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Atmospheric near-surface nitrate at coastal Antarctic sites

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Abstract. Records of atmospheric nitrate were obtained by year-round aerosol sampling at Neumayer and Dumont D'Urville stations, located in the Atlantic and Pacific sector of coastal Antarctica, respectively. Where possible, evaluation of the nitrate records is mainly based on concurrently measured radioisotopes (^{10}Be, ^{7}Be, ^{210}Pb) as well as δ^{15}N in nitrate nitrogen. Observations made at these (and two other coastal Antarctic sites [*Savoie et al.*, 1993]) reveal a uniform nitrate background near 10 ng m^{-3} persisting throughout coastal Antarctica between approximately April and June. The dominant seasonal nitrate maximum, which occurred between spring and midsummer and ranged from 20 to 70 ng m^{-3}, tended to increase with latitude. An estimate based on Neumayer mineral dust concentrations suggests that an average of less than 5% of the observed atmospheric nitrate load may be associated with continental tropospheric sources, while a separate estimate based on ^{210}Pb records implies a much higher proportion of up to 60%. Stratospheric nitrate influx rates seen at coastal sites, deduced from Neumayer ^{10}Be/^{7}Be records for stratospheric air mass intrusions and from tritium for the sedimentation of polar stratospheric clouds (PSC), exceed the theoretical stratospheric odd nitrogen production rate from N_2O oxidation by almost a factor of 5 and are found to be in close agreement with the observed surface nitrate flux, implying again that the continental source contribution is relatively unimportant. Consideration of nitrate reemission from near-surface snow layers reveals a minor effect of this flux on the global Antarctic troposphere but possibly a substantial influence on the nitrate load of a persistent surface inversion layer. Evaluation of the mean seasonal nitrate pattern, based on concurrent ^{10}Be, ^{210}Pb, and δ^{15}N records at Neumayer and on tritium in precipitation at Halley, suggests that the period of significant enhancement above the background mainly reflects inputs of stratospheric nitrate with secondary peaks in winter and late summer most likely dominated by PSC sedimentation and stratospheric air mass intrusions, respectively.

1. Introduction

Nitrate, removed from the atmosphere as HNO_3 or particulate nitrate, is a major component in polar precipitation for both hemispheres. Ice core studies in these regions may allow reconstruction of the depositional history of nitrate on the decadal to the 100 millennium timescale [*Legrand and Delmas*, 1985; *Wolff*, 1995]. Important questions still exist, however, about the dominant NO_x sources even responsible for the present-day background nitrate level observed at remote sites [*Kasibhatla et al.*, 1993; *Levy et al.*, 1980]. This is true for tropical marine areas in the southern hemisphere [*Savoie et al.*, 1989] and especially for the most remote tropospheric compartment overlying the Antarctic continent [*Legrand and Kirchner*, 1990].

Up to now, this uncertainty has limited considerably the usefulness of nitrate records recovered from Antarctic ice cores for paleo-environmental studies despite the relatively large data set available [*Mulvaney and Wolff*, 1994]. For the Holocene period the most likely nitrate sources to the Antarctic troposphere are believed to be tropical lightning activity and various stratospheric sources (see review by *Wolff* [1995]), but the relative contributions of these sources are still a matter of controversy [*Legrand and Delmas*, 1988]. Detailed investigations of the Antarctic nitrate cycle by glacio-chemical studies are ambiguous due to inadequate time resolution and also to nonconservative behavior of HNO_3 in the snow pack which may lead to serious reemission effects [*Dibb and Whitlow*, 1996; *Mulvaney et al.*, this issue]. Multi year-round atmospheric observations of nitrate which would be needed for interpreting Antarctic ice core records are sparse, however, and confined to two coastal sites only: Mawson station in the Indian Ocean sector [*Prospero et al.*, 1991] and Neumayer in the Atlantic sector [*Wagenbach et al.*, 1988a; *Wagenbach*, 1996]. Here we report on year-round atmospheric nitrate records obtained from Neumayer (hereinafter denoted as NM) and Dumont D'Urville (DDU) in the Pacific sector, which extend the temporal and spatial coverage of the existing nitrate observations. These records are discussed mainly in terms of intersite variability and major sources, which drive the regular seasonal cycle. Concurrent nitrate analyses obtained in surface snow by year-round sampling, at daily resolution at Halley Station (Weddell Sea sector) and at much lower resolution at NM, are discussed in detail by *Mulvaney et al.* [this issue].

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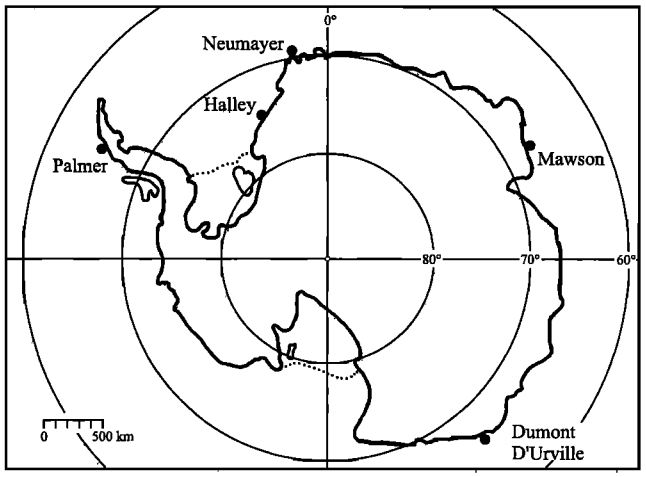

Figure 1. Location of Antarctic sites where year-round atmospheric records of nitrate are available for the stations Mawson and Palmer [see *Savoie et al.*, 1993].

2. Sampling Sites and Methods

The climatologies of DDU and NM are described in detail by *König-Langlo et al.* [this issue], while sampling and analytical protocols for the aerosol and snow chemical studies are given by *Wolff et al.* [this issue] as well as by *Wagenbach et al.* [1988a] specifically for NM. In the following section, only a brief overview is presented, focusing on certain aspects important for the evaluation of the site specific atmospheric nitrate records.

2.1. Site Description

The locations of the sampling sites used in this work are indicated in Figure 1, together with those of Mawson and Palmer stations where year-round atmospheric nitrate records are also available [*Savoie et al.*, 1993]. Climatological differences between the various sites which may be relevant in assessing the nitrate records include the following aspects:

1. Their position relative to the Antarctic vortex is established during winter, and the vortex has a reduced upper atmospheric exchange with lower latitude air masses during that time. The probability of being within the vortex clearly decreases going from NM (via Mawson) to DDU, whereas Palmer is expected to remain outside the vortex edge throughout the year.

2. The seasonal change in the occurrence and strength of the surface inversion may contribute to the variability of all short-lived species in the boundary layer except locally produced sea-salt aerosol. As summarized by *König-Langlo et al.* [this issue], the period from November to February shows a relatively weak or absent surface inversion at NM and DDU but generally stronger temperature gradients at NM (due to radiative cooling). Cyclonic activity, however, may regularly interrupt the isolation from higher atmospheric levels at both sites throughout all seasons.

3. The surface wind system is dominated by zonal flow at NM but by a meridional one at DDU and Mawson [*Parish*, 1988]. The latter two sites are therefore more directly influenced by air masses flowing down from the Antarctic plateau and by upper tropospheric air from midlatitudes eventually entrained in the downslope winds.

In summary, the climatologies at DDU and Mawson are similar, whereas NM is characterized by its ice shelf position (leading to zonal winds) and by its relatively more frequent location inside the polar vortex. Palmer station stands out by its position on the Antarctic Peninsula and reflects mainly the subpolar maritime regime.

2.2. Sampling and Analyses

Details on the sampling procedure and analytical methods used for aerosol chemical analyses are summarized in Table 1. Auxiliary measurements at NM used here to back up the nitrate data come from the following analyses performed on the same high-volume filters: radio isotopes ^{210}Pb, ^{7}Be [*Wagenbach et al.*, 1988a], and ^{10}Be [*Wagenbach et al.*, 1988b; *Wagenbach*, 1996] and stable isotope ratio ^{15}N/^{14}N in nitrate [*Pichlmayer and Wagenbach*, 1995].

For DDU, concurrent ^{210}Pb analyses are obtained on separate filters at a daily time resolution [*Lambert et al.*, 1990]. Ion chromatographic nitrate analyses of the filter extracts from both sites had uncertainties typically better than 5% [*Wolff et al.*, this issue], and the nitrate concentration of filter blanks exposed in the field is generally insignificant. Critical aspects in evaluating the atmospheric nitrate data are, however, the risk of ambient air contamination from the station at DDU, and the problem of obtaining total atmospheric nitrate concentrations by the sampling procedures applied. While local contamination (at least) by anthropogenic sources is prevented at NM by a wind and condensation particle controlled sampling procedure [see *Wagenbach et al.*, 1988a], aerosol samples from DDU are subject to potential contamination by natural and anthropogenic sources from the local station environment.

