

Sea-spray and marine biogenic seasonal contribution to snow composition at Terra Nova Bay, Antarctica

R. UDISTI,^{1*} S. BECAGLI,² E. CASTELLANO,² R. TRAVERSI,² S. VERMIGLI,² G. PICCARDI²

¹*Department of Chemistry, University of Calabria, I-87030 Arcavacata di Rende (Cosenza), Italy*

²*Department of Public Health and Environmental Analytical Chemistry, University of Florence, Via G. Capponi 9, I-50121 Florence, Italy*

ABSTRACT. Primary and secondary marine aerosol contributions to snow composition in Terra Nova Bay, Antarctica, were evaluated by chemical analysis of surface and snow-pit samples. A seasonal pattern of marine inputs, very clear for secondary aerosol (mainly constituted by nssSO_4^{2-} and methanesulphonic acid (MSA) coming from phytoplanktonic activity) and less evident for sea spray (Na^+ , Cl^- , Mg^{2+}), was shown by snow-pit samples. Altitude and distance from the coast were found to be the main parameters affecting seasonal change in the composition of snow collected within about a 200 km radius of the Terra Nova Bay Italian base. Using Na^+ as a sea-spray indicator and MSA as a biogenic marker, fractionating aerosol effects (which are altitude-induced) as well as source contributions for Cl^- and nssSO_4^{2-} were found. A nssSO_4^{2-} /MSA ratio of 2.7 (w/w), indicating their distribution from the common source dimethylsulphide, was calculated from analysis of fresh summer snow collected in horizontal and vertical transects in northern Victoria Land.

INTRODUCTION

Primary and secondary marine aerosols constitute the main contributions to the snow composition in coastal regions in Antarctica and may play an important role in the climate control of remote marine regions, as principal factors for cloud-condensation-nuclei formation (Charlson and others, 1987; Ayers and Gras, 1991). Antarctic coastal areas are directly exposed to marine air masses and are characterised by high annual snow accumulation. Chemical analysis of samples from snow pits and firn cores gives high-resolution records of the environmental and climatic history of the Southern Ocean (Wagenbach, 1996). Snow sampling at stations located in different geographic positions (altitude and distance from the sea) in the area surrounding Terra Nova Bay can give useful information about aerosol sources and transport processes (such as short- and long-range transport and fractionating effects). Variations in marine productivity can also be investigated by means of the seasonal pattern and the temporal and spatial distribution of some biogenic markers, such as non-sea-salt sulphate (nssSO_4^{2-}) and methanesulphonic acid (MSA). Since these sulphur-cycle compounds are quite stable in glacial ice, the climatic conditions and phytoplanktonic-activity variations can also be evaluated for the past (Legrand and others, 1991; Saltzman, 1995).

Cl^- , Na^+ , Mg^{2+} and, partially, SO_4^{2-} are the typical components of primary marine aerosol (sea spray) which is the dominant component in snow collected in low-altitude coastal areas. When the distance from the sea and/or more importantly the altitude increases, the contribution of secondary

atmospheric aerosol becomes important. In unpolluted marine areas such as Antarctica, where the impact of other aerosol sources is low, the secondary marine aerosol is closely related to biologic processes. The main compound emitted by the oceanic phytoplanktonic activity is dimethylsulphide (DMS) which is oxidised in the atmosphere mainly to H_2SO_4 (determined as nssSO_4^{2-}) and MSA (Andreae and Raemdonck, 1983; Saltzman, 1995). MSA is exclusively produced by marine life (Savoie and Prospero, 1989; Legrand and others, 1991; Wagenbach, 1996), whereas nssSO_4^{2-} has other potential sources such as volcanic, anthropogenic and crustal inputs (Legrand and Delmas, 1987; Shaw, 1988). In Antarctic coastal areas, however, the nssSO_4^{2-} biogenic source is dominant, especially during summer (Legrand, 1995; Wagenbach, 1996; Udisti and others, 1998). The seasonal pattern of DMS emissions gives an analogous seasonal character to the MSA and nssSO_4^{2-} content in aerosol and snow, with concentration maxima during the phytoplanktonic bloom periods and immediately thereafter (Prospero and others, 1991; Saltzman, 1995; Wagenbach, 1996; de Mora and others, 1997). Previous studies on the distribution of marine components in snow and firn samples collected in northern Victoria Land (Udisti and others, 1993, 1998; Piccardi and others, 1996a, b) revealed a sharp seasonal pattern for MSA and nssSO_4^{2-} (so their summer maxima can be used as reliable seasonal markers in firn-core dating; Udisti, 1996). There is a less evident seasonal trend for sea-spray components (Cl^- , Na^+ , Mg^{2+}), but higher concentrations are found in winter snowfalls. A relevant influence of altitude on the chemical composition of snow and on aerosol fractionating effects was also observed.

The aim of this paper is to confirm and complete such observations with a large new dataset derived from chemical analysis of four snow pits sampled at different positions in coastal areas of Terra Nova Bay. A spatial evaluation of the

*Present address: Analytical Chemistry Section, University of Florence, Via G. Capponi 9, I-50121 Florence, Italy.

summer marine contribution was also performed by analyzing fresh summer snow samples collected in vertical transects (stations located very close together but at different altitudes) and horizontal transects (stations at different distances from the coastline arranged along a sea-inland direction).

