

**Nitrate in polar ice**

E. W. Wolff et al.

# Reassessment of the factors controlling temporal profiles of nitrate in polar ice cores using evidence from snow and atmospheric measurements

E. W. Wolff, A. E. Jones, S. J.-B. Bauguitte, and R. A. Salmon

British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, UK

Received: 5 May 2008 – Accepted: 19 May 2008 – Published: 9 June 2008

Correspondence to: E. Wolff (ewwo@bas.ac.uk)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Nitrate is frequently measured in ice cores, but its interpretation remains immature. Using daily snow surface concentrations of nitrate at Halley (Antarctica) for 2004–2005, we show that sharp spikes ( $>$ factor 2) in nitrate concentration can occur from day to day. Some of these spikes will be preserved in ice cores. Many of them are associated with sharp increases in the concentration of sea salt in the snow. There is also a close association between the concentrations of aerosol nitrate and sea salt aerosol. This evidence is consistent with many of the spikes in deposited nitrate being due to the conversion or trapping of gas-phase nitrate, i.e. to enhanced deposition rather than enhanced atmospheric concentrations of  $\text{NO}_y$ . Previously, sharp spikes in nitrate concentration (with concentration increases of up to a factor 4 seen in probably just one snowfall) have been assigned to sharp production events such as solar proton events (SPEs). We find that it is unlikely that SPEs can produce spikes of the kind seen. Taken together with our evidence that such spikes can be produced depositionally, we find that it is not possible to track past SPEs without carrying out a new multi-site and multi-analyte programme. Seasonal and interannual trends in nitrate concentration in cores from any single site cannot be interpreted in terms of production changes until the recycling of nitrate from central Antarctica to coastal Antarctica is better quantified. It might be possible to assess the interannual input of  $\text{NO}_y$  to the Antarctic lower troposphere by using a network of cores to estimate variability in the total annual deposition across the continent (which we estimate to be  $9 \pm 2 \times 10^7$  kg/a (as  $\text{NO}_3^-$ )), but it will first have to be established that the outflow across the coast can be ignored.

## 1 Introduction

Ice cores provide chronologically-ordered profiles of the concentrations of chemicals deposited from the atmosphere and preserved in the ice. Once these concentrations have been measured, the main challenge is to interpret them in terms of a desired

ACPD

8, 11039–11062, 2008

## Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



environmental unknown. For aerosol components such as sea salt and terrestrial dust, interpretations in terms of specific sources are available, even if not fully verified (Wolff et al., 2006). However, there are additional complications for other components, especially those that include multiple production and loss pathways, and a gas-phase chemistry.

It is relatively simple to analyse nitrate in melted snow and ice, and numerous datasets of nitrate variability along ice cores exist (Fischer et al., 1998; Herron, 1982; Legrand et al., 1988; Mayewski et al., 1990). However, the interpretation of these datasets has proved extremely complicated (Legrand et al., 1999; Röthlisberger et al., 2000; Wolff, 1995), and it seems difficult to relate the concentrations unequivocally to an important environmental parameter. There are two major reasons for this: firstly, it has proven difficult to clearly determine the main controls on the concentrations of oxidised nitrogen in the polar lower troposphere (Savarino et al., 2007; Wagenbach et al., 1998b). There are probably significant contributions from the stratosphere, as well as from lower latitudes, and recycling of material from central Antarctica to the coast adds complexity. Secondly, the conversions between different oxidised nitrogen chemicals in the polar atmosphere are complex (Jones et al., 2007), and the processes leading to and after deposition of nitrate itself have a strong effect on the concentrations actually recorded in the ice (e.g. Röthlisberger et al., 2000).

In some cases, attempts have been made to relate changes in concentration to different environmental parameters. For example (Mayewski et al., 1990), the increase over recent decades in nitrate concentration in Greenland snow has been attributed to increasing industrial emissions of  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). Given that other factors that might control deposition and preservation of nitrate have probably not altered over recent decades in a way that could explain the increase, this conclusion is robust. Over longer timescales, different authors have attempted to relate measured nitrate concentration profiles to factors such as aspects of solar activity (McCracken et al., 2001; Zeller and Dreschhoff, 1995; Zeller et al., 1986), or to changes in stratospheric processes (Mayewski and Legrand, 1990; McElroy, 1989; Mulvaney and Wolff, 1993),

**Nitrate in polar ice**

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



but there is no consensus about their success.

In a very general sense, the parameter of most interest that one might hope to derive from ice cores is the production strength of new  $\text{NO}_y$  (the sum of all oxidised forms of nitrogen), or more specifically  $\text{NO}_x$ , molecules in the atmosphere. Changes in the production rate itself would be indicative of changing influences on the source strength: for example,  $\text{NO}_y$  production in the middle and upper atmosphere through dissociation of  $\text{O}_2$  and  $\text{N}_2$  by solar and geomagnetic charged particles should be modulated by solar activity. Additionally, knowledge of such changes in production would be of value in modelling other aspects of atmospheric chemistry. New  $\text{NO}_y$  production does not generally occur in the snowpack, although  $\text{NO}_y$  can be recycled between the snowpack and the atmosphere. In the absence of significant surface sources, production occurs mainly at higher altitudes (upper troposphere and above), or (as in the case of pollution  $\text{NO}_x$ ) at lower latitudes. The concentrations present in the Antarctic lower troposphere therefore depend not only on production but also on the strength of lateral and vertical transport. At an individual atmospheric measurement site, the concentrations of nitrate depend additionally on the speciation and spatial distribution of  $\text{NO}_y$ , and what is seen in ice cores depends additionally on the deposition of nitrate to the snow and its subsequent preservation. The crucial question for the interpretation of ice cores is: which of these factors dominates in causing variability and trends in ice core nitrate concentrations? In particular, is information about changes in large-scale production of nitrate discernible in ice cores against the background of change in the other factors. This question can be asked at different time and space scales, and therefore we need to understand how all the other processes affect the spatial and temporal pattern of nitrate in ice cores.

