Ice-core evidence for a small solar-source of atmospheric nitrate

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Abstract. A precision-dated ice-core nitrate record from Law Dome, coastal East Antarctica is compared to the timing of known solar proton events and geomagnetic storms over the period 1888 to 1995. We find statistical evidence for a significant ($P < 0.03$) but small elevation in mean nitrate concentrations following the solar events (11% over the 12 months beginning 3 months post-event). While some solar events are identifiable in the nitrate record, most are not distinguishable from the background noisy signal (which has numerous large peaks), and some solar events show no nitrate elevation above even mean levels.

Introduction

Considerable uncertainties exist regarding atmospheric nitrate sources and their relative strengths [*Legrand and Kirchner*, 1990]. Odd nitrogen species, precursors for atmospheric nitrate, are produced by solar proton events [*Crutzen et al.*, 1975; *Rusch et al.*, 1981; *Jackman et al.*, 1993], however ice core studies have provided conflicting data regarding the significance of such production in the overall budget. In particular, some authors [*Dreschhoff and Zeller*, 1990, 1998; *Shea et al.*, 1999] report the existence of relatively short-lived, but large, nitrate enhancements in polar snow following solar proton events while others [*Legrand and Kirchner*, 1990; *Legrand and Delmas*, 1986; *Herron*, 1982; *Mosley-Thompson et al.*, 1991] find no such effect.

This study is based upon a nitrate record from the DSS97 ice core, recovered in November 1997 from a site ($66\ 47^0$S, $112\ 49^0$E) 5.5 km S of the summit of Law Dome, East Antarctica. The high accumulation and the absence of strong katabatic winds at Law Dome [*Morgan et al.*, 1997] result in exceptionally well-preserved stratigraphy. This is evident in readily identifiable seasonal variations in water isotopes [*van Ommen and Morgan*, 1997; *Morgan and van Ommen*, 1997], major ions [*Curran et al.*, 1998] and peroxides[*van Ommen and Morgan*, 1996]. High-resolution sampling (12 samples per annual-layer) of cores from the region not only allows precision dating of individual cores by layer counting in several parameters, but also provides unambiguous registration of sub-seasonal features between separate cores up to 16 km apart. In this way, the DSS97 layer-counted chronology has been cross-validated against DSS core [*Morgan et al.*, 1997] (0.9 km N of DSS97), the DE08 core [*Morgan et al.*, 1991] (16 km E) and the BHD core [*Morgan*, 1985] (5.5 km N). This cross-validation provides reference-horizon checks from several volcanic events seen in DSS and atmospheric nuclear tests (1965) seen in BHD.

The resolution of the records is illustrated by the fact that oxygen isotopes and peroxide data show an average 3-week lag between the peroxide 'mid-summer' peak and the isotopic 'mid-summer' peak, which has been interpreted as the lag between radiation maximum at the solstice and temperature maximum somewhat later [*van Ommen and Morgan*, 1996]. Also, the good agreement between isotope seasonality and measured temperature seasonality [*van Ommen and Morgan*, 1997] indicates that the records are not affected by strong seasonal bias in accumulation.

Methods

The DSS97 ice core was sampled at 5 cm intervals using clean techniques [*Curran et al.*, 1998]. High-resolution sampling of the core provided around 20 samples per annual layer at the top of the core, decreasing to around 12 samples at 96 m (age 100 yr). Since the sampling density varies considerably with depth, the data presented here have been averaged down to 12 samples-per-year and interpolated onto a uniform scale. Annual dating horizons are adopted that align the year origin with the oxygen isotope mid-summer peak. On average this has the effect of placing the nitrate dating 10 days behind the actual calendar [*van Ommen and Morgan*, 1996]. Thus the "first" month in a nitrate year is centred on January 10, which is sufficiently close to mid-month for the comparisons in this study.

The ice cores were analyzed for a range of ions using suppressed ion chromatography techniques [*Legrand et al.*, 1993] and Dionex equipment. Nitrate and other anions were preconcentrated from a 6 mL sample using a 4 mm TAC-LP1 concentrator column and determined on a DX500 ion chromatograph with a 2 mm Ionpac AS14 column. Nitrate eluted at 12 minutes using a gradient method with a sodium tetraborate eluent.

Results

The nitrate record (Figure 1) from the DSS97 ice core spans the period 1888–1995 with a mean concentration of 0.288 μEq/L ($\sigma = 0.057\mu$Eq/L for 1-year averages), which is similar to that found at other Antarctic sites when consideration is made for accumulation and elevation differences [*Mulvaney and Wolff*, 1993]. The record is noisy with many

