



Atmospheric nitric oxide and ozone at the WAIS Divide deep coring site: a discussion of local sources and transport in West Antarctica

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Abstract. The first measurements of atmospheric nitric oxide (NO) along with observations of ozone (O₃), hydroperoxides (H₂O₂ and MHP) and snow nitrate (NO₃⁻) on the West Antarctic Ice Sheet (WAIS) were carried out at the WAIS Divide deep ice-coring site between 10 December 2008 and 11 January 2009. Average $\pm 1\sigma$ mixing ratios of NO were 19 ± 31 pptv and confirmed prior model estimates for the summer boundary layer above WAIS. Mean $\pm 1\sigma$ mixing ratios of O₃ of 14 ± 4 ppbv were in the range of previous measurements from overland traverses across WAIS during summer, while average $\pm 1\sigma$ concentrations of H₂O₂ and MHP revealed higher levels with mixing ratios of 743 ± 362 and 519 ± 238 pptv, respectively.

An upper limit for daily average NO₂ and NO emission fluxes from snow of 8.6×10^8 and 33.9×10^8 molecule cm⁻² s⁻¹, respectively, were estimated based on photolysis of measured NO₃⁻ and nitrite (NO₂⁻) in the surface snowpack. The resulting high NO_x emission flux may explain the little preservation of NO₃⁻ in snow ($\sim 30\%$) when compared to Summit, Greenland (75–93%). Assuming rapid and complete mixing into the overlying atmosphere, and steady state of NO_x, these snow emissions are equivalent to an average (range) production of atmospheric NO_x of 30 (21–566) pptv h⁻¹ for a typical atmospheric boundary-layer depth of 250 (354–13) m. These upper bounds indicate that local emissions from the snowpack are a significant source of short-lived nitrogen oxides above the inner WAIS.

The net O₃ production of 0.8 ppbv day⁻¹ triggered with NO higher than 2 pptv is too small to explain the observed O₃ variability. Thus, the origins of the air masses reaching

WAIS Divide during this campaign were investigated with a 4-day back-trajectory analysis every 4 h. The resulting 168 back trajectories revealed that in 75 % of all runs air originated from the Antarctic coastal slopes (58 %) and the inner WAIS (17 %). For these air sources O₃ levels were on average 13 ± 3 ppbv. The remaining 25 % are katabatic outflows from the East Antarctic Plateau above 2500 m. When near-surface air from the East Antarctic Plateau reaches WAIS Divide through a rapid transport of less than 3 days, O₃ levels are on average 19 ± 4 ppbv with maximum mixing ratios of 30 ppbv. Episodes of elevated ozone at WAIS Divide are therefore linked to air mass export off the East Antarctic Plateau, demonstrating that outflows from the highly oxidizing summer atmospheric boundary layer in the interior of the continent can episodically raise the mixing ratios of long-lived atmospheric chemical species such as O₃ and enhance the oxidative capacity of the atmosphere above WAIS.

1 Introduction

Over the last decade, a large number of field and lab studies have provided evidence of the importance of snow photochemistry on the chemical composition of air above snow-covered surfaces in the polar and mid-latitudes (Grannas et al., 2007, and references therein). The upper snowpack is seen not only as a chemical reservoir but as a chemical reactor. Trace gases emitted by the snowpack include hydrogen peroxide (H₂O₂), formaldehyde (CH₂O) and nitrogen oxides (NO_x = NO + NO₂), and increase the oxidizing potential of the atmospheric boundary layer through production of

the hydroxyl radical (OH) and ozone (O_3) (Grannas et al., 2007; Thomas et al., 2012). Measurements of atmospheric and snow concentrations and also fluxes from snow surfaces indicate that the polar snowpack emits NO_x mainly through the photolysis of nitrate (NO_3^-) in near-surface snow (Grannas et al., 2007; Bauguutte et al., 2012; Frey et al., 2013). Snowpack emissions of NO_x can contribute significantly to the NO_y (NO_x + other oxidized nitrogen species) budget above snow, as observed in continental and coastal Antarctica (Jones et al., 2000; Frey et al., 2013). Bauguutte et al. (2012) reached a similar conclusion at Halley station by highlighting that halogen chemistry over the Antarctic coast controls the lifetime of NO_x species and reduces the nitric oxide (NO) mixing ratios. When atmospheric turbulence is low or atmospheric boundary layer depths are shallow, these emissions contribute to high NO_x levels, several hundred pptv, as observed at South Pole and over the East Antarctic Plateau (Davis et al., 2004, 2008; Slusher et al., 2010; Frey et al., 2013). Chen et al. (2004) and Mauldin et al. (2004) showed that at South Pole these high levels of NO_x shift the HO_x (OH + HO_2) partitioning towards OH:



NO_x emissions from snow can also lead to net production of O_3 over the East Antarctic Plateau (Helmig et al., 2008a, and references therein), and thereby shift HO_x partitioning of the overlying atmosphere.

Above the West Antarctic Ice Sheet (WAIS), enhanced snowpack emissions of NO_x associated with events of stratospheric O_3 depletion may lower the formation rate of atmospheric H_2O_2 (Frey et al., 2005). Photochemical modeling suggests that atmospheric H_2O_2 is sensitive to the NO background, opening up the possibility of constraining past NO_x and OH levels using the H_2O_2 ice-core record (Frey et al., 2005, 2006). Therefore, investigation of the current atmospheric boundary-layer photochemistry at a WAIS ice-core drilling site is essential to interpret ice-core records of photochemically active species such as H_2O_2 and NO_3^- . This can also provide information regarding the contribution of air advection from the East Antarctic Plateau to levels of oxidants above WAIS, similar to Legrand et al. (2009) who observed outflows from the Antarctic Plateau increasing O_3 concentrations at the East Antarctic coastal site Dumont D'Urville.

So far, atmospheric-sampling campaigns in the Antarctic have taken place at existing stations on the coast (Dumont D'Urville, Halley, Neumayer) and on the East Antarctic Plateau (South Pole, Dome C). Only recent airborne campaigns (Eisele and Davis, 2008; Slusher et al., 2010) or scientific overland traverses (Frey et al., 2005) provided information on the composition of the lower atmosphere across the interior of the continent. Thus, spatial data coverage of the lower atmosphere in Antarctica is still sparse and little is known about the variability of O_3 and its precursors above WAIS. For example, the first ground-based measurements across WAIS lasting several days included at-

mospheric records of H_2O_2 , methyl hydroperoxide (MHP), CH_2O , O_3 but not NO_x (Frey et al., 2005).

The current study includes multi-week first observations of NO and complementary measurements of atmospheric O_3 , H_2O_2 , MHP and of surface-snow H_2O_2 , NO_3^- and nitrite (NO_2^-) in the WAIS region. The aims were to determine the summer composition of the lower atmosphere in the interior of West Antarctica and the relative importance of local production versus air mass transport on the local atmospheric budgets of NO_x and O_3 .

2 Methods

From 10 December 2008 to 11 January 2009, atmospheric concentrations of NO and O_3 were continuously measured at WAIS Divide (local time: LT = UTC - 07:30). Mixing ratios of ROOH (H_2O_2 and MHP) were recorded between 31 December 2008 to 7 January 2009. Snow samples were collected daily from the surface and weekly from 30 cm snow pits for chemical analysis of NO_3^- , NO_2^- and H_2O_2 .

Atmospheric sampling took place 5 km NW of the WAIS Divide drilling camp (79.467° S, 112.085° W, 1766 m a.m.s.l., <http://www.waisdivide.unh.edu>). All instruments were run out of a Polarhaven tent heated by a prewatt heater. Atmospheric measurements were made 1 m above the snow, 10 m upwind (prevailing winds from NE) from the tent, with ambient air drawn through an insulated and heated PFA (1/4" I.D.) intake line (typically 1.4 STP - L min⁻¹) of 12 m for ROOH, and of 20 m for NO and O_3 . In an attempt to minimize artifacts in our atmospheric records, the two generators (3.5 and 5 KW) that provided electricity to the lab were located about 30 m downwind from the sampling lines, and all activities around the site were restricted. However, the heater exhaust was located on the top of the Polarhaven tent.

2.1 Atmospheric sampling

NO was measured using a modified chemiluminescence instrument used previously at South Pole (Davis et al., 2001, 2004). NO mixing ratios recorded at 1 Hz were aggregated to 1 min averages. The limit of detection (LOD), defined as 2- σ of the background count rate, was 5 pptv. A two-minute background signal was monitored every 20 min and an automatic 4 min calibration was performed every 2 h by addition of a 2 ppmv NO standard. Due to late delivery of this NO gas standard to the site, calibration was only run during the last 3 days of the campaign. The instrument sensitivity remained fairly constant over the three days, with an average over 16 calibrations of 7.10 ± 0.18 Hz pptv⁻¹, similar to the pre-season value of 7.00 Hz pptv⁻¹ determined in the lab. We therefore used the 3-day average value of these calibrations to process the overall dataset. NO spikes related to pollution from generators and heater exhaust were removed using a moving standard deviation filter with a maximum standard deviation

of 30 (1.5 times the interquartile range of the dataset). This led to the removal of 25 % from the raw NO record.

Surface O₃ was monitored at 1 min resolution using a 2B Technologies (Golden, Colorado) O₃ monitor, model 205, similar to those previously used in the remote Antarctic such as on the ITASE traverses (Frey et al., 2005) and in an O₃ monitoring network (Bauguitte et al., 2011). LOD was 1 ppbv.

Atmospheric ROOH were measured based on continuous scrubbing of sample air followed by separation in an HPLC column and fluorescence detection, described in detail by Frey et al. (2005, 2009a). The detector was calibrated 1–2 times per day with H₂O₂ solution and MHP standards synthesized in our lab following the protocol described by Frey et al. (2009a). The LOD, 2- σ of the baseline, were 87 pptv for H₂O₂ and 167 pptv for MHP. Unexpected variations of the coil-scrubber temperatures may have caused higher LOD than those reported by Frey et al. (2005, 2009a).

2.2 Snow sampling

All surface snow and snow pits were sampled in a 7200 m² clean area upwind from the Polarhaven tent. The top 1 cm of the non-cohesive surface snow, referred to as the skin layer (Frey et al., 2009b; Erbland et al., 2013), was collected daily with a 10 mL glass test tube to assess temporal changes in snow chemistry. Twice during the campaign, the skin layer was sampled simultaneously at five different spots inside the clean area to assess possible local spatial variability of NO₃⁻, NO₂⁻ and H₂O₂.

Weekly snow pits were sampled at 2 cm resolution to a depth of 30 cm, covering the snowpack zone where 85 % of NO₃⁻ photolysis is expected to occur (France et al., 2011). Snowflakes were collected on aluminum foil during the only snow precipitation event observed during the campaign, on 12 December 2008.

All snow samples were collected in 100 mL SCHOTT bottles and kept frozen during storage and transport until analysis 14 months later. The analysis involved melting the snow 1 hour before injecting the sample into a self-built continuous flow analysis (CFA) system, as described by Frey et al. (2006). The LOD, defined as 3 σ of the baseline, was 0.4 ppbw for NO₃⁻, NO₂⁻ and H₂O₂. Only values above LOD were used for further calculations. Some loss of NO₂⁻ in the samples may have occurred between the time of collection and analysis, as Takenaka and Bandow (2007) and O'Driscoll et al. (2012) showed that NO₂⁻ may be oxidized during freezing and storage.