SAMPLING AND ANALYTICAL METHODS

Sampling stations

Terra Nova Bay is located between the Ross Sea and the Transantarctic Mountains, in a region affected by intense katabatic winds (Bromwich and Kurtz, 1984). Study of the seasonal pattern of snow components from snow-pit or firn-core samples calls for undisturbed annual snow deposition. To avoid areas where wind effects on the snow cover (e.g. ablation or redistribution) can perturb the snow-layer deposition, a detailed analysis of satellite photos was performed (Stenni and others, unpublished). In this way, it was possible to choose stations where wind morphologies (e.g. sastrugi and snowdrift) were missing, so that an undisturbed snow deposition was highly probable.

Samples were obtained from four snow pits (2.5–3.5 m deep) dug at stations located within about 200 km of the Terra Nova Bay Italian base, during the 1993–94 Italian Antarctic campaign.

During the Italian Antarctic campaigns from 1993–94 to 1996–97, about 100 samples of surface snow were collected in summer at different stations in the same area. In particular, surface snow from coast-inland transects was obtained along the Reeves–Priestley Névé and Rennick Névé. The surface snow was collected as soon as possible after deposition (maximum 2 days), so the samples can be considered as “fresh snow” samples, little affected by post-depositional processes.

Sampling procedures and analytical methods

All samples were collected using a sampling protocol to avoid contamination (Udisti and others, 1991, 1994; Piccardi and others 1994). The snow pits were hand-excavated by personnel wearing clean-room clothing. Pit walls were cleaned by removing a 5–10 cm snow layer with a stainless-steel scraper just before sampling. Pre-cleaned polypropylene vials (inside diameter 35 mm) were inserted into the vertical snow walls, and after removal each sampling vial was sealed in a double polyethylene bag. The vials were kept frozen (–20°C) until analysis (usually a few months after sampling).

Snow components were determined using an integrated system of three ion chromatographs (ICs) with conductivity detectors. The separation columns were Dionex ASI2A (Cl^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-}), ASI1A (F^- , acetate, propionate, formate, MSA and pyruvate) and Dionex CS12A (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}), followed by electrochemical micro-membrane conductivity suppressors. All components were analyzed as soon as possible after melting (usually 30 min). The samples were melted under a class 100 laminar hood and filtered on a 0.45 μm Teflon membrane just before analysis. A 1 mL sample loop was sufficient to determine the lowest concentrations of the components without pre-concentration. Blank control procedures, sample treatment and IC methods are described in Udisti and others, (1991, 1994), Piccardi and others, (1994) and Udisti (1996).

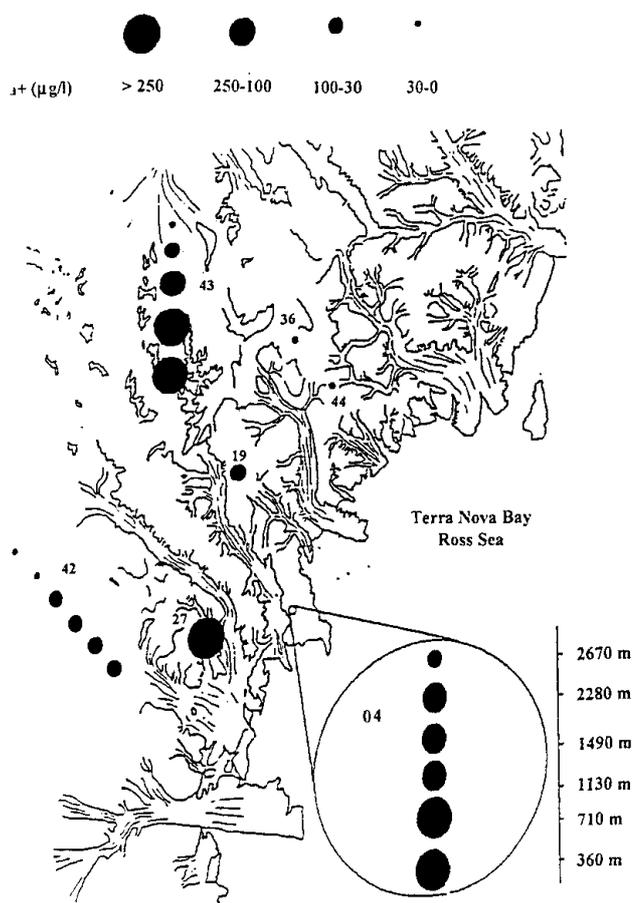


Fig. 1. Sampling area and distribution of Na^+ concentration. The Na^+ mean snow contents are grouped by concentration classes. Sampling stations:

04, Mount Melbourne. Surface snow: six sites between $74^\circ 32' \text{S}$, $164^\circ 46' \text{E}$ and $74^\circ 21' \text{S}$, $164^\circ 41' \text{E}$ (360–2670 m a.s.l.).

19, Styx Glacier plateau. Snow pit: $73^\circ 52' \text{S}$, $63^\circ 42' \text{E}$ (1660 m a.s.l.).

27, McCarthy Ridge. Snow pit: $74^\circ 36' \text{S}$, $163^\circ 03' \text{E}$ (870 m a.s.l.).

36, Hercules Névé. Snow pit: $73^\circ 06' \text{S}$, $165^\circ 28' \text{E}$ (2960 m a.s.l.).

44, Pilot Glacier. Snow pit: $73^\circ 16' \text{S}$, $165^\circ 31' \text{E}$ (2100 m a.s.l.).

Transect 42, Reeves–Priestley Plateau. Surface snow: eight sites spaced 10–20 km apart from $74^\circ 29' \text{S}$, $161^\circ 00' \text{E}$ (1540 m a.s.l.) to $73^\circ 37' \text{S}$, $157^\circ 54' \text{E}$ (2320 m a.s.l.).