2.2.1. Assessing local contamination at DDU. The very small size of the island (Ile des Pétrels) on which DDU is located makes it impossible to define a "clean air sector" there. In order to estimate the effects both of human activities (which

Table 1. Sampling and Analytical Procedures for Aerosol Chemical Records Obtained at Dumont D'Urville and Neumayer Stations

	Dumont d'Urville (DDU) 66°S, 140°E	Neumayer (NM) 70°S, 8°W
Observational period	Jan. 1991 to Dec. 1995	March 1983 to Jan. 1996
Collection interval	1–7 days	3–20 days (typical 2 weeks)
Sampling system		
Air intake height	1.8 m above snow level	7 m above snow level
Aerosol filter	47 mm Ø, 0.4 μm PTFE, open face	240 mm Ø, double cellulose filters, in line
Filter face velocity	0.6 m s^{-1}	1.1 m s^{-1}*
Analyzed ion species and methods	NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, Br^-, MSA: ion chromatography	NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, Br^-, MSA: ion chromatography

*Corresponds to 13% of air intake velocity.

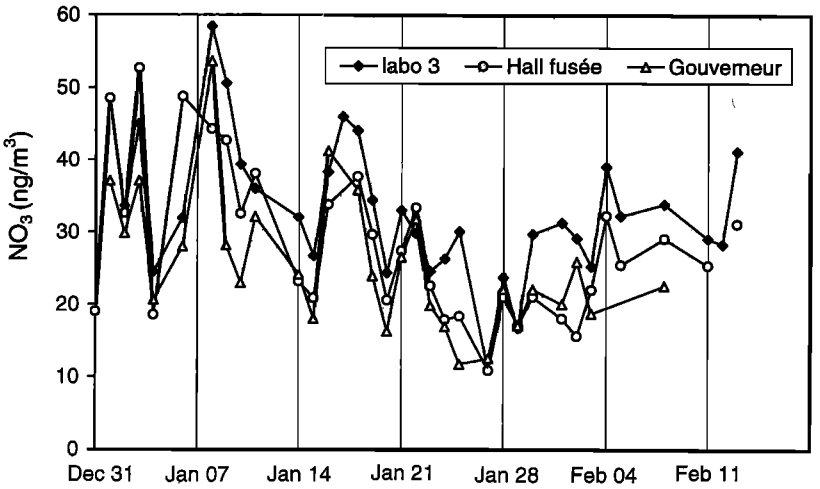

Figure 2. Concurrent nitrate records observed at three sites in the close station environment of Dumont D'Urville. The anthropogenic and natural contamination risk is generally highest at Labo 3 and lowest at Gouverneur.

occur over the entire year) and of large penguin colonies (located at this site in summer), simultaneous aerosol collections were performed using three sampling lines set up at the main station and 3 km away (see details given by *Legrand et al.* [this issue]). As shown in Figure 2, based on 26 common samplings performed in summer 1993/1994 at the three sites, nitrate concentrations are very similar, ranging from 33.0 ± 9.2 at "Labo 3" to 27.0 ± 9.1 ng m^{-3} at "Ile du Gouverneur." Visual inspection of the filter color for soot suggests that contamination by station activities, when it occurs, can provide a slight contribution to nitrate [*Ducroz*, 1996]. For instance, the filter collected at Labo 3 on February 1 which exhibits a gray color has a nitrate concentration of 31 ng m^{-3} instead of 20 ng m^{-3} as at the two other sites.

The main cause of contamination at DDU was found to be related to wildlife as discussed by *Legrand et al.* [this issue]. The bacterial decomposition of uric acid from ornithogenic soils is responsible for extremely high ammonia and ammonium levels observed at Dumont d'Urville. Nitrate has not been detected in freshly occupied ornithogenic soils in Antarctica [*Ugolini*, 1972]. In a more recent study of Antarctic ornithogenic soils at Cape Bird, *Speir and Cowling* [1984] found amounts of nitrate which were significantly higher than the ones observed in normal soil standards (70 ppm instead of 10 ppm) but which were 3 orders of magnitude lower than the ammonium content (4.2% as N). *Legrand et al.* [this issue] find that primary particle mobilization from ornithogenic soils at DDU may contribute up to 100 ng m^{-3} to the excess of ammonium detected at Labo 3 with respect to the level observed at Ile du Gouverneur. Using these numbers, it appears that the contribution of primary particle emissions from ornithogenic soils may account for 0.5 ng m^{-3} of nitrate at most at the principle site Labo 3. Also, the atmospheric oxidation of ammonia by hydroxyl radicals could be a source of nitrogen oxides in the atmosphere. Assuming a typical OH concentration of 5 10^5 radicals per cm^3 for these regions in summer [*Crutzen and Gidel*, 1983] and a kinetic rate for the oxidation reaction of 1.25 10^{13} cm^3 molecules^{-1} s^{-1} [*Jet Propulsion Laboratory (JPL)*, 1994], we calculate a lifetime of 180 days for ammonia. The 6 month lifetime suggests that this oxidation process is not rapid enough, compared to other processes such as ammoniation of acidic particles or dissolution in water, to be an effective source of nitrogen oxides. In conclusion, it is very unlikely that the presence of large penguin colonies at the DDU site leads to nitrate contamination of the local atmosphere.

2.2.2. Collection of total nitrate. Analyses of aerosol filter extracts sampled at marine sites is reported by *Savoie et al.* [1989] generally to provide total nitrate (i.e., HNO_3 plus particulate nitrate) concentrations. This is mainly because large amounts of sea-salt accumulated on the aerosol filters may react with HNO_3 to form $NaNO_3$ [*Appel et al.*, 1981]. This working hypothesis might not be valid a priori, however, for coastal Antarctic sampling sites which have been found to show roughly 1–2 orders of magnitude lower atmospheric sea-salt loads compared to open ocean sites [*Wagenbach et al.*, this issue] and which have highly acidic aerosol properties during midsummer. Although teflon filters (which retain only a minor HNO_3 fraction) are used at DDU, no substantial HNO_3 loss is expected there. This is because the sea-salt level during summer is relatively high (2 μg m^{-3}) and, more importantly, extremely high NH_3 concentrations of about 5 μg m^{-3} occur during that time [*Legrand et al.*, this issue]. Preliminary denuder tube and mist chamber measurements performed by *Ducroz* [1996, also unpublished results, 1996] at DDU have revealed that only 10% of total nitrate is found in the gas phase. There is also no indication of substantial nitrate remobilization from the filters by the acidic species (i.e., non-sea-salt (NSS) sulphate and methane sulfonic acid (MSA)) at DDU since on the basis of 1–2 day samples, no significant relationship was found between nitrate and biogenic sulphur or nitrate and sea-salt loads.

The ambient conditions for total nitrate sampling during summer appear to be less favorable at NM than at DDU due to much lower ammonium (20 ng m^{-3}) and sea-salt (0.6 μg m^{-3}) levels. Weekly low-volume nitrate samples collected on teflon filters followed by two nylon filters (retaining HNO_3) indicate that less than 40% of the total nitrate occurs in the gas phase. Nitrate mobilization from the accumulated aerosol matrix on the high-volume filters is clearly seen at NM through the existence of relatively higher nitrate amounts sometimes found on the backup cellulose filter (which is arranged face to face with the first one and regularly analyzed). Such events are

