Atmos. Chem. Phys., 11, 9271–9285, 2011
www.atmos-chem-phys.net/11/9271/2011/
doi:10.5194/acp-11-9271-2011

Atmospheric Chemistry and Physics

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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Received: 13 March 2007 – Published in Atmos. Chem. Phys. Discuss.: 28 March 2007
Revised: 5 August 2011 – Accepted: 30 August 2011 – Published: 8 September 2011

Abstract. Measurements of a suite of individual NO_y components were carried out at Halley station in coastal Antarctica as part of the CHABLIS campaign (Chemistry of the Antarctic Boundary Layer and the Interface with Snow). Conincident measurements cover over half a year, from austral winter 2004 through to austral summer 2005. Results show clear dominance of organic NO_y compounds (PAN and $MeONO_2$) during the winter months, with low concentrations of inorganic NO_y. During summer, concentrations of inorganic NO_y compounds are considerably greater, while those of organic compounds, although lower than in winter, are nonetheless significant. The relative concentrations of the alkyl nitrates, as well as their seasonality, are consistent with an oceanic source. Multi-seasonal measurements of surface snow nitrate correlate strongly with inorganic NO_y species (especially HNO_3) rather than organic. One case study in August suggested that, on that occasion, 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 overwhelmingly dominate over gas-phase sources. This result suggests that, for certain periods in the past, the flux of NO_x into the Antarctic boundary layer can be calculated from ice core nitrate data.

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1 Introduction

The chemistry of oxidised nitrogen (NO_y = NO + NO_2 + NO_3 + HONO + HNO_3 + p-NO_3^- + $RONO_2$ + PAN + HNO_4 + N_2O_5 + $XONO_2$ + XNO_2 + …, where p-NO_3^- is particulate nitrate, PAN is peroxyacetyl 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 (=NO + NO_2) in tropospheric chemistry, the sources, concentrations and associated chemistry of NO_x are important to understand and quantify in order to determine its influence on high latitude boundary layer composition. Various studies have explored the concentrations and considered sources of NO_y component species. 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 a NO_x source (Bottenheim et al., 1993). Alkyl nitrates were shown to be significant components of NO_y in summertime coastal Antarctica, and a Southern Ocean source was postulated (Jones et al., 1999).

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Nitrate impurities within surface snow have been shown to be sources of NO_x to the boundary layer in both polar regions (Honrath et al., 1999; Jones et al., 2000, 2001; Beine et al., 2002). In some polar locations, concentrations of NO_x from this snowpack source are high enough to drive local ozone production (Crawford et al., 2001; Davis et al., 2001, 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. Furthermore, we need to understand the depositional processes that generate the record of nitrate in ice and the post-depositional processes that drive NO_x release from the condensed phase nitrate.

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 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; 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 springtime 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 the seasonality of surface snow nitrate (NO_3^-) concentrations and look for associations with changing NO_y components through the year.

2 Methodology

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., 2008). A full description of the site and meteorological conditions during the campaign are provided in Jones et al. (2008). Altogether 10 different gaseous NO_y components were measured during the campaign using 6 different methods and techniques, with snow samples also analysed to derive nitrate concentrations (see Table 1). The majority of these measurements have been presented at full resolution in specific data papers (see below). Here we present monthly means when assessing the NO_y budget, but also present as-yet unpublished data.

Descriptions of instrument techniques and full resolution datasets can be found for PAN (Mills et al., 2007), NO and NO_2 (Bauguitte et al., 2009), HNO_3, p-NO_3^- and surface snow nitrate (Jones et al., 2008). Measurements for the atmospheric nitrate radical, NO_3, were made using the long-path DOAS system employed for halogen measurements during CHABLIS (Saiz-Lopez et al., 2007). An attempt to measure HONO was made using a wet chemical method (scrubbing gas-phase HONO into water followed by optical detection of an azo dye derivative of HONO) Clemitshaw, 2006). While such wet chemical methods have been used widely in polar studies, it now appears, both from modelling studies (Chen et al., 2004; Sjostedt et al., 2007) and instrument intercomparisons (Liao et al., 2006), that the resulting HONO measurements over-estimate ambient values. Indeed, subsequent assessments of the CHABLIS data showed that the derived HONO concentrations were inconsistent with both the HO_x and NO_x observations, yielding significant overpredictions in both (Bloss et al., 2007, 2010). Consequently we do not present these data here, but describe their features qualitatively when appropriate.

2.1 Alkyl nitrates

Alkyl nitrates were measured for the NO_y budget analysis using whole air sampling into flasks. Sampling was carried out at weekly resolution from end March 2004 through to end January 2005. In order to look for higher temporal variability, in each season for 1 week, flasks were filled on a daily basis, and for one of those days, they were filled every 6 h. At the end of the CHABLIS campaign, the flasks were returned to the UK for analysis using a GC-MS.