Transect 43, Rennick Glacier plateau. Surface snow: nine sites spaced 10–20 km apart from $73^\circ 20' \text{S}$, $162^\circ 30' \text{E}$ (2210 m a.s.l.) to $72^\circ 20' \text{S}$, $162^\circ 26' \text{E}$ (1350 m a.s.l.). The elevation decreases away from the sea.

Not all the stations are visible, because some sampling points are obscured by the dark patches indicating the Na^+ concentrations.

For each sample, the nssSO_4^{2-} concentration was calculated (Maupetit and Delmas, 1992) by

$$[\text{nssSO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{tot}} - 0.253 [\text{Na}^+] \text{ or } -0.139 [\text{Cl}^-] \text{ (w/V)}.$$

Previous nssSO_4^{2-} measurements on samples collected in the same region indicated that Na^+ is the best sea-spray marker. In the lowest-elevation station (station 27, McCarthy Ridge, 870 m a.s.l.) some negative nssSO_4^{2-}

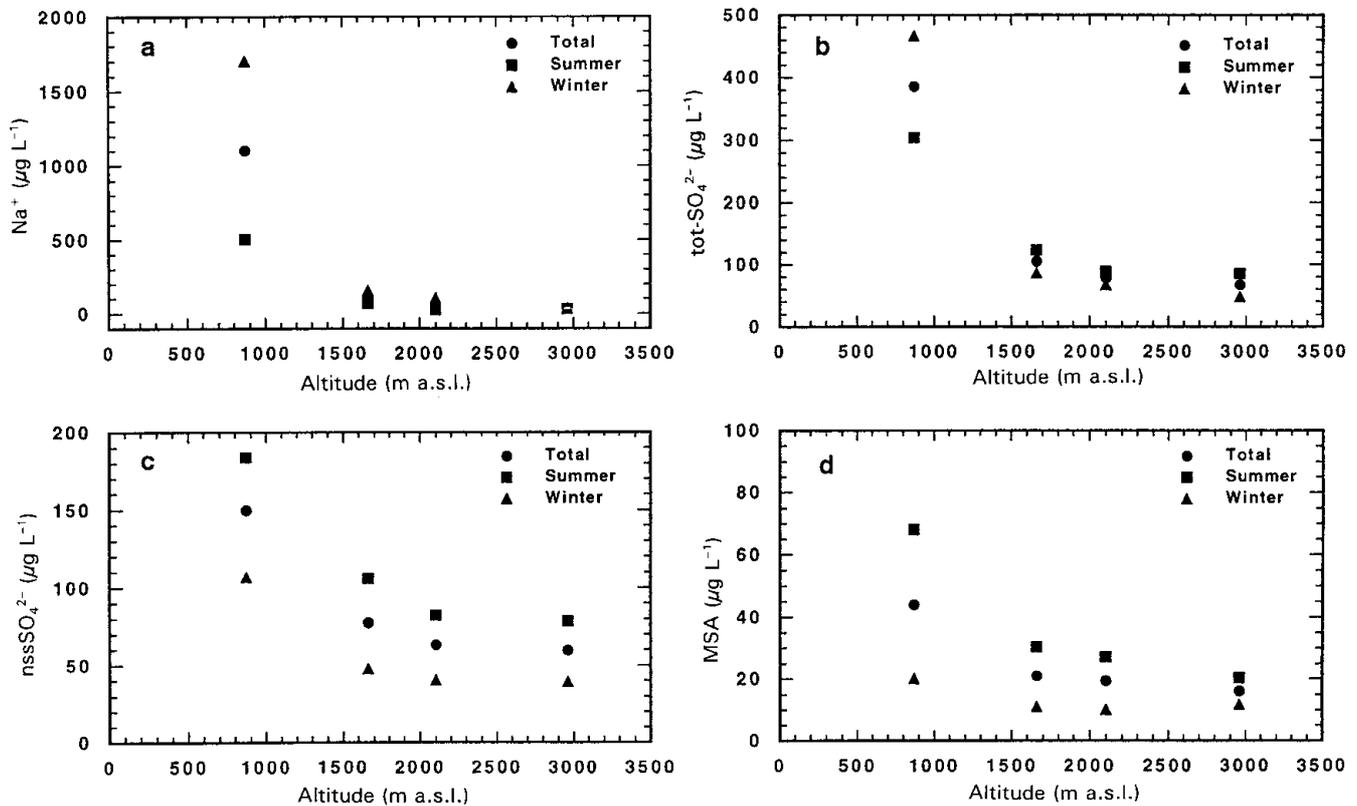


Fig. 2. Seasonal mean trends of Na^+ (a), total sulphate (b), non-sea-salt sulphate (c) and MSA (d) as functions of altitude in snow-pit samples collected at stations 27 (870 m), 19 (1660 m), 44 (2100 m) and 36 (2960 m).

values were found in winter samples, when the biogenic contribution was very low. For a reliable comparison of all snow-pit data, only positive nssSO_4^{2-} values were used for the statistical treatments. A detailed discussion of the nssSO_4^{2-} calculation can be found in Udisti (1996).

The snow-pit dating was performed using a multiparametric method based on normalisation of the concentration/depth profiles of H_2O_2 , nssSO_4^{2-} and MSA (Udisti, 1996). The dating results are reported in Piccardi and others (1995). The normalised profiles of the three seasonal indicators gave a new, more reliable seasonal profile (designated the "normalised sum"), with a sinusoidal pattern, where the maximum values are related to summer samples and the minimum values to winter samples. Summer samples are those with a normalised sum value higher than half of the relative annual peak height, and winter samples those with lower normalised sum values.