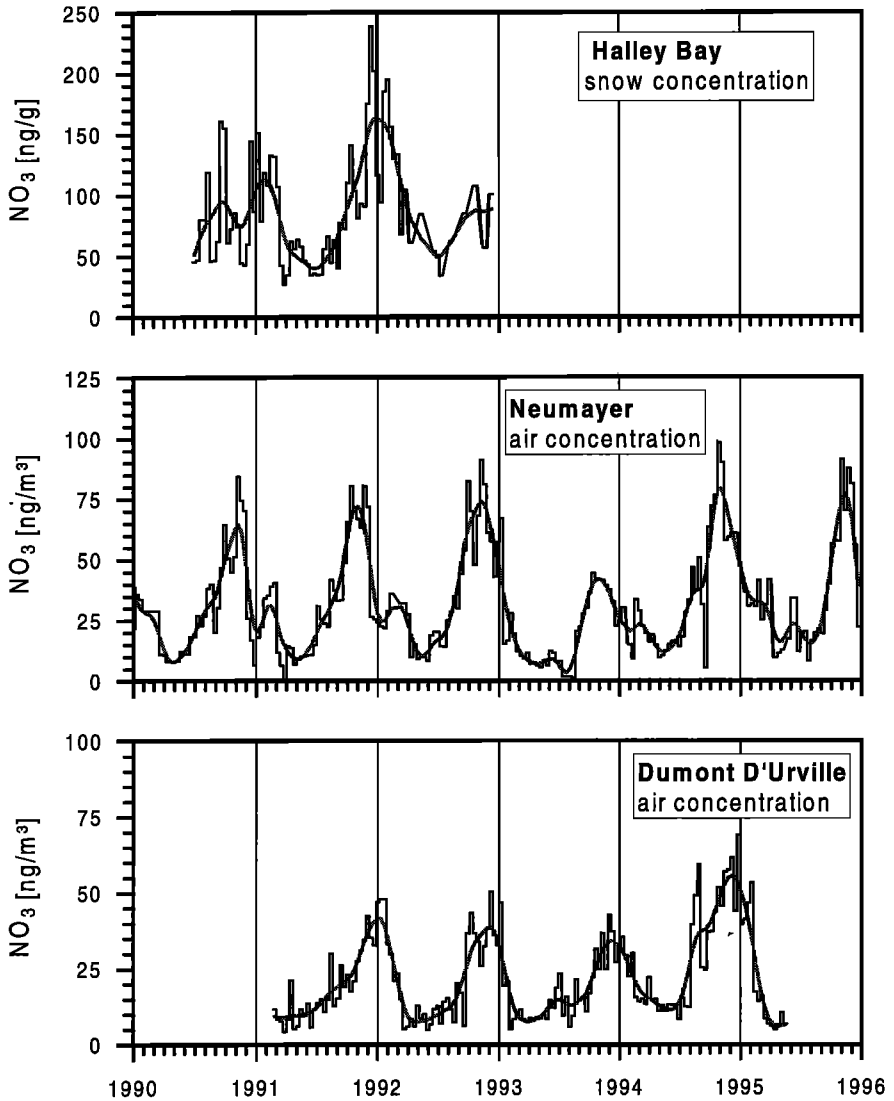

Figure 3. Continuous atmospheric nitrate records at Neumayer and Dumont D'Urville displayed as 10 day means. For comparison with the situation at Halley station, 10 day mean concentrations obtained from daily surface snow samplings [*Mulvaney et al.*, this issue] are shown as well. Solid gray lines from spline smoothing are added for convenience.

confined to the summer period and to individual filters with very low sea-salt loads. On the other hand, the HNO_3 collection efficiency for the backup aerosol filter was found to be between 60 and 90%, allowing resampling of most of the evaporated nitrate. Again, inspection of the summer nitrate variability at NM did not reveal a systematic relationship to the sea-salt or acidity loads of the filters. In particular, the general nitrate trend during the summer season is not substantially influenced by the dramatic change in the aerosol acidity during that season. We cannot exclude, however, the possibility that some filters collected during the acidity peak in January under low sea-salt loads may underestimate the total atmospheric nitrate concentration. We expect that the same holds true for the total nitrate data reported by *Savoie et al.* [1992] from Mawson station since sea salt is lower there by a factor of ~4 compared to NM and since nonhygroscopic polycarbonate fibre filters are used.

In conclusion, total atmospheric nitrate records reported here are affected to a minor extent by year-round contamination events at DDU and by HNO_3 remobilization from summer filters at NM, respectively. None of these shortcomings occurring on individual filter samples could, however, substantially perturb the observed mean nitrate levels and their seasonal patterns.

3. Results

Because of the large difference in the sampling intervals (ranging from 1 to 2 days to 1 week at DDU and from 3 to 14 days to up to 3 weeks at NM), the continuous raw data were transformed into series of 10 day means to make the data variability more comparable. This compromise is also quite comparable to the regular collection time of 1 week applied by *Savoie et al.* [1992] at Mawson station. The main features of the DDU and NM records shown in Figure 3 for the overlapping years 1991–1995 include the following:

1. There is a steadily decreasing mean nitrate level going from NM (36 ng m^{-3}) via Mawson (28 ng m^{-3}) to DDU (23 ng

Table 2. Annual Mean and Dissected Seasonal Mean Concentrations of Atmospheric Nitrate Observed in Coastal Antarctica and the Southern Hemisphere

	Neumayer	Dumont d'Urville	Mawson*	Palmer*	SH†
Years	1983–1995	1991–1994	1987–1991	April 1990 to Feb. 1991	...
Annual mean ± s.d.	35.60 ± 6.70	23.00 ± 5.8	28 ± 2.3	~17	~113
Background					
Timing	April 1 to May 30	April 1 to May 30	April–June	April–June	...
Mean ± s.d.	13 ± 3.4	11 ± 3.3	9–12	~10	~80
Winter peak					
Timing	July 15 to Sept. 15	July 15 to Sept. 15	Aug.	July to mid-Oct.	...
Mean ± s.d.	32 ± 11	20 ± 11	34	17	...
Primary summer peak					
Timing	Oct. 1 to Nov. 30	Nov. 1 to Jan. 15	Nov.	mid-Oct. to mid-Dec.	...
Mean ± s.d.	73 ± 16	41 ± 11	60	22	...
Secondary summer peak					
Timing	Jan. 1 to March 15	...	mid-Dec. 1990 to early Feb. 1991	mid-Dec. to early Feb.	...
Mean ± s.d.	31 ± 8	...	39	22	...

*Values given by *Savoie et al.* [1992].
†Southern hemisphere values from remote sea level sites [*Prospero and Savoie*, 1989].

m^{-3}). Note that the sampling artifacts discussed above would lead to a higher nitrate level at DDU compared to NM. Mean total nitrate concentrations (Table 2) at higher latitudes in coastal Antarctica are significantly higher than those at the Antarctic Peninsula (Palmer station), but lower by more than a factor of 3 than those observed at remote marine sites at low latitudes in the southern hemisphere. In particular, the rather uniform nitrate background concentration in coastal Antarctica is roughly a factor of 8 lower than at tropical sites.

2. There is a lack of an obvious synchroneity between the interannual variability at NM and DDU (except for the year 1993 which stands out in both records by relatively low nitrate concentrations unprecedented in the 1983–1995 record at NM). Similarly, no common interannual change is seen between Mawson [*Savoie et al.*, 1993] and NM for the overlapping period 1987–1990.

To illustrate the mean annual nitrate cycle, corresponding 10 day means are averaged over the total observed years and are shown in Figure 4 in comparison with the cycle at Mawson [*Savoie et al.*, 1993]. The regular annual nitrate cycle occurring at all three sites is characterized by a stable background of the order of 10 ng m^{-3} between April and June underlying a bimodal or trimodal peak region during the rest of the year. The trimodal peak shape appearing at Mawson and NM was proved to be a significant pattern at NM through Monte Carlo singular spectrum analyses [*Allen and Smith*, 1994] of the 12 year record available from this site. Seasonal means compiled in Table 2 suggest a quite regular reproducibility of the seasonal nitrate cycle from year to year which is driven by a dominant spring-early summer enhancement. The main intersite differences in the timing of the seasonal nitrate cycles are an apparent phase lag in the absolute maxima, occurring in November at NM and Mawson but in December–January at DDU, and the lack of a clear secondary late summer peak around February at DDU. The secondary summer peak was not considered separately therefore in the calculated seasonal means for DDU given in Table 2. We cannot entirely exclude that the latter finding may be partly connected to the contamination problem at DDU or, conversely, to an incomplete sampling during January at NM and Mawson (see section 2).

Special attention is directed, however, to the late winter secondary peak which regularly appears at all three sites for approximately the same period (July–September) and which shows comparable mean nitrate levels. The interannual variability during this period (represented by error bars in Figure 3) is much higher than during the background period, suggesting that an Antarctic source may be responsible for the winter nitrate enhancement. The regular annual nitrate cycle seen at all high-latitude sites in coastal Antarctica basically reflects the strength of the relevant sources and the transport conditions, which may both vary seasonally.

4. Discussion

The most crucial problem in evaluating the atmospheric nitrate records in Antarctica is to constrain the dominant source responsible for the mean nitrate level and to identify the process governing the seasonal cycle. Previous studies based on ice core nitrate profiles and backed up by modeling efforts [*Legrand and Delmas*, 1986; *Legrand and Kirchner*, 1990] suggested that tropical lightning and stratospheric odd nitrogen (from a variety of natural sources including N_2O oxidation) provide the dominant nitrate fluxes to the Antarctic troposphere. The relative contribution of these two major sources to the Antarctic nitrate budget are essentially unknown, however. In view of this basic lack of information as to whether a tropospheric or a stratospheric source is the main contributor to Antarctic nitrate, the controversial question of what may be the controlling source of stratospheric NO_x [*Legrand and Delmas*, 1988] appears to be of only secondary importance.

On the one hand, *Savoie et al.* [1993] hypothesized that their nonbackground signal of atmospheric nitrate seen at Mawson is of (unspecified) continental origin, based on the existence of a seasonal cycle similar to that of ^{210}Pb. On the other hand, reinforced by current evidence on the denitrification and dehydration of the winter stratosphere by sedimenting polar stratospheric clouds (PSC) [*Solomon*, 1988], several authors have suggested that Antarctic surface nitrate is possibly associated with that phenomenon [*Mulvaney and Wolff*, 1993; *Wagenbach*, 1996; *Legrand and Kirchner*, 1990; *McElroy*, 1989; *Mayewski and Legrand*, 1990]. In the following sections, the potential sources and processes governing the atmospheric nitrate records in coastal Antarctica are evaluated mainly on the basis of concurrently observed atmospheric tracers (i.e., radioisotopes and $\delta^{15}N$).