Much effort in recent years has been applied to understanding the details of changes over short time periods (hours to weeks) in snowpack concentrations of nitrate (Mulaney et al., 1998), and in concentrations of  $\text{NO}_x$  in the lowest levels of the polar atmosphere (Grannas et al., 2007; Honrath et al., 1999; Jones et al., 2000). However, there has been little reanalysis of the joint consequences of the detailed processes be-

**Nitrate in polar ice**

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ing observed at short timescales and the long-term records observed in ice cores. In this paper, we will start from the new CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) measurements at Halley (Antarctica), in order to understand what controls nitrate deposition on shorter (day to seasonal) timescales, and therefore to assess whether short-lived events can be diagnosed from the ice core record. We will then expand to consider other recent data, in order to determine what information measurements of nitrate in ice cores at single sites are capable of delivering. Finally, we will take a very broad view to assess strategies by which past large-scale changes in  $\text{NO}_y$  production might be assessed. Our aim is to define the kinds of studies that might be needed in order to turn the dream of deriving production information into reality.

## 2 Observations at Halley

The new observations relevant to this study made at Halley in the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) campaign consist of aerosol nitrate, gas phase nitric acid, and surface snow nitrate measurements made between February or March 2004, and February 2005 (Jones et al., 2007). Aerosol filters were collected typically weekly (but occasionally daily or 6-hourly), and analysed for a range of anions and cations, including nitrate and sodium. Annular denuders were used on the same intervals, and analysed for gas-phase nitric acid. The collection efficiency for gas-phase nitrate was checked by the use of two denuders in series at all times; a correction was made to account for this. Surface snow samples were collected daily (with some exceptions), and analysed for the same range of anions and cations as the aerosol filters (Jones et al., 2008).

### Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Nitrate deposition on short (sub-seasonal) timescales

Sharp spikes in nitrate concentration have been observed in ice cores from both Greenland and Antarctica (McCracken et al., 2001; Palmer et al., 2001; Zeller and Dreschhoff, 1995). It has been proposed that such spikes in nitrate concentration in ice cores may be recording the occurrence of short-lived solar proton events (SPEs) (e.g. McCracken et al., 2001; Zeller and Dreschhoff, 1995). The peaks in nitrate concentration shown in these studies typically exhibit concentrations up to a factor 4 higher than the surrounding background, and appear to represent often less than 10% of the annual snow accumulation, and thus probably correspond to a single snowfall (McCracken et al., 2001). In this section, we examine whether such spikes can have causes other than sharp production events such as SPEs and, conversely, whether such spikes are consistent with the signal expected for SPEs.

#### 3.1 Short-term variations in concentration of nitrate in Halley snow

Nitrate concentrations in surface snow at Halley show strong short-term variability during the CHABLIS year. Whilst we have no information on how much of this variability is preserved in the ice core record, the data (Fig. 1) show numerous events that appear analogous to those reported elsewhere, and which have sometimes been ascribed to SPEs. In particular, concentrations sometimes increased by a factor 2 or more from day to day. In Fig. 1, we have marked the two largest SPEs of the period (peaks occurring on 26 July 2004 and 17 January 2005). We note that these have no special relationship to the spikes in the nitrate record. The maximum proton fluxes of these two SPEs are an order of magnitude less than that of the two largest SPEs recorded in the last 30 years (based on data supplied by NOAA Space Environment Center at <http://www.swpc.noaa.gov/ftpd/indices/SPE.txt>).

For summer 2004 and 2005, we observe that many of the largest spikes in surface snow nitrate concentration are accompanied by increased concentrations of other ions, and in particular by high concentrations of sea salt ions (Fig. 2). This applies, for

### Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

example, to the spikes seen at day 386 and day 369 (note though that two surface snow samples were taken on day 369 at nearby positions, and only one of them has high concentrations, implying heterogeneity in snow deposition). On both of these days, the meteorological records show that fresh snow fell. We therefore have a scenario in which a fresh snowfall occurred, laden with both high sea salt concentrations and high nitrate. In the two cases picked out here, the high concentrations were seen only for one day, implying that the snow was either removed by wind, or covered by cleaner snow. However, it is clear that either of these events, if preserved, could have shown up in an ice core as an event that resembled the sharp peaks previously described.

The nitrate concentration variability seen in summer 2004 and 2005 appears to be greater than that observed in a previous year of daily snow sample collections at Halley (Mulvaney et al., 1998). In fact, the sea salt concentrations are also particularly high and variable in this summer: the CHABLIS year shows a summer maximum in sea salt concentrations, in contrast to two earlier reported years where a winter maximum in Halley snow (Wolff et al., 1998) and aerosol (Wagenbach et al., 1998a) concentrations was reported.

There is also one prominent peak in snow concentration of nitrate observed in winter 2004. This has already been noted (Jones et al., 2007): on 15 August the surface snow concentration of nitrate increased to around  $200 \mu\text{g kg}^{-1}$ , many times higher than the concentrations during the rest of the spring-winter-autumn period. The increase was clearly the result of a new snowfall, and the concentrations remained high until another snowfall on 28 August. The high concentrations in surface snow appear to have been associated with a fresh snowfall during a period with relatively high concentrations of aerosol nitrate, but no unusual values of other  $\text{NO}_y$  species. This episode probably contributed a significant proportion of the total nitrate deposition to snow in the winter season. An increase in sea salt concentration in snow was associated with this event, but the sea salt concentrations are not unusual compared to many other times of the winter when no nitrate enhancement is apparent in the snow. We can therefore only surmise that this event is associated with an enhancement of partitioning of nitrate to

aerosol, without definitely attributing a cause.

### 3.2 Sea salt and nitrate aerosol

It has previously been assumed that the concentration of nitrate archived in ice cores is determined by the deposition and retention of nitrate (as nitrate ion or nitric acid) from the atmosphere, rather than by any important conversion of other  $\text{NO}_y$  species at the snow surface or within the snowpack. In the CHABLIS campaign at Halley, it was indeed found that the seasonality of nitrate concentrations in surface snow was similar to that of inorganic nitrate and not organic nitrate (Jones et al., 2007). This suggests that, although organic nitrate has higher concentrations than inorganic for much of the year, it probably has a very long lifetime against deposition to snow, and plays little role in determining snow concentrations. We therefore feel reasonably confident in concentrating on inorganic nitrate in air ( $\text{HNO}_3$  in gas phase, plus aerosol nitrate) and snow to assess the short-term depositional processes.