RESULTS AND DISCUSSION

Sea-salt concentrations in Antarctic snow show the largest spatial and temporal variations, compared to other source components. In aerosol measurements, the mean concentrations range from $0.062 \mu\text{g m}^{-3}$ at the South Pole (Tuncel and others, 1989) to $3.2 \mu\text{g m}^{-3}$ on the Antarctic Peninsula (Palmer station; Wagenbach, 1996). Coastal sites influenced by katabatic winds, which are able to blow away the marine air masses from the coastal areas, show an intermediate sea-salt aerosol content ($0.27 \mu\text{g m}^{-3}$ at Mawson; Wagenbach, 1996).

Allen and others (1985), analyzing two ice cores collected at two stations located in northern Victoria Land (Evans Névé and Morozumi Range), found the following respective

median values for some of the compounds discussed here: chloride 147 and $163 \mu\text{g L}^{-1}$; sodium 81.6 and $87.6 \mu\text{g L}^{-1}$; sulphate 68.2 and $73 \mu\text{g L}^{-1}$.

Figure 1 shows the firn-core and surface-snow sampling stations. For each station, the mean concentration of Na^+ (considered as a specific sea-spray marker) is reported (proportional to the symbol size). The importance of location in examining the contribution of sea spray to the snow composition is shown by the fact that the highest mean Na^+ contents are at the lower-altitude coastal stations (Fig. 1). In particular, the importance of distance from the sea and altitude is highlighted by the Reeves–Priestley (horizontal) and Melbourne (vertical) transects, respectively. For the Reeves–Priestley transects, the sampling sites were spaced about 10–20 km apart and located at high altitudes (1540–2320 m a.s.l.). A progressive decrease of the Na^+ mean concentration is evident for the low absolute values. The Melbourne transect gives very useful information concerning the altitude effect. In fact, the samples were collected at closely spaced stations but at very different altitudes. The Na^+ decrease is very sharp for the first 1000 m. At higher altitudes, the decreasing trend is less evident.

The Rennick transect shows an apparent anomaly. The Na^+ concentration decreases as the altitude decreases. This glacier is located behind the Transantarctic Mountains, and therefore the altitude decreases in the inland direction. The marine air masses coming from the Ross Sea and up Campbell Glacier must rise over 2500 m before they reach the Rennick Glacier plateau, and so the sea-spray aerosol content is deposited preferentially at the highest Rennick site (first site at 2210 m a.s.l.; see also Fig. 1 caption).

Figure 2 shows the altitude effect and the seasonal pattern of the primary (Na^+ ; Fig. 2a) and secondary (nssSO_4^{2-}

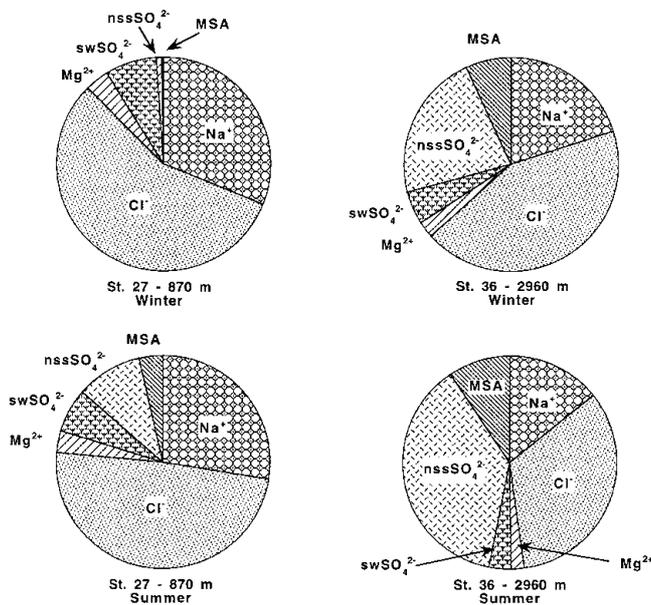


Fig. 3. Winter and summer percentage contributions of primary (Na^+ , Cl^- , Mg^{2+} , sea-water sulphate) and secondary (non-sea-water sulphate, MSA) marine inputs at the lowest (station 27, McCarthy Ridge) and highest (station 36, Hercules Nève) snow-pit stations.

and MSA; Fig. 2c and d) marine aerosol in the four snow pits. The Na^+ concentration is high in the lower station, with a maximum mean value in winter, but decreases quickly in the first altitude step (870–1660 m). Above 1500 m, the concentrations are very low and the seasonal differences less evident. At Hercules Nève station (2960 m a.s.l.), a seasonal trend is lacking. A similar pattern is shown by Cl^- and Mg^{2+} . On the other hand, $nssSO_4^{2-}$ concentrations are higher in summer at all stations, and the tendency to decrease as a function of altitude is more gradual. For altitudes above 2000 m, the concentration approaches $60 \mu g L^{-1}$. This pattern is confirmed by the MSA concentration trend (Fig. 2d), but a lower seasonal variation is observed for the highest station, where summer and winter mean concentration values are quite similar, ranging from 10 to $20 \mu g L^{-1}$. Figure 2b shows the behaviour of total sulphate. At the lowest station, sulphate follows the same trend as Na^+ , with high winter values. From 870 to 1660 m, the concentration drops quickly, while the decrease in percentage is lower than for Na^+ . From 1660 to 2960 m, the sulphate shows an opposite seasonal pattern, with maxima in summer. As for $nssSO_4^{2-}$, a seasonal distribution is also revealed by $totSO_4^{2-}$ for the highest station. This shows that the SO_4^{2-} contribution from sea spray is partially counter-balanced by the presence of biogenic sources, which gain importance as altitude increases.