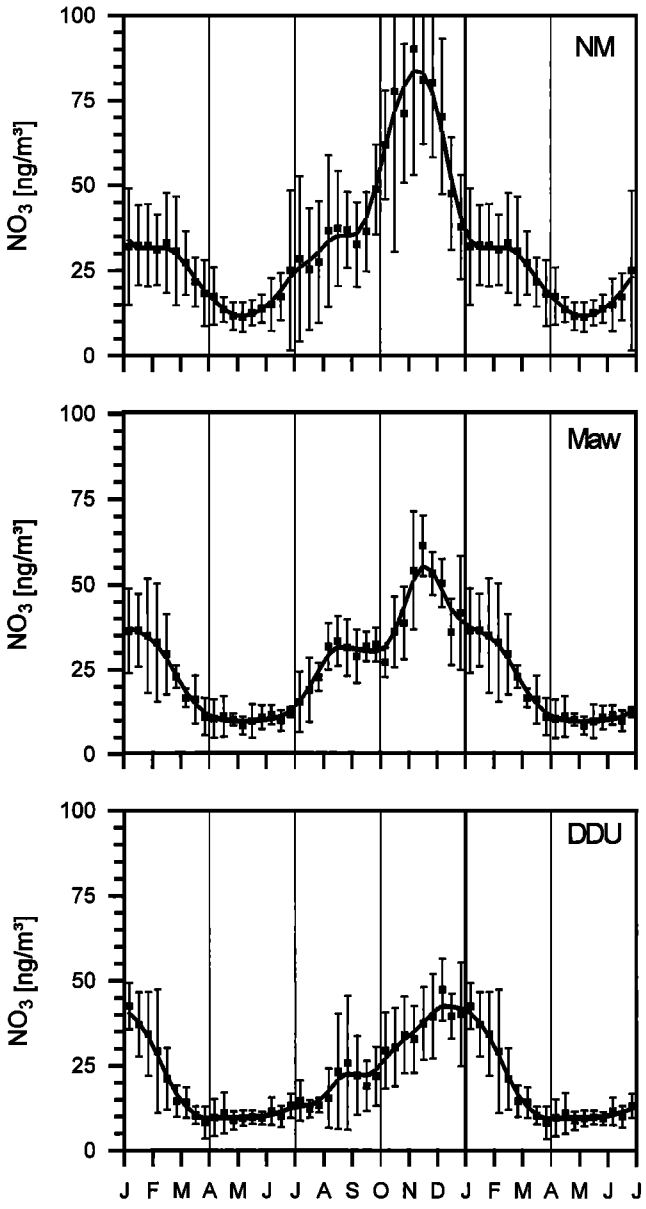

Figure 4. Mean annual nitrate cycles calculated as arithmetic means observed at Dumont D'Urville (1991–1994), Neumayer (1983–1995), and at Mawson (1987–1990). The latter data are taken from *Savoie et al.* [1993]. Error bars refer to the $\pm 1\ \sigma$ standard deviation in the interannual variability.

4.1. Tropospheric Sources

Marine sources, possibly provided by nitrite photolysis in surface water [*Zafirou and True*, 1979] or by emission of organic nitrate species [*Mopper and Zika*, 1987], are neglected here since, in contrast to biogenic sulphur, decreasing nitrate concentrations have not been observed in Antarctic snow with increasing distance from the coast [*Minikin et al.*, 1994]. For continental NO_x sources, we consider mainly soil exhalation of NO, anthropogenic activities, biomass burning, and N fixation by lightning (assumed here to occur mainly within the continental upper troposphere).

The simplest estimate of the overall contribution of continental sources to the Antarctic nitrate budget can be derived from the clear correlation of nonbackground nitrate at remote tropical sites in the northern hemisphere with mineral dust (as observed by *Prospero and Savoie* [1989] mainly during spring due to the advection of Asian dust plumes). Taking their average mass ratio of excess nitrate to excess mineral dust of 0.2 for Midway (30° N), and using the mineral dust annual cycle reported by *Wagenbach* [1996] for NM (winter: ~7 ng m^{-3}; summer: ~18 ng m^{-3}), we calculate continental inputs of 1.4 and 3.6 ng m^{-3} for winter and summer nitrate at NM, respectively. This estimate, pointing to a continental nitrate fraction of the order of 5% only, is governed by the effective removal of mineral dust during long-range transport and disregards the support of HNO_3 by its precursor gases. It provides therefore a lower limit for the atmospheric level of continental nitrate expected in coastal Antarctica.

Lead 210 produced in the atmosphere by radioactive decay of the terrigenous noble gas ^{222}Rn (τ = 5.5 days) may be better suited for tracing the transport, transformation, and removal of continental NO_x and nitrate to Antarctica. Since it is expected that the long-range transport of aerosol and water-reactive trace gases operates more efficiently in the upper troposphere (where the residence time of those species is longer), we refer here to total nitrate and ^{210}Pb data reported by *Dibb et al.* [1996] for the mid to upper troposphere over the tropical North Pacific. From their data covering an altitude range between 2 and 13 km and including the influence of the Asian dust plume we deduce a mean ratio of (total) nitrate to ^{210}Pb of 17 ng fCi^{-1}. Assuming no further fractionation during transport between ^{210}Pb and total nitrate, and similar lifetimes of the HNO_3 precursors and ^{222}Rn (i.e., 5.5 days), the fraction of continental nitrate in coastal Antarctica may be estimated from the above ratio and the atmospheric ^{210}Pb concentration there. This calculation gives an annual mean of about 15 ng m^{-3} nitrate at DDU, NM, and Mawson based on the common mean ^{210}Pb level of ~0.9 fCi m^{-3} observed at all three sites (for the seasonal cycle of this continental nitrate fraction, see section 4.4). According to the seasonal means given in Table 2 the 15 ng m^{-3} continental nitrate (still overestimated by roughly 10–20% due to the neglected marine ^{222}Rn exhalation) may easily explain the 10 ng m^{-3} background level seen throughout coastal Antarctica and would account for 40, 54, and 60% of the annual means at NM, Mawson, and DDU, respectively.

Continental nitrate may specifically contribute to the dominant summer peak at all coastal sites. Particularly at DDU where the most distinct ^{210}Pb summer peak occurs the (^{210}Pb deduced) continental nitrate fraction might add again up to 60% to the major nitrate peak seen during that season (see section 4.2). It is not clear, however, if the used nitrate to ^{210}Pb source ratio (which is confined to the northern fall season) is representative for continental plumes in the upper marine troposphere of the southern hemisphere as well. The above estimates are too uncertain therefore to draw a final conclusion on the overall influence of the tropospheric nitrate source. However, the following qualitative aspects suggest that continental sources do not dominate:

1. Both fossil fuel and biomass-burning nitrate sources are expected to have increased in strength over recent decades. There is, however, no clear ice core evidence for such systematic change above the natural variability seen throughout the Antarctic continent [*Wolff*, 1995] confirming the previous estimate that Antarctic troposphere is relatively insensitive to the continental NO_x source.
2. The relative summer nitrate maximum may partly be

due to the weakening or frequent absence of the surface inversion during that time. The broad covariance between the seasonal cycles of nitrate and continental aerosol species such as mineral dust [*Wagenbach*, 1996], ^{210}Pb, and black carbon [*Wolff and Cachier*, this issue] is therefore not necessarily the result of a common continental source.

3. The spatial variability of the atmospheric nitrate level does not follow the spatial pattern of ^{210}Pb. For example, the pronounced ^{210}Pb summer peak is significantly higher at DDU [*Lambert et al.*, 1990] compared to the rather flat summer maximum at NM, although a relatively lower nitrate level was found at DDU. Also in contrast to DDU, there is no clear correspondence at NM between the outstanding summer nitrate peak in November and the weak seasonal pattern of ^{210}Pb or ^{222}Rn [*Winkler et al.*, 1991].