The GC-MS instrument consisted of an online air preconcentrator (UNITY and Online Air Server, Markes International Ltd.) coupled to a gas chromatograph mass spectrometer (Agilent Technologies GC 6890 and MS 5973N). The system is described in detail elsewhere (Worton et al., 2008). In brief, 1 l air samples were dried using a counter-flow nafion dryer before being pre-concentrated for 30 min on a packed (Carbograph-TD™ and Carboxen-1000™) quartz capillary cold trap at −15 °C. Samples were injected hourly onto the analytical column by resistively

Table 1. Details of techniques used to measure components for the NO_y budget analysis during CHABLIS.

Molecule	Technique	Detection Limit	Normal sampling resolution	Data capture
NO	Chemiluminesence	1.5 pptv	1 min	July onwards
NO_2	Chemiluminesence	5.0 pptv	1 min	July 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
snow NO_3^-	IC	< 1 ppb	daily	March onwards

heating the trap to 250–300 °C for 8 min. The analytes were separated on an RTX-502.2 capillary column (105 m, 320 µm OD, 1.8 µm film, Restek Corporation) using Helium carrier gas. The oven was held at 35 °C for 8 min before being ramped to 150 °C (at 10 °C per minute) where it was held for 15 min before being heated to 220 °C (at 20 °C per minute) for 10 min. Detection was by Negative Ion Mass spectrometry (using Methane as the buffer gas at 2 sccm) operating in selective ion mode and monitoring mass to charge ratio (*m/z*) 46 for the alkyl nitrates. Duplicate analyses of each canister were performed and calibrations carried out every 8 injections using a compressed air gas standard that had been assigned calibrated values on the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) scale for the alkyl nitrates though an intercalibration of air samples from a remote California research site (Reeves et al., 2007). The mean precision of measurements was calculated to be 4.6 % (3σ), estimated from calibrations and sample replicates. Detection limits for the alkyl nitrates were <0.02 parts per trillion by volume (pptv) (Worton et al., 2008).

As the alkyl nitrate measurements have not previously been published, we present below the full dataset from whole air samples, as well as the monthly means for the NO_y budget analysis.

2.2 Data handling for budget analysis

Instruments measuring the various NO_y 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 addition, surface snow was sampled each day from March 2004 onwards, and stored for subsequent analysis for nitrate.

In this paper we present data from the various NO_y component species as monthly-averages and standard error of the monthly mean. For instruments whose data were collected at higher 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. As alkyl nitrate concentrations were derived from whole air flask samples, the data are spot measurements made on a number of occasions (not always evenly spaced) during the month. To derive representative averages, 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 Alkyl nitrates

Figure 1 shows the seasonal variation observed in the C_1 to C_3 alkyl nitrates measured in the whole air samples throughout the campaign. Methyl nitrate ($MeONO_2$) dominates in terms of concentration, with progressively lower mixing ratios for the higher nitrates, and with 2-propyl nitrate dominating over 1-propyl nitrate. These relative concentrations (methyl > ethyl > propyl) are consistent with two earlier studies of summertime alkyl nitrates in coastal Antarctica (Jones et al., 1999; Fischer et al., 2002). Over the seasons, the highest mixing ratios for all the alkyl nitrates were measured during the autumn. An apparent steady decline in concentration was then observed through the winter and into the spring for methyl, ethyl and 2-propyl nitrate, while 1-propyl nitrate mixing ratios were low and constant. From late spring 2004 through summer 2005, mixing ratios for all the alkyl nitrates were relatively constant. The earlier Antarctic

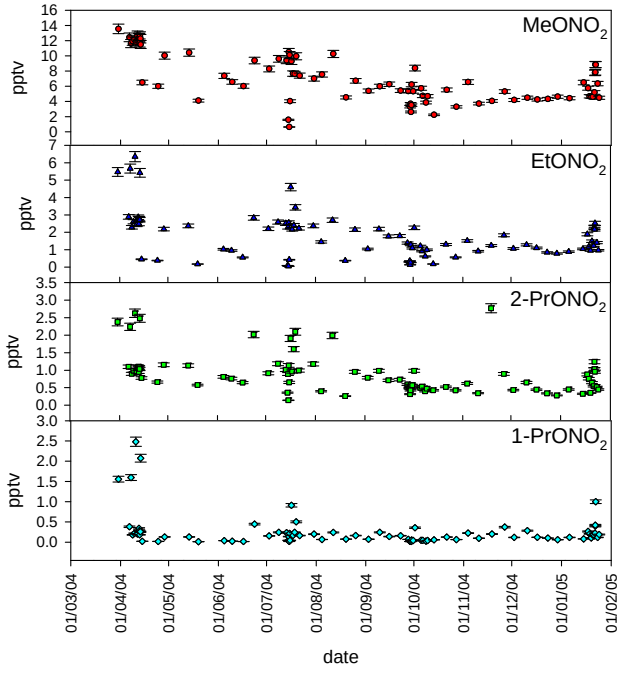

Fig. 1. Measurements of methyl, ethyl, 2-propyl and 1-propyl nitrate from whole air samples. The error bars show the 4.6 % mean precision derived from all the alkyl nitrate measurements during the campaign. Note the data are plotted on different scales.