The different contributions of primary and secondary marine aerosols as a function of altitude and seasonality are shown in Figure 3. In winter, at the lowest station (station 27), the sea-spray content (Na^+ , Cl^- , Mg^{2+} and $swSO_4^{2-}$) is more than 95% of the total marine contribution. On the other hand, in summer at the highest station (station 36) the secondary marine aerosol ($nssSO_4^{2-}$ and MSA) constitutes about 50% of the marine input. These data are in agreement with long-term aerosol observations at Neumayer station (Wagenbach, 1996). In winter, 90% of the dry aerosol mass concentration consists of sea salt, and

the other 10% consists of $nssSO_4^{2-}$ and NO_3^- in a ratio of approximately 1:1. In summer, the sea-spray content is reduced to 50%, while the marine biogenic compounds ($nssSO_4^{2-}$ and MSA) constitute the remaining 50%.

The seasonal variations of the sea-salt load are relatively weak (at least for stations above 1000 m a.s.l.) and are not in phase with the annual sea-ice cycle. Minimum sea-spray values in aerosol and snow samples are found in summer when the sea surface is open, and maximum concentrations are measured in autumn and spring when the sea-ice extent is usually greater. Sudden high concentration peaks of sea spray are evident in winter, with values 10–100 times higher than mean seasonal values, especially at the lowest station (Piccardi and others, 1994). A similar pattern is shown by aerosol measurements from other coastal stations (Mawson, Neumayer and Dumont D'Urville; Wagenbach, 1996 and references therein). The sea-spray source areas and the transport pathways of such highly enriched sea-spray aerosol are not well known. Heavy salt storms, which are more probable in winter, could be the primary cause, although local sea-ice conditions must also be considered. A winter polynya in Terra Nova Bay is well documented (Bromwich and Kurtz, 1984) and a combination between such a polynya

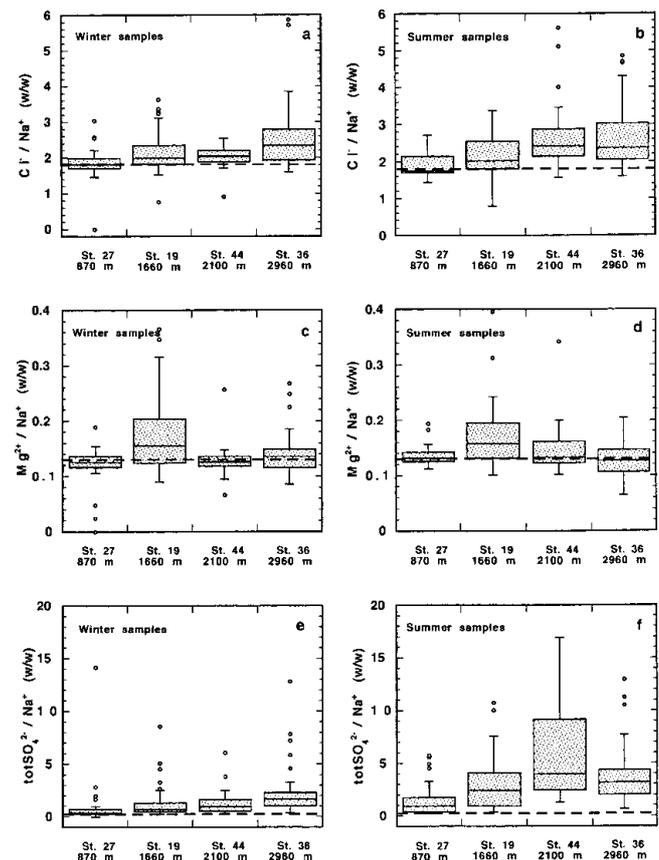


Fig. 4. Distribution plots of Cl^- / Na^+ , Mg^{2+} / Na^+ and $totSO_4^{2-} / Na^+$ ratios in winter (a, c, e) and summer (b, d, f), for the four snow-pit stations. Each box contains 50% of the data, with the median value displayed as a line. The top and bottom of the box mark the limits of $\pm 25\%$ of the variable population (25th and 75th percentiles). The lines extending from the top and bottom of each box mark the minimum and maximum values that fall within an acceptable range (1.5 times the box width). Any value outside this range (outlier) is shown as an individual point. The dashed lines indicate the sea-water composition.

