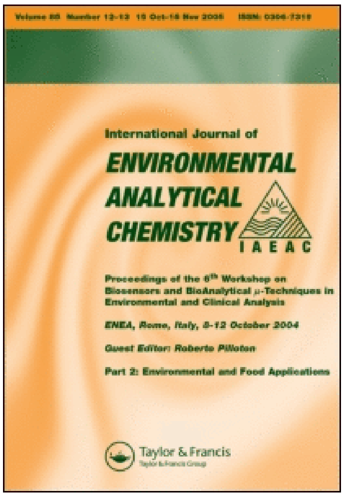

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Spatial and temporal distribution of environmental markers from Coastal to Plateau areas in Antarctica by firn core chemical analysis

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SPATIAL AND TEMPORAL DISTRIBUTION OF ENVIRONMENTAL MARKERS FROM COASTAL TO PLATEAU AREAS IN ANTARCTICA BY FIRN CORE CHEMICAL ANALYSIS

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The chemical analysis of shallow firn cores sampled in coastal and plateau areas in Northern Victoria Land and along a transect from Talos Dome to Dome C (East Antarctica, Pacific Ocean sector) allowed a global view of spatial and temporal changes in chemical composition of snow depositions over the last 100 years. Variations in concentration of primary (sea spray) and secondary (biogenic emission, atmospheric inputs) source markers were observed and discussed as a function of distance from the sea and altitude.

In the stations characterized by relatively high snow accumulation rates, the sub-sampling resolution was sufficient to obtain a stratigraphic dating by using the periodical variations of seasonal markers. In these stations, a subdivision in "summer" and "winter" samples was carried out in order to study the seasonal changes of the contributions of the measured compounds to the snow composition as elevation and distance from the sea increase.

Some evidence of post-depositional effects which are able to change the original deposition of chloride and nitrate, was observed at stations with low accumulation rates. The reliability of the depth/concentration profile of these substances for reconstructing past deposition was also discussed.

Keywords: Firn cores; Antarctica; Spatial distribution; Post-deposition effects; Ion chromatography

INTRODUCTION

Polar ice caps represent a powerful and unique archive of past climatic and environmental changes and offer the possibility of understanding the forcing factors and the positive and negative feedback mechanisms of the climatic system of the Earth [1–5]. Ice cores drilled in Greenland and Antarctic ice sheets allow a detailed reconstruction of the chemical composition of snow precipitation with a temporal resolution and over time periods that depend on the depth of the ice cap and on the snow accumulation rate

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at the sampling station. Among the several ice coring projects in progress at present, EPICA (European Project for Ice Coring in Antarctica) aims to obtain paleo-climatic and paleo-environmental information for the last 500 000 years from a deep ice core drilled at Dome C (Pacific/Indian Ocean sector, East Antarctica) [6–11]. However, a reliable relationship between glaciological data and paleo-atmospheric composition is closely dependent on our understanding of how changes in source intensity and transport efficiency can be memorised in the snow in different climatic conditions, and how changes in chemical and physical features of snow deposition (e.g., accumulation rate, snow acidity, temperature), varying the depositional and post-depositional processes, affect the ice layer composition [12–17]. Therefore, for a better understanding of paleo-data coming from the Dome C area, it is necessary to study the present relationship between atmospheric aerosol composition and snow chemistry, assessing the spatial and temporal (over the last decades) distribution of compounds that can be used as reliable markers of aerosol sources and of transport and depositional processes. It is also very important to evaluate the real significance of their signatures in the snow layers i.e., whether the observed parameters are conservative in the ice.

In order to study the spatial and temporal distribution of aerosol components in the Pacific/Indian Ocean sector of East Antarctica, several stations located at different altitudes and distances from the sea were sampled during the Italian Antarctic Campaigns from 1991/92 to 1998/99, in the framework of the PNRA (Progetto Nazionale di Ricerche in Antartide) and ITASE (International Trans-Antarctic Scientific Expeditions) projects.

Here we report the study of the spatial and temporal distribution of primary (sea spray) and secondary (biogenic sulphur compounds and atmospheric nitrate) aerosol components in coastal areas of northern Victoria Land and in plateau areas, along a transect between Talos Dome and Dome C [18,19]. Another topic discussed in this paper is the influence of accumulation rate on snow composition, both by dilution and by post-depositional effects particularly for volatile species, such as HCl and HNO_3.