The deposition of nitrate to the Antarctic snowpack (neglecting for the moment its continued preservation after deposition) consists of: nitric acid incorporation in cloud by dissolution in cloud droplets, by co-deposition during the formation of snowflakes, or by surface uptake onto ice crystals; aerosol deposition of nitrate (both wet and dry deposition); and various processes on the ground, including trapping of gas phase nitric acid on the surface of ice (Röthlisberger et al., 2002).

High concentrations of sea salt aerosol are expected to promote conversion of gas-phase nitrate to aerosol nitrate, as well as trapping of gas-phase nitrate on salty snow surfaces. It has previously been shown (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Teinila et al., 2000) using size-segregated aerosol collection, that aerosol nitrate is found in the same size range as sea salt aerosol, and this supports the conclusion that sea salt (as well as terrestrial dust, but this is a small component at coastal sites in the present day) is responsible for converting nitric acid to aerosol. In Fig. 3, we present aerosol sea salt concentrations from Halley in parallel to aerosol nitrate data for the CHABLIS period; it is apparent that there is a general tendency for short-

## Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

term enhancements of concentrations of aerosol nitrate to be associated with similar enhancements of sea salt. The typical ratio of aerosol nitrate: Na is lower during the winter months when total nitrate (aerosol + gas-phase) is low, so that a single correlation covering the whole year cannot be made, but the relationship is present in both summer and winter. We therefore suggest that increased aerosol sea salt concentrations are tending to partition nitrate towards the aerosol phase. It is difficult to test this directly and quantitatively by estimating the aerosol/gas-phase ratio for two reasons: firstly, the gas phase HNO<sub>3</sub> concentrations are not available at similar resolution, because the data above the detection limit are rather sparse; and secondly, the conversion towards the aerosol phase could be taking place at higher levels in the atmosphere not sampled by our experiments. During a snowfall it is certainly the concentrations at higher levels (up to that of the cloud) that are important.

We therefore note that the presence of sea salt can promote the conversion of gas phase nitrate to the aerosol phase, and tentatively conclude that this would allow an efficient deposition of nitrate through aerosol mechanisms. Highly saline (or dusty) ice may also promote the direct uptake of gas phase nitric acid onto the ice surface. Whichever process is dominant, we indeed see some examples where the highest spikes of nitrate in surface snow are clearly associated with exceptionally high concentrations of sea salt. The importance of this conclusion is that sea salt excursions can be highly episodic, with high concentrations often lasting for just a few days; short-term excursions in nitrate deposition, at least at coastal Antarctic sites, may therefore be controlled by episodes of sea salt production that happen to coincide with a period of snowfall.

### 3.3 SPEs and nitrate deposition

SPEs last for periods of hours to days and should enhance the production of nitrogen oxides in the middle and upper atmosphere. However, the question arises whether such events are capable of leading to a signal in deposited snow that consists of an increase in nitrate concentration of factor 4, confined to perhaps a single snowfall or a few

**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

weeks. Modelling (using a two-dimensional zonally-averaged photochemical transport model) suggested that, even for the largest SPEs of the last 30 years, the stratospheric burden of  $\text{NO}_y$  should only have increased by just over 10%, or up to 40% at specific altitudes and latitudes in the stratosphere (Vitt et al., 2000); another process, oxidation of  $\text{N}_2\text{O}$  by  $\text{O}^1\text{D}$ , remains the dominant stratospheric source. It is hard to see how a spike of larger magnitude than this relative to the background concentration could be generated in polar snow by an SPE. The propagation of the SPE event in  $\text{NO}_y$  downwards into the stratosphere as a rapid and sharp signal is also influenced by very variable atmospheric dynamics (Cilliverd et al., 2007); further transport from the stratosphere into the troposphere depends either on stratosphere-troposphere exchange or on descent in polar stratospheric cloud particles (PSCs), and it is not obvious that the episodicity of the SPE itself can be maintained during these processes. Finally, we note that in the most comprehensive statistical study of the relationship between nitrate in (20th century Antarctic) snow and SPEs, a small increase in nitrate after such events was observed, but the increase was just a few percent (Palmer et al., 2001). On current understanding, it is therefore hard to understand how spikes of the magnitude seen in polar snow can be generated by SPEs, and it is not clear that enhancements should be so sharp in the snow for such events.

### 3.4 The origin of sharp spikes in nitrate concentration in polar ice

In the last section, we showed that, while SPEs can lead to some enhancement of nitrate deposition to snow, it appears difficult to produce snow concentration spikes of sufficient magnitude from them. We have shown for Halley in coastal Antarctica, that the episodic deposition of aerosol nitrate, associated with high concentrations of sea salt, does provide a simple mechanism by which spikes of this sort can occur.

Of the sites where nitrate signals attributed to SPEs have been observed, one (Windless Bight) (McCracken et al., 2001) is a site close to sea level in the Ross Ice Shelf, which has high concentrations of sea salt (Palais et al., 1989). The mechanisms we have proposed for Halley should operate at such sites.

**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

For central Greenland and central Antarctica, although sea salt input may be rather episodic, it will rarely be at concentrations that could cause the effects described above. However, similar effects can be expected in association with other cations, such as ammonium or calcium. These ions are at insignificant concentrations relative to nitrate in present-day snow at Halley. However, ammonium shows strong and sharp concentration spikes in Greenland ice, arising from very short-lived episodes of transport of biomass burning material from North America (Fuhrer et al., 1996). Biomass burning may also be a direct source of nitrate reaching Greenland. Whatever the cause, there are definitely short-lived spikes in nitrate in snow from Summit and other Arctic sites that are strongly associated with spikes in ammonium (Whitlow et al., 1994). Summit is the second site where nitrate signals have previously been attributed to SPEs (McCracken et al., 2001).

Finally, for central Antarctica, neither sea salt nor ammonium will generally be at elevated concentrations. However, for sites with very low accumulation rates such as Dome C and Vostok, extensive post-depositional loss (Röthlisberger et al., 2000) makes it highly unlikely that original short-term signals are preserved in any recognizable form. Even at South Pole, deposition peaks are substantially modified after burial (Dibb and Whitlow, 1996).