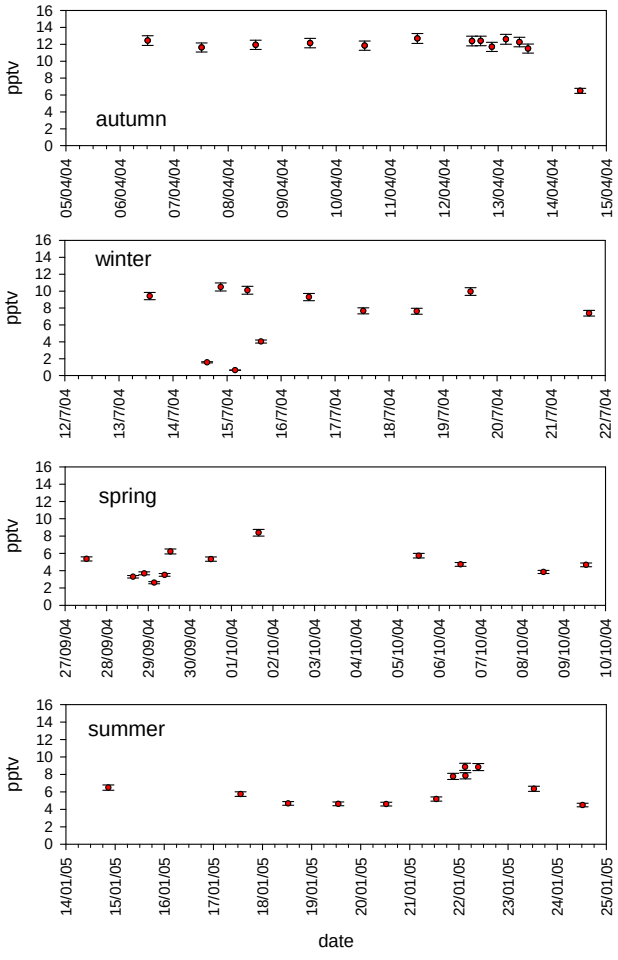

Fig. 2. Higher resolution (roughly daily or 6-hourly) flask sampling for methyl nitrate during each season. Data are irregular at times when inclement weather prevented sampling.

measurements found mixing ratios increasing from summer to early autumn (Jones et al., 1999).

On top of this general seasonal trend, the amount of variability in sample concentrations varied at different times of the year, particularly for methyl and ethyl nitrate. For example, considerable scatter can be seen in the weekly data during the first part of the record, while in the latter part, mixing ratios varied very little. As the sampling and analysis system appear to have been operating well (as discussed further below), we assume that these features are real.

Methyl nitrate measured from the flasks sampled each season at higher resolution, are shown in Fig. 2. During the autumn, mixing ratios of methyl nitrate are extremely constant for both the daily and the 6-hourly flasks. Such consistency in measured $MeONO_2$ suggests that the experimental approach is robust and that the alkyl nitrate data are reliable. During the winter, some smooth variability can be seen, the exception being three samples with unusually low methyl nitrate mixing ratios on 14 and 15 July. Alkyl nitrates are destroyed by photolysis (Clemitshaw et al., 1997; Talukdar et al., 1997a) and reaction with the OH radical (Talukdar et al., 1997b). Given that during the Antarctic winter the sun remains below the horizon for 24 h each day, no local (or even regional) destruction mechanisms can account for the low concentrations. Five-day back trajectories calculated with the HYSPLIT model (Draxler and Rolf, 2003) show no unusual air mass origin, and the local wind speed/direction and temperature are likewise not atypical. The cause for the low methyl nitrate concentrations is therefore not obvious, but we note that ethyl nitrate and 2-propyl nitrate concentrations are also suppressed in these flask samples suggesting either that it is an artefact that affects all these alkyl nitrates, or that it is real. During both spring and summer, more regular variation in methyl nitrate mixing ratios was observed, with smooth increases/decreases in mixing ratio suggesting changes in source/sinks and/or transport mechanisms. The variability during January compares extremely well with high resolution in situ GC-MS measurements made at Halley (unpublished data) which provides further support to the variability being real.