EXPERIMENTAL

Sampling

During several Italian Antarctic Campaigns (from 1991/92 to 1998/99) many shallow firn cores were drilled in coastal and plateau areas located in the Pacific/Indian Ocean sector of East Antarctica. In this article we report the main results of the chemical analysis carried out on eight shallow firn cores drilled both in stations located around the Italian base "Terra Nova Bay" (northern Victoria Land, Ross Sea sector), in the framework of the PNRA (Programma Nazionale di Ricerche in Antartide) Italian Project, and in plateau sites along a transect from Terra Nova Bay to Talos Dome to Dome C. The latest sampling (Talos Dome, Mid Point and D2 stations) was carried out during the 1996/1997 and 1998/99 scientific traverse, in the framework of the ITASE (International Trans-Antarctic Scientific Expedition) project [18,19]. Locations and geographical features of the sampling stations are reported in Fig. 1 and Table I. The drilled firn core sections were stored frozen in pre-cleaned polyethylene bags and brought to Italy. In cold laboratories, under class 100 laminar

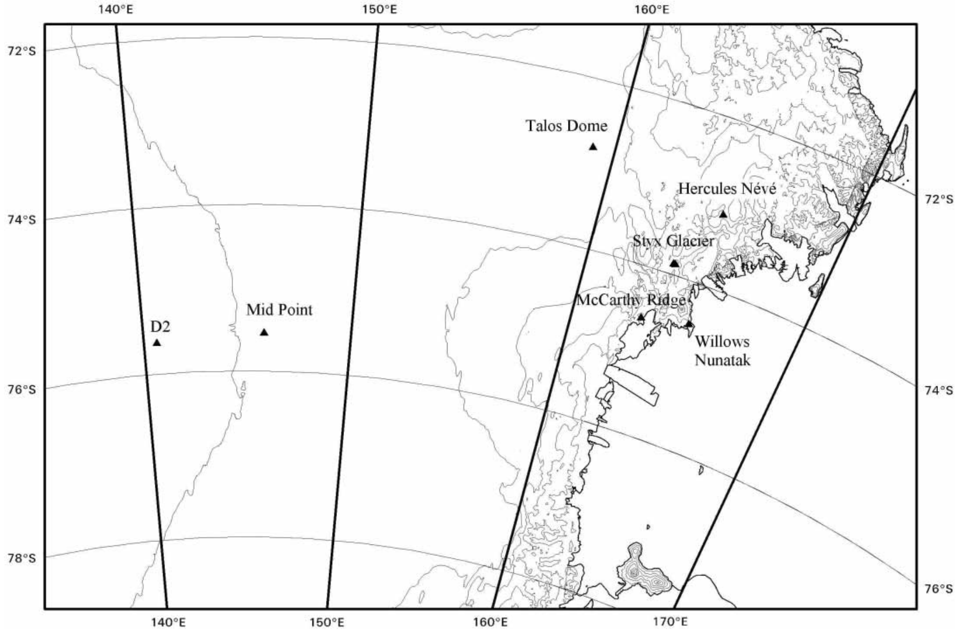

FIGURE 1 Map of the sampling sites in northern Victoria Land and Dome C areas.

TABLE I Geographical location of the sampling sites and core features

Station	*Antarctic Campaign*	*Longitude*	*Latitude*	*Elevation* (m a.s.l.)	*Distance from coast* (km)	*Analysed core length* (m)	*Estimated covered time* (yr)	*Acc. rate* (kg m^{-2} yr^{-1} w.eq)
Willows Nunatak	1991/92	165° 11′ E	74° 29′ S	400	4	3.3		
McCarthy Ridge	1991/92	163° 03′ E	74° 36′ S	700	40	7.2	12	260[a] [38], 270[a] [22]
Styx Glacier	1991/92	163° 45′ E	73° 52′ S	1800	50	9.5	20	203[a] [38], 160[a] [22]
Styx Glacier	1995/96	163° 41′ E	73° 52′ S	1700	50	25	80	
Talos Dome	1996/97	159° 06′ E	72° 48′ S	2330	300	36	250	80[a] [37]
Mid Point	1998/99	145° 49′ E	75° 32′ S	2454	460	5	50	47[a]
D2	1998/99	140° 38′ E	75° 37′ S	2611	598	12	200	30[b]
Hercules Névé	1992/93	164° 58′ E	73° 07′ S	3000	80	7.5	20	145[a] [38], 119[a] [39], 131[a] [39], 161[a] [40], 142[a] [40]

[a] From firn cores and snow-pits chemical analysis. [b] From 1998–2002 stakes farm measurements.

flow hood, the firn core sections were superficially decontaminated by mechanically removing a thin external layer, and sub-sampled in polyethylene containers with a 3-cm resolution.