3 Results

3.1 Atmospheric concentrations

The average $\pm 1\sigma$ (median) of NO over the campaign was 19 ± 31 (10) pptv (Table 1). Some noise remained in the NO dataset after filtering; however, the 4 h running median (Fig. 1a) shows very little change in the overall trend of the data due to filtering, with the median value after filtering similar to that of the raw dataset (6 pptv). One-minute data did not exhibit any clear diel cycle (Fig. 1), but 1 h binned data centered on each hour for the measurement period revealed a diel cycle that can be interpreted with the variations of the average solar elevation angle (Fig. 2b). NO mixing ratios increased at 07:00–08:00 LT with a maximum rise of 36 % from the daily median of 10 pptv. A decrease was observed afterwards and followed by a second increase of 20 % above the median value at 19:00 LT. These peaks in NO occurred as solar elevation angle increased and decreased, with lower values of NO at the maxima and minima of solar elevation angle.

Average $\pm 1\sigma$ (median) mixing ratios of O₃ at WAIS Divide were 14 ± 4 (13) ppbv (Table 1). The mean is two thirds of the 20 ± 2 ppbv average mixing ratio observed at Byrd Station in summer 2002, but is in the range of values from previous measurements between 79.06° S and 85.00° S above the WAIS (Frey et al., 2005) (Fig. 3). Two events of elevated O₃ levels were recorded between 24 and 25 December, and between 27 and 29 December, with concentrations in the range of 20 to 30 ppbv (Fig. 1). Concentrations above 25 ppbv were only observed for winds blowing from ENE to SWS. This 135° sector represents 67 % of all the wind directions observed during the field campaign (Fig. 4). The hourly binned O₃ data (Fig. 2b) show a small diel cycle in phase with solar elevation angle and wind speed. The mixing ratios rose by 5 % of the median value (13 ppbv) in the morning, reaching a maximum at 14:00 LT and dropping thereafter in the afternoon.

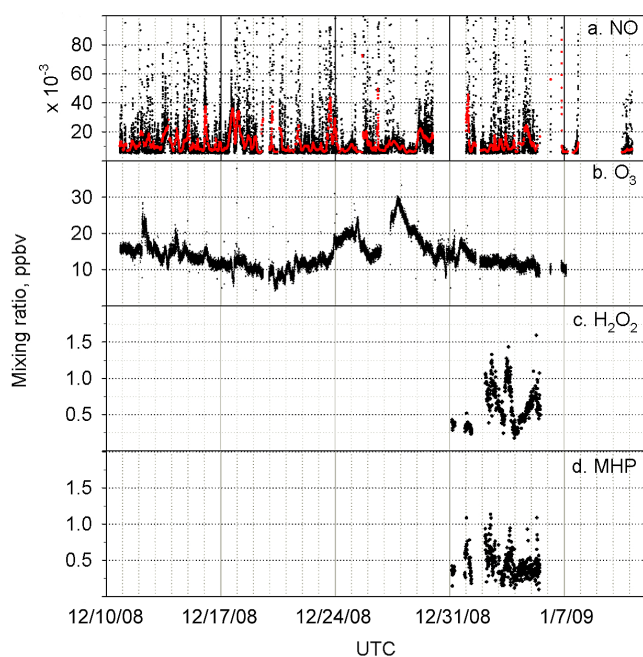
Concentrations of H₂O₂ and MHP were measured between 31 December 2008 and 5 January 2009 (Fig. 1). Averages $\pm 1\sigma$ (medians) were 743 ± 362 (695) and 519 ± 238 (464) pptv for H₂O₂ and MHP, respectively. Our records are closer to values observed at West Antarctic sites below 1500 m a.m.s.l. and higher than measurements made in the surrounding area (Fig. 3), with mixing ratios of H₂O₂ that were twice those observed at Byrd station in late November 2002 (Table 1) (Frey et al., 2005). Average $\pm 1\sigma$ (range) of the MHP:(H₂O₂ + MHP) ratios were 0.42 ± 0.10 (0.12–0.76). These values are in the range of those previously recorded over WAIS (Frey et al., 2005). Binned values suggest, for both H₂O₂ and MHP, a diel cycle with respective maximum 44 and 37 % above their medians (695 and 464 pptv) observed in the morning (Fig. 2c).

Table 1. Averages $\pm 1\sigma$ (medians) of atmospheric and snow concentrations of the chemical species observed at WAIS Divide and nearby sites.

Site	atmospheric				skin layer		
	NO (pptv)	O ₃ (ppbv)	H ₂ O ₂ (pptv)	MHP (pptv)	H ₂ O ₂ (ppbw)	NO ₃ ⁻ (ppbw)	NO ₂ ⁻ (ppbw)
WAIS Divide	19 ± 31 (10)	14 ± 4 (13)	743 ± 362 (695)	519 ± 238 (464)	238 ± 37 (238)	137 ± 37 (142)	0.6 ± 0.4 (0.5)
ITASE 00-1 ^a	–	–	303 ± 159	–	175	–	–
Byrd ^b	10	20 ± 2 (20)	364 ± 138 (348)	422 ± 162 (411)	25 ± 4 (25)	–	–

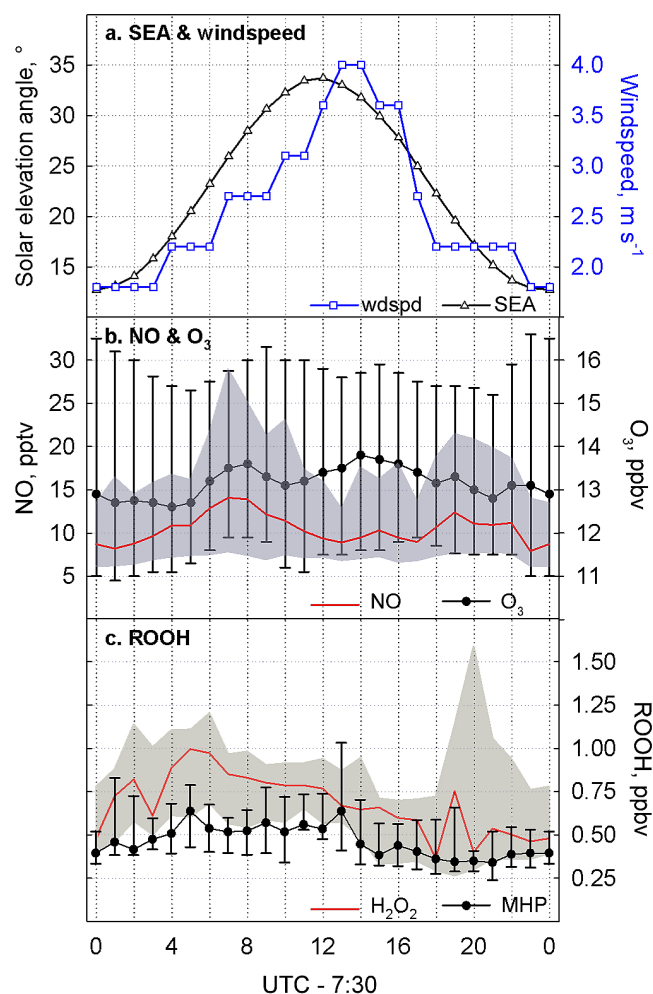
^a 79.38° S, 111.23° W, 1791 m a.m.s.l. (from Frey et al., 2005)

^b 80.02° S, 119.60° W, 1537 m a.m.s.l. (from Frey et al., 2005); NO based on optimum model runs; atmospheric H₂O₂ from sampling at site RIDS-C (80.00° S, 119.53° W, 1575 m a.m.s.l.); H₂O₂ in snow from sampling at site RIDS-B in 1996 (79.46° S, 118.04° W, 1650 m a.m.s.l.)

**Fig. 1.** Atmospheric mixing ratios of NO after filtering and O₃ (1 min averages), and of H₂O₂ and MHP (10-minute averages) during austral summer 2008–2009 at WAIS Divide. The 4 h running median of NO is also shown (red symbols).

3.2 Concentrations in snow

Average $\pm 1\sigma$ (median) concentrations of NO₂⁻, NO₃⁻ and H₂O₂ in the skin layer at WAIS Divide were 0.6 ± 0.4 (0.5), 137 ± 37 (142) and 238 ± 37 (238) ppbw, respectively (Table 1). Daily concentrations of NO₂⁻ in the skin layer showed a decrease of 30 pptw per day ($R^2 = 0.36$) over the campaign (Fig. 5). This decrease represents a rate of 5 % per day of the average concentration of NO₂⁻ measured in all of the snow-surface samples. Unlike NO₂⁻, NO₃⁻ and H₂O₂ exhibited some variation but no trend was observed for these species.

**Fig. 2.** Diel variation of (a) average solar elevation angle (SEA) and wind speed, (b) median NO (left axis) and O₃ (right axis), and (c) median H₂O₂ and MHP. Symbols and lines are 1 h binned values centered on each hour; shaded area and error bars indicate the range between the first and third quartiles; local time is UTC – 07:30.

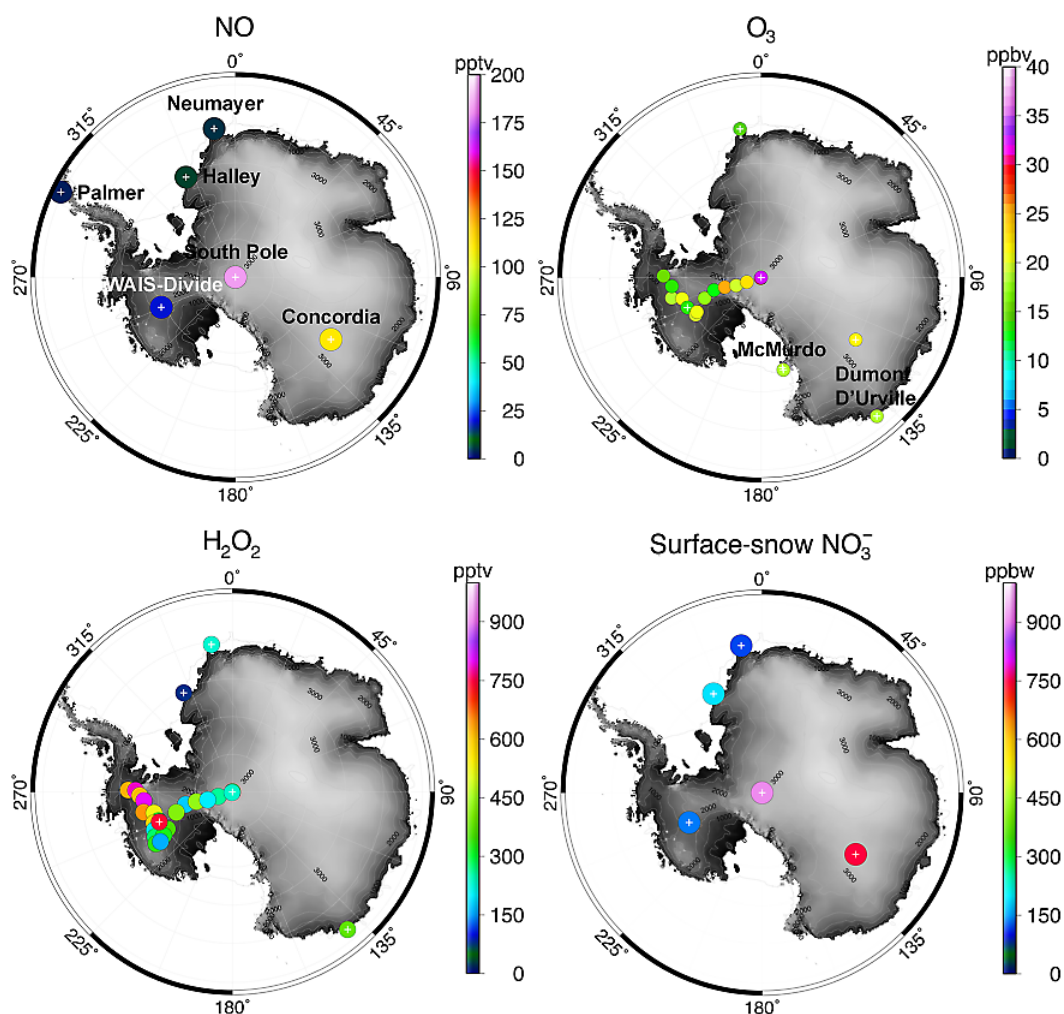


Fig. 3. Report of some previous Antarctic measurements of atmospheric NO, surface O₃, H₂O₂, plus NO₃⁻ in surface snow. Data from Frey et al. (2013), Preunkert et al. (2012), Frey et al. (2009a), Legrand et al. (2009), Frey et al. (2005), Dibb et al. (2004), Davis et al. (2004), Rothlisberger et al. (2000), Jacobi et al. (2000), Jones et al. (1999), Mulvaney et al. (1998), Jefferson et al. (1998), NOAA/GMD, and AWI (<http://ds.data.jma.go.jp/gmd/wdcgg/>).