The atmospheric lifetime of alkyl nitrates ranges from a few days to a month, depending on alkyl chain length as well as latitude and season (Roberts, 1990; Chuck et al., 2002). The mixing ratios measured at Halley are likely to

reflect, to a certain extent, well-mixed baseline concentrations. However, they are also consistent with a source from the ocean. It is known that the oceans are a source of light alkyl nitrates (e.g. Atlas et al., 1993; Chuck et al., 2002; Blake et al., 2003; Dahl et al., 2005, 2007), and that in regions of high oceanic emissions, $MeONO_2$ and $EtONO_2$ dominate over other alkyl nitrates (Atlas et al., 1997; Blake et al., 2003). An October cruise observed significant sea-to-air fluxes of methyl and ethyl nitrate from the Atlantic Ocean off Africa (methyl > ethyl), and for methyl nitrate from the Southern Ocean (Chuck et al., 2002). Further, multi-year measurements in coastal Antarctica of the short-lived alkenes, ethene and propene, both with known oceanic sources, found the maximum annual concentration occurred in late autumn (Rudolph et al., 1989), concurrent with the maximum in alkyl nitrates. A detailed exploration of alkyl nitrate sources would require high time-resolution observations. However it seems that some contribution from marine emissions of alkyl nitrates is inevitable at Halley and may account for some of the variability in the data observed, as well as the seasonality.

3.2 Budget of monthly-averaged NO_y components

The variation of the monthly-averaged NO_y components measured during CHABLIS is shown in Fig. 3. Figure 3a shows the inorganic NO_y species. The lowest mixing ratios for HNO_3 were measured during the winter, with monthly-averaged mixing ratios around 1 pptv. Boundary layer HNO_3 increased with the onset of spring, and by December (austral summer) had reached monthly mean mixing ratios of ~6 pptv. These observations for gas-phase HNO_3 are consistent with measurements made by nylon filter sampling at Neumayer, both in terms of seasonality (Weller et al., 2002) and summertime mixing ratio (Jones et al., 1999; Jacobi et al., 2000). As shown on Fig. 3a), 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 (Weller et al., 2002). 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 cycle of "total inorganic nitrate" (TIN = HNO_3 + p-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 (Wagenbach et al., 1998; Savarino et al., 2007). Monthly averages of NO and NO_2 for the summer months (November–January) are also shown in Fig. 3a). Wintertime mixing ratios of NO and NO_2 were below the instrumental detection limit, consistent with the winter observations of NO made at Neumayer (Weller et al., 2002). Finally, NO_3 measurements were made during the year, but mixing ratios never exceeded the detection limit of 2 pptv.

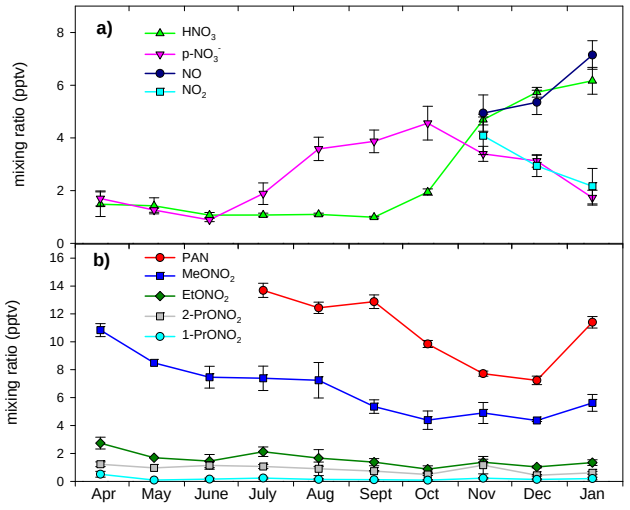

Fig. 3. Comparison of monthly-averaged NO_y components (mean and standard error of the mean) during the measurement period from April 2004 to January 2005; **(a)** measured inorganic and aerosol components; **(b)** measured organic components. Note data are plotted on different scales.

The monthly-averaged mixing ratios for the organic NO_y components measured during CHABLIS are shown in Fig. 3b. The organic NO_y components are dominated by PAN and $MeONO_2$. For PAN, the highest monthly-averaged mixing ratio observed was in July, reaching 13.7 pptv, but as measurements for PAN only began in July, it is not possible to tell from these data whether the annual maximum occurred then or during an earlier month. For $MeONO_2$, the highest measured monthly average mixing ratios was also at the start of the record, with an average 14.0 pptv measured during April. By July, mixing ratios of $MeONO_2$ were still elevated compared with the rest of the year, at 9.5 pptv. For both PAN and $MeONO_2$, mixing ratios declined toward austral summer, but were still maintained at 7.2 and 5.6 respectively for the month of December. This declining concentration in $MeONO_2$ throughout winter darkness and into the spring months is in line with measurements from South Pole (Beyersdorf et al., 2006). The noticeably high January mean for PAN is driven by two events with exceptionally high concentrations, as discussed by Mills et al. (2007). The higher alkyl nitrates exhibit a similar seasonality to that of $MeONO_2$, albeit at lower mixing ratios as discussed in Sect. 3.1 above. They reach monthly averages of 2.5 pptv (ethyl nitrate), 1.4 pptv (2-propyl nitrate) and 0.2 pptv (1-propyl nitrate) during July (austral winter) and drop to 1.2 pptv, 0.6 pptv and 0.1 pptv respectively in December (austral summer). Sources of PAN during the measurement period are considered in detail by Mills et al. (2007),