Instrumentation and Reagents

Chemical analysis was performed with an integrated system obtained by coupling two ion chromatographs (conductometric detection) with a flow analysis device. The

TABLE II Ion chromatographic methods for analytical determinations

Inorganic anions: Cl^-, NO_3^-, SO_4^{2-}	
Separation column	Dionex AS4A 4 mm
Guard column	Dionex AG4A 4 mm
Eluent	$NaHCO_3$1.3 mM + Na_2CO_3 1.4 mM
Eluent flow	2.5 mL/min
Conductivity suppressor	Dionex AMMS-1 and ASRS ULTRA 4 mm
Regenerant	H_2SO_4 1.25×10^{-2} M with AMMS-1 Ultrapure H_2O with ASRS ULTRA
Cations: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	
Separation column	Dionex CS12 4 mm
Guard column	Dionex CG12 4 mm
Eluent	H_2SO_4 25 mN
Eluent flow	1.5 mL/min
Conductivity suppressor	Dionex CMMS-2 and CSRS ULTRA 4 mm
Regenerant	Tetrabutyl-ammonium hydroxide 5×10^{-2} M with CMMS-2 Ultrapure H_2O with CSRS ULTRA

samples were left melting but closed in their containers under a laminar flow hood (class 100) and introduced into the chromatographs just after melting through a teflon tube connected to a peristaltic pump. In this way, the simultaneous determination of cations and inorganic anions was carried out without any sample manipulation, reducing contamination risk from uptake of substances distributed in particulate and gas phases in the laboratory environment.

Table II summarises the used IC methods and the chosen operative variables.

Further details concerning handling of samples, blank control and procedures to minimise contamination have been described in previous papers [20–22].

Eluent, regenerant and standard solutions were prepared using ultra pure water ($> 18\,M\Omega$), obtained from a Millipore MilliQ apparatus and continuously recycled in an Elga UHQ device. Stock standard solutions ($1000\,mg\,L^{-1}$) were obtained from Merck suprapur, when available, or Merck or Fluka reagent grade reagents.

RESULTS AND DISCUSSION

Sea Spray

Sea spray constitutes the main source of the primary atmospheric aerosol in Antarctic coastal regions affected by marine air masses. Na^+, Cl^-, Mg^{2+} and part of SO_4^{2-} are the typical components of the primary marine aerosol.

In order to show the different pattern of the two main sea spray components (Na^+ and Cl^-), as a function of altitude and distance from the coastline, Fig. 2 shows the correlations between chloride and sodium, the latter used as a univocal and conservative sea spray marker. Plots are related to five of the examined stations and arranged by increasing distance from the coast (downward); a straight line represents the calculated linear correlation and a dashed line indicates Cl^-/Na^+ sea water ratio. A very good correlation can be observed in the first three stations (R ranging from 0.86 to 0.98) but it becomes less significant for station D2 ($R = 0.74$) and it even disappears at Mid Point, where no trend in data dispersion can be detected. The slope of the regression line, representing the Cl^-/Na^+ ratio, decreases inland, ranging from 1.68 w/w (close to the theoretical sea water ratio 1.81 w/w) for the station nearest to the coastline, to 1.11 w/w for station D2. This progressive depletion of the Cl^-/Na^+ ratio moving inland reveals a loss of Cl^-, probably due to the removal of HCl, produced by an exchange reaction between NaCl and atmospheric H_2SO_4 [23–25]. As HCl is distributed in the gas phase, it undergoes different transport processes from NaCl aerosol particles.

An apparent anomaly is visible for Mid Point station, where both correlation and mean Cl/Na ratio are lower than D2, which is located at a higher elevation and a longer distance from the sea. A probable explanation for this pattern could lie in the particular wind conditions characterising this station, which are likely to enhance the re-emission of acidic volatile species (HCl and HNO_3) into the atmosphere.

The most inland stations, Mid Point and D2, show positive intercepts, although this may only be significant for D2, because of the low regression coefficient calculated at