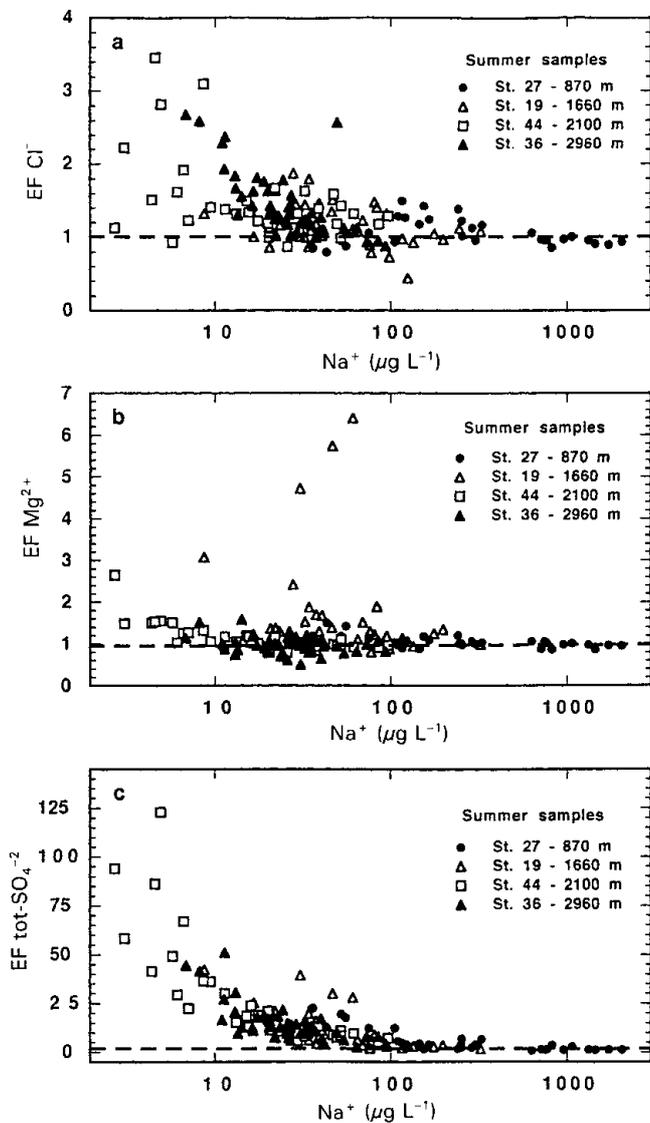


Fig. 5. Enrichment factors of Cl^- (a), Mg^{2+} (b) and totSO_4^{2-} (c) (by using Na^+ as sea-spray marker) in summer samples for the four snow-pit stations plotted vs Na^+ concentration. The dashed lines indicate the sea-water composition.

and a heavy storm with marine winds seems to be a reliable explanation for sea-spray winter maxima.

By using Na^+ concentrations as a sea-spray marker, it is possible to demonstrate the fractionation phenomena related to the increase in altitude. Figure 4 a–f show the distribution diagrams (box plots) of the Cl^-/Na^+ , $\text{Mg}^{2+}/\text{Na}^+$ and $\text{totSO}_4^{2-}/\text{Na}^+$ concentration ratios for the four snow pits sampled as a function of seasonality and altitude. Each box indicates the concentration range of 50% of the samples, and its height is correlated to the variability in the data. The lines in the boxes indicate the median values, and the dashed lines represent the sea-water ratios. In winter, the data variability is generally low and the median ratio values are similar to those of sea water. In summer on the other hand, only the $\text{Mg}^{2+}/\text{Na}^+$ ratio remains similar to the sea-water composition (except at station 19, where a Mg^{2+} crustal contribution occurs; Piccardi and others, 1996a), while Cl^-/Na^+ and, above all, $\text{totSO}_4^{2-}/\text{Na}^+$ ratios are higher. This difference, relative to the sea-water composition, increases with altitude. For the $\text{totSO}_4^{2-}/\text{Na}^+$ trend, the explanation is clear. The biogenic contribution, which is very important in summer, increases the ratio with re-

spect to the sea-water content. For Cl^- , fractionation of the aerosol during transport must be considered. So too must other non-sea-salt Cl^- sources such as volcanic inputs, long-range HCl transport or HCl formation from a reaction between NaCl and H_2SO_4 in aerosol. To illustrate the Na^+ effect, the enrichment factors for Cl^- , Mg^{2+} and totSO_4^{2-} in summer samples are reported as a function of Na^+ concentration (Fig. 5a–c). The enrichment factor (EF) for compound X is calculated as:

$$\text{EF} = ([X]/[\text{Na}])_{\text{snow}} / ([X]/[\text{Na}])_{\text{sea water}}$$

The Na^+ scale is logarithmic to point out the trend at the lowest Na^+ concentrations. A general increase in Cl^- and totSO_4^{2-} EF when the Na^+ concentration decreases is evident in all snow-pit stations. The increase in the Cl^-/Na^+ ratio, which is more evident in summer, may be related to seasonality (aerosol transport processes or seasonal pattern of other Cl^- sources). On the other hand, the non-sea-salt contribution to the Cl^- concentration could be quite constant all year round, but with the Cl^- excess (with respect to the sea-water Cl^-/Na^+ ratio) becoming evident only in summer when the sea-spray contribution is lower (low values of Na^+). This second hypothesis is supported by the experimental observation that at the highest elevation, where the Na^+ content is always low (low contribution of sea spray), the Cl^- enrichments are similar both in summer and in winter (Fig. 4a and b).

Figure 5c shows high sulphate enrichment with respect to the sea-water composition in all stations. Enrichment factors in the range 20–100 are found for Na^+ concentrations of $<10 \mu\text{g L}^{-1}$. For this component both the above hypotheses are true. The seasonality of the biogenic source of nssSO_4^{2-} is clear, and its contribution to the total sulphate budget is even more evident when the sea-spray contribution is low, as it is in summer and at high-altitude stations.