but proved difficult to pin down. Trajectory analyses did not suggest any clear source regions throughout the year, most likely because the lifetime of PAN at high latitudes is long compared with the trajectory duration (up to 8 days in their study). Nor was there any clear association between PAN mixing ratios and those of either CO or O_3, which might otherwise have been taken as indicating a pollutant source. Of note, however, was a qualitative relationship with ethene (and some with propene), and that the ratio of these alkenes was consistent with an oceanic source. Further, the highest PAN mixing ratios observed during the summer months corresponded with the longest marine trajectory to the north of the station.

From the measurements made, long-range transport of organic NO_y components appears to be the dominant source of gaseous NO_y to this coastal Antarctic station during the winter months. During the summer, although there is relatively less organic NO_y compared with inorganic NO_y, the organics nonetheless make a significant contribution to total NO_y. Their role as a source of boundary layer NO_x is discussed later. 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 (December) data is given in Table 1 of Grannas et al. (2007). 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, NO_2 and HNO_3. These data highlight the large differences in the boundary layer chemistry between coastal and inland, plateau, sites.

3.3 Linking boundary layer and snowpack measurements

3.3.1 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, the magnitude and balance of which will be determined by factors such as e-folding depth (e.g. France et al., 2011), snow accumulation rate and temperature (Röthlisberger et al., 2000), mobility of NO_3^- in the snow and the mineral loading (Beine et al., 2003). The incorporation of impurities into precipitating 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. This picture is confirmed from field studies in the Arctic (e.g. Dibb et al., 1998; Toom-Sauntry and Barrie, 2002; Beine et al., 2003).

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 between 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.

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^{-1} (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^{-1} (e.g. Park and Lee, 1988; Becker et al., 1996). Particulate nitrate, p-NO_3^- can be scrubbed from the atmosphere by falling snow, or deposit directly to the surface of the snowpack, so is also a potential 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 an order of magnitude smaller than for HONO (Kames and Schurath, 1992, 1995), so at the concentrations measured, their contribution to snowpack nitrate is expected to be negligible.

Figure 4 shows measured HNO_3, p-NO_3^-, PAN and $MeONO_2$ together with daily surface snow nitrate concentrations. HNO_3 is clearly the most closely correlated with nitrate in surface snow, with the winter minima increasing through spring to the summer maxima. Particulate nitrate shows a similar seasonality during winter and spring, but

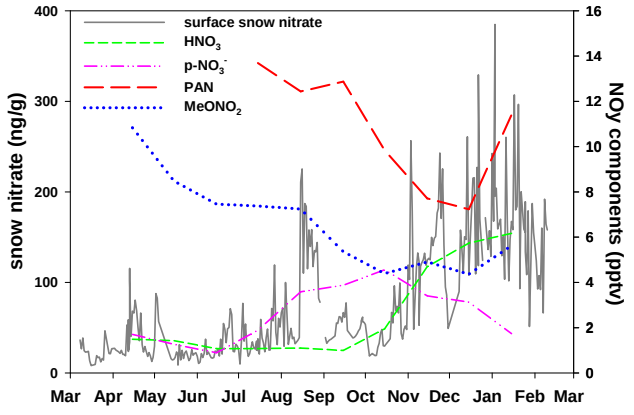

Fig. 4. Daily surface snow nitrate plotted against certain NO_y components.

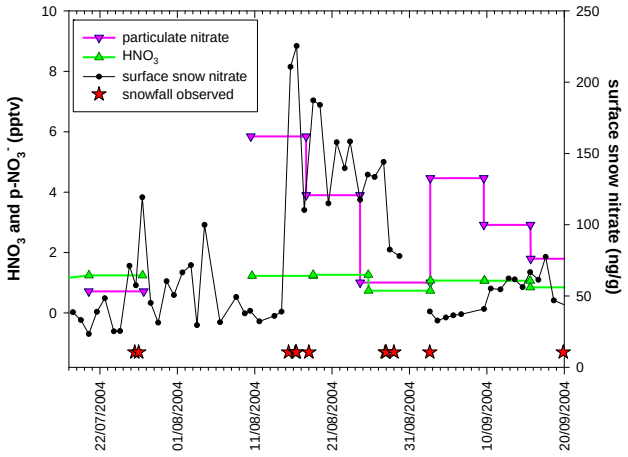

Fig. 5. The period in August when surface snow nitrate concentrations (black line) increased markedly. Also shown are atmospheric concentrations of HNO_3 and p-NO_3^-. Also shown are snowfall observations which indicate either whether it was snowing at that time or whether it had snowed during the previous 3 h.

differs during summer. As anticipated, there is no equivalent association between surface snow nitrate and the organic NO_y components.