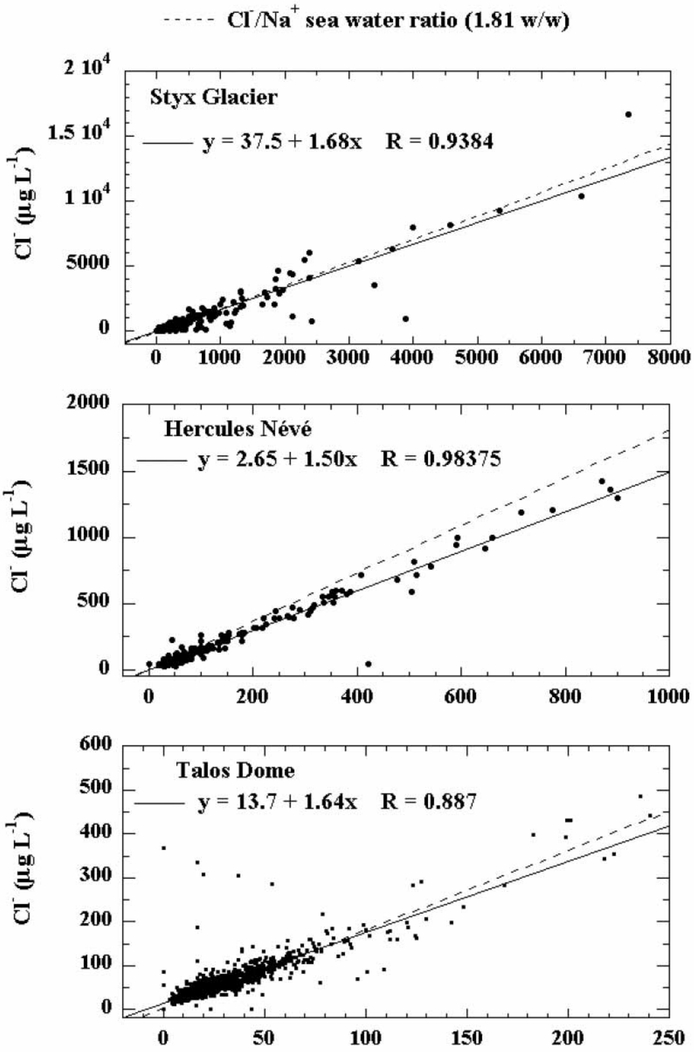

FIGURE 2 Cl^- vs Na^+ correlations for some of the sampling stations; distance from the sea increases from top (Styx Glacier) to bottom (D2).

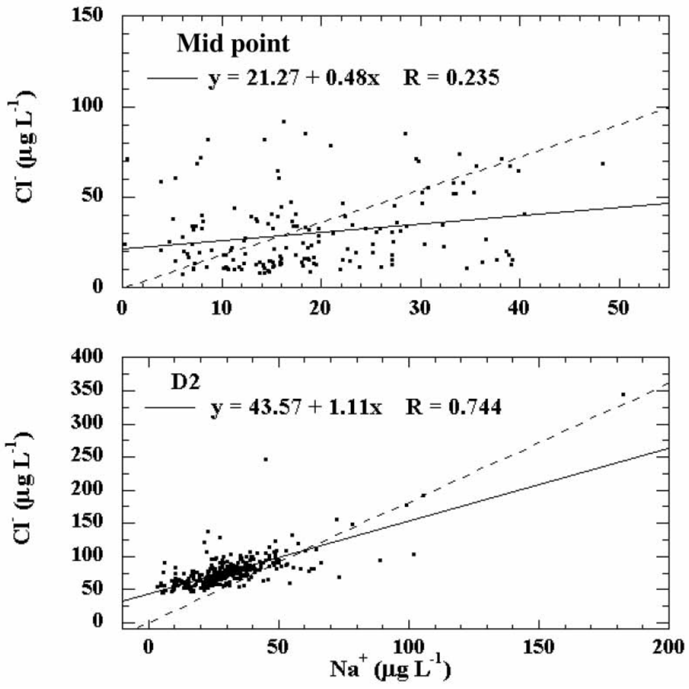

FIGURE 2 Continued.

Mid Point. A positive intercept on the Cl/Na correlation means an extra NaCl source for chloride, attributed to HCl deposition from long-range transport of volcanic emissions, anthropogenic input and NaCl–H_2SO_4 acid–base exchange. HCl can thus play a double role in Antarctic snow: first, when it is formed during NaCl transport or after deposition, HCl removal is able to decrease the initial Cl/Na ratio. Second, when deposition of HCl occurs, the Cl/Na increases above the sea water ratio. The second effect is more visible when sea spray input is lower, i.e., when the Na content is low.

In order to discriminate between the variation of primary marine aerosol contribution as a function of elevation or of distance from the coast, the two geographical parameters were studied separately. For each station, median concentrations of sea spray components (Na, Cl and Mg) are reported as a function of the distance from the coastline (top of Fig. 3) and the altitude (bottom of Fig. 3). A general rapid decrease (note that the concentration scale is logarithmic) of all three components is evident along the first 300 km from the coast, because of deposition of the coarsest sea salt particles (1–20 μm). Beyond this distance, concentrations reach fairly constant values, about two orders of magnitude lower than the coastal ones, which may be considered the background levels for this sector. As elevation increases, a similar trend can be observed and, in this case, background levels are reached at an altitude ranging from 1500 to 2000 m. The Hercules Névé site (3000 m a.s.l.) shows higher concentrations than those measured at stations at lower elevations. This apparent anomaly is due to the geographical position of this site which is the highest station among the ones studied, but it is located quite near the coast (about 80 km). This pattern seems to confirm that the more critical parameter limiting atmospheric transport of sea salt aerosol is the distance from the coast rather than the elevation: in fact, while the sea