In summary, the importance of short-term variability in deposition of the aerosol component, such as we have documented above, makes it very unlikely that spikes in nitrate concentration in ice can be simply or reliably correlated with short-lived production events, such as solar proton events (e.g. Shea et al., 1999; Zeller and Dreschhoff, 1995) at most sites. It might however be possible, through careful screening of data in which multiple ions were measured to remove sea salt (or other cation) associated deposition events, and through the independent use of multiple carefully-chosen sites, to isolate any events that are not due to local deposition signals. Such a study has not yet been attempted.

## 4 The seasonal and interannual signal of nitrate deposition

We have shown in Sect. 3 that variability in nitrate deposition (at least in coastal Antarctica) at synoptic timescales is most likely related to atmospheric dynamics and deposition rather than to source changes. However, we can consider whether such controls average out over longer periods, leaving production changes to dominate the budget of nitrate reaching the ground. In order to do this, we briefly consider what controls the seasonal and interannual concentrations seen in snow at Halley and other sites.

The seasonal cycle of snow nitrate concentrations at Halley shows a summer peak that appears to be closely related to a summer increase in gas-phase  $\text{HNO}_3$  concentrations (Jones et al., 2007). The summer peak in snow concentration has already been reported from both Halley and Neumayer stations from earlier years (Mulvaney et al., 1998). An early to mid-summer peak in nitrate concentrations in air (based on measurements assumed to be of total (gas-phase plus aerosol) nitrate) has also been noted previously for different coastal sites (Wagenbach et al., 1998b), while a summer maximum of gas-phase nitric acid was clearly measured at one site (Jourdain and Legrand, 2002). Whilst it is difficult to interpret this in the absence of seasonal information about nitrate concentrations at higher (cloud-formation) levels in the atmosphere, it seems reasonable to assume that the summer peak in nitrate deposition to snow (at a time when both sea salt and continental dust concentrations are often low) is indeed related to increased source strengths, i.e. to an increased input of nitrate to the relevant part of the atmosphere.

It has proved difficult to determine what are the main sources of nitrate to the polar troposphere (Wolff, 1995). In earlier work, it has been proposed that the most important source of nitrate to the coastal Antarctic lower atmosphere was the stratosphere, both through air mass exchange from the stratosphere to the troposphere, and through sedimentation of nitrate-rich polar stratospheric cloud particles (Wagenbach et al., 1998b). A small spring seasonal maximum in concentration could be related to the time of PSC sedimentation, but it was less clear why there was a main maximum in mid-summer.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Recently, using a combination of aerosol concentration and isotopic measurements (Savarino et al., 2007) for the Dumont d'Urville site, it was suggested that, while the stratosphere likely did contribute to the spring peak, the summer peak was most likely caused by the appearance of nitrate that had been re-emitted from inland sites and then transported from the Antarctic plateau. The idea behind this is that it has been clearly shown that central Antarctic sites (with very low snow accumulation rates) have extremely high initial concentrations of nitrate (as high as  $1000 \mu\text{g kg}^{-1}$ ), but that these values decay to much lower ones (as low as  $10 \mu\text{g kg}^{-1}$ ) at depths of 1–2 m (Röthlisberger et al., 2000). This loss of nitrate may be partly to do with the photolysis of nitrate in near-surface snow that contributes strongly to the  $\text{NO}_x$  content of the atmosphere at sites such as South Pole (Davis et al., 2004). However, it is likely that it is dominated by the simple evaporative re-emission of nitric acid (Blunier et al., 2005), and that this emission (depleted in  $^{15}\text{N}$ ) also explains the very low  $^{15}\text{N}$  content of aerosol at coastal sites during the summer maximum (Savarino et al., 2007; Wagenbach et al., 1998b).

In either case, the implication of this finding is that the summer maximum in concentration of gas-phase nitric acid, and of deposition to snow at coastal sites, is not due to an input from primary sources, but is rather the result of a recycling from inland regions. In that case the strength of the summer maximum in a given year (and because it dominates the annual deposition, therefore the average annual value) will be controlled by the strength of emission and transport from the central plateau regions. Emission strength must be controlled mainly by factors in central Antarctica: the initially deposited concentrations there, and the temperature, accumulation rate and available sunlight. Transport strength to a particular site will depend on the directions of air mass movement in the near-surface layers, and the extent of mixing to higher levels.

There is an urgent need to confirm whether it is correct that material recycled from and within the interior is a major source of nitrate for Antarctic ice. This will likely require painstaking concentration and isotopic studies along lines of transport from the interior, coupled with a new generation of models. If it is correct, it implies that time series of

nitrate in ice at individual sites in Antarctica cannot be used to diagnose changes in  $\text{NO}_y$  source strength until the meteorological factors controlling losses at interior sites and gains at coastal sites are understood well enough to account for them.

## 5 Can we derive information about $\text{NO}_y$ production from nitrate concentrations in Antarctic snow?

In Sect. 4, we conclude that, based on the most likely cause of the summer peak in atmospheric nitrate concentration, which appears to be related to the summer peak in nitrate deposition, it is unlikely that the interannual variations in nitrate concentration in ice cores at a single site can be related to primary production of  $\text{NO}_y$ ; secondary transport phenomena are likely to dominate. Only if these can be accounted for can nitrate concentrations at some timescale be considered in terms of production rates.

The situation was probably very different during parts of the last glacial period, when concentrations of both sea salt and terrestrial dust in Antarctica were much higher than at present (Wolff et al., 2006). Under such circumstances we can imagine that post-depositional loss was almost stopped (Legrand et al., 1999; Röthlisberger et al., 2000), transport of recycled nitrate from the plateau to the coast may have been minimal, and although deposition strength at high resolution could still have been controlled by the concentrations of aerosol material, at low resolution, the concentration of nitrate in snow at Halley and other coastal sites might indeed have been determined by the amount of input from other sources, notably the stratosphere. Analysis of the nitrate isotopic content of glacial ice from coastal and inland sites would test whether it is correct that the recycling had ceased, and whether the remaining material was likely to be of stratospheric origin.