Just as Na^+ was used for the evaluation of the sea-spray contribution, MSA can be used as a biogenic marker to explain the biogenic contribution of nssSO_4^{2-} and to estimate the distribution processes between MSA and H_2SO_4 coming from DMS. Such evaluations have to be performed on summer samples, where the biogenic contribution is higher, and in the absence of any post-depositional processes which can change the snow composition. For this reason, samples of fresh summer snow were collected just after deposition within about a 200 km radius of the Terra Nova Bay Italian base. Figure 6a shows the relationship between nssSO_4^{2-} and MSA. There is a good correlation ($R = 0.82$, $n = 95$), with a slope (indicating the summer mean $\text{nssSO}_4^{2-}/\text{MSA}$ ratio) of 2.7. Figure 6b shows the trend of the $\text{nssSO}_4^{2-}/\text{MSA}$ (w/w) ratio as a function of MSA concentration. In the same figure, the dashed line indicates the ratio value of 2.7. For MSA concentrations as high as $50 \mu\text{g L}^{-1}$, the $\text{nssSO}_4^{2-}/\text{MSA}$ clearly tends to a value very near to 2.7. When the MSA concentration decreases, the ratio progressively increases to values even higher than 20. The highest values of the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio are mainly obtained at the highest-elevation stations. The trend in the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio could be explained by one or more of the following:

- (1) the relative importance of non-DMS sources to the nssSO_4^{2-} budget;
- (2) the effect of aerosol fractionation during transport progressively enriching nssSO_4^{2-} (with respect to the original $\text{nssSO}_4^{2-}/\text{MSA}$ ratio from DMS), as distance from

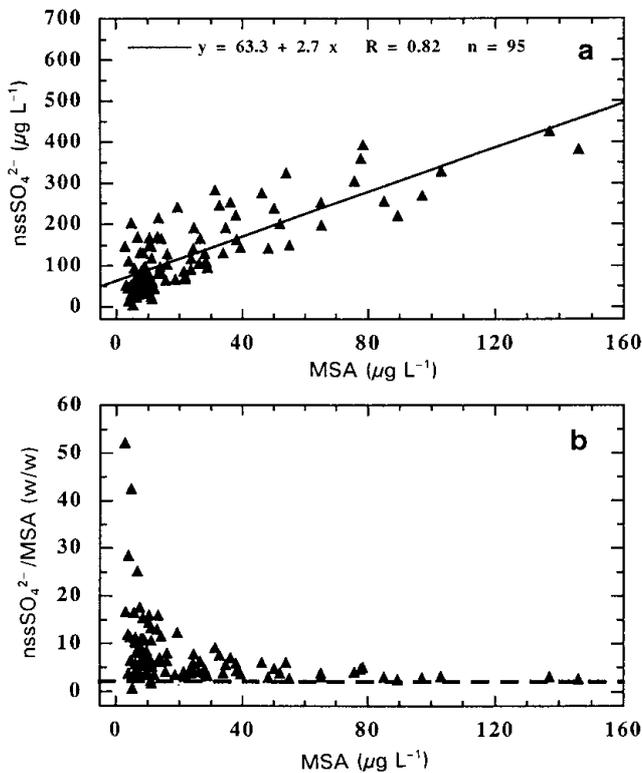


Fig. 6. (a) nssSO_4^{2-} as a function of MSA concentration for summer fresh samples collected within a 200 km radius of the Terra Nova Bay Italian base, and (b) $\text{nssSO}_4^{2-}/\text{MSA}$ ratio as a function of MSA concentration for the same samples.

the sea and altitude increase;

- (3) the contribution of marine air masses coming from lower latitudes (long-range aerosol transport) with an original $\text{nssSO}_4^{2-}/\text{MSA}$ ratio higher than that obtained in the Antarctic oceans.

In fact, the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio is strongly affected by latitude (Bates and others, 1992). At medium latitudes, the $\text{nssSO}_4^{2-}/\text{MSA}$ aerosol ratio can reach values more than ten times greater than those found in the polar regions (Berresheim, 1987; Saltzman, 1995). Moreover, the positive relationship between altitude and $\text{nssSO}_4^{2-}/\text{MSA}$ ratio leads us to believe that the different sizes of aerosol particles can play a relevant role. For example, the smaller aerosol particles are more involved in long-range aerosol transport from Southern mid-latitudes to Antarctic coastal areas (Wagenbach, 1996).

A simpler explanation for the pattern of the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio as a function of the MSA concentration is obtained by considering a quite constant and globally distributed background nssSO_4^{2-} contribution (volcanic, crustal and/or from long-range transport), with a superimposed biogenic contribution. When the biogenic source decreases (due to seasonal variation and/or altitude effects) the background nssSO_4^{2-} concentration becomes more important, leading to a progressive increase in the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio.

CONCLUSIONS

The principal contributions to snow composition in northern Victoria Land are primary and secondary marine aerosol, and their relative importance varies as a function of season and position. This phenomenon can be demonstrated by observing the spatial and seasonal distribution of some compo-

nents chosen as primary (Na^+ , Mg^{2+} , Cl^- and totSO_4^{2-}) and secondary (MSA and nssSO_4^{2-}) aerosol markers.

Altitude and distance from the sea are fundamental parameters in understanding the distribution processes of components coming from sea spray as well as from marine biogenic activity. When altitude and distance from the sea increase, fractionation phenomena related to the aerosol particle size occur. In particular, we found larger Cl^- enrichments in summer samples than in winter samples, but this seasonal difference disappears in the highest stations. This proves the existence of other Cl^- sources, evident only when the Na^+ concentration is lower (summer precipitation and/or high altitudes, where the relatively large sea-spray particles arrive with difficulty).

For total sulphate, the enrichment with respect to sea-water composition prevalently found in summer is mainly due to the seasonality of the biogenic source (nssSO_4^{2-} from DMS).

Evaluation of the biogenic contribution to the nssSO_4^{2-} budget as a function of seasonality is difficult because of the contributions of other sulphate sources such as volcanic and crustal inputs.