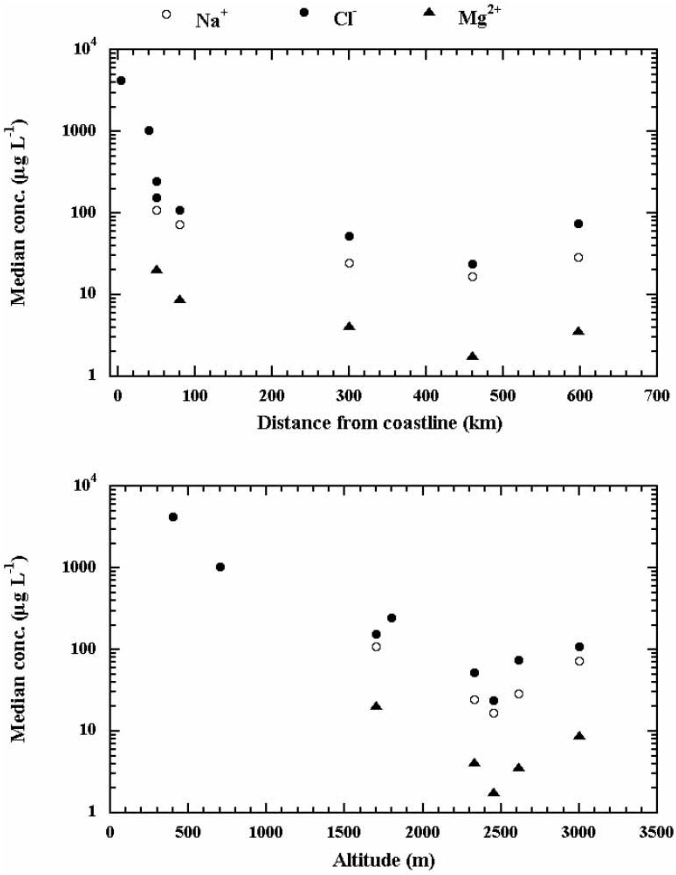

FIGURE 3. Na^+, Cl^- and Mg^{2+} median concentrations plotted vs. the distance from the coastline (upper plot) and the altitude (lower plot).

spray contribution drops sharply on moving inland, elevation is not able to reduce this contribution in coastal stations.

For most inland stations, the sea spray load is shown to be independent of distance from the sea, owing to transport processes involving the finest particles (micrometric and sub-micrometric size).

Sulphate

The most important sources of sulphur on a global scale in Antarctica are sea spray, crustal erosion, marine biogenic emissions (showing a strong seasonal pattern) and volcanic emissions (characterised by sudden and large atmospheric depositions of sulphuric acid aerosol) [26]. The sulphate contribution arising from sources other than sea spray is defined as the non-sea-salt sulphate ($nssSO_4^{2-}$) and has been calculated by the equation [27,28]:

$$[nssSO_4^{2-}] = [totSO_4^{2-}] - 0.253[Na^+],$$

where concentrations are expressed as w/V, Na^+ is used as a univocal sea spray marker and 0.253 is the SO_4^{2-}/Na (w/w) ratio in sea water. For McCarthy Ridge, the Na^+ content was not available, so $nssSO_4^{2-}$ was calculated from the Cl^- content using the equation

$$[nssSO_4^{-2}] = [totSO_4^{2-}] - 0.139[Cl^-],$$

where 0.139 is the SO_4^{2-}/Cl^- (w/w) ratio in sea water. Although Na^+ is the most reliable sea spray marker, using Cl^- for $nssSO_4^{2-}$ calculation at coastal stations leads to a negligible error, as shown by Piccardi *et al.* [29] from snow-pit samples collected at the same site.

Plots (a) and (b) in Fig. 4 show the median values of the two sulphate contributions, sea water sulphate ($swSO_4^{2-}$) and $nssSO_4^{2-}$ respectively, for the examined firn cores, as a function of distance from the sea. In the same plots, summer and winter $swSO_4^{2-}$ and $nssSO_4^{2-}$ values were also reported for stations where a clear seasonal pattern was observed.

As distance from the coast increases, $swSO_4^{2-}$ values show a sharp and progressive decrease, reaching median values at plateau stations about 1% of that measured at the most coastal station. This pattern is consistent with the one already observed for the other primary marine markers. Also $nssSO_4^{2-}$ concentrations decrease in the first three stations, reaching in the Hercules Névé firn core the lowest median values, around 9% of the level measured at Willows Nunatak. The different extent of $swSO_4^{2-}$ and $nssSO_4^{2-}$ decrease with distance from coastline can be explained by the difference in the residence time of the relative aerosol dimensional classes: the first is mainly distributed in the 1–20 µm range, whereas $nssSO_4^{2-}$ is included in submicrometric particles.