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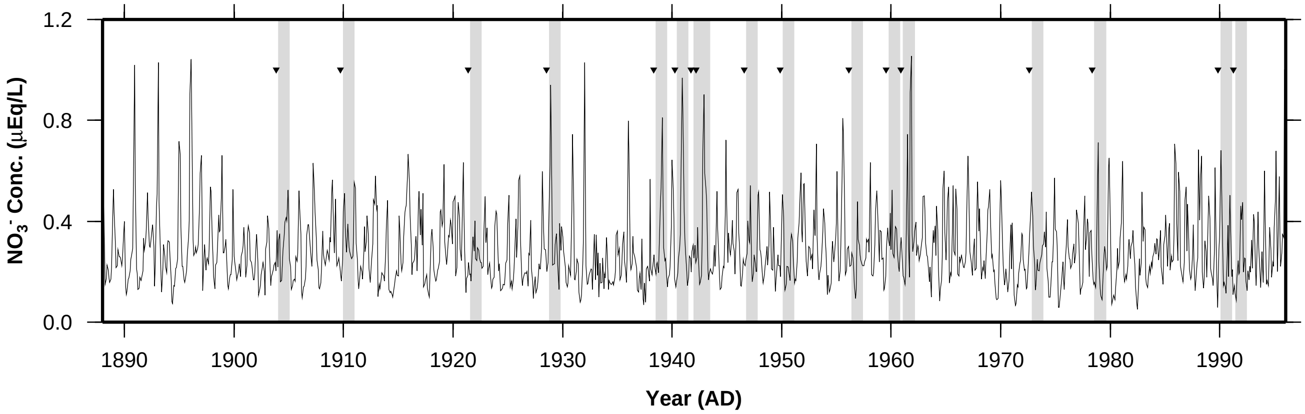

Figure 1. Nitrate record and solar events, 1888 to 1995. Small markers denote epochs of events from Table 1, and shaded bars indicate the 3-month lagged, 1-year intervals described in the text. Dating of the ice-core record over this period is absolutely unambiguous at the annual level and typically resolved with an accuracy of a month (see text).

nitrate peaks above the typical summer envelope. Possible sources and transport mechanisms that may produce such peaks include spring deposition from polar stratospheric cloud (PSC) sedimentation, and advection of low latitude air over Law Dome as this site is dominated by marine air [*Curran et al.*, 1998]. The presence of high peaks in this record and the existing debate surrounding the putative link between solar-events and nitrate peaks leads us to investigate whether these data support such a connection.

To compare, we use events listed by *Shea et al.* [1999] covering the period 1942–1995 and augment these with the July 1928 white-light flare [*Dreschhoff and Zeller*, 1990], and the Royal Greenwich Observatory's tabulation of "The Greatest Storms" (1874–1954) [*Royal Greenwich Observatory*, 1955] (see Table 1). The latter source clearly only gives a possible indicator of proton-events, and will not necessarily correlate as well with potential nitrate production as the 1942–1995 events which are based on direct particle flux measurements (either from earth or space-borne detectors). From Figure 1 it is possible that some of the higher peaks do appear in proximity with events, but it is clearly not a general relationship as exemplified by the large solar event of 1972 [*Legrand and Kirchner*, 1990; *Dreschhoff and Zeller*, 1990; *Mosley-Thompson et al.*, 1991] which is not evident in our record. More generally, comparison of the fluences listed by *Shea et al.* [1999] for the 1942–1995 events reveals no correlation with nitrate concentrations. Also, several large nitrate peaks appear which are not readily associated with any solar events. Hence a statistical approach has been adopted.

Ensemble-mean nitrate data following the 17 event years were computed and compared to the population as a whole, the null-hypothesis being that both populations share the same distribution. Standard t-test significances are quoted in this discussion, however alternative statistical tests were also used and we return to this issue shortly. The mean flux in the 12-months following the events was elevated with respect to the population as a whole, by 7% ($P < 0.08$).

Table 1. List of solar events used in this study

Event(s)[a]	Year	$[NO_3^-]$[b]	Ref.
31/10	1903	0.334	1
25/9	1909	0.334	1,2
13/5	1921	0.273	1
15/7	1928	0.389	2
25/1; 16/4	1938	0.353	1
24/3	1940	0.405	1
1/3; 18/9	1941	0.341	3
28/2; 7/3	1942	0.379	3
28/3; 25/7	1946	0.279	3
19/11	1949	0.242	3
23/2	1956	0.247	3
10-12/5; 17/7	1959	0.320	3
4/5; 15/11	1960	0.437	3
7/8	1972	0.246	3
7/5	1978	0.268	3
12-18/8; 29/9; 30/10	1989	0.328	3
26/3	1991	0.259	3

[a] Day/month of events in that calendar year.
[b] Mean concentration (Eq/L) over 12 months beginning 3 months after the last event in that year.
References: 1–*Royal Greenwich Observatory* [1955]; 2–*Dreschhoff et al.* [1990]; 3–*Shea et al.* [1999]