There remains the question as to whether there are other ways of deriving information at an annual resolution. At some scale, all the material that subsides from the stratosphere into the lowest levels of the polar atmosphere must either be deposited in Antarctica or advected across the coast. Would it be possible through a network of

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



cores to assess temporal variability in the total deposition of nitrate to Antarctica? If we could assume that the amount of nitrate advected across the coast is either relatively small or rather constant, then it might be possible to make a crude assessment of variations in the input of nitrate to the entire Antarctic troposphere.

5 To estimate the feasibility of such an approach, we note that the net surface mass balance of snow in Antarctica has been calculated as  $2288 \text{ Gt a}^{-1}$  over the whole continent including ice shelves (Vaughan et al., 1999). The average nitrate concentration retained in snow (i.e. below the surface layer) across Antarctica varies with snow accumulation rate, being very low ( $\sim 15 \mu\text{g kg}^{-1}$ ) due to post-depositional loss at the  
10 sites with extremely low accumulation rate ( $< 50 \text{ kg m}^{-2} \text{ a}^{-1}$ ), relatively high (up to about  $100 \mu\text{g kg}^{-1}$ ) at sites with moderately low accumulation rate, falling with increasing accumulation rate to about  $20 \mu\text{g kg}^{-1}$  at sites with very high accumulation rates (Mulvaney and Wolff, 1994). To estimate the total nitrate accumulation across Antarctica, we used the snow accumulation rates recently derived from satellite measurements  
15 (Arthern et al., 2006). We applied a transformation in which we estimated the concentration of nitrate to be  $15 \mu\text{g kg}^{-1}$  wherever the snow accumulation rate is lower than  $50 \text{ kg m}^{-2} \text{ a}^{-1}$ ; for sites with accumulation rate above the threshold, we applied an exponential function for nitrate concentration based on the observed spatial distribution (Mulvaney and Wolff, 1994) (giving  $23 \mu\text{g kg}^{-1}$  at very high snow accumulation rates, and  $90 \mu\text{g kg}^{-1}$  just above the  $50 \text{ kg m}^{-2} \text{ a}^{-1}$  accumulation threshold). Using this, we  
20 estimate the total deposition over the ice (grounded plus ice shelf) of Antarctica to be around  $8.6 \times 10^7 \text{ kg}$  (as  $\text{NO}_3^-$ ) per year (with an uncertainty based mainly on uncertainty in the nitrate/accumulation rate relationship, of about 20%). If we also estimate the average concentration of nitrate in near surface air at coastal sites to be around  
25  $30 \text{ ng m}^{-3}$  (average of 3 coastal sites (Wagenbach et al., 1998b)), and assume a net meridional wind speed of  $\sim 5 \text{ m s}^{-1}$  (König-Langlo et al., 1998), then the net outflow of nitrate across the coast (circle at  $70^\circ \text{ S}$  of  $14\,000 \text{ km}$ ) would be  $7 \times 10^4 \cdot h \text{ kg yr}^{-1}$ , where  $h$  is the height over which outflow of air occurs across the coast. Other  $\text{NO}_y$  species could also contribute to the net loss from the region. The outflow of nitrate is there-

## Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



fore only negligible compared to the deposition in Antarctica if the depth of outflow is  $<<1000$  m. There are few data with which to estimate this however.

It can be seen that it would not be a simple undertaking to estimate changes in source strength even from a network of cores. It may be feasible to estimate the total deposition to Antarctica within a few percent with a large enough network of cores, but only if the outflow can be constrained will it be possible to estimate net production over the continent to the same precision. Far more study of what controls the distribution of nitrate across Antarctica is needed if one is to have any confidence that nitrate concentrations either at a single site or from a network can be used to estimate changes in production of  $\text{NO}_y$  across Antarctica.

## 6 Conclusions

Numerous short-lived spikes of high nitrate concentrations certainly occur in records of snowfall at Halley, and these are likely to translate into a smaller number of preserved spikes in ice core records, and to be seen at other sites. However, at least some of these spikes certainly relate to episodic inputs of high sea salt concentrations that cause a partitioning of nitrate to aerosol and/or a trapping of nitrate in snow. Although we cannot rule out that some spikes could also be related to an increase in the production of  $\text{NO}_y$  (for example in SPEs), there will certainly be no one-to-one correlation. A realistic search for such production changes calls for a major study of different ice core sites, influenced by different transport pathways and sea salt influences, in order to search for contemporaneous spikes that are not influenced by deposition strength. Further modelling studies to estimate how a brief SPE should be recorded in the polar lower troposphere (and ultimately in snow) should also be carried out. Until such work is complete, it is not possible to use nitrate spikes in ice cores as indications of solar proton activity.

On longer timescales, significant recycling of material from central to coastal Antarctica may confound efforts to assess nitrate input on an interannual basis using any

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





single core. More work is needed to assess the importance of this process before proceeding. Studies are needed to assess the spatial extent of regions that experience loss of nitrate, and to determine more closely the conditions that control the extent of such losses; further studies of isotopic balance would also contribute quantitative information on the importance of this process.

Finally, we estimate that carrying out an Antarctic-wide survey of nitrate deposition as a proxy for the continent-wide input of  $\text{NO}_y$  to the Antarctic troposphere can only succeed when the relative budgets of nitrate that is deposited and advected out of the continent is pinned down. This calls for profiling studies of  $\text{NO}_y$  above the surface of Antarctica, especially in the outflow regions, to assess horizontal fluxes.

In short, except over time periods and spatial scales when transport and deposition can be assumed to be reasonably constant, we are not yet in a position to use nitrate in polar ice cores to assess large-scale changes in polar  $\text{NO}_y$  production quantitatively.

*Acknowledgements.* We gratefully acknowledge the assistance of the overwinterers at Halley research station who conducted the filter sampling discussed in this work, and Andrew Rankin who carried out some of the chemical analyses. We thank Robert Arthern for providing the dataset of Antarctic snow accumulation and showing EWW how to use it. The work was funded by the Natural Environment Research Council through Antarctic Funding Initiative grant number NER/G/S/2001/00010, and through the BAS core project CACHE-CEFAC.