The coefficients of variation of concentrations of NO₂⁻, NO₃⁻ and H₂O₂ in the skin layer are 49 %, 26 % and 17 %, respectively. The coefficients of variation for samples collected simultaneously on 1 and 8 January 2009 (Fig. 5) are 17 %, 31 % and 7 % for NO₂⁻, NO₃⁻ and H₂O₂, respectively. The similar coefficients of variation for NO₃⁻ concentrations in snow imply that spatial variability contributes significantly to the overall variability and thus a temporal trend may be difficult to detect. For NO₂⁻ and H₂O₂, the coefficients of temporal variability (49 % and 17 %, respectively) are more than double those calculated from spatial variability (17 % and 7 %, respectively). The variations of daily concentrations of NO₂⁻ and H₂O₂ in near-surface snow may then be interpreted as temporal trends. Concentrations of H₂O₂ in the top 5–15 cm of the profile (Fig. 6) may also indicate a temporal trend; seasonal increase in concentrations measured over

this period was apparent not only in the top 5 cm of snow, but also down to at least 15 cm. Although there was no new snow accumulation during this period, there was wind redistribution and atmosphere–snow exchange of H₂O₂ and other atmospheric gas species, or nighttime deposition of fog.

The 30 cm deep profiles of NO₂⁻, NO₃⁻ and H₂O₂ illustrated in Fig. 6 represent concentration changes of these species in snow over the last 6 months of 2008, based on local mean annual snow accumulation rate of 0.20 m_{weq} yr⁻¹ (Banta et al., 2008) and an average snow density of 0.37. Total concentrations of NO₃⁻ in the snow column dropped by about 19 % between the first and last snow-pit samplings. NO₃⁻ concentrations decrease by 94–188 ppbw over the top 5 cm of snow, reaching ~ 30 ppbw below. Total NO₂⁻ stored in the 30 cm column decreased by about 65 % across the three snow-pit samplings. Unlike NO₂⁻ and NO₃⁻, total

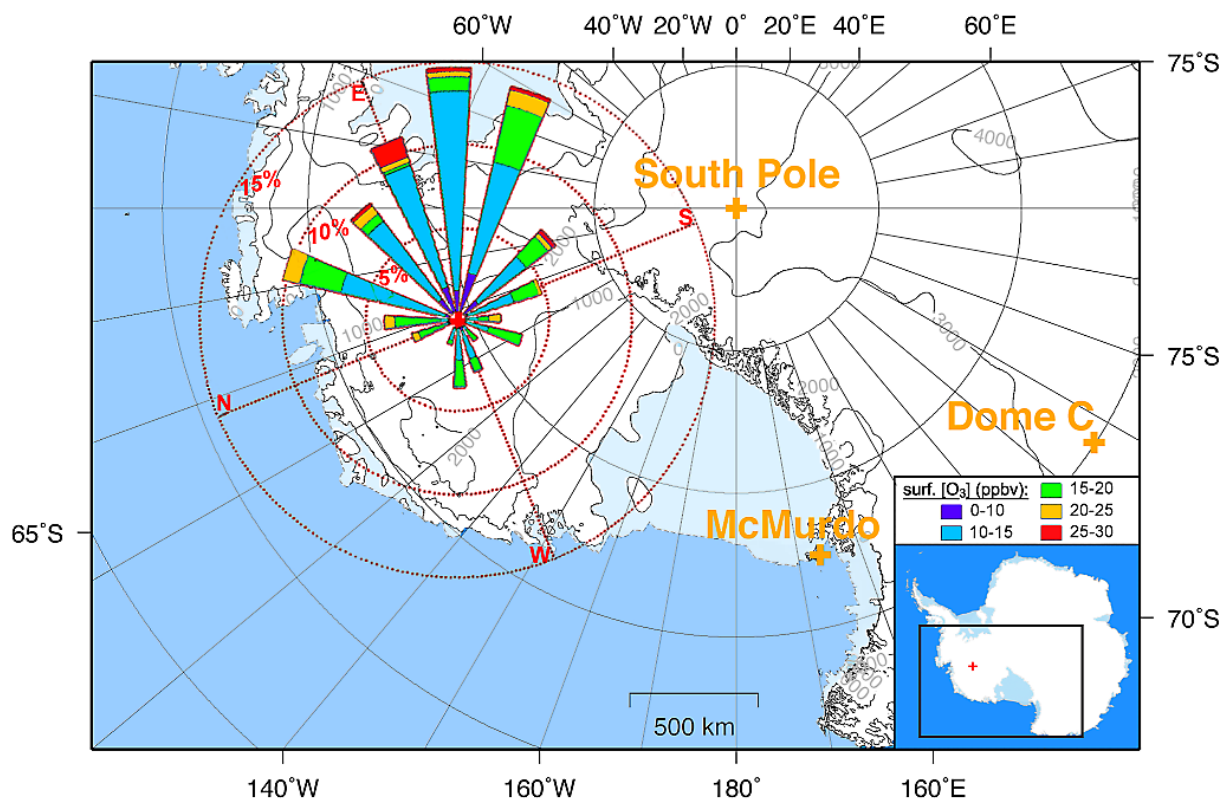


Fig. 4. The windrose for WAIS Divide for period of 10 December 2008 to 5 January 2009 and O_3 concentrations from each direction for the same period.

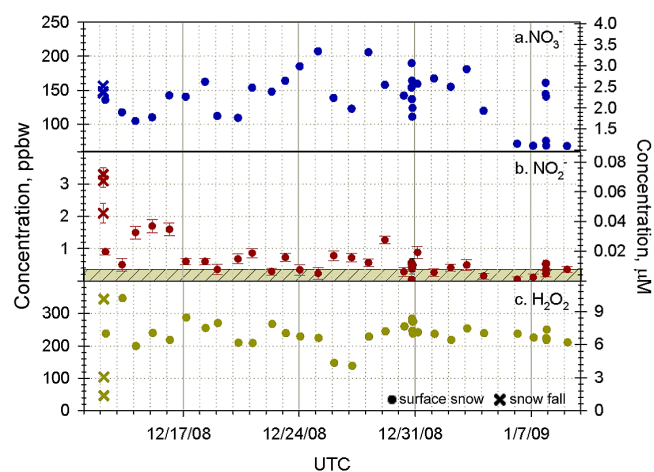


Fig. 5. Surface-snow concentrations and snow concentrations from the 12 December 2008 precipitation of (a) NO_3^- , (b) NO_2^- , (c) H_2O_2 . The shaded area in (b) represents the NO_2^- LOD.

concentrations of H_2O_2 in the top 30 cm of snowpack doubled over the 18 days of sampling. A 233–298 ppbw decrease of H_2O_2 concentrations in the first 10 cm of each snow pit was generally observed.

4 Discussion

4.1 Local photochemistry

4.1.1 Factors controlling atmospheric levels of ROOH, NO, O_3 and snow content of NO_3^- , NO_2^- and H_2O_2

Levels of NO and O_3 measured at WAIS Divide during summer 2008–2009 are slightly higher than coastal values but lower than observed concentrations on the Antarctic Plateau (Fig. 3). The observed mean of NO mixing ratios are close to the 10 pptv modeled by Frey et al. (2005) at Byrd, about 160 km from WAIS Divide. Their potential NO concentrations were computed with the NASA Goddard Flight Center (GSFC) point photochemical model that included a snowpack source of H_2O_2 and CH_2O .

The diel cycle of NO (Fig. 2b) does not compare well with either measurements from the East Antarctic Plateau (Dome C) (Frey et al., 2013) or from the West Antarctic coast (Halley) (Bauguitte et al., 2012). Data show a symmetry of the NO diel cycle with respect to local noon that is similar to predictions and observations from Summit/Greenland (Thomas et al., 2012), but with lower mixing ratios and a diel amplitude of 6.5 pptv. The NO variability is mainly in phase with solar radiations but presents two minima around local

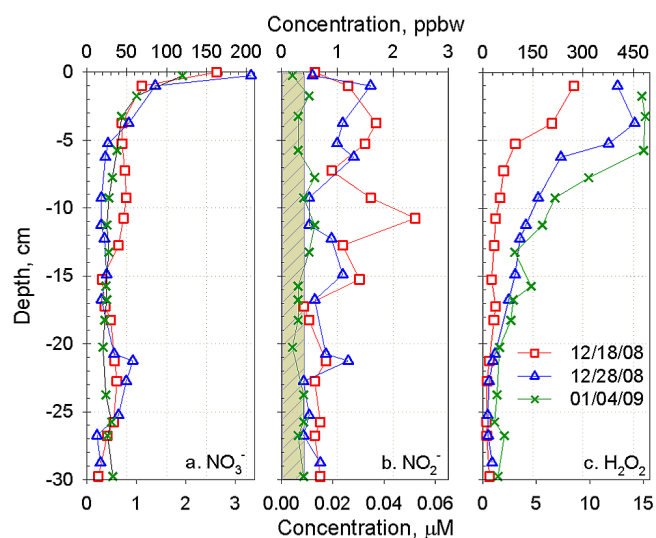


Fig. 6. Snow concentrations of (a) NO_3^- , (b) NO_2^- and (c) H_2O_2 measured in the 30 cm-depth snow pits dug on 18 December 2008 (red squares), 28 December 2008 (blue triangles) and 04 January 2009 (green crosses). The shaded area in (b) represents the NO_2^- LOD.

noon and midnight and two daily maxima around 07:00 and 19:00 LT. The 36 % rise from the NO median of 10 pptv observed in the morning along with the increase of solar elevation angle suggests that the increase of solar elevation angle enhances the photolytic production of NO from the snowpack. The 2 h binned data of NO and wind speed (data not shown) suggest that higher NO mixing ratios were observed for wind speeds less than 3 m s^{-1} , indicating a potential local production of NO from surface snow. The decrease observed after 09:00 LT at high solar elevation angle may result from the increase of the atmospheric boundary layer height and of the wind speed. Higher wind speeds would result in an increase of turbulent mixing and therefore in efficient vertical upward transport and dilution of surface emissions into a growing volume given by the developing boundary layer (Frey et al., 2013). The increase of NO levels by 20 % of the median value around 19:00 LT may result from the decrease of the atmospheric boundary layer height and wind speed along with solar elevation angle. However, no measurements of the diel variability of the atmospheric boundary layer height were performed during the campaign to confirm this point. These data suggest that both snow photochemistry and physical mixing control the diel cycle of NO at WAIS Divide. Through its different sinks and sources, the NO_x photochemistry may also drive the NO variability but this contribution cannot be defined here as it requires a more detailed analysis using a 1-D model (Thomas et al., 2012).