Moving from Hercules Névé towards more inland sites, an increase in $nssSO_4^{2-}$ content is shown. This pattern was found by Mulvaney and Wolff [30] for central East Antarctic sites and ascribed to the effect of dry deposition.

Figure 4c shows $nssSO_4^{2-}$ flux as a function of distance from the coastline; unlike the concentration trend, $nssSO_4^{2-}$ flux exhibits a progressive decrease as distance increases, reaching quite constant $nssSO_4^{2-}$ background levels in plateau areas, located very far from the oceanic source. Therefore, it seems more likely that the concentration increasing trend is related to the contemporaneously decreasing accumulation rate, leading to a lower dilution factor of the $nssSO_4^{2-}$ atmospheric scavenging.

From Fig. 4b, it is evident that $nssSO_4^{2-}$ values are always higher in summer than in winter (about double), in accord with the seasonality of their dominant source (marine biogenic activity). As a consequence, $nssSO_4^{2-}$ represents the main sulphate contribution in summer and also for the most coastal stations. On the contrary, $swSO_4^{2-}$ values (Fig. 4a) are higher in winter than in summer because of the higher frequency of sea storms occurring in winter; this pattern is consistent with the other sea spray components' behaviour observed at these stations [31].

In summer, $nssSO_4^{2-}$ represents the main contribution at all the stations (from 64 to 75%). On the contrary, in winter, $swSO_4^{2-}$ is dominant at the McCarthy Ridge (67%) and Styx Glacier (56%) sites; at Hercules Névé, the primary and secondary contributions to the total sulphate budget are equivalent.

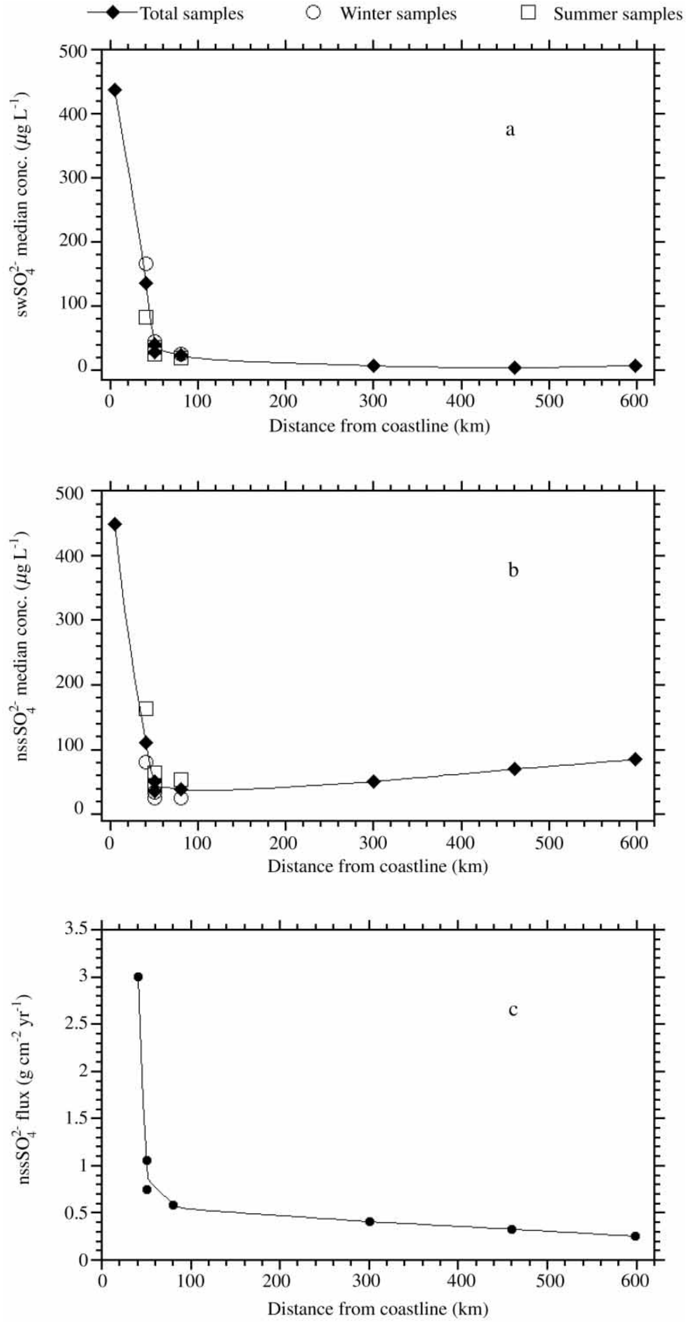

FIGURE 4 $swSO_4^{2-}$ and $nssSO_4^{2-}$ median concentrations (reported as function of seasonality) and $nssSO_4^{2-}$ median flux vs. the distance from the coastline.