3.3.2 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 ng g^{-1}; on 16 August, the sample collected had a concentration of over 200 ng g^{-1}. These high concentrations were maintained through until the end of August. By 30 August, concentrations of nitrate had fallen to roughly 80 ng g^{-1}, and following a short data gap, by 2 September, concentrations had returned to background.

As the most likely contributors to surface snow nitrate are the inorganic NO_y components, Fig. 5 also shows the coincident measurements for HNO_3 and p-NO_3^- at the weekly sampling resolution used at this time. Although not presented, we note that the measurements for HONO, which likely represent some sort of soluble nitrite, show very little variability prior to and during the high snow nitrate event, so do not appear connected with the surface snow nitrate signal. Interestingly, also very little variation in HNO_3 is evident during this period, with mixing ratios consistently around the detection limit of ∼1 pptv. 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 ng g^{-1}; by the time the sample of surface snow was collected, at 15:00 on 15 August, nitrate concentrations had risen to over 200 ng g^{-1}. 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 to 17 August, the concentration of p-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-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-NO_3^- available to be scrubbed from the atmosphere. Although p-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 chemistry and ground level aerosol, 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 concentration 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). Variability in the aerosol profile may go some way to explain why, for this event, it appears that the source of surface snow nitrate was wet deposition and scrubbing of boundary layer p-NO_3^-, while on a seasonal basis, there is no obvious link between the two. We note, however, that Wolff et al. (2008) further explored the role of snowfall in depositing aerosol nitrate during the CHABLIS campaign and found that spikes in the surface snow nitrate data were regularly accompanied by fresh snowfall.

3.4 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 (Ridley et al., 2000; Davis et al., 2001; Jones et al., 2001; Honrath et al., 2002; Wolff et al., 2002; Beine et al., 2002) from the snowpack, but the relative contribution compared 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.

3.4.1 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 (unpublished) 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 from flasks every 6 h – the highest resolution alkyl nitrate data available for the spring period. Uncertainties in this approach are discussed in some detail in Sect. 4.3 below.

3.4.2 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 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 HNO_3, sampled over a longer timeframe, it was necessary to reconstruct higher resolution data. Summertime HNO_3 was measured as a 24-h-mean centred around 23:59 on both 17 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 HNO_3 data measured previously at Neumayer station (Weller 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 HNO_3, the 6-hourly-resolution data were below the detection limit, so the daily mean for 27 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. NO_3 and the higher alkyl nitrates), and they were ignored for this calculation.

3.4.3 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

Table 2a. 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 (molecs cm^{-3} s^{-1})	
	mid-January	end-September
$HNO_3 + h\nu \rightarrow OH + NO_2$	7.60×10	2.57
$PAN + h\nu \rightarrow CH_3C(O)OO + NO_2$ $CH_3C(O) + O_2 + NO_2$	6.48×10	3.24×10
$MeONO_2 + h\nu \rightarrow CH_3ONO_2 + NO_2$	7.26×10	2.01×10
$EtONO_2 + h\nu \rightarrow C_2H_5ONO_2 + NO_2$	3.41×10	4.71
$PAN + M \rightarrow CH_3C(O)OO + NO_2$	1.22×10^2	4.74

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 $j(O^1D)$ (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 $(28/29\ \text{September})_{\text{calculated}} = 0.561\ (15\ \text{January})_{\text{calculated}}$. A diurnally-varying OH for 28/29 September was calculated from 0.561 × each 3-hourly measured January OH. Temperature data were taken from measured values. For PAN thermal decomposition, the upper limit was calculated according to $-d[\text{PAN}]/dt = k[\text{PAN}]$.

3.4.4 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), which were previously found to be in good agreement (taking into account the different conditions) with similar ones related to measurements from Alert, Canada (Simpson 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 main feature of such models is that, beyond a shallow skin, actinic fluxes fall exponentially with depth. In the earlier work (Wolff et al., 2002), the e-fold depth calculated with the model was 3.7 cm, in line with earlier measurements at South Pole. More recent data shows much larger e-fold depths (typically 10–20 cm) at Dome C (France et al., 2011). In the absence of direct measurements at Halley, we have, in Table 2b, scaled the values for an e-fold depth of 7 cm. This value roughly bisects the original choice and the value of 10 cm derived for windpacked snow at Dome C, while the uncertainty we use encompasses these two values. 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, 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^{-1} for September and 157 ng g^{-1} for January.