The interpretation of the 1 month record of O_3 in terms of seasonal trend is made difficult given the short period of measurement. However, its comparison with the annual cycles of

O_3 observed at other Antarctic stations, with concentrations between those observed at Halley and South Pole, suggests a possible influence of both marine and continental air on the WAIS Divide level, and shows characteristic low mixing ratios around the Austral solstice.

The O_3 diel cycle (Fig. 2b) is similar to observations from Dome C (Legrand et al., 2009) but with lower amplitude and concentrations. The increase of 5 % of the median value is consistent with O_3 produced locally from the snowpack NO_x emissions and confined into a shallow atmospheric boundary layer. Similarly to the NO diel cycle, the following decrease of O_3 in the afternoon can be attributed to a deeper atmospheric boundary layer and higher wind speeds that dilute all the produced O_3 . Because the chemical lifetime of O_3 in polar regions is in the order of days (Grannas et al., 2007), it is not expected that photochemical loss is a main driver of the diel cycle of O_3 . Lack of higher mixing ratios during periods with wind speed less than 3 m s^{-1} (data not shown) suggests that local production of O_3 over the surface snow is not the predominant process at WAIS Divide during the austral summer. The amplitude of the diel cycle is relatively low in comparison with the average daily O_3 which indicates that another source may be considered to explain the change of O_3 over the campaign. The ENE to SWS wind directions associated with high O_3 values (Fig. 4) point to a possible contribution of air mass transport of this chemical species at WAIS Divide, e.g. outflow from the East Antarctic Plateau (see Sect. 4.2). A similar conclusion was reached by Helmig et al. (2007a) from the review of other Antarctic station data.

H_2O_2 concentrations at WAIS Divide are similar to those observed above WAIS at lower latitudes (below 1500 m a.m.s.l.) but 3 times the mixing ratios measured at South Pole (Frey et al., 2009a). As shown in Table 1 and in Fig. 3, the concentrations of H_2O_2 measured at WAIS Divide are higher than those measured at nearby sites (Frey et al., 2005). A similar comparison between our average MHP mixing ratios and prior measurements across WAIS (Frey et al., 2005, 2009a) is also observed. The average specific humidity of 1.1 g kg^{-1} calculated for the period of ROOH measurement is higher than previous records from nearby sites (Frey et al., 2005). This high value may explain the elevated mixing ratios of H_2O_2 and MHP measured at WAIS Divide, as water vapor is an important precursor for both species.

H_2O_2 and MHP exhibited a simultaneous increase with solar elevation angle between 03:00–13:00 LT, followed by a decrease (Fig. 2). The maximum amplitude of H_2O_2 is observed at 05:00 LT, with a rise of 43 % above the median value of 695 pptv. For MHP, mixing ratios rose to a maximum of 37 % above the median (464 pptv) at 05:00 and 13:00 LT. These results also suggest that both H_2O_2 and MHP may be affected by photochemistry and an increase of the atmospheric boundary layer depth during the day. Unlike NO, ROOH did not show an increase in the second part of the day but the levels remained low, consistent with an increased uptake by the snowpack when the temperature decreased in

the evening (Hutterli, 2003, and references therein). The temperature record at the WAIS Divide camp was, however, too intermittent to further investigate the influence of temperature on atmospheric H_2O_2 . A source from the snowpack is not considered significant for MHP since it has a solubility only 0.1 % that of H_2O_2 (Lind and Kok, 1994) and because no MHP has been detected in snow and ice above the current LOD (Frey et al., 2005, 2009a). The change of MHP may depend on the photochemistry of its precursors such as CH_4 , NMHCs and water vapor, which may decrease with solar elevation angle. Higher H_2O_2 and MHP levels at low wind speeds (less than 4 m s^{-1}) (data not shown) suggest that ROOH are produced locally, coherent with a local photochemical production of MHP and a physical snow-air exchange controlling H_2O_2 (Frey et al., 2009a). They are then diluted through turbulent transport after production.

NO_3^- values are closer to those measured at coastal sites such as Halley or Neumayer stations (Mulvaney et al., 1998), than to the values observed at higher-altitude sites such as South Pole and Concordia stations (Dibb et al., 2004; France et al., 2011). Concentrations of skin-layer NO_3^- present short-term and local spatial variations as Jarvis et al. (2009) and Wolff et al. (2008) also observed at Summit and Halley. These variations cannot be explained with a scenario of fresh snowfall since only one snow precipitation occurred during the campaign (Fig. 5). Part of these variations of NO_3^- in the skin layer as H_2O_2 may be caused by processes such as nighttime deposition of NO_3^- , in the form of nitric oxide (HNO_3) and H_2O_2 or HNO_3 and H_2O_2 gas exchange. Other part can be attributed to some events of snow removed by the wind since this snow removal would also impact on chemical species other than NO_3^- (such as H_2O_2 , which presents similar variations to NO_3^-) on 26–27 December 2008 and on 1–2 January 2009. However, these events are too episodic to explain the overall variations of skin-layer NO_3^- . It is suggested that part of NO_3^- in the top snowpack undergoes some possible post-depositional processes such as photolysis.

The contents of NO_3^- and H_2O_2 in fresh snowfall are in the range of skin-layer concentrations, while previous observations showed that fresh snowfall contains higher concentrations of these species than does aged snow (e.g., Mulvaney et al., 1998). In addition to post-depositional equilibrium with the atmosphere, it is possible that either the snow may have degassed during its collection or prior to analysis. Anastasio and Robles (2007) showed that NO_3^- and H_2O_2 contribute to half the light absorption in polar snow for wavelengths of 280 nm and above. Since the snowflakes from this diamond-dust-like precipitation stayed exposed to the sun under a clear sky until their collection at the end of the event – over 5 h – it is possible that photochemical loss of NO_3^- and H_2O_2 may have occurred during the collection process.

The NO_3^- and H_2O_2 profiles measured in the 30 cm snow pits show a summer peak, as observed in earlier studies (Kreutz et al., 1999, and references therein). The increase

over the campaign of H_2O_2 concentrations in the top 15 cm of snow (Fig. 6) may point to a significant deposition of H_2O_2 during summer, and may also reflect changes in the overlying atmospheric H_2O_2 levels, as discussed in Hutterli (2003). NO_3^- in the skin layer does not show a constant increase with time, unlike H_2O_2 . However, a 70 % decrease of NO_3^- concentrations with increasing depth in the snow is observed, unlike reported snow-pit measurements from polar sites with similar surface temperature and snow accumulation rate, such as Summit, Greenland (e.g., Burkhart et al., 2004). These NO_3^- profiles are similar to those observed at Dome C (e.g., Frey et al., 2009b; France et al., 2011). Based on the interpretation of these authors, this sharp decrease may therefore indicate that NO_3^- in the top snowpack can be significantly reduced by photolysis. A similar photochemical depletion can be suggested to explain the slight decrease of NO_2^- concentration observed in the 30 cm deep profiles over the campaign.

4.1.2 Post-depositional loss of NO_3^- in surface snowpack

WAIS Divide and Summit, Greenland, have similar latitudes, surface temperature and snow accumulation rate (Table 2 and Fig. 7a). Concentrations of NO_3^- in the skin layer are also in the same range for both sites, between 24–206 ppbw for WAIS Divide and 61–207 ppbw for Summit (Fig. 8a, b).

However, the median NO_3^- concentrations in the top 1 m of snow at WAIS Divide is lower than at Summit, 38 vs. 138 ppbw. At very dry and cold sites on the East Antarctic Plateau such as Dome C, mean NO_3^- concentrations are as low as 10–20 ppbw if one excludes the surface layer (Fig. 8c). Note that at Dome C most NO_3^- is concentrated in the top layer with levels 1–2 orders of magnitude larger than at depth (Frey et al., 2009b; Erbland et al., 2013). Comparison of concentrations at the surface and at depth allows estimating net preservation of NO_3^- in snow, which is about 30 % at WAIS Divide, 75–93 % at Summit (Burkhart et al., 2004; Dibb et al., 2007) and less than 10 % at Dome C (Rothlisberger et al., 2002; Frey et al., 2009b).

Differences in average NO_3^- concentrations in the skin layer and preserved at depth between WAIS Divide and Summit can be attributed to (a) a lower background of atmospheric reactive nitrogen in Antarctica compared to the Arctic due to a larger distance from anthropogenic pollution sources, and (b) differences in processes occurring during and after deposition.

Regarding (b), the relative contributions of the processes involved may vary significantly between different locations, i.e., both physical (evaporation and adsorption of HNO_3) and photochemical (photolysis of NO_3^-) processes have been put forward to explain NO_3^- net preservation (sum of gain and loss) in polar snow (Rothlisberger et al., 2002; Frey et al., 2009b). Both processes will be sensitive to accumulation rate and timing. For example, little snowfall in the sunlit season

Table 2. Concentrations of major ions (in ppbw) measured in surface snow at WAIS Divide and Summit, Greenland, and the respective estimated pH and alkalinity.

Sampling year	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	pH ^a	Alk. ^b	
WAIS Divide ($T_{\text{air}} = -28.5\text{ }^{\circ}\text{C}$; $\text{Acc} = 20\text{ cm}_{\text{weq}}\text{ yr}^{-1}$)											
2000 ^c	13	–	16	1	8	24	24	24	6.1	0.37	
2006 ^d	6	4	2	1	1	33	61	43	5.6	0.34	
2006 ^g	4	2	0.4	1	2	31	62	42	5.6	0.27	
2008 ^e	31	–	2	5	5	54	67	41	5.8	0.29	
									Average	5.8	0.32
Summit ($T_{\text{air}} = -29.5\text{ }^{\circ}\text{C}$; $\text{Acc} = 24\text{ cm}_{\text{weq}}\text{ yr}^{-1}$)											
1987 ^f	2	6	1	1	15	8	40	40	5.6	1.2	
2003–2009 ^g	8	21	10	2	18	42	234	107	5.2	2.4	
2007 ^h	4	10	3	2	19	23	195	72	5.3	1.6	
2008 ^e	3	5	3	1	6	19	239	54	5.3	0.65	
									Average	5.3	1.5

^a Based on $[\text{H}^+] = ([\text{SO}_4^{2-}] - 0.12 \times [\text{Na}^+] + [\text{NO}_3^-] + ([\text{Cl}^-] - 1.17 \times [\text{Na}^+])$ (Legrand and Delmas, 1988).

^b In μeqL^{-1} , derived from the ionic balance and attributing the missing part of anions to dissolved carbonate.

^c Site ITASE 00-1, top 2 cm of surface snow; unpublished data (Mayewski and Dixon, 2005).

^d Top 3 cm of surface snow with the first cm removed, unpublished data from <http://www.waisdivide.unh.edu>.

^e Top 3 cm of surface snow, unpublished data (Kreutz and Koffman, 2011).

^f Top 3 cm of surface snow (Mayewski et al., 1990).

^g Top 1 cm of surface snow, unpublished data from <http://niflheim.nilu.no/geosummit/>.

^h Top 0.5 cm of surface snow (range 0.1–6 cm, Dibb et al., 2010).