## References

- Arthern, R. J., Winebrenner, D. P., and Vaughan, D. G.: Antarctic snow accumulation mapped using polarization of 4.3-cm wavelength microwave emission, *J. Geophys. Res.*, 111, D06107, doi:10.1029/2004JD005667, 2006.
- Blunier, T., Floch, G. L., Jacobi, H. W., and Quansah, E.: Isotopic view on nitrate loss in Antarctic surface snow, *Geophys. Res. Lett.*, 32, L13501, doi:10.1029/2005GL023011, 2005.
- Clilverd, M. A., Seppala, A., Rodger, C. J., Thomson, N. R., Lichtenberger, J., and Steinbach, P.: Temporal variability of the descent of high-altitude NO<sub>x</sub> inferred from ionospheric data, *J. Geophys. Res.*, 112, A09307, doi:10.1029/2006JA012085, 2007.

## Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Nitrate in polar ice

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Davis, D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F., Mauldin, L., and Hogan, A.: South Pole NO<sub>x</sub> chemistry: an assessment of factors controlling variability and absolute levels, *Atmos. Environ.*, 38, 5375–5388, 2004.

Dibb, J. E. and Whitlow, S. I.: Recent climate anomalies and their impact on snow chemistry at South Pole, 1987–1994, *Geophys. Res. Lett.*, 23, 1115–1118, 1996.

Fischer, H., Wagenbach, D., and Kipfstuhl, J.: Sulfate and nitrate firn concentrations on the Greenland ice sheet. 2. Temporal anthropogenic deposition changes, *J. Geophys. Res.*, 103, 21935–21942, 1998.

Fuhrer, K., Neftel, A., Anclin, M., Staffelbach, T., and Legrand, M.: High-resolution ammonium ice core record covering a complete glacial-interglacial cycle, *J. Geophys. Res.*, 101, 4147–4164, 1996.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Dominé, F., Frey, M. M., Guzmán, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klán, P., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: Evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, 7, 4329–4373, 2007,  
<http://www.atmos-chem-phys.net/7/4329/2007/>.

Herron, M. M.: Impurity sources of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in Greenland and Antarctic precipitation, *J. Geophys. Res.*, 87, 3052–3060, 1982.

Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B., and Campbell, B.: Evidence of NO<sub>x</sub> production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, 26, 695–698, 1999.

Jones, A. E., Weller, R., Wolff, E. W., and Jacobi, H.-W.: Speciation and rate of photochemical NO and NO<sub>2</sub> production in Antarctic snow, *Geophys. Res. Lett.*, 27, 345–348, 2000.

Jones, A. E., Wolff, E. W., Ames, D., Bauguitte, S. J.-B., Clemitshaw, K. C., Fleming, Z., Mills, G. P., Saiz-Lopez, A., Salmon, R. A., Sturges, W. T., and Worton, D. R.: The multi-seasonal NO<sub>y</sub> budget in coastal Antarctica and its link with surface snow and ice core nitrate: Results from the CHABLIS campaign, *Atmos. Chem. Phys. Discuss.*, 7, 4127–4163, 2007,  
<http://www.atmos-chem-phys-discuss.net/7/4127/2007/>.

Jones, A. E., Wolff, E. W., Salmon, R. A., Bauguitte, S. J.-B., Roscoe, H. K., Anderson, P. S., Ames, D., Clemitshaw, K. C., Fleming, Z., Bloss, W. J., Heard, D. E., Lee, J. D., Read, K. A.,

**Nitrate in polar ice**

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Hamer, P., Shallcross, D. E., Jackson, A., Walker, S., Lewis, A. C., Mills, G. P., Plane, J. M. C., Saiz-Lopez, A., Sturges, W. T. and Worton, D. R.: Chemistry of the Antarctic boundary layer and the interface with snow: an overview of the CHABLIS campaign, *Atmos. Chem. Phys. Discuss.*, 8, 5137–5181, 2008,

<http://www.atmos-chem-phys-discuss.net/8/5137/2008/>.

Jourdain, B. and Legrand, M.: Year-round records of bulk and size-segregated aerosol composition and HCl and HNO<sub>3</sub> levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer, *J. Geophys. Res.*, 107, 4645, doi:10.1029/2002JD002471, 2002.

König-Langlo, G., King, J., and Pettre, P.: Climatology of the three coastal Antarctic stations Dumont d'Urville, Neumayer and Halley, *J. Geophys. Res.*, 103, 10935–10946, 1998.

Legrand, M., Wolff, E. W., and Wagenbach, D.: Antarctic aerosol and snowfall chemistry: implications for deep Antarctic ice core chemistry, *Ann. Glaciol.*, 29, 66–72, 1999.

Legrand, M. R., Lorius, C., Barkov, N. I., and Petrov, V. N.: Vostok (Antarctica) ice core: atmospheric chemistry changes over the last climatic cycle (160 000 years), *Atmos. Environ.*, 22, 317–331, 1988.

Mayewski, P. A. and Legrand, M. R.: Recent increase in nitrate concentration of Antarctic snow, *Nature*, 346, 258–260, 1990.

Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M. S., Buck, C. F., and Whitlow, S.: An ice-core record of atmospheric response to anthropogenic sulphate and nitrate, *Nature*, 346, 554–556, 1990.

McCracken, K. G., Dreschhoff, G. A. M., Zeller, E. J., Smart, D. F., and Shea, M. A.: Solar cosmic ray events for the period 1561–1994 1. Identification in polar ice, 1561–1950, *J. Geophys. Res.*, 106, 21585–21598, 2001.

McElroy, M. B.: Studies of polar ice: insights for atmospheric chemistry, in: *The environmental record in glaciers and ice sheets*, edited by: Oeschger, H. and Langway Jr., C. C., John Wiley, Chichester, 363–377, 1989.

Mulvaney, R., Wagenbach, D., and Wolff, E. W.: Post-depositional change in snowpack nitrate from observation of year-round near-surface snow in coastal Antarctica, *J. Geophys. Res.*, 103, 11 021–11 031, 1998.