4.2. Stratospheric Sources

In evaluating the importance of the stratospheric nitrate source, two transport mechanisms are considered to contribute to the near-surface Antarctic nitrate budget: air mass exchange across the Antarctic or midlatitude tropopause and the sedimentation of polar stratospheric cloud (PSC) particles mainly made up by nitric acid and water. To quantify the intrusion of stratospheric air, we used the cosmogenic radioisotopes ^{10}Be ($T_{1/2} = 1.5 \times 10^6$ years) and ^{7}Be ($T_{1/2} = 53$ days) both of which show maximum production rates in the lower stratosphere. Although ^{10}Be and ^{7}Be, which are most likely attached to stratospheric sulphate particles, may also become incorporated in PSCs, this removal mechanism is assumed here to be insignificant compared to the air mass exchange of the aerosol across the tropopause. To identify PSC-related nitrate, we used tritium (^{3}H), which is also mainly produced in the lower stratosphere by cosmic rays and which currently shows a higher abundance in stratospheric water vapor compared to tropospheric values by 4 orders of magnitude [*Schott*, 1991]. The influx of material evaporated from PSCs (somewhere above or below the tropopause region) is expected therefore to be sensitively traced by the ^{3}H abundance of Antarctic precipitation or near-surface water vapor. A possible link between the PSC downward transport and bomb-produced ^{3}H observed in Antarctic winter precipitation was previously mentioned by *Jouzel et al.* [1982].

As illustrated in Figure 5, the seasonal timing of the stratospheric air mass signals ^{10}Be and ^{7}Be (measured at NM) and ^{3}H (observed in precipitation at Halley [*International Atomic Energy Agency* (*IAEA*), 1986, 1990]) differs by roughly 6 months, with an absolute ^{3}H maximum in September, suggesting that this approach should help us to distinguish the relative importance of the two downward transport mechanisms for stratospheric nitrate. The applicability of the ^{10}Be, ^{7}Be, and ^{3}H tracers for quantifying the stratospheric nitrate inputs is essentially based, however, on the assumption that their residence times in the Antarctic troposphere are comparable to that of HNO_3 (or particulate nitrate). Unlike at NM, at DDU, only ^{7}Be is available as an stratospheric air mass tracer (possibly indicating mainly the subsidence of upper tropospheric air). As shown in Figure 6, the distinct summer peak of ^{210}Pb at this site prevents use of the ^{7}Be/^{210}Pb ratio for identification of the season with maximum stratospheric aerosol arrival. Nevertheless, the ^{7}Be level at DDU is among the highest measured in Antarctica, suggesting at least a close coupling to upper tropospheric air, and shows a broad absolute maximum between December and March which is clearly delayed compared to the nitrate summer peak occurring in December.

We calculated mean stratospheric influx rates of nitrate, ^{10}Be, and ^{3}H to the (coastal) Antarctic troposphere associated with air mass exchange and with PSC sedimentation, respectively. The results are presented in Table 3 together with the observed deposition fluxes as well as with the (theoretical) global stratospheric production rates of these species. The overall influence of stratospheric air masses seen at coastal sites is estimated from the mean ^{10}Be/^{7}Be ratio (denoted by $R_{10/7}$) observed in aerosol sampled at NM [*Wagenbach*, 1996]. Under steady state conditions, $R_{10/7}$ is linearly related to the atmospheric residence time τ of the Be-bearing aerosol body in an isolated atmospheric box according to

$$R_{10/7} = \frac{P_{10}}{P_7}\left(1 + \frac{\tau}{\tau_7}\right)$$

with P_{10}/P_7 being the (uniform) ^{10}Be/^{7}Be production ratio and τ_7 the radioactive lifetime of ^{7}Be (i.e., 77 days). $R_{10/7}$ values are thus significantly higher in the stratosphere ($\tau \approx 1$ year) than in the troposphere, where τ is of the order of some weeks. Following *Raisbeck et al.* [1981], we calculated the influx rate of stratospheric ^{10}Be to the troposphere that is needed to maintain the mean $R_{10/7}$ value of 1.7 observed at NM by considering isotope mass balance of the Antarctic troposphere. The parameters still required for that mixing calculation are the ^{10}Be/^{7}Be production ratio, taken as 0.6 [*Dibb et al.*, 1994], the stratospheric $R_{10/7}$ value, calculated as 3.3 from τ (stratosphere) of 1 year, the tropospheric ^{10}Be production rate, taken as 0.01 at cm^{-2} s^{-1} [*Lal*, 1988], and τ in the Antarctic troposphere, assumed to be 30 days [*Shaw*, 1982].

Given a typical ^{10}Be atom concentration for the high-latitude lower stratosphere of 9.10^6 at m^{-3} STP [*Raisbeck and Yiou*, 1985], the ^{10}Be influx rate calculated via the above as procedure 0.54. 10^6 atoms cm^{-2} yr^{-1} corresponds to a stratospheric air mass influx rate (seen at NM) of close to 79 g cm^{-2} yr^{-1}. This number was used to derive the stratospheric nitrate and ^{3}H inputs associated with air mass exchange. In the case of nitrate we adopted for that calculation a lower stratospheric NO_y level of 3 ppbv from the data of *Fahey et al.* [1996], *Tuck et al.* [1994], and *Jones and MacKenzie* [1995] as representative for the winter Antarctic and midlatitude stratosphere. For ^{3}H we assumed a uniform water vapor mixing ratio in the lower stratosphere of 5 ppmv marked by a ^{3}H/H ratio of 5 10^{-13} (i.e., 5 10^5 TU) [*Schott*, 1991].

For the PSC sedimentation inputs of ^{3}H and nitrate we simply assumed that the missing stratospheric water vapor and HNO_3 inventories observed during the dehydration and denitrification of the winter Antarctic stratosphere is entirely carried by PSC particles into the upper Antarctic troposphere. Hence no attempts were made here to consider lateral exchanges across the boundary of the vortex. The annual PSC-related ^{3}H input given in Table 3 is derived from the depletion in the water vapor mixing ratio (~2.5 ppmv) observed by *Vömel et al.* [1995] over the altitude range of 12 to 20 km and the above stratospheric ^{3}H/H ratio. The annual PSC nitrate input was derived from the winter depletion of the total HNO_3 column reported by *Van Allen et al.* [1995] for south pole. Note that unlike the air mass exchange inputs, which are site specific since they are essentially based on ^{10}Be/^{7}Be ground level observations, the PSC-related inputs are taken as distributed homogeneously over the Antarctic continent.

In view of the crude estimates and the large uncertainties of

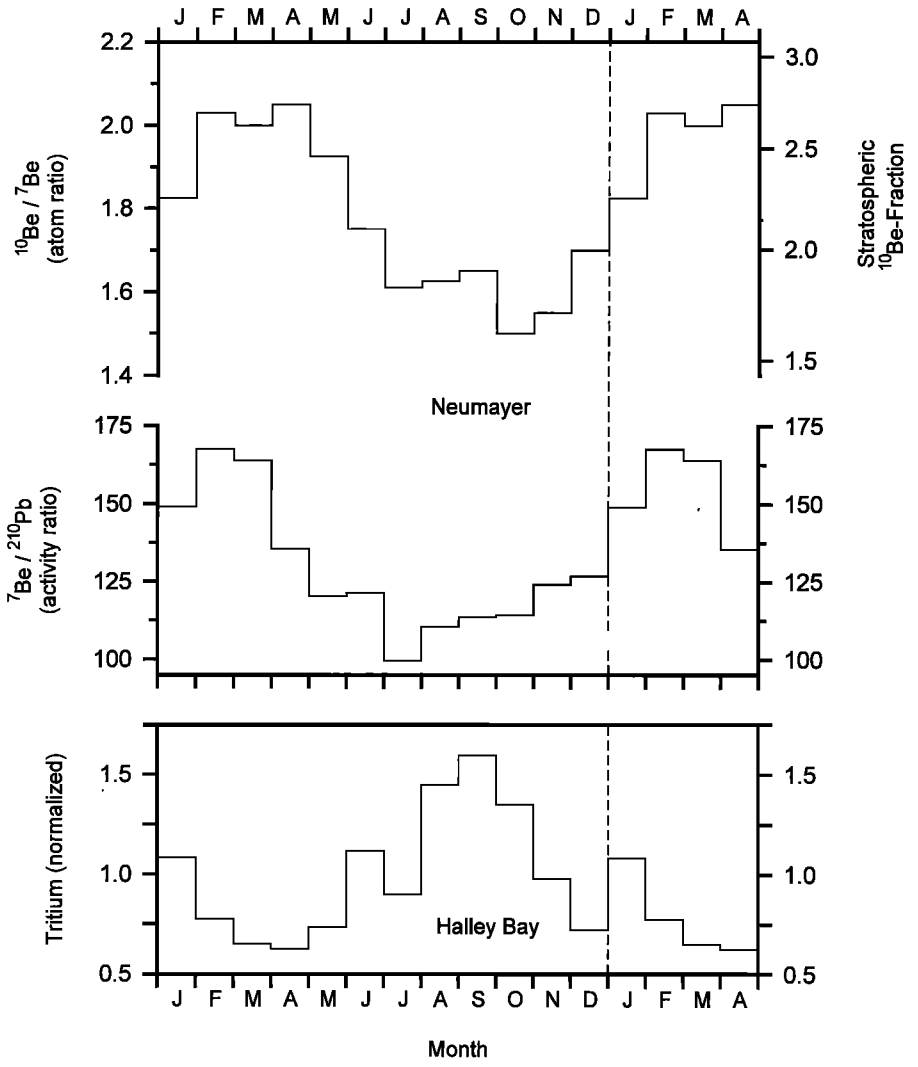

Figure 5. Seasonal pattern of the arrival of stratospheric aerosol tracers at Neumayer Station, indicated by enhanced ^{10}Be/^{7}Be (1983–1985) or ^{7}Be/^{210}Pb (1983–1993) ratios. The ^{7}Be/^{210}Pb ratio is displayed instead of ^{7}Be to compensate for changes in the downward transport from higher tropospheric levels. On the basis of stratospheric and tropospheric aerosol residence times of 15 and 1 months, respectively, the apparent stratospheric input flux, normalized to the tropospheric ^{10}Be production rate, is displayed on a nonlinear scale on the right-hand ordinate. To indicate the arrival of PSC-related material, tritium values are shown in monthly precipitation samples (normalized to the individual annual means) as reported by IAEA from Halley during 1983–1993 (adopted from *Wagenbach* [1996]).