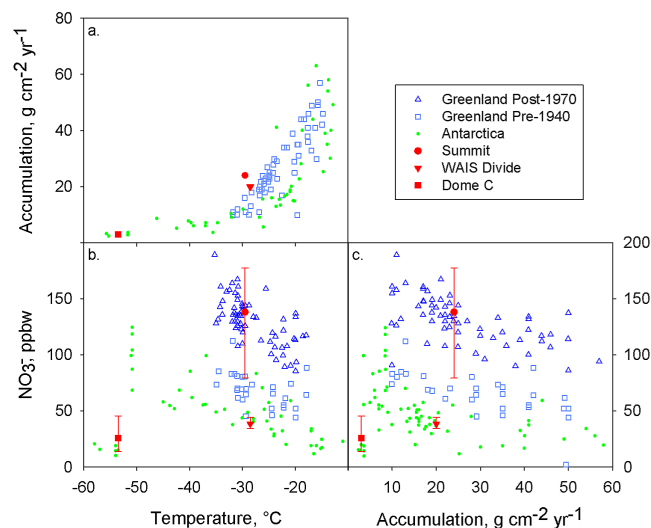


Fig. 7. Updated Figs. 2, 3 and 4 from Rothlisberger et al. (2002) with additional measurements from WAIS Divide, Summit, and Dome C (median and range). Data reported from Greenland are NO₃⁻ concentrations in snow deposited either before 1940 (squares) or after 1970 (triangles). The NO₃⁻ levels observed in the snow deposited after 1970 over Greenland are influenced by anthropogenic emissions that do not reach the Antarctic continent, whereas the difference between the pre-1940s records and the Antarctic data is likely due to a difference in alkalinity.

implies longer exposure of surface snow to UV radiation, leading to significant loss of NO₃⁻ at some sites from photolysis (Frey et al., 2009b; Erbland et al., 2013).

In general, NO₃⁻ concentration preserved in polar snow scale with mean annual temperature and accumulation rate (Rothlisberger et al., 2002, Fig. 7). Comparison shows that NO₃⁻ concentrations at WAIS Divide are not unusual at all since they do fall into the range expected in Antarctica (Fig. 7b, c). They are, however, still lower than those in pre-1940 snow at Greenlandic sites of similar accumulation rate and temperature. The slightly lower accumulation and thus slower burial rate of annual snow deposition at WAIS Divide vs. Summit may contribute to this difference in NO₃⁻ preservation.

But, as suggested by the recent literature, variables linked to (post)depositional processes other than accumulation rate may contribute as well to the observed difference and include micro-physical properties and chemical heterogeneity in the snow matrix. Regarding the latter, observations of atmospheric and snow NO₃⁻ in coastal Antarctica showed that deposition of NO₃⁻ spikes is linked to sea salt aerosol, i.e., by conversion of gas-phase NO₃⁻ to NO₃⁻ aerosol and enhanced trapping of gas-phase NO₃⁻ on salty surfaces (Wolff et al., 2008). This enhanced deposition efficiency will be less important further inland. However, higher NO₃⁻ concentrations were also associated with higher dust content (i.e., calcium (Ca²⁺)), suggesting reduced post-depositional loss of NO₃⁻ by photolysis or evaporation (Rothlisberger et al., 2000). In

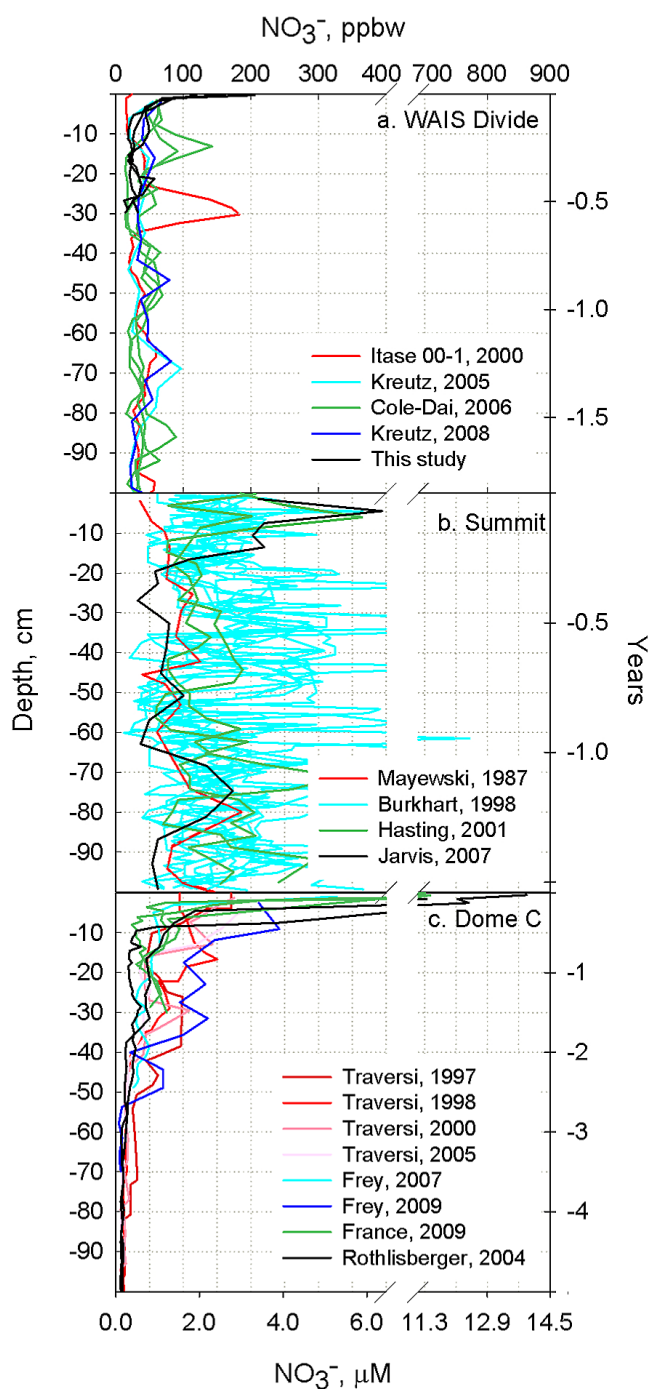


Fig. 8. The 1 m NO_3^- profiles from snowpits reported from WAIS Divide, Summit, and Dome C (Frey et al., 2013; France et al., 2011; Traversi et al., 2009; Burkhart et al., 2004; Hastings, 2004; Rothlisberger et al., 2000; Mayewski et al., 1990; Jarvis (unpublished data)).

comparison with Summit, the lower dust content in WAIS Divide snow, $\sim 20\%$ as alkaline and $\sim 30\%$ as much Ca^{2+} (Table 2), may reduce the preservation of NO_3^- in snow and enhance the NO_x emission flux in summer. Systematic dif-

ferences of NO_x emissions from surface snow could indeed further support increased loss rates and thus less preservation of NO_3^- in surface snow at WAIS Divide. At Summit, Honrath et al. (2002) measured 24 h average NO_x fluxes of $2.5 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$, significantly less than what we calculated for WAIS Divide (see Sect. 4.1.5). However, based on a similar approach to our study, Zatzko et al. (2013) recently modeled an NO_x flux at Summit 5–10 times that reported by Honrath et al. (2002). These results point to significant NO_x emissions from NO_3^- in the snowpack at both sites. Our calculations suggest high loss rates, higher than at Summit (see Sect. 4.1.5), but uncertainties in available measurements and model estimates prevent concluding that emission rates are significantly higher at WAIS Divide than at Summit.

Further, the stable isotopic composition of NO_3^- in snow can provide information on the amount of post-depositional NO_3^- loss (e.g., Frey et al., 2009b; Erbland et al., 2013). At Summit, the N and O isotopes of NO_3^- showed that most of the NO_x emitted from the surface snow is recycled back to the snow as NO_3^- , explaining high NO_3^- preservation (Hastings, 2004). It can be speculated that if the NO_3^- loss rate was similar at WAIS Divide, then some of the emitted gas phase species may be lost through lateral export, implying a lower recycling efficiency and therefore lower NO_3^- preservation. Thus, NO_3^- post-depositional loss is a nonlinear combination of both accumulation and temperature, but other parameters need also to be considered including snow chemistry to get a more complete process understanding.

4.1.3 Steady-state estimation of atmospheric NO_2

Considering the NO – NO_2 – O_3 system, it is reasonable to assume a photo-stationary steady state between NO and NO_2 at 1 m above the snowpack (Frey et al., 2013) to infer the potential atmospheric NO_2 concentrations from reactions:



The conversion of NO to NO_2 described in Reaction (R4) is also achieved through different channels (Reactions R1, R5–R6) with the presence of oxidants such as HO_x , peroxy (RO_2) or halogen ($\text{XO} = \text{ClO}, \text{BrO}, \text{IO}$) radicals:



NO_2 mixing ratios can therefore be estimated from the extended Leighton ratio as derived in Ridley et al. (2000):

$$[\text{NO}_2] = [\text{NO}] \frac{k_{\text{R4}}[\text{O}_3] + k_{\text{R1}}[\text{OX}]}{j_{\text{R2}}} \quad (1)$$

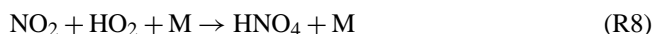
with OX the total radical concentration ($[OX] = [HO_2] + [RO_2] + 2[XO]$) as XO represents the halogen radicals (Ridley et al., 2000). The photolytic rate constant j_{R2} was calculated from the NCAR/ACD radiative-transfer model TUV version 5.0 (Lee-Taylor and Madronich, 2002) with O₃ columns measured by total ozone mapping spectrometer (TOMS) (http://ozoneaq.gsfc.nasa.gov/ozone_overhead_current_v8.md) and assuming clear-sky conditions. k_{R4} and k_{R1} were estimated through the temperature-dependent expressions from Sander et al. (2006). An NO₂ concentration of 5 pptv was computed based on the averages of NO and O₃ observed at WAIS Divide, and on 4.9×10^7 molecule cm⁻³ HO₂ + RO₂ mixing ratios derived from the 1.3×10^6 molecule cm⁻³ OH radical concentrations computed for Byrd (Frey et al., 2005). Because the mixing ratios of HO_x for WAIS Divide are estimates, we calculated the steady-state NO₂ concentrations with reported HO_x levels from Halley (2.3×10^7 molecule cm⁻³) (Bloss et al., 2007) and South Pole (8.3×10^7 molecule cm⁻³) (Eisele and Davis, 2008), resulting in NO₂ concentrations of 5.1 and 6.1 pptv, respectively. These results show that this steady state relationship depends essentially on NO and O₃ mixing ratios.

Note that halogen radicals were not considered in these calculations, and no records have yet been reported above WAIS. Coastal sea ice is the main source of active halogen (Saiz-Lopez and von Glasow, 2012, and references therein) and measurements from Antarctic coastal sites showed a strong spatial variability in concentrations of halogens and their potential impact on boundary layer photochemistry. Summertime measurements of IO and BrO ranged from 0.7 to 5.5 pptv at Halley (Saiz-Lopez et al., 2007), while mixing ratios at Dumont D'Urville were observed between 0.04 and 0.15 pptv for IO and below or equal to 2 pptv for BrO (Grilli et al., 2013). The back-trajectory analysis described in Sect. 4.2.1 shows that marine intrusions over WAIS are frequent (58 % of all back trajectories) and have therefore the potential to export halogen compounds over the ice sheet. However, from measurements by the satellite spectrometer SCIAMACHY (Schönhardt et al., 2012), monthly mean IO and BrO vertical column amounts averaged over 2004 to 2009 revealed insignificant concentrations of both species over WAIS Divide between December and January. Thus, it is reasonable to assume that little or insignificant halogen chemistry is occurring at WAIS Divide.

The NO : NO₂ ratio of 3.8 is significantly higher than the ratios of 1.3–2 and 1.5 observed respectively at Halley (Bauguitte et al., 2012, and references therein) and Dome C (Frey et al., 2013). These studies showed evidence of large discrepancies between observed and steady-state estimated ratios that are attributed to halogen chemistry for the coastal station and to the presence of HO₂ + RO₂ on the plateau. Therefore, the estimated atmospheric NO₂ from the steady-state assumption has to be considered as a lower limit of true value.