Mulvaney, R. and Wolff, E. W.: Evidence for winter/spring denitrification of the stratosphere in the nitrate record of Antarctic ice cores, *J. Geophys. Res.*, 98, 5213–5220, 1993.

Mulvaney, R. and Wolff, E. W.: Spatial variability of the major chemistry of the Antarctic ice

**Nitrate in polar ice**

E. W. Wolff et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- sheet, *Ann. Glaciol.*, 20, 440–447, 1994.
- Palais, J. M., Chuan, R., and Spencer, M. J.: Soluble and insoluble impurities in snow samples from Ross Island, Antarctica, *Ant. J. U.S.*, 24, 89–91, 1989.
- Palmer, A. S., van Ommen, T. D., Curran, M. A. J., and Morgan, V.: Ice-core evidence for a small solar-source of atmospheric nitrate, *Geophys. Res. Lett.*, 28, 1953–1956, 2001.
- Rankin, A. M. and Wolff, E. W.: A year-round record of size-segregated aerosol composition at Halley, Antarctica, *J. Geophys. Res.*, 108, 4775, doi:10.1029/2003JD003993, 2003.
- Röthlisberger, R., Hutterli, M. A., Sommer, S., Wolff, E. W., and Mulvaney, R.: Factors controlling nitrate in ice cores: evidence from the Dome C deep ice core, *J. Geophys. Res.*, 105, 20 565–20 572, 2000.
- Röthlisberger, R., Hutterli, M. A., Wolff, E. W., Mulvaney, R., Fischer, H., Bigler, M., Goto-Azuma, K., Hansson, M. E., Ruth, U., Siggaard-Andersen, M.-L., and Steffensen, J. P.: Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes, *Ann. Glaciol.*, 35, 209–216, 2002.
- Savarino, J., Kaiser, J., Morin, S., Sigman, D., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, *Atmos. Chem. Phys.*, 7, 1925–1945, 2007, <http://www.atmos-chem-phys.net/7/1925/2007/>.
- Shea, M. A., Smart, D. F., and Dreschhoff, G. A. M.: Identification of major proton fluence events from nitrates in polar ice cores, *Radiation Measurements*, 30, 309–316, 1999.
- Teinila, K., Kerminen, V. M., and Hillamo, R.: A study of size-segregated aerosol chemistry in the Antarctic atmosphere, *J. Geophys. Res.-Atmos.*, 105, 3893–3904, 2000.
- Vaughan, D. G., Bamber, J. L., Giovinetto, M., Russell, J., and Cooper, A. P. R.: Reassessment of net surface mass balance in Antarctica, *J. Clim.*, 12, 933–946, 1999.
- Vitt, F. M., Armstrong, T. P., Cravens, T. E., Dreschhoff, G. A. M., Jackman, C. H., and Laird, C. M.: Computed contributions to odd nitrogen concentrations in the Earth's polar middle atmosphere by energetic charged particles, *J. Atmos. Sol.-Terr. Phys.*, 62, 669–683, 2000.
- Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A., Legrand, M., Hall, J. S., and Wolff, E. W.: Seasalt aerosol in coastal Antarctic regions, *J. Geophys. Res.*, 103, 10 961–10 974, 1998a.
- Wagenbach, D., Legrand, M., Fischer, H., Pichlmayer, F., and Wolff, E. W.: Atmospheric near-surface nitrate at coastal Antarctic sites, *J. Geophys. Res.*, 103, 11 007–11 020, 1998b.
- Whitlow, S., Mayewski, P., Dibb, J., Holdsworth, G., and Twickler, M.: An ice-core-based record

- of biomass burning in the Arctic and Subarctic, 1750–1980, *Tellus*, 46B, 234–242, 1994.
- Wolff, E. W.: Nitrate in Polar Ice, in: *Ice core studies of global biogeochemical cycles*, edited by: Delmas, R. J., Springer-Verlag, Berlin, 195–224, 1995.
- 5 Wolff, E. W., Fischer, H., Fundel, F., Ruth, U., Twarloh, B., Littot, G. C., Mulvaney, R., Rothlisberger, R., de Angelis, M., Boutron, C. F., Hansson, M., Jonsell, U., Hutterli, M. A., Bigler, M., Lambert, F., Kaufmann, P., Stauffer, B., Stocker, T. F., Steffensen, J. P., Siggaard-Andersen, M. L., Udisti, R., Becagli, S., Castellano, E., Severi, M., Wagenbach, D., Barbante, C., Gabrielli, P., and Gaspari, V.: Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles, *Nature*, 440, 491–496, 2006.
- 10 Wolff, E. W., Hall, J. S., Mulvaney, R., Pasteur, E., Wagenbach, D., and Legrand, M.: Relationship between chemistry of air, fresh snow and firn cores for aerosol species in coastal Antarctica, *J. Geophys. Res.*, 103, 11 057–11 070, 1998.
- Zeller, E. J. and Dreschhoff, G. A. M.: Anomalous nitrate concentrations in polar ice cores – do they result from solar particle injections into the polar atmosphere?, *Geophys. Res. Lett.*, 22, 2521–2524, 1995.
- 15 Zeller, E. J., Dreschhoff, G. A. M., and Laird, C. M.: Nitrate flux on the Ross Ice Shelf, Antarctica and its relation to solar cosmic rays, *Geophys. Res. Lett.*, 13, 1264–1267, 1986.