the parameters used, the agreement between predicted stratospheric influx rates of ^{10}Be, ^{3}H, and nitrate and observed deposition rates is surprisingly good (see Table 3). This would leave little room for a supplementary tropospheric nitrate component. The deposition rate of stratospheric ^{10}Be which is obtained by subtracting the tropospheric contribution (roughly accounting for 33%) falls below the expected stratospheric input by a factor of 2. If real, this shortfall may imply an important horizontal ^{10}Be flux out of the lower Antarctic troposphere, that is, toward the surrounding areas where the aerosol lifetime is much shorter. This reasoning may not be valid for tritiated water vapor, which also can be removed by molecular exchange with the snow surface. Assuming that stratospheric nitrate would undergo a net outflow similar to that of ^{10}Be, the corresponding deposition flux would be lower by a factor of 2 than the expected total influx rate from the stratosphere of 2.1 μg cm^{-2} yr^{-1}. The deposition flux (based on the above calculation) of 1 μg cm^{-2} yr^{-1} stratospheric nitrate is still well within the range of the values typically observed in coastal areas. However, this does not hold true for low accumulation sites in central Antarctica (e.g., Dome C, Vostok) where the observed nitrate deposition fluxes [*Wolff*, 1995] are up to 1 order of magnitude lower than what can be expected (by a similar calculation based on ^{10}Be snow concentrations) from the stratospheric fraction alone. As addressed below, this points to a substantial net nitrate loss from such sites by remobilization out of the near surface firn layer.

Comparing the calculated stratospheric influx rates in Table 3 with the (theoretical) global stratospheric production rates, it appears that, as a result of the PSC sedimentation, the stratospheric odd nitrogen and ^{3}H inventories of the southern hemisphere are mainly leaking through the Antarctic tropopause, implying also a significant outflow toward lower latitudes. The same suggestion was made by Taylor [1968] for ^{3}H based on an

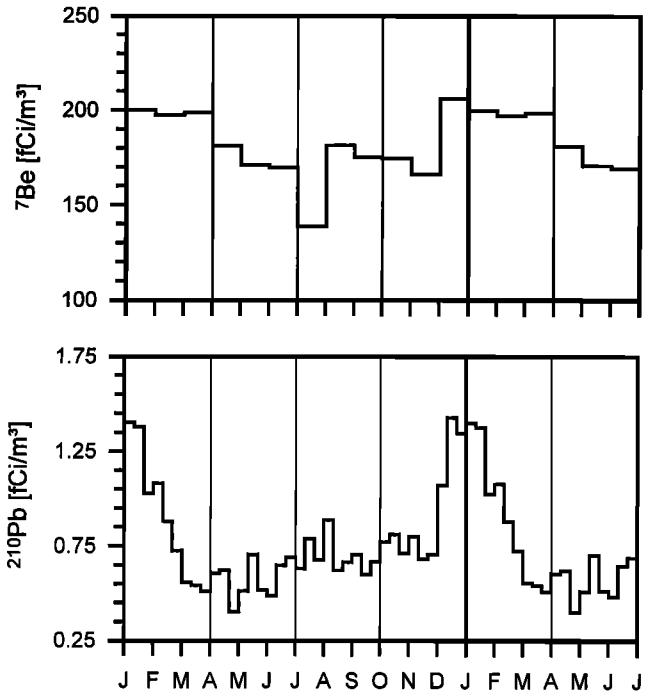

Figure 6. Mean annual cycles of atmospheric ^{7}Be and ^{210}Pb concentrations observed at Dumont D'Urville. The monthly ^{7}Be means are taken from *Lambert et al.* [1990]; 10 day means of ^{210}Pb are calculated from daily observations (G. Lambert, personal communication, 1996) over the years 1990–1992.

evaluation of the phase shift in the southern hemisphere ^{90}Sr and ^{3}H seasonal cycles, although PSCs were not considered. In conclusion, the observed net nitrate deposition in Antarctica may be entirely explained by stratospheric nitrate with almost 80% provided by PSC sedimentation.

4.3. Nitrate Reemission From Snow

Another potential source of nitrate to Antarctic boundary layer air is the reemission of nitrate from surface snow or firn, both in central and coastal Antarctica. This nitrate must already have been deposited and therefore does not represent a net source. It is nonetheless important as it could alter the seasonality, interannual variability, and isotopic properties of the nitrate signal seen in coastal air.

At sites with very low snow accumulation rates (mainly in central Antarctica), there is clear evidence of a slow reemission of nitrate from the top meter of snow [*Mayewski and Legrand*, 1990; *Wolff*, 1995; *Legrand et al.*, 1996]. This appears at sites such as Dome C and Vostok as a decrease from concentrations of 100 ng g^{-1} at the surface, to less than 20 ng g^{-1} at about 1 m depth [*Mayewski and Legrand*, 1990], implying a process occurring over a period of about 10 years. Extraordinarily high δ^{15}N-nitrate values in deeper ice at Dome C [*Freyer et al.*, 1996] are also probably a result of kinetic fractionation operating during this reemission process. Although this slow reemission is probably mainly confined to sites with less than 5.0 g cm^{-2} yr^{-1} snow accumulation, at south pole (8.5 g cm^{-2} yr^{-1} snow accumulation) a reduction with depth in the amplitude of near-surface seasonal peaks in nitrate is probably also due to a less severe version of this process [*Dibb and Whitlow*, 1996]. A similar smoothing was observed in coastal firn cores at Berkner Island (17 g cm^{-2} yr^{-1} of snow accumulation) by *Wagenbach et al.* [1994].

A second process appears to be the much faster emission occurring in probably a matter of days after deposition. This has been reported at a coastal site, where very high nitrate concentrations in fresh snow (300 ng g^{-1} or more) decayed to generally <100 ng g^{-1} in older surface snow, over a period of a few days [*Neubauer and Heumann*, 1988a]. At Halley (HB), however, surface snow was collected daily over almost 3 years (see Figure 3), and significant losses from one day to the next were not observed [*Mulvaney et al.*, this issue]. Fresh snow collected at all three stations (HB, NM, and DDU) has an average concentration higher than that seen in nearby cores (Table 4), and a few very high concentrations of 300 ng g^{-1} or more are seen in fresh snow at all three sites, but never seen in deeper firn. Therefore, although the evidence is unclear, it appears likely that there is a fast (days) attenuation of some very high initial concentrations and thereafter a slower loss (<1 year) from the upper tens of centimeters of the firn even at coastal sites.

We now estimate the importance of these reemitted nitrate fluxes on the observed atmospheric records. For the slow emission in central Antarctica the concentration typically decays from 100 to 20 ng g^{-1}. At a typical site with a snow accumulation rate of 5.0 g cm^{-2} yr^{-1} this amounts to a nitrate loss rate of 0.4 μg cm^{-2} yr^{-1}, which would be sufficient to replenish the nitrate inventory of a roughly 200 m thick column of the atmospheric boundary layer every day. Assuming that this slow loss occurs at all sites with snow accumulation rates less than

Table 3. Estimates of Stratospheric Influx Rates of Nitrate and Cosmogenic Radioisotopes to the Coastal Antarctic Troposphere in Comparison to Observed Deposition and Theoretical Production Rates

	^{10}Be, 10^{6} at cm^{-2} yr^{-1}	^{3}H, 10^{6} at cm^{-2} yr^{-1}	Nitrate, μg cm^{-2} yr^{-1}
Stratospheric influx rates			
Air mass exchange	0.54	7.9	0.5
PSC sedimentation	...	7	1.6
Total	0.54	14.9	2.1
Observed surface deposition fluxes	0.4	20*	(0.6–1.5)†
Global stratospheric production rate	1.1‡	6.9‡	0.45§

*Recent ^{3}H in precipitation at Halley Bay [*IAEA*, 1986, 1990; K. Rozanski, personal communication, 1995].