4.1.4 Potential NO_x lifetime

The NO_x lifetime was calculated to investigate the factors controlling its atmospheric concentration. Assuming that halogen chemistry is not significant at WAIS Divide, Reactions (R7)–(R8) are the main sink of NO₂ during polar day:



Based on these reactions, the lifetime of NO₂ (τ_{NO_2}) was estimated with $[OH] = 1.3 \times 10^6$ molecule cm⁻³ and $[HO_2] = 4.9 \times 10^7$ molecule cm⁻³ (Sect. 4.1.3). The lifetime of NO_x (τ_{NO_x}) was then deduced through Eq. (2) (Seinfeld and Pandis, 1998):

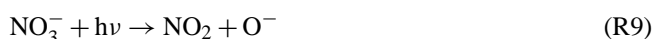
$$\tau_{NO_x} = \tau_{NO_2} \times \left(1 + \frac{[NO]}{[NO_2]}\right). \quad (2)$$

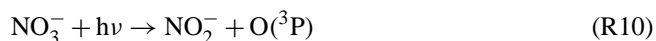
The resulting lifetime of NO_x at WAIS Divide of 15 h represents an upper bound, given that the NO : NO₂ ratio of 3.8 is an upper limit. This value is less than the 24 h estimated by Jones et al. (2000) from a snow block at Neumayer, but it is longer than the 6.4 h estimated at Halley (Bauguitte et al., 2012) and 8 h at South Pole (Davis et al., 2004). Bauguitte et al. (2012) showed that NO₂ lifetime at Halley is mainly controlled by halogen oxidation processes, while low temperatures at South Pole prevent thermal decomposition of pernitric acid and therefore enhance NO₂ removal through its oxidation with HO₂ (Slusher et al., 2002). Thus, our potential NO_x lifetime seems plausible since we expect to observe none of these conditions at WAIS Divide. NO_x lifetimes computed with reported HO_x concentrations from South Pole and Halley (Sect. 4.1.3) are respectively 9 and 33 h and represent the potential lower and upper bounds for the NO_x lifetime in the inner WAIS.

Considering a photochemical lifetime of other NO_x precursors, such as HNO₄ and HNO₃ (HNO₃ compared to dry deposition), of less than a day above the East Antarctic Plateau (Davis et al., 2008; Slusher et al., 2002) and an air mass transport between WAIS Divide and the Plateau longer than 33 h (Sect. 4.2), outflows from this region are not expected to be a major NO_x source for the boundary layer at WAIS.

4.1.5 Calculation of upper-limit NO_x emission from NO₃⁻ and NO₂⁻ photolysis

The simplified reaction scheme (R9) to (R12) summarizes the currently known NO₃⁻ photochemistry in near-surface snow:





While NO_3^- photolysis is the major source of NO_2 (Reaction R9) (Grannas et al., 2007), recent studies also pointed at the potential contribution of the photolysis of NO_2^- to produce nitric oxide (Reaction R11) (France et al., 2012, and references therein). Therefore, calculations of the NO_x emission flux in snow were based on Reactions (R9) and (R11) for the respective wavelengths 280–360 nm and 280–400 nm (Chu and Anastasio, 2003, 2007, and references therein). The first-order rate constants for the photolysis of NO_3^- at the snowpack surface $j_{\text{NO}_3^-,z_0}$ were calculated as defined in Seinfeld and Pandis (1998):

$$j_{\text{NO}_3^-,z_0} = \int_{\lambda_i}^{\lambda_j} \sigma_{\text{NO}_3^-}(\lambda, T) \phi_{\text{NO}_3^-}(\lambda, T) I(\lambda, \theta, z_0) d\lambda. \quad (3)$$

Based on the results of Chu and Anastasio (2003), the spectral UV absorptivity $\sigma_{\text{NO}_3^-}(\lambda, T)$ was derived between 280 to 360 nm from the measured molar absorption coefficients of aqueous NO_3^- at 278 K and a quantum yield $\phi_{\text{NO}_3^-}(\lambda, T)$ of 2.79×10^{-3} was estimated for $T = 259$ K, the average temperature over the three sampling days. The first-order rate constants for the photolysis of NO_2^- at the snow surface $j_{\text{NO}_2^-,z_0}$ were calculated with the same approach. $\sigma_{\text{NO}_2^-}(\lambda, T)$ was calculated between 280 to 400 nm from reported molar absorptivities for aqueous NO_2^- at 274 K and a range of $\phi_{\text{NO}_2^-}(\lambda, T)$ of $3.4 \times 10^{-2} - 0.9 \times 10^{-2}$ for λ between 280 and 400 nm was also determined for $T = 259$ K (Chu and Anastasio, 2007). The actinic fluxes $I(\lambda, \theta, z_0)$ were computed with the NCAR/ACD radiative transfer model TUV version 5.0 under clear-sky conditions for a 23° solar elevation angle ($\text{SEA} = 90^\circ - \theta$, with θ the solar zenith angle) averaged over the three sampling days.

The transmission of light in snow that drives the photochemistry in the top snowpack is controlled by optical processes: scattering and absorption (Dominé et al., 2008; Grannas et al., 2007, and references therein). These processes are summarized in the parameter *e*-folding depth (EFD), which in turn depends on snow physical properties – grain size, density, liquid water content – and the concentration of light-absorbing impurities such as black carbon. Studies at Dome C (France et al., 2011) and Barrow, Alaska (Reay et al., 2012), showed that absorption in snow layers, and therefore EFD, is inversely proportional to the content of black carbon in snow. Reported concentrations of black carbon in snow at WAIS Divide of $0.08 \pm 0.4 \text{ ng g}^{-1}$ (average

$\pm 1\sigma$) are in the range of those measured at South Pole, $0.2\text{--}0.3 \text{ ng g}^{-1}$ (Bisiaux et al., 2012, and references therein). Values of $j_{\text{NO}_3^-,z_0}$ and $j_{\text{NO}_2^-,z_0}$ were then scaled as a function of depth (z) using an EFD of 30 cm (Table 3), based on the similar value calculated for South Pole by Zatzko et al. (2013):

$$j_{\text{NO}_3^-} = j_{\text{NO}_3^-,z_0} \times \exp\left(\frac{-z}{\text{EFD}}\right). \quad (4)$$

The depth-integrated emission flux of NO_x was calculated for 18 and 28 December 2008 and 4 January 2009 with

$$F_{\text{NO}_2} = \int_{z=0 \text{ cm}}^{z=30 \text{ cm}} [\text{NO}_3^-]_z j_{\text{NO}_3^-,z} dz \quad (5)$$

$$F_{\text{NO}} = \int_{z=0 \text{ cm}}^{z=30 \text{ cm}} [\text{NO}_2^-]_z j_{\text{NO}_2^-,z} dz, \quad (6)$$

with respectively $[\text{NO}_3^-]_z$ and $[\text{NO}_2^-]_z$ in molecule cm^{-3} measured at each depth z (Fig. 6).

In order to convert flux F_{NO_x} ($\text{molecule cm}^{-2} \text{ s}^{-1}$) into a volumetric production rate P_{NO_x} (pptv h^{-1}), F_{NO_x} was multiplied by the height of the boundary layer estimated from prior balloon soundings above the West Antarctic Ice Sheet in summer, with an average height of 250 m (range 13–354 m) between morning and late afternoon (Frey et al., 2005). Note that atmospheric boundary layer height as low as 13 m may be infrequent at WAIS Divide. Therefore, estimation of the potential NO_x production from snow for an atmospheric boundary layer height of 13 m will be an upper bound.

Recent studies (Chu and Anastasio, 2007; Boxe and Saiz-Lopez, 2008, and references therein) suggest that only NO_3^- and NO_2^- in quasi-liquid layers are available for photolysis as photochemistry of these species does not occur in the bulk ice. Because the distribution of NO_3^- and NO_2^- between the quasi-liquid layers and the lattice ice is unknown, these calculations assumed that all NO_3^- and NO_2^- can be photolyzed. It is also assumed that the totality of the NO_x produced escapes from the snowpack and is released into the overlying atmosphere without considering any chemical loss. These fluxes and production rates are therefore an upper limit of the potential NO_x source from the snow.

4.1.6 Potential NO_x production from top snowpack

The resulting potential daily NO_2 emission fluxes from NO_3^- photolysis in the surface snowpack were $8.6 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$ (Table 3). This value is in agreement with previous reported NO_2 emission fluxes on the Antarctic continent (Table 4). For NO , the estimated value is $33.9 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$. Maximum daily NO_x emission fluxes from snow are therefore F_{NO_x} of $42.5 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$, with 20 % and 80 % from

Table 3. Potential depth integrated NO_x emission fluxes and equivalent NO_x production rates from NO₃⁻ and NO₂⁻ photolysis for an EFD of 30 cm, a solar elevation angle of 23° and three different atmospheric boundary layer heights (ABL) from previous measurements (Frey et al., 2005).

Compound	Potential emission fluxes (10 ⁸ molecule cm ⁻² s ⁻¹)	Potential production rates (pptv h ⁻¹)		
		ABL = 13 m	ABL = 250 m	ABL = 354 m
NO ₂	8.6	114	6	4
NO	33.9	452	24	17

NO₃⁻ and NO₂⁻ photolysis, respectively. This contribution is similar to that found by France et al. (2012) at Barrow.

The resulting local NO_x production is 30 pptv h⁻¹ for a mean atmospheric boundary layer height of 250 m (Table 3). Average production rates of 21 and 566 pptv h⁻¹ were calculated for boundary layer depths of 354 and 13 m, respectively. Comparison between the potential NO_x production rate and the mixing ratios of NO_x estimated from the extended Leighton mechanism with measured NO (Sect. 4.1.3) indicates that the snow source contributes significantly to the NO_x budget at WAIS Divide. However, values of P_{NO_x} suggest that the estimated production rates are an upper limit since the observed levels of NO (19 pptv) and the estimated NO₂ mixing ratios (5 pptv) are inconsistent with an NO_x production rate of 566 pptv h⁻¹ for atmospheric boundary layer height of 13 m.

These calculated NO_x emissions are higher than reported values from other Antarctic sites, where modeled and measured fluxes reached between 2.4×10^8 and 22×10^8 molecule cm⁻² s⁻¹ (Table 4). In a recent study, Zatzko et al. (2013) suggested that local contamination from nearby stations increases the content of impurities in snow, therefore reducing the EFD of the actinic flux in the top snowpack, resulting in a possible underestimation of the NO_x emissions modeled or measured nearby stations by a factor of 1.4–2.4. Thus, high NO_x emissions could be expected in our study since the sampling site was 5 km upwind of the main WAIS camp emissions (Sect. 2). However, the results from Zatzko et al. (2013) can be discussed since most of the measurements or estimations of NO_x nearby Antarctic stations were from sites located in clean air sector, upwind of the stations (Table 4). With said precautions, local contamination from nearby stations should not reach these sites and impact on the measured or calculated snowpack emissions.

The above estimates do have uncertainties: a) daily surface-snow samples revealed that the local-scale spatial variability of NO₃⁻ in the near-surface snowpack is significant, and b) our calculations assume that all of the NO₃⁻ and NO₂⁻ in snow is available for photolysis followed by emission into the atmosphere of all the photo-produced NO and NO₂. Concerning b), Anastasio and Chu (2009) suggested that 30% of the NO₂ produced from NO₃⁻ photolysis may be converted to NO₂⁻ within the snow matrix before being

released into the atmosphere. Also, the decrease of 5% per day of NO₂⁻ in surface snow (Sect. 3.2) indicates that only a small amount of NO₂⁻ may actually undergo photolysis to produce NO. Nevertheless, these results show the key role of the boundary-layer depth in determining the contribution of snowpack emissions to the overlying photochemistry. Our estimates imply that both the variability of boundary layer height with an observed range in summer of 13 to 354 m and local NO_x emissions from snow impact the atmospheric NO_x mixing ratios.