The seasonal timing described above for $nssSO_4^{2-}$ and $swSO_4^{2-}$ is in agreement with the available data from Antarctic firn samples such as South Pole snow-pit measurements showing sea-salt species (Na^+, Mg^{2+}) peaking in winter layers and $nssSO_4^{2-}$ reaching their maximum in summer [32].

Nitrate

Nitrate is one of the main components in Antarctic depositions both in present times and from past glacial periods [33], but the study of nitrate temporal and spatial distribution is made difficult because of its huge variety of sources, the controversial understanding of its formation and transport processes and some evidence of post-depositional effects (atmospheric re-emission of HNO_3 from superficial layers and/or solar decomposition), able to change the original snow composition. Nitrate in polar areas arises mainly from stratosphere/troposphere interchanges, lightning and other photo-induced atmospheric processes. Also its atmospheric distribution is related to its presence in the aerosol gaseous phase as acidic species (HNO_3) [34,35].

Nitrate median concentrations have been plotted as a function of distance from the coastline and altitude in Fig. 5: the concentration values fall within the range 5–60 μg L^{-1} with no particular trend as distance and elevation increase.

The same figure shows a higher nitrate content in summer samples than in winter ones in some coastal stations. Such behaviour is consistent with the seasonal character of nitrate sources and transport mechanisms, which are enhanced in spring/summer periods when a more efficient stratosphere/troposphere exchange occurs [36].

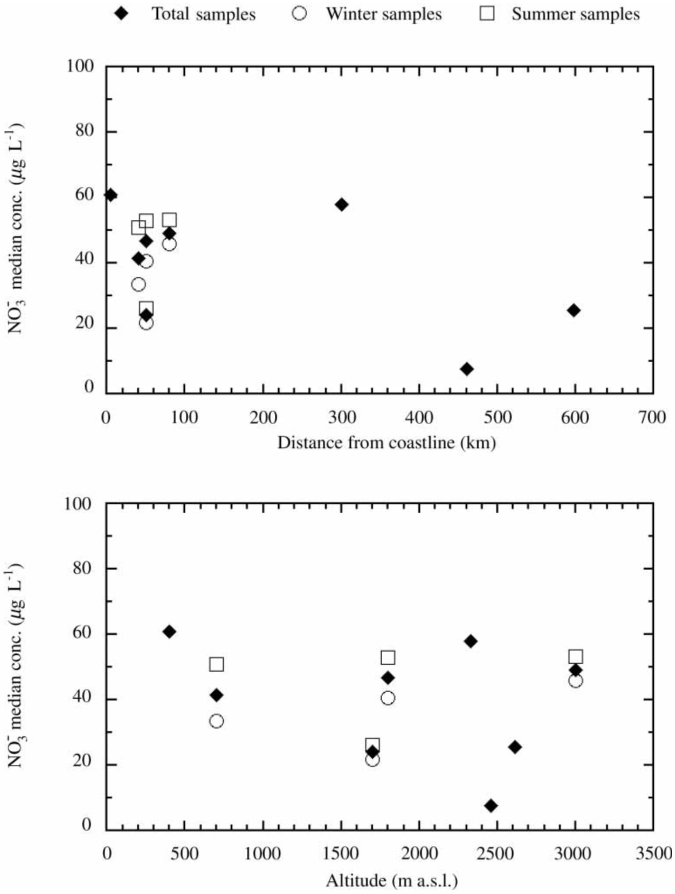

FIGURE 5 No_3^- median concentrations plotted as function of seasonality vs. the distance from the coastline (top) and the altitude (bottom).

