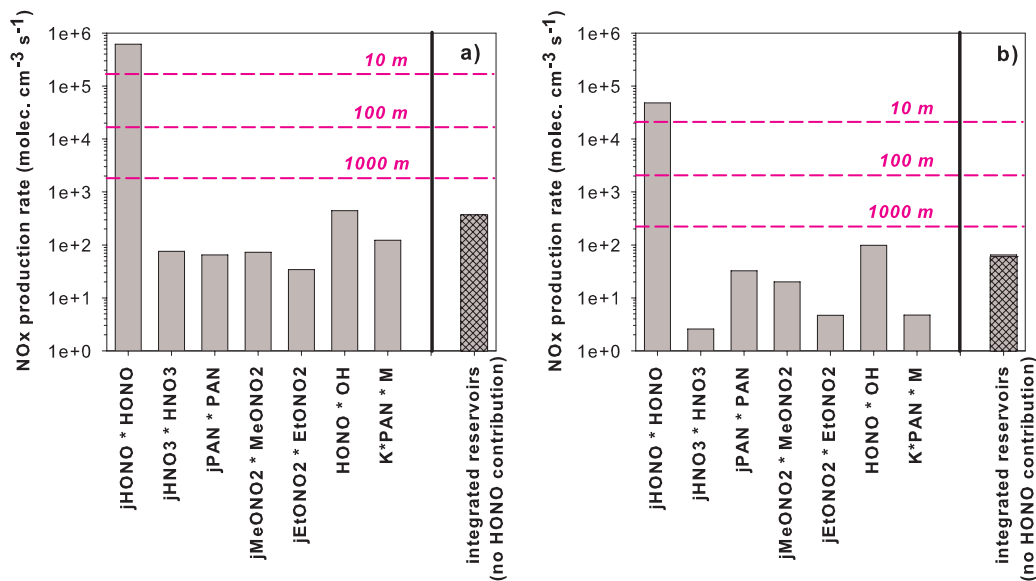


Fig. 6. Rate of NO_x production from gas phase reactions as 24-h averages during **(a)** summer (January) and **(b)** spring (September). Also shown (by the pink dashed lines) is the contribution of NO_x produced from snowpack photochemistry assuming various boundary layer heights. Note the log scale.

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