4.1.7 Local production of O₃

The oxidation of methane is the main in situ chemical source of tropospheric O₃. Thus, Reaction (R1) leads to production of O₃ while Reaction (R13) leads to its destruction (Seinfeld and Pandis, 1998):



The ratio between these two rates indicates whether WAIS Divide is an O₃ production or destruction site:

$$\frac{(\text{R13})}{(\text{R1})} = \frac{k_{\text{R13}} [\text{O}_3]}{k_{\text{R1}} [\text{NO}]} \quad (7)$$

This ratio was calculated with $k_{\text{R1}} = 9.49 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_{\text{R13}} = 1.62 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, derived from Sander et al. (2006), and an average temperature of 255.6 K measured during the campaign. Note that this estimation from the photo stationary state relation accounts for the NO_x emitted from the snowpack. In the case of Summit, Thomas et al. (2012) showed that NO_x emitted from the snowpack can increase the boundary layer O₃ by an additional 2–3 ppbv. Frey et al. (2013) show that under calm conditions typical for Dome C, East Antarctica, NO and NO₂ emitted by surface snow reach steady-state at 1 m. Thus, it is expected that our measured mixing ratios of O₃ at 1 m above surface snow already reflect the contribution from the NO_x emissions. Also, it is assumed that halogen chemistry does not occur at WAIS Divide, otherwise the reaction of BrO with O₃ and NO_x in the snowpack would reduce the local O₃ production (Thomas et al., 2012).

The ratio (R13):(R1) equals 0.216 and confirms that WAIS Divide is a surface ozone production site (Sect. 4.1.1).

Table 4. Potential emission flux of NO_x from NO₃⁻ and NO₂⁻ photolysis in snow at WAIS Divide compared to other Antarctic sites.

Site & reference	$F_{\text{NO}_x} \pm 1\sigma$ (10^8 molecule cm ⁻² s ⁻¹)		Period	Notes
	Measured	Modeled		
WAIS Divide				
<i>This study</i>		$F_{\text{NO}_x} = 42.5^{\text{a}}$	12/08–01/09	Daily average, 23° SEA
Neumayer				
Jones et al. (2001)	3(+0.3/–0.9) ^b		05–07/02/99	Noon maxima
Halley V:				
Jones et al. (2011)		2.42 ^a	18/01/05	Daily average
Bauguitte et al. (2012)	12.6 ^b 7.3 ^b	3.48 ^c	02/02/05	Noon maxima (07:05–15:05 UTC) average
South Pole				
Oncley et al. (2004)		3.9 ± 0.4 ^d	26–30/11/00	Overall average
Wang et al. (2008)		3.2–4.2 ^e	11–12/03	
Zatko et al. (2013)		3.3–9.8 ^f 7.7–22 ^f	January	Noon maxima, near station Noon maxima, remote
Dome C				
Frey et al. (2013)	6.9 ± 7.2 ^b		12/09–01/10	
Zatko et al. (2013)		3.2–12 ^f 4.4–17 ^f	January	Noon maxima, near station Noon maxima, remote
WAIS Divide				
<i>This study</i>		$F_{\text{NO}_2} = 8.6^{\text{a}}$ $F_{\text{NO}} = 33.9^{\text{a}}$	12/08–01/09	Daily average, 23° SEA
South Pole				
Oncley et al. (2004)		$F_{\text{NO}} = 2.6 \pm 0.3^{\text{d}}$	26–30/11/00	Overall average
Dome C				
France et al. (2011)		$F_{\text{NO}_2} = 2.4–3.8^{\text{g}}$	12/09–01/10	Values for 22° SEA

^a Depth-integrated F_{NO_x} with spectral irradiance from the TUV model.

^b From measured gradients of NO_x concentrations and turbulent diffusivity.

^c From 1-D model of NO_x concentrations based on production from NO₃⁻ photolysis and chemical loss.

^d Based on observed NO gradients and assuming photochemical steady-state.

^e From 1-D chemistry-diffusion model based on trace gas measurements.

^f Based on depth-dependent actinic flux profiles derived from snowpack radiative transfer model and snow-impurity measurements.

^g Depth-integrated F_{NO_x} with measured spectral irradiance.

From Eq. (7), a threshold value of 2 pptv for NO is found to trigger O₃ production at WAIS Divide, whereas this threshold is reached at 5 pptv in the remote continental troposphere of mid-latitude regions (Seinfeld and Pandis, 1998) and of high latitude sites, such as Dome C (derived from Chen et al., 2007). An atmospheric HO₂ concentration of 4.9×10^7 molecule cm⁻³ leads to a potential O₃ production of 0.8 ppbv day⁻¹. This is about 5% of the observed O₃ mixing ratios and respectively 20% and 50% of the rates calculated above the East Antarctic Plateau. O₃ production rates are ~4 ppbv day⁻¹ at South Pole (Chen et al., 2004, and references therein) and ~1.5 ppbv day⁻¹ at Dome C (Legrand et al., 2009). Our result is consistent with these previous studies since WAIS Divide is a lower-altitude site with a deeper atmospheric boundary layer that is influenced by a diel cycle of UV irradiance.

It is apparent that local O₃ production is too small to account for the observed increases between 24–25 and 27–29

December of 0.3 ppbv h⁻¹. We therefore consider the impact of air mass transport, as detailed below.

4.2 Impacts of air mass transport

Analysis of wind direction and O₃ mixing ratios indicate that air masses from the ENE-SWS sector have typically the highest O₃ concentrations (Sect. 2, Fig. 4). O₃ can be considered a long-lived chemical species compared to NO_x (Sect. 4.1.5) with a lifetime of about 22 days in the polar regions (Grannas et al., 2007). It is therefore expected that local O₃ is affected by transport, so the origin and transport of air at WAIS Divide were further investigated using 4-day back trajectories.

A total 168 trajectories were computed with the NOAA Hysplit(Hybrid Single-Particle Lagrangian Integrated Trajectory; see <http://ready.arl.noaa.gov/hysplit4.html>) model (R. R. Draxler and G. D. Rolph, 2003) every 4 h using global meteorological data from the NCEP Global Data Assimilation System (GDAS) with a 3 h temporal resolution, a

$1^\circ \times 1^\circ$ (latitude \times longitude) spatial resolution, an endpoint at the latitude and longitude of WAIS Divide and 10 m above ground level from 10 December 2008 to 8 January 2009. A comparison of the resulting 168 trajectories with another set generated from the NCEP-NCAR archived data shows similar results (Fig. 9), while Sinclair et al. (2013) showed that back trajectories from NCEP-NCAR and ECMWF Interim Re-Analysis (ERA-Interim) were comparable during austral summer. Therefore, the following discussion is based on trajectories produced from the GDAS archives. The back trajectories were combined to create daily maps (Fig. 10) and we distinguish three regions of air mass origin based on elevation, slope and previous O_3 and temperature measurements (Fig. 9).

We refer to the East Antarctic Plateau as the East Antarctic region above 2500 m a.m.s.l. with a slope of less than 1° since elevated O_3 has not been observed below 2500 m a.m.s.l. during the Antarctic summer (Frey et al., 2005). Surface O_3 is produced over the East Antarctic Plateau and possibly exported through air outflow (Sect. 4.2.2). The inner WAIS refers to the West Antarctic area above 1750 m a.m.s.l. with a slope inferior to 1° . An average temperature of about -25°C was reported in the inner WAIS compared to -15°C in the lower-elevated regions (Frey et al., 2005). Finally, based on a slope higher than 1° and on the previous observations, the areas below 2500 m a.m.s.l. in East Antarctica and 1750 m a.m.s.l. in West Antarctica are referred to as Antarctic coastal slopes.

Figure 9 shows that over the campaign, 58 % of the air masses originated from the Antarctic coastal slopes with 2 % possibly flowing from the distant King Haakon VII coast. An estimated 17 % was transported from the inner WAIS and 25 % of the air was advected from the East Antarctic Plateau. About 71 % of the air reaching WAIS Divide flowed from East Antarctica and 29 % from West Antarctica.

4.2.1 Air mass origins related to low O_3 levels

Except for outflows from the East Antarctic Plateau, all air mass origins are associated with low O_3 , averaging 13 ± 3 ppbv (Fig. 11). This represents therefore 75 % of the air mass reaching WAIS Divide, which includes air from the coastal slopes (Fig. 10a, b) and the inner WAIS (Fig. 10e). In coastal Antarctica, halogen-catalyzed chemistry has been found to prevent O_3 production in summer and even leads to the well-known episodic O_3 depletion events during spring (Jones et al., 2008, and references therein). The little vertical-column amounts of IO and BrO observed at WAIS Divide from satellite in December and January 2004–2009 (Schönhardt et al., 2012) suggest that contribution of halogens from intrusions of coastal air (58 % of all back trajectories) to the WAIS Divide photochemistry is not significant. Thus, reduction of O_3 levels at WAIS Divide by halogen chemistry may not occur, as assumed in the previous sections.

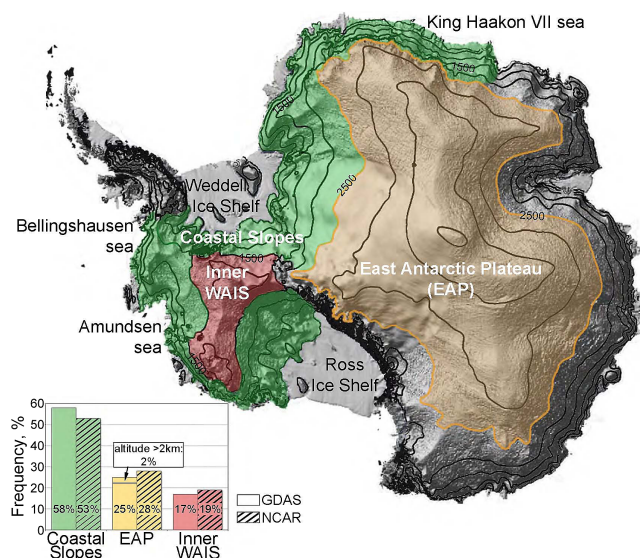


Fig. 9. Map of the different origins of air reaching WAIS Divide identified by the 4-day back-trajectory analysis and topography: East Antarctic Plateau (yellow), inner WAIS (red) and the Antarctic coastal slopes (green). Comparison between the results from analyses using the GDAS and NCAR meteorological archived data is shown.

Air masses from the interior of WAIS (17 % of all back trajectories, Fig. 10e) are also associated with low O_3 mixing ratios. Influence from local halogen chemistry or halogens exported from the Antarctic coasts is not consistent with observations of Schönhardt et al. (2012).

It is therefore suggested that the O_3 levels of the air masses from the coastal slopes and the interior of WAIS are low, so these airflows can reduce the O_3 levels of WAIS Divide when reaching the site. From these results and the wind-speed record (Fig. 11), it is also expected that O_3 production over WAIS is less than or equal to our estimated O_3 production rate for WAIS Divide.

Airflows from long-distance sources such as King Haakon VII sea coast (2 % of all back trajectories, Fig. 10f) appear infrequently, with no obvious impact on local O_3 . The O_3 signature of these air masses likely disappeared during their transport over more than 2500 km.

4.2.2 Air mass origins associated with elevated O_3 levels

Approximately 25 % of all back trajectories point to airflows from the East Antarctic Plateau (Fig. 10c, d and Fig. 9), which are mainly related to the highest O_3 measured at WAIS Divide, with an average $\pm 1\sigma$ of 19 ± 4 ppbv (Fig. 11).