†Depicted from compilation of *Mulvaney and Wolff* [1994] for coastal sites with an annual snow deposition larger than 14 cm H_2O.

‡*Lal and Peters* [1967].

§*Levy et al.* [1980], photochemical N_2O oxidation only.

Table 4. Concentrations of Nitrate in Fresh Snow and in Firn Cores Drilled Close to Coastal Antarctic Stations

Station	Fresh Snow, ng g^{-1}	Core Site	Firn Core, ng g^{-1}	Reference for Core Data
Dumont d'Urville	65*	D10†, 4 km south	38	*Legrand and Delmas* [1985]
Halley	84‡	Halley	64§	*Mulvaney et al.* [this issue]
Neumayer	79‖	Ekstrøm Shelf Ice, 40 km south	42	*Moser* [1991]

*Average of fresh snow collected at Dumont d'Urville, January 1991 to December 1993, but includes less summer samples as snow melts at this station in summer.

†Average of upper 14–30 m.

‡Average of accumulated snow collected at Halley, January 1991 to December 1992, but may include drifted as well as fresh snow (see Figure 3).

§Average of 0.3 to 2.4 m depth.

‖Average of fresh snow collected at Neumayer, January 1984 to December 1992.

10 g cm^{-2} yr^{-1} (which then includes sites with the smaller effect as seen at south pole), we can estimate that outgassing over the relevant area of about 6 million km^2 contributes 0.02 Tg yr^{-1} of nitrate. This estimate has to be compared to about 0.28 Tg (as nitrate) calculated for the total stratospheric nitrate source from Table 3 (i.e., 2.1 μg cm^{-2} yr^{-1} over an area of ~12 million km^2) and suggests that this should not be an important source to the Antarctic atmosphere as a whole. It might be important, however, for near-surface air in some seasons.

Losses occurring over a longer time period (<1 year) from coastal snow could play a role in modulating the seasonal signal. Calculations similar to those carried out for central Antarctica and based on Table 4 would suggest a comparable source strength (loss of 20 ng g^{-1} associated with a snow accumulation of 30 g cm^{-2} yr^{-1}, leading to a loss rate of 0.6 μg cm^{-2} yr^{-1} over some millions of square kilometers). Although small compared for instance to the total stratospheric input, this emission, though rather uncertain, could make a major impact on a surface inversion layer if it persisted for a longer time period. Note also that the reemitted nitrate, if not instantaneously removed from the boundary layer, may be deposited again. Because we do not know the exact loss mechanism, it is hard to estimate the likely seasonality of the reemitted nitrate. If either photochemistry [*Neubauer and Heumann*, 1988b] or a temperature-dependent air-surface equilibrium were involved, then we might expect maximum loss during summer. However, losses may also be due to changes in grain size and specific surface area during metamorphosis and could occur throughout the year.

4.4. Seasonal Changes

On the basis of the previous evaluation of major nitrate sources we may expect for the seasonal timing of nitrate seen in the coastal Antarctic boundary layer the following pattern:

1. A midsummer maximum for continental nitrate is suggested by the mineral dust [*Wagenbach*, 1996], ^{210}Pb-^{222}Rn [*Lambert et al.*, 1990], and black carbon cycles [*Wolff and Cachier*, this issue] and appears to be mainly driven by enhanced meridional long-range transport and a less frequent surface inversion during that time of the year.

2. Following *Poole and Pitts* [1994], significant PSC sighting probabilities typically prevail (depending on longitude) between mid-May and early October with maximum values seen in August at an altitude range of 18–20 km. There is no precise information on the representative settling velocity associated with the downward transport of the major PSC mass load. Indirect observations are restricted to single events (and particle size modes) only and range from 26 km/month [*Vömel et al.*, 1997] and 10 km/month [*Vömel et al.*, 1995] down to 3.5 km/month [*David*, 1995]. Estimates on the arrival of PSC-related signals are therefore extremely uncertain. Disregarding differences in the timing and size distribution of PSC 1 (nitric acid-water mixture) and PSC 2 (mainly water ice) particles, we speculate that the PSC nitrate and ^{3}H signals may arrive concurrently in the upper troposphere several weeks after PSC formation. Considering a tropospheric residence time of 1 month, this would be in reasonable agreement with the maximum values in the abundance of ^{3}H which are observed in fresh snow at Halley between August and October [*IAEA*, 1986, 1990] (see Figure 5), in atmospheric water vapor at NM between mid-July and mid-September (I. Levin, personal communication, 1996), and in central Antarctic firn during the stratigraphical winter half year [*Jouzel et al.*, 1979]. For unknown reasons the absolute atmospheric nitrate maximum is delayed, however, by up to 2 months with respect to the absolute ^{3}H maximum, complicating a straightforward link with PSC nitrate.

3. For the stratospheric nitrate delivered by air mass exchange, enhanced values should be seen in late summer to fall according to seasonal cycles of the ^{10}Be/^{7}Be or ^{7}Be/^{210}Pb ratios (see Figure 5).

4. For regionally reemitted nitrate the seasonality remains unclear, but if there is a substantial signal, we would expect a contribution delayed by some weeks from the time generally showing maximum nitrate concentrations in surface snow. Referring to the nitrate record recovered by daily surface snow sampling at Halley [*Mulvaney et al.*, this issue] and displayed in Figure 3, the relevant period may be between September and March.

This picture may qualitatively explain the secondary winter nitrate peak around August and the secondary summer nitrate peak in February as stratospheric inputs related to PSC and air mass exchange, respectively, leaving, however, the main nitrate events in November (NM, Mawson) and December (DDU) still partly unexplained.

We therefore made an attempt to quantify the seasonal change in the atmospheric near-surface nitrate load expected from stratosphere/troposphere air mass exchange on the basis of the observed annual cycles of the atmospheric ^{10}Be record at NM. Here a constant nitrate to ^{10}Be ratio of 13 10^{-6} μg m^{-1} is taken from the respective mean stratospheric input rates given in Table 3 and multiplied by the mean annual ^{10}Be

cycle at NM after correcting it for the tropospheric ^{10}Be contribution. This correction was based on the mean annual cycle of the stratospheric ^{10}Be influx rate J_{10} (calculated as described in section 4.2) as

$$[^{10}Be]_{str} = [^{10}Be]_{tot}\left(1 + \frac{P_{10}}{J_{10}}\right)^{-1}$$

with $[^{10}Be]_{str}$ denoting the stratospheric fraction of the total ^{10}Be concentration $[^{10}Be]_{tot}$ observed at NM. The resulting annual nitrate cycle associated with stratospheric air mass exchange fractions estimated in this way is shown in Figure 7 together with the NM cycle of the tropospheric nitrate fraction previously derived via ^{210}Pb using a nitrate to ^{210}Pb ratio in the continental outflow of 15 ng fCi^{-1}. The seasonal nitrate maximum associated with stratospheric air mass exchange corresponds quite well with the observed February nitrate peak, whereas the expected tropospheric (continental) contribution does not add substantially to the observed nitrate variability.

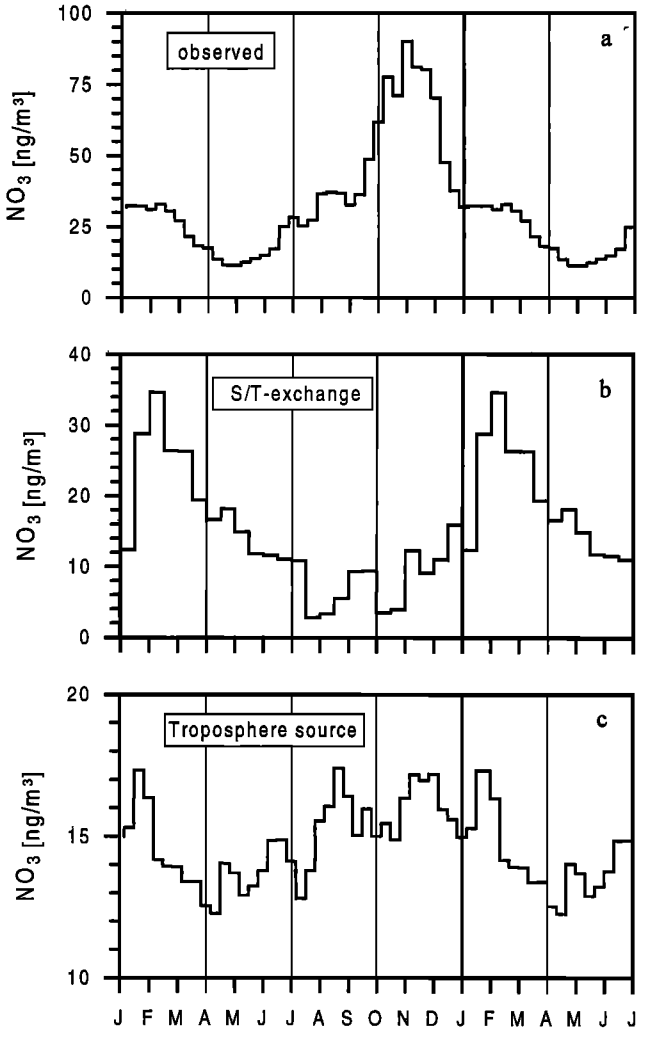

Figure 7. Observed and predicted mean annual cycles of atmospheric nitrate at Neumayer station dissected in different source components (see text): (a) observed cycle 1983–1995, same as in Figure 4, (b) nitrate related to stratospheric air mass exchange derived from ^{10}Be and ^{7}Be records, and (c) continental nitrate component derived from ^{210}Pb cycle using an initial nitrate/^{210}Pb ratio of 17 ng fCi^{-1}.