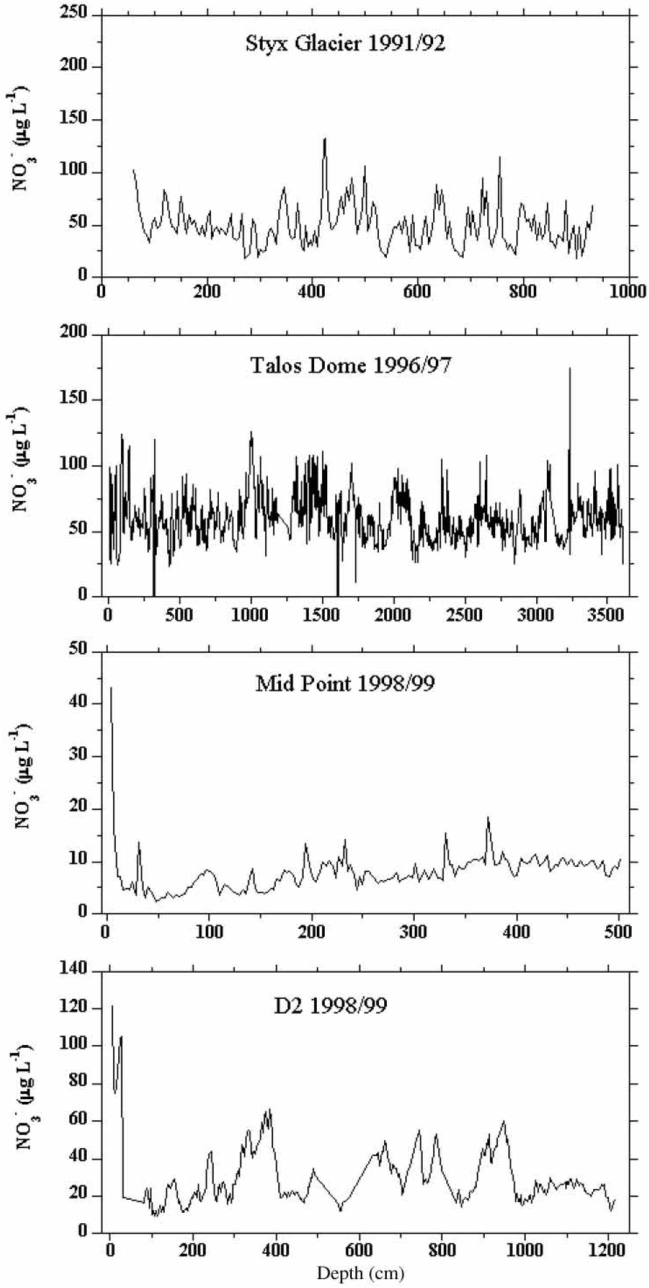

FIGURE 6 Depth profiles for NO_3^- concentrations in four selected sampling stations.

In the most internal stations (Mid Point and D2), characterized by low accumulation rate, higher nitrate concentrations were expected, bearing in mind the reduced dilution factor observed for $nssSO_4^{2-}$. Indeed, these stations do show the lowest nitrate concentrations: this result can be explained by post-depositional processes occurring at these sites just because of the low accumulation rate as already found at Vostok (23 kg m^{-2} yr^{-1}) [14] and at Dome C (30 kg m^{-2} yr^{-1}) [17].

Figure 6 shows NO_3^- concentration/depth profiles for four of the examined stations. Background values do not show any particular trend in the coastal site (Styx Glacier) and in the semi-plateau site (Talos Dome). On the contrary, at the most inland sites (Mid Point and D2) nitrate shows high concentrations at the surface (within the top 50 cm), about four times higher than the background values measured in the deeper layers. Such a large difference in concentration clearly reveals post-depositional processes affecting nitrate concentration in the firn, occurring through a re-emission of HNO_3 from the uppermost snow layers to the atmosphere [14,17].

Within the examined sites, the mean accumulation rate determined at Talos Dome, 80 kg m^{-2} yr^{-1} [37], seems to be the threshold value able to preserve nitrate in the snow layers.

CONCLUSIONS

Chemical analysis of shallow and deep firn cores collected both at coastal sites (Ross Sea) and at plateau sites provided information about the spatial and temporal variability of snow composition in the Pacific sector of the East Antarctic ice sheet. Coastal Antarctic aerosol appears to be greatly affected by primary and secondary oceanic sources. While the sea spray contribution quickly falls as distance from the coast and altitude increase, showing low background values beginning from 300 km inland or 1500 m a.s.l., biogenic sulphate, coming from phytoplanktonic activity, is able to reach the central regions owing to the lower aerodynamic diameter of their particles. Also, because coastal stations are characterized by relatively high accumulation rates, it is possible to perform here a temporal study of snow composition on a seasonal scale. Moreover, the high accumulation rate at these sites is able to prevent snow post-deposition changes, due to re-emission into the atmosphere or photochemical reactions of some components.

The low accumulation rates characterizing the more inland stations do not allow a sufficient sampling resolution to study the seasonal variations in snow composition. Here, the lower dilution factor and the long distance from local sources make longer temporal data sets available. Nevertheless, the interpretation of temporal records has to take post-depositional effects into account, involving particularly volatile acidic species, such as HNO_3 and, to a lesser extent, HCl. In particular, it was shown that a value around 80 kg m^{-2} yr^{-1} can be considered as the limiting accumulation rate for nitrate preservation in the snow layers.

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