This is consistent with the O_3 production above the East Antarctic Plateau (Helmig et al., 2008a, and references therein) that enhances the O_3 levels of WAIS through air transport, as previously reported by Legrand et al. (2009), who only observed high O_3 mixing ratios at Dumont

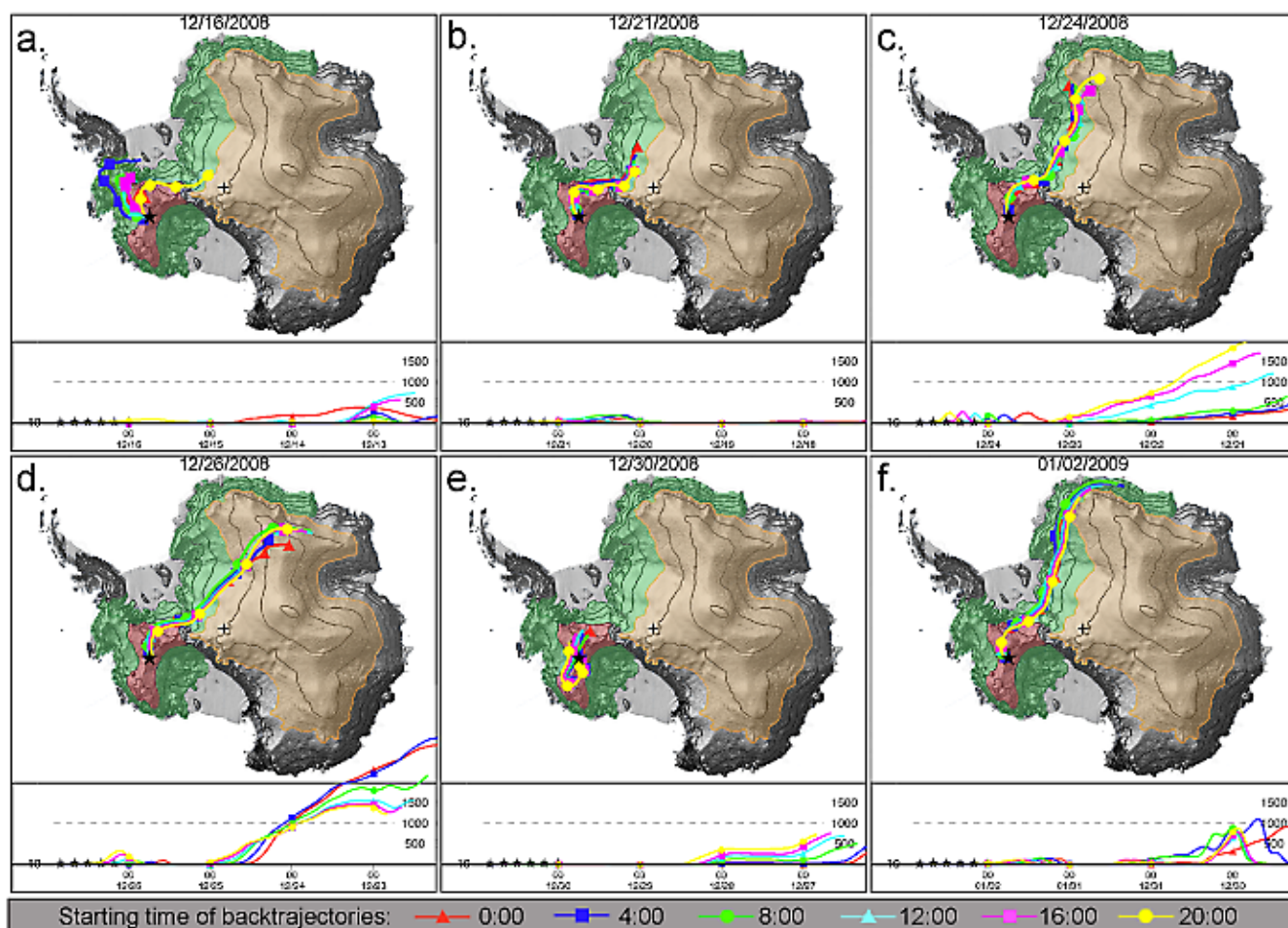


Fig. 10. Combined 4-day back-trajectory maps of some specific events identified in Fig. 11. Each daily map contains 6 trajectories of 4-hour intervals and symbols are plotted for every 24 h time step. The different regions of air origin are identified in Fig. 9. Trajectory colors do not correspond to map colors. Trajectory elevations are meters above ground level.

D'Urville for air masses originating from the Antarctic Plateau. Such an oxidizing environment is confirmed by the O_3 observations at South Pole (S. J. Oltmans, <http://ds.data.jma.go.jp/gmd/wdcgg>) over the same period that shows an average concentration of 31 ppbv, 17 ppbv more than the average observed at WAIS Divide (Fig. 11).

Further back-trajectory analysis reveals two conditions in which high O_3 concentrations are observed above WAIS Divide. First, elevated O_3 mixing ratios were only observed for lower atmosphere air coming from the East Antarctic Plateau (below 1500 m above ground level). The trajectories of these near-surface airflows are in good agreement with the katabatic streamlines described by Parish and Bromwich (2007). This suggests that air exported off the East Antarctic Plateau via katabatic outflows raises significantly the O_3 mixing ratios at WAIS Divide. The ozone depletion recorded between 25 and 27 December 2008 (Fig. 10d and Fig. 11) is attributed to an air mass coming from altitude as high as ~ 3000 m above ground level.

Secondly, high O_3 was only observed at WAIS Divide when the transport time from the East Antarctic Plateau was less than 3 days (Fig. 10c and d). To investigate this condition, the total O_3 loss during transport from the Antarctic Plateau to WAIS Divide was estimated. The back trajectories indicate that O_3 maxima during 24–28 December at WAIS Divide are due to rich O_3 air originating from the South Pole region, as local records show similar but higher peaks about 2 days before (Fig. 11). From this delay, a loss rate of $0.25 (\pm 0.04)$ ppbv h^{-1} was calculated. This represents an O_3 loss rate of $5.5 (\pm 0.9)$ ppbv day^{-1} when averaged O_3 mixing ratios were 30 and 14 ppbv, respectively, at South Pole and WAIS Divide over the campaign. If these loss rates (from dilution, net destruction, etc.) are typical, then it follows that O_3 export off the Plateau has to be rapid (less than 3 days) in order to have an impact on WAIS Divide's levels.

Observations of elevated O_3 levels are frequently related to vertical transport from the free troposphere/lower stratosphere at Summit, Greenland (Helmig et al., 2007b) and

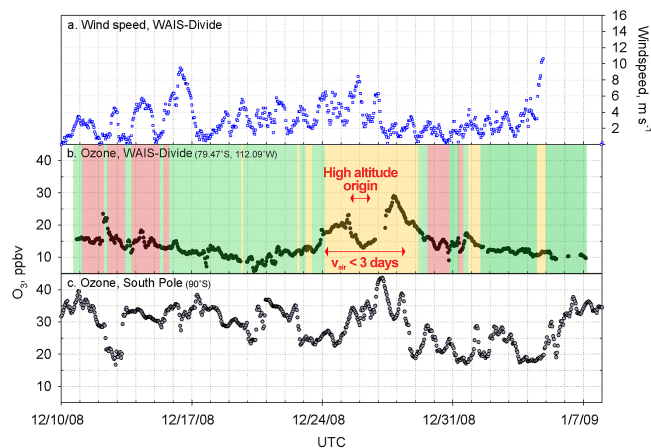


Fig. 11. The 1 h averages of observed (a) wind speed at WAIS Divide, (b) O₃ at WAIS Divide, and (c) O₃ at South Pole (data available at: <http://ds.data.jma.go.jp/gmd/wdcgg>) for austral summer 2008–2009. Air mass origins are reported with the identical color coding used in Fig. 9: East Antarctic Plateau (yellow), inner WAIS (red) and Antarctic coastal slopes (green). Events of air transport less than 3 days between East Antarctic Plateau and WAIS Divide ($v_{\text{air}} < 3$ days) and of high-altitude air origin (< 2 km above ground level) are also reported.

other Arctic sites (Helmig et al., 2007a, and references therein). These stratospheric-intrusion events are promoted by boundary-layer instabilities, which are caused by significant diel radiation cycles and by the size of the Greenland ice sheet (Helmig et al., 2007b). All of the vertical O₃ profiles over the East Antarctic Plateau from tethered-balloon measurements (Helmig et al., 2008a; Johnson et al., 2008; Oltmans et al., 2008) and an airborne study (Slusher et al., 2010) present higher O₃ mixing ratios in the atmospheric boundary layer than in the free troposphere, indicating that no contribution of stratospheric O₃ occurs over the Antarctic Plateau. Enhancement of the O₃ levels at WAIS Divide from vertical transport is neither supported by the back-trajectory analysis nor by the vertical O₃ profiles measured at South Pole during this period (<http://www.esrl.noaa.gov/gmd/dv/data/index.php>), confirming the previous observations from the East Antarctic Plateau.

However, not all elevated O₃ mixing ratios at this site could be explained with the air origin. This is the case for the 5 h rise of O₃ mixing ratios that reached 24 ppbv on 12 December and occurred during the only snowfall observed during the campaign (Fig. 5). With low wind speeds (Fig. 11) and airflow from the inner WAIS observed during this event, it is possible that more O₃ accumulated in the boundary layer from local production. However, given the O₃ production rate we estimated previously (Sect. 4.1.7), it seems unlikely that only the local production of O₃ could cause this specific increase.

5 Conclusions

Being from a geographically intermediate site between the Antarctic coast and the East Antarctic Plateau, our results show that concentrations of atmospheric NO, O₃, H₂O₂ and skin-layer NO₃⁻ at WAIS Divide during summer 2008–2009 are similar to coastal levels.

Comparison of local potential NO_x production from daily average depth-integrated emission fluxes of NO_x and the NO_x mixing ratios estimated from a steady-state assumption shows that NO₃⁻ and NO₂⁻ photolysis in the local snowpack are a significant source of NO_x at WAIS Divide. The upper limit of 15 h NO_x lifetime confirms that short-lived NO_x species are more sensitive to local production above WAIS than to outflows from the East Antarctic Plateau. Lower NO₃⁻ preservation in snow at WAIS Divide than at Summit is coherent with the potential NO_x emission flux and suggests stronger lateral export of emitted NO_x than local recycling.

O₃ production at WAIS Divide can be triggered with NO mixing ratios higher than 2 pptv, but the small O₃ production rate cannot explain the observed O₃ variability, which suggests a significant air mass transport contribution. Air flows from the East Antarctic Plateau are only associated with high O₃ mixing ratios if the air transport is near surface by gravity driven winds and less than 3 days from the East Antarctic Plateau. With levels of O₃ over the East Antarctic Plateau twice those observed at WAIS Divide, outflows from the interior of the continent therefore have the potential to enhance the mixing ratios of long-lived atmospheric chemical species such as O₃ over WAIS. During this 28-day campaign, outflows from the Antarctic Plateau were observed over 7.5 days, raising the summer O₃ average by about 20 % (2 ppbv). The possibility of halogen chemistry above inland WAIS that would impact the atmospheric photochemistry is not consistent with satellite observations and cannot therefore explain the low O₃ levels that are associated with air mass origins from the interior of WAIS.

Results from the back-trajectory analysis over December 2008 and January 2009 at WAIS Divide (Fig. 9) compare well with those of Markle et al. (2012) calculated over thirty years in the Ross Sea region. For the same months, the authors found that 45 % of the air mass trajectories have an oceanic/West Antarctic origin and 55 % a continental/East Antarctic source, while we observed respective values of 29 % and 71 % at WAIS Divide. These results confirm the minor contribution of oceanic/West Antarctic inflows to the WAIS atmosphere during austral summer shown by Nicolas and Bromwich (2011), and the predominance of continental/East Antarctic air masses that may significantly impact the oxidative capacity of the atmosphere above the interior of WAIS.

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