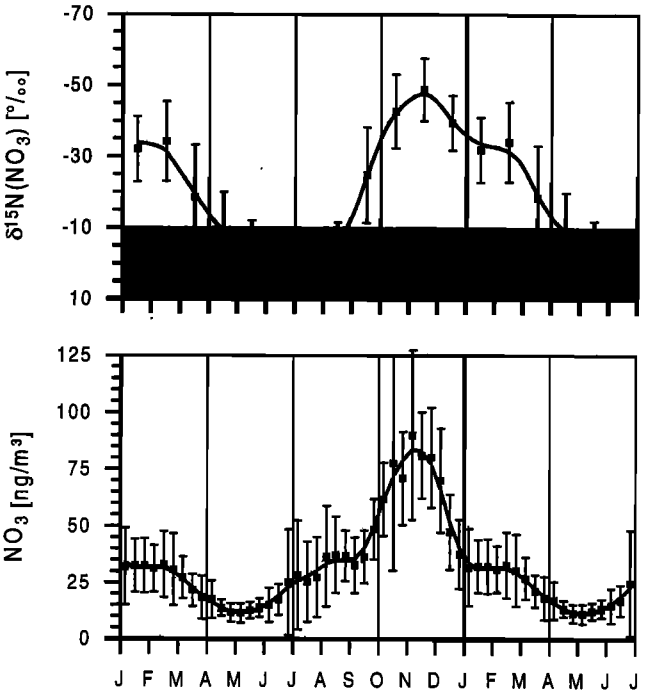

Figure 8. Mean annual cycles of atmospheric nitrate (1983–1995) at Neumayer and of $\delta^{15}N$ in nitrate (displayed as monthly means from composite samples for the years 1986–1992). Error bars refer to the $\pm 1\ \sigma$ standard deviation in the interannual variability. Solid lines are derived by spline smoothing. Shaded area for $\delta^{15}N$ indicates the overall range commonly observed in tropospheric nitrate.

Obviously, these two predicted nitrate fractions are not able to fully explain the observed seasonality. In view of the still ambiguous source apportionment for the dominant November nitrate peak we have some preliminary evidence from the continuous ^{3}H records in atmospheric water vapor investigated at NM (I. Levin, personal communication, 1996) that this main nitrate event might be also associated with PSC nitrate. This is because the most prominent positive ^{3}H-excess values as defined by the deviation of the atmospheric ^{3}H concentration (expressed in Bq m^{-3}) from its mean annual cycle (which is strongly governed by the seasonality of the absolute humidity) regularly appears in November.

Furthermore, we gained independent evidence from the isotopic signature of nitrate nitrogen at NM that a common non-tropospheric source may be responsible for the nitrate signal whenever it is significantly above the background level. Typical $\delta^{15}N$ values (defined as the per mil deviation of the $^{15}N/^{14}N$ ratio relative to atmospheric N_2) of troposopheric nitrate and NO_x species are generally found to be within a range of $\pm 10‰$ [*Moore*, 1977]. For example, nitrate in South African precipitation exhibited a range around -7 to $+3‰$ [*Heaton*, 1987]. As shown by the mean seasonal $\delta^{15}N$ cycle displayed in Figure 8, such typical $\delta^{15}N$ values are only seen at NM for the background nitrate level (April–June) which is easily explained by continental sources. An extraordinary ^{15}N depletion, however, of up to $-50‰$ shows up in covariance with the enhanced nitrate concentration, suggesting, at least, a qualitative agreement among the different nitrate peak modes regularly appearing between August and March. Note that for unknown reasons the onset of the $\delta^{15}N$ decrease is delayed by roughly 1

month with respect to the (PSC related) nitrate increase starting in midwinter. We do not know the fractionation process or any correspondingly depleted nitrate source which may govern this extremely strong ^{15}N depletion (in particular, no experimental data on $\delta^{15}N$ in stratospheric odd nitrogen species exist), preventing use of the isotopic evidence for a quantitative source apportionment. Although nitrate slowly reemitted from central Antarctic firn is likely to be depleted in ^{15}N by some ten per mil (according to the $\delta^{15}N$ firn data by Freyer et al. [1996]), no substantial contribution of this source is expected for the isotopic nitrate signal seen in the coastal Antarctic troposphere (see section 4.3). Despite the basic uncertainty, the $\delta^{15}N$ evidence strongly suggests that at NM the absolute nitrate maximum in November is also mainly associated with a nontropospheric source which (like the secondary peaks around August and February) is most likely of stratospheric origin.

With respect to the other coastal sites, the situation for the seasonal nitrate cycle at Mawson appears to be quite similar to that at NM since the seasonal cycles of both ^{7}Be and ^{210}Pb show no big intersite differences [*Savoie et al.*, 1992]. As shown in Figure 6, the situation at DDU is more complex due to the strong ^{210}Pb summer peak (somewhat lagging nitrate) and the surprisingly high ^{7}Be level (almost twice as high as at NM and Mawson). Since there is no ^{10}Be information available at DDU, it is hard to elucidate the net stratospheric air mass influence on the broad summer nitrate peak around December–January. Nevertheless, the observation of an unresolved late summer nitrate peak at DDU which is otherwise clearly seen around February at NM and Mawson (see Figure 4) might be simply due to the generally higher level of stratospheric (or upper tropospheric) aerosol species at DDU during that time possibly masking the relatively weak early summer nitrate peak there. As shown by *Savoie et al.* [1993], the seasonal nitrate cycle at the far north site Palmer is rather flat and delayed with respect to the other sites, although exhibiting a quite similar nitrate background (see also intersite comparison in Table 2). Such a meridional difference may be anticipated if, as proposed here, the major nitrate inputs above background occur from the stratosphere via PSC sedimentation within the polar vortex.

5. Summary and Conclusions

Multiyear records of atmospheric nitrate obtained by continuous aerosol sampling at two sites in the Atlantic and Pacific sector of coastal Antarctica revealed the following:

1. There is a remaining uncertainty about the reliability of such records in terms of the total nitrate sampled and of the contamination risk (although small) from local ornithogenic soil, which should be carefully considered in future studies.

2. Although background nitrate levels are uniformly distributed throughout coastal Antarctica, different levels and seasonal timings are seen in the annual nitrate maximum. This major nitrate peak regularly appears at all sites between late spring and midsummer and increases systematically with the latitude of the site.

A crude source apportionment of the mean near-surface nitrate level in coastal Antarctica via concurrent mineral dust and radioisotope records (^{7}Be, ^{10}Be, ^{210}Pb, ^{3}H) and the relative abundance of these tracers with respect to the free tropospheric and stratospheric nitrate inventories suggests the following:

1. Continental sources can explain the background nitrate level and may also contribute substantially to the Antarctic nitrate budget but are probably not the dominant sources.

2. The stratospheric nitrate (and also the ^{3}H) source to the Antarctic troposphere is governed by the sedimentation of PSCs and may provide the major depositional flux to the Antarctic ice sheet, making again continental sources relatively unimportant. This nitrate input may be partially masked by an apparent reemission flux most relevant in low snow accumulation areas of central Antarctica.

Evaluation of the seasonal nitrate variability revealed that the secondary winter peak around August and the secondary summer peak in February are most likely associated with PSC sedimentation and stratospheric air mass exchange, respectively. Indirect evidence for a stratospheric origin of the major nitrate peak, regularly occurring in November at Neumayer comes from concurrent $\delta^{15}N$-nitrate values much lower than hitherto observed in tropospheric samples.

In order to obtain a comprehensive picture on the Antarctic nitrate issue which can eventually be used for the interpretation of nitrate ice core signals, atmospheric records from the interior of the continent are still required. Backing up such atmospheric observations with concurrent records and snow profiles of isotopic tracers (as ^{10}Be, ^{7}Be, ^{222}Rn, ^{210}Pb, ^{3}H, and $\delta^{15}N$) would greatly help the quantification of the various source contributions and also give information on the competitive nitrate reemission process operating in near-surface firn. However, representative concentrations of the above isotope species in the stratosphere and upper troposphere needed to gain a quantitative source apportionment of Antarctic surface nitrate are not available yet.

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