A $\text{nssSO}_4^{2-}/\text{MSA}$ ratio of 2.7 was calculated from fresh summer snow samples, and this value could be representative for their distribution from DMS in northern Victoria Land coastal areas. The $\text{nssSO}_4^{2-}/\text{MSA}$ ratio plotted vs MSA concentration, used as a specific biogenic marker, confirms this ratio for high MSA concentrations, but shows a progressive increase when the MSA concentration decreases. Several factors may explain this increase, e.g. the contribution of a background nssSO_4^{2-} value from non-DMS sources (volcanic and crustal), the effect of aerosol fractionation during transport (related to altitude and distance from the sea) or the contribution of marine air masses coming from mid-latitudes with different $\text{nssSO}_4^{2-}/\text{MSA}$ ratios from DMS.

ACKNOWLEDGEMENTS

This research was carried out in the framework of the Programma Nazionale di Ricerche in Antartide. It was financially supported by Ente per le Nuove Tecnologie, l'Energia e l'Ambiente.

REFERENCES

- Allen, B., III, P. A. Mayewski, W. B. Lyons and M. J. Spencer. 1985. Glaciochemical studies and estimated net mass balances for Rennick Glacier area, Antarctica. *Ann. Glaciol.*, **7**, 1–6.
- Andreae, M. O. and H. Raemdonck. 1983. Dimethyl sulphide in the surface ocean and the marine atmosphere: a global view. *Science*, **221**(4612), 744–747.
- Ayers, G. P. and J. L. Gras. 1991. Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air. *Nature*, **353**(6347), 834–835.
- Bates, T. S., J. A. Calhoun and P. K. Quinn. 1992. Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosol particles over the south Pacific Ocean. *J. Geophys. Res.*, **97**(D9), 9859–9865.
- Berresheim, H. 1987. Biogenic sulfur emissions from the subantarctic and Antarctic oceans. *J. Geophys. Res.*, **92**(D11), 13,245–13,262.
- Bromwich, D. H. and D. D. Kurtz. 1984. Katabatic wind forcing of the Terra Nova Bay polynya. *J. Geophys. Res.*, **89**(C3), 3561–3572.
- Charlson, R. J., J. E. Lovelock, M. O. Andreae and S. G. Warren. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, **326**(6114), 655–661.
- de Mora, S. J., D. J. Wylie and A. L. Dick. 1997. Methanesulphonate and non-sea-salt sulphate in aerosol, snow and ice on the East Antarctic Plateau. *Antarct. Sci.*, **9**(1), 46–55.
- Legrand, M. 1995. Sulphur-derived species in polar ice: a review. In Delmas, R. J., ed. *Ice core studies of global biogeochemical cycles*. Berlin, etc., Springer-

- Verlag, 91–119. (NATO ASI Series I: Global Environmental Change 30)
- Legrand, M. R. and R. J. Delmas. 1987. A 220-year continuous record of volcanic H_2SO_4 in the Antarctic ice sheet. *Nature*, **327**(6124), 671–676.
- Legrand, M., C. Feniet-Saigne, E. S. Saltzman, C. Germain, N. I. Barkov and V. N. Petrov. 1991. Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature*, **350**(6314), 144–146.
- Maupetit, F. and R. J. Delmas. 1992. Chemical composition of falling snow at Dumont d'Urville, Antarctica. *J. Atmos. Chem.*, **14**(1), 31–42.
- Piccardi, G., R. Udisti and F. Casella. 1994. Seasonal trends and chemical composition of snow at Terra Nova Bay (Antarctica). *Int. J. Environ. Anal. Chem.*, **55**, 219–234.
- Piccardi, G., E. Barbolani, S. Becagli, R. Traversi and R. Udisti. 1995. Ruolo della stagionalità e dell'altitudine su fenomeni di frazionamento atmosferico e sulla identificazione di fonti secondarie nelle precipitazioni nevose in Antartide. In Csecon, P., ed. *Progetto Nazionale di Ricerche in Antartide, IV Convegno Nazionale Contaminazione Ambientale, 6–7 December 1995, Venezia, Italy. Proceedings*. Venezia, Università di Venezia, 53–62.
- Piccardi, G., S. Becagli, R. Traversi and R. Udisti. 1996a. Fractionating phenomena, altitude induced, on snow composition in northern Victoria Land (Antarctica). In Colacino, M., G. Giovannelli and L. Stefanutti, eds. *Conference on Italian Research on Antarctic Atmosphere, 6–8 November 1995, Florence, Italy. Proceedings. Vol. 51*. Bologna, Società Italiana di Fisica, 229–245.
- Piccardi, G., F. Casella and R. Udisti. 1996b. Non-sea-salt contribution of some chemical species to the snow composition at Terra Nova Bay (Antarctica). *Int. J. Environ. Anal. Chem.*, **63**, 207–223.
- Prospero, J. M., D. L. Savoie, E. S. Saltzman and R. Larson. 1991. Impact of oceanic sources of biogenic sulphur on sulphate aerosol concentrations at Mawson, Antarctica. *Nature*, **350**(6315), 221–223.
- Saltzman, E. S. 1995. Ocean/atmosphere cycling of dimethylsulphide. In Delmas, R. J., ed. *Ice core studies of global biogeochemical cycles*. Berlin, etc., Springer-Verlag, 65–90. (NATO ASI Series I: Global Environmental Change 30)
- Savoie, D. L. and J. M. Prospero. 1989. Comparison of oceanic