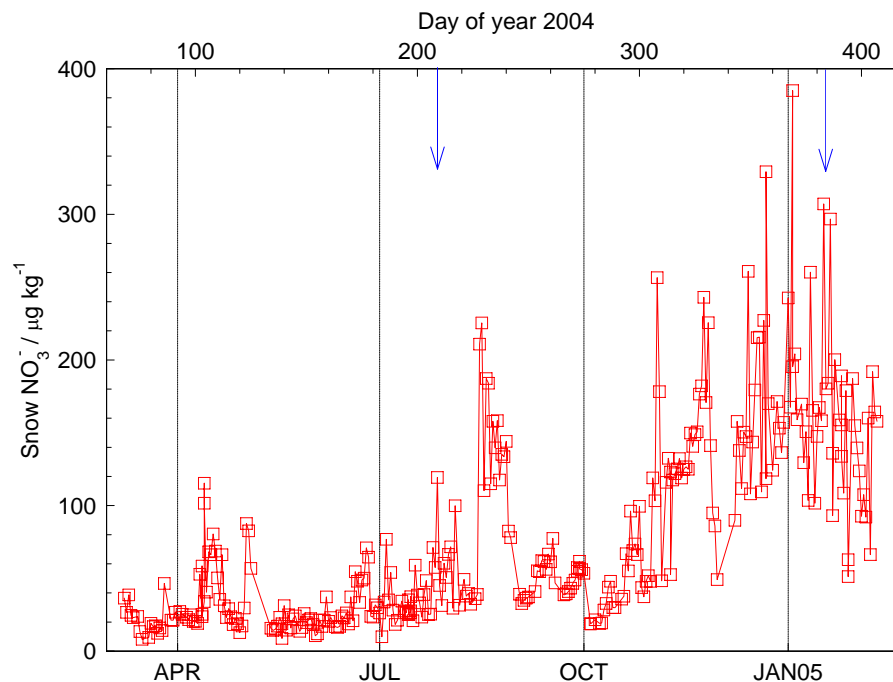
**Nitrate in polar ice**

E. W. Wolff et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## Nitrate in polar ice

E. W. Wolff et al.

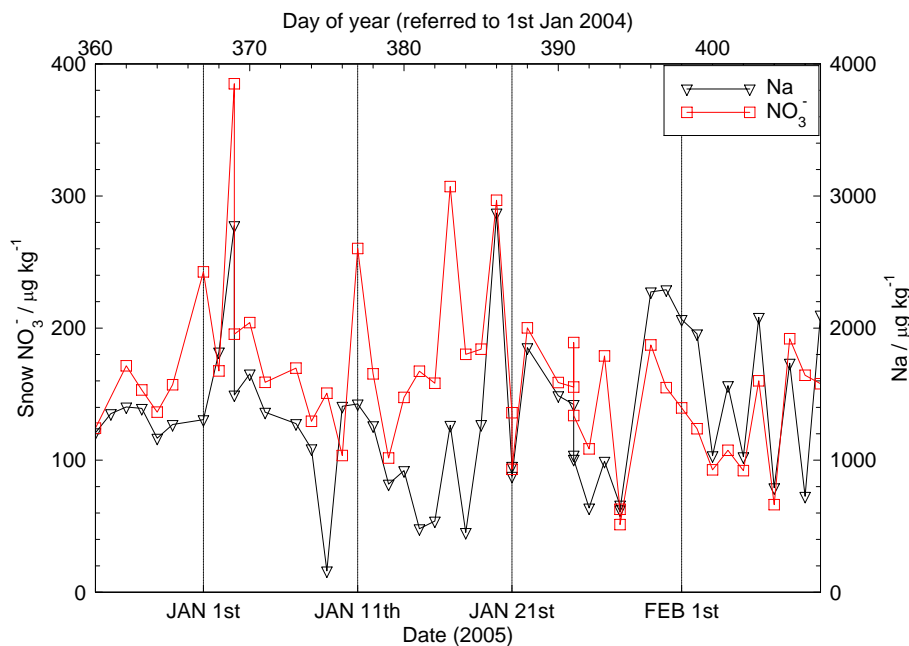


**Fig. 1.** Nitrate concentrations measured in surface snow samples collected approximately daily at Halley, Antarctica, in 2004 and early 2005. Month markers and grid lines refer to the start of the respective months. The timing of the maximum of the two largest SPE's of the period (proton flux at  $>10$  MeV more than 1000 pfu, based on NOAA Space Environment Center listing) is shown as arrows.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## Nitrate in polar ice

E. W. Wolff et al.

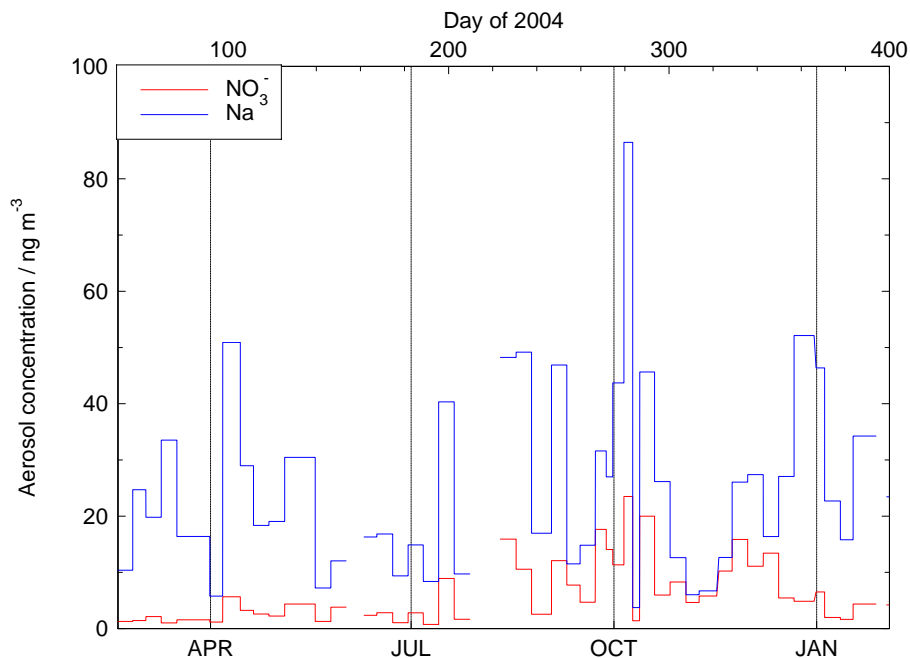


**Fig. 2.** Nitrate and sodium concentrations measured in daily surface snow samples in summer 2004 and 2005 at Halley, Antarctica.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## Nitrate in polar ice

E. W. Wolff et al.



**Fig. 3.** Nitrate and sodium concentrations measured on aerosol filters collected at Halley, Antarctica, in 2004 and early 2005. Month markers and grid lines refer to the start of the respective months.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)