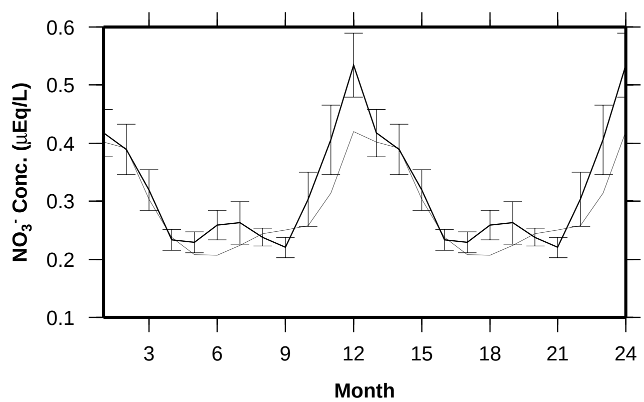

Figure 2. Mean annual cycles in nitrate. Bold curve is the ensemble mean of the 17 solar-event years and the fine curve is the mean for the entire 1888-1995 time-period. Error bars are ±1 standard errors in the mean of the 17 event years.
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This elevation is further enhanced to 11% ($P < 0.02$) if the "event-window" is lagged by 3 months from the actual event date (i.e. an average from 3 to 14 months post-event, which is thus centered 8-9 months following the event). In the following we shall denote this as the "maximum annual enhancement". The elevated nitrate at some months' lag reflects the time taken for the nitrate to reach the continent from the upper atmospheric layers. Varying this lag through a 160 month window showed no other significant correlations (i.e. correlations with $P < 0.1$). Likewise, instantaneous monthly values for the events were compared to the population mean and a significant elevation (22%, $P < 0.04$) was detected at a lag of 8 months post-event (we denote this as the "maximum monthly enhancement"). Indeed significantly elevated ($P < 0.1$) monthly values were seen at lags between 7 and 11 months inclusive. Note that this maximum monthly enhancement at some 8 months post-event is consistent with the central lag of the maximum annual enhancement. As a complementary and non-parametric statistical test, the above significances were also assessed using the Mann-Whitney statistic. The 11% maximum annual enhancement remains significant with $P < 0.03$, but the 22% maximum monthly enhancement is no longer significant, with a null probability of 0.22. A final test of these significances was undertaken using a "bootstrapping" technique [*von Storch and Zwiers*, 1999], wherein candidate sets of 17 randomly generated "events" were compared to the given ensemble of events. Over 10000 resamplings the enhanced nitrate levels noted above remained significant, with $P < 0.013$ for the maximum annual enhancement and $P < 0.046$ for the maximum monthly enhancement.

Discussion and Conclusion

The mean annual cycles for the 17 solar-event years and the whole record were computed and are shown in Figure **??**. The solar-event ensemble-mean shows an enhancement in nitrate during the early austral winter months (months 5-7), with a mean of 0.250μEq/L ($\sigma = 0.113, N = 51$) compared to the same three months in all years, which have mean 0.213μEq/L ($\sigma = 0.0926, N = 324$). This elevation is significant, with $P < 0.005$ (t-test). Likewise the solar-event ensemble-mean is elevated in the early austral summer months (months 10-12), with a mean of 0.414μEq/L ($\sigma = 0.216, N = 51$) compared to the same three months in all years, which have mean 0.330μEq/L ($\sigma = 0.152, N = 324$). This elevation is significant, with $P < 0.0003$ (t-test).

The spring nitrate enhancement has been observed in other ice core [*Mulvaney and Wolff*, 1993; *Mayewski and Legrand*, 1990] and aerosol records [*Wagenbach et al.*, 1998] and is attributed to sedimentation of PSCs. The polar vortex dominates atmospheric transport from the stratosphere to the troposphere during the winter with the vortex strongest south of 80 S latitude and weakening towards the coast [*Fromm et al.*, 1997]. Law Dome, at 67 S latitude is likely to be only marginally influenced by air-masses from within the vortex region during the winter. It is known that observations of PSCs are rare in the region [*Fromm et al.*, 1997] and that air-masses of cyclonic, maritime origin dominate. Thus, the spring enhancement at Law Dome probably accompanies the outflow of nitrate enriched stratospheric air-masses during the decay of the vortex itself. On the other hand, the early-winter peak is most probably nitrate produced in the preceding months (even into the preceding winter, but outside the vortex) and arriving with the maritime air. Such production is likely, since the auroral zone is certainly not confined to within the polar vortex. This more general mixing outside of the vortex is also more consistent with the several months to 1-year delay seen here between events and deposition, since areas outside the vortex lack the potential rapid mechanism of precipitation from the stratospheric clouds.

It is known from observations of volcanic fallout [*Morgan et al.*, 1997] that Law Dome is not as sensitive to stratospheric air masses as high-plateau sites, partly because of its maritime exposure, but also because of dilution effects of the high accumulation. In light of this and the uncertainties in deposition relating to timing of vortex formation, breakdown and the stochastic nature of precipitation events, it is not surprising that stronger or more reliable enhancements are not seen.

Nevertheless, it would appear that there is a detectable solar contribution to the nitrate budget, at least at Law Dome, but this falls short of the impulsive, readily identifiable temporal markers suggested by other workers. On average, this production takes several months to reach peak deposition rates and somewhat over a year to return to baseline levels. The noisy nature of the nitrate record and the present inability to identify sources for many of the larger events sounds a cautionary note for registering peaks with solar events in the absence of sufficient corroborating chronological control. Certainly, on present evidence, hopes of reconstructing paleorecords of short-lived solar events from records of ice-core nitrates are unlikely to be realized.

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