Table 2b. As for Table 2a, but now the rate of NO_x emission from the snowpack into the overlying boundary layer. See text for full discussion.

NO_x production mechanism	NO_x emission rate (molec. cm^{-2} s^{-1})	
	mid-January	end-September
Snowpack emission of NO_x	$2.42\times10^8 \pm 50\,\%$	$1.53\times10^7 \pm 50\,\%$

3.4.5 Outcome

The results for the gas-phase production rates are given in Table 2a. The dominant gas-phase mechanism for NO_x production in January is thermal decomposition of PAN with contributions from photolysis of PAN, HNO_3 and $MeONO_2$ 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, 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 in Table 2b. For 28/29 September, an emission rate of 1.53×10^7 molec. cm^{-2} s^{-1} is calculated, with almost all production in about 6 h around midday. For 18 January, a daily averaged emission rate of 2.42×10^8 molec. cm^{-2} s^{-1} is calculated, spread a little more evenly throughout the day (midday value being roughly a factor 10 higher than the midnight value). Field

observations of NO_x fluxes have been made predominantly during summer months (e.g. Jones et al., 2001; Honrath et al., 2002; Oncley et al., 2004; Bauguitte et al., 2009) in both the Antarctic and Arctic. Measurements of daily-averaged NO_x emissions range from 1.7×10^8 molec. cm^{-2} s^{-1} (Bauguitte et al., 2009) to 3.9×10^8 molec. cm^{-2} s^{-1} (Oncley et al., 2004). The values derived for the Antarctic summer in this study therefore concur with the field measurements. No published field data exist with which to compare the springtime values derived in this study.

In order to compare with the gas-phase NO_x sources, we need to convert the snowpack emissions to units of molecs. cm^{-3} 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, 2008). 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 2a. It also shows the integrated rate of NO_x production from the reservoir species PAN + HNO_3 + $MeONO_2$ + $EtONO_2$. The figure also indicates the equivalent emission of NO_x from snow for various boundary layer 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.

3.4.6 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 measurements 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. We have also made noticeable assumptions in the way we reconstructed diurnally-varying cycles of HNO_3 and September OH. Again, however, the uncertainty here will not affect the overall conclusion. Snow at Halley is acidic such that NO_3^- in snow is unlikely to be severely constrained by association with mineral salts, as was found in other parts of Antarctica in snow with a high mineral loading (Beine et al., 2006). 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 similar to those implied by using the Neumayer data to "calibrate" our model. Bearing in mind the much higher values measured in central Antarctica and the lack of e-fold data for coastal sites, the values we use should therefore be assumed to have an uncertainty of ± 50 %, as shown in Table 2b. 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 %. However, the overriding purpose of this analysis is to compare sources of NO_x to the boundary layer. Given that the boundary layer at Halley, although highly variable from day to day lies somewhere between 10 m and a few hundred meters, the uncertainty on calculated snowpack emissions does not alter the conclusion that the snowpack source dominates over the gas-phase sources, and indeed to a considerable extent.

4 Discussion and conclusions

The analysis presented here is based upon NO_y component species that were measured at Halley during the CHABLIS campaign. Noticeable gaps in the measurement suite include N_2O_5, HONO and HNO_4 so their respective concentrations need to be assessed using other methods. For N_2O_5, we use output from the GEOS-Chem model (Evans and Jacob, 2005). The model was run at a resolution of 4° by 5° using meteorological input from the NASA Global Modeling and Assimilation Office. Results suggested that N_2O_5 mixing ratios at Halley never exceeded 0.5 pptv at any time during the year (M. Evans, personal communication, 2006). Bloss et al. (2010) used a detailed zero-dimensional photochemical box model to study radical chemistry at Halley during the CHABLIS summer campaign, 2004/05. The model was constrained by observations of long-lived chemical species, measured photolysis frequencies and meteorological parameters. They calculated gas phase HONO from the reaction OH + NO, and derived a daily mean of 0.1 pptv, and maximum of 0.22 pptv. Using this value they were able to reproduce mean observed levels and diurnal variation in IO, BrO and NO_x. HNO_4 has been measured at Halley subsequent to the CHABLIS campaign (N. Brough, unpublished data), using the chemical ionisation mass spectrometer

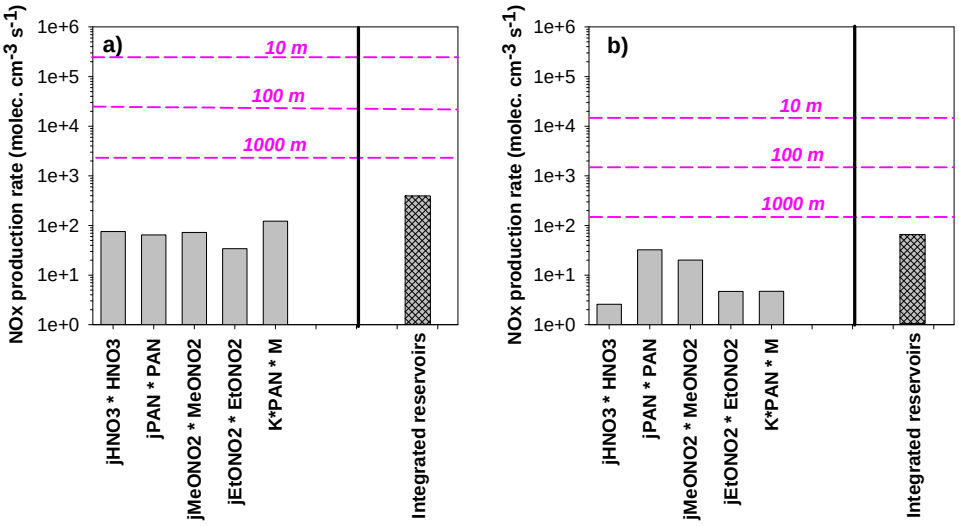

Fig. 6. Rate of NO_X production from gas phase reactions as 24-h averages during **(a)** summer (January) and **(b)** spring (September). Also shown (pink dashed lines) is the NO_X produced directly from photolysis of snowpack nitrate assuming boundary layer heights of 10 m, 100 m and 1000 m. Note the log scale.

(CIMS) technique described by Slusher et al. (2001). Winter time mixing ratios closely tracked those of HNO_3, which was measured concurrently at Halley with the CIMS. During summertime CIMS measurements of HNO_4 and HNO_3 at South Pole, HNO_4 mixing ratios again showed very similar magnitude and variability to HNO_3 (Slusher et al., 2002). Given that HNO_4 more readily undergoes thermal decomposition than does HNO_3, the mixing ratios of HNO_3 at Halley are likely to be an upper limit for HNO_4 during the warmer summer months.

The results from CHABLIS measurements suggest that, as a source of boundary layer NO_x, the snowpack overwhelmingly dominates over any of the gas phase NO_x sources. This conclusion is robust to a range of boundary layer heights, given the importance, but also uncertainty, in this parameter. Extending the suite of NO_y components to include also N_2O_5, HONO and HNO_4, given the assumptions described above, does not alter this conclusion. Further, the calculated snowpack source did not account for emissions from snowpack nitrite, which has been shown to be a significant contributor albeit present at considerably smaller concentrations in the snowpack than nitrate (Jones et al., 2008). 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 from the snowpack would then be different from those of today. However, during past interglacials, when mineral loading was similar to those of the present day, snowpack nitrate should be similarly 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. It thus seems that for some periods in the past, we should be able to derive a flux of NO_x to the Antarctic (and Arctic) boundary layer using ice core data.

Regarding sources of nitrate to the snowpack, various mechanisms are supported/suggested by the CHABLIS data. The late winter/spring peak in total inorganic nitrate apparent in the CHABLIS data (see Jones et al., Fig. 11) is in line with previous observations from coastal Antarctic stations that have been interpreted as nitrate originating in the stratosphere (Wagenbach et al., 1998; Savarino et al., 2007). The case study in August suggests that, at least at certain times, particulate nitrate is the prime source of nitrate to the snowpack. This role is explored further in Wolff et al. (2008). The seasonality of HNO_3 closely matches that of surface snow nitrate, suggesting a strong link between these chemical species, most likely driven by the recycling mechanisms that exist between snowpack and boundary layer air (e.g. Davis et al., 2004, 2008; Frey et al., 2009). A striking result from this long-duration budget study is the sustained significant concentrations of organic nitrates (PAN and alkyl nitrates) observed throughout the campaign at Halley. They completely dominated the NO_y budget during the winter, and were on a par with the measured inorganic nitrate compounds during the summer. Although not a direct source of snowpack nitrate, organic nitrates would act as a source of NO_x to coastal Antarctica that would ultimately contribute to nitrate within the snowpack.

Acknowledgements. We gratefully acknowledge the assistance of the overwinterers at Halley research station who conducted the filter sampling for this work. The authors would like to thank Mat Evans for producing the CHABLIS data merger which was used as a source of data for some of the analyses presented here. We also thank Bill Bloss for providing us with the OH data used in Sect. 4. Finally, we are indebted to the Natural Environment Research Council Antarctic Funding Initiative for providing funding for this research under grant numbers NER/G/S/2001/00010, and the BAS core project CACHE-CEFAC.

Edited by: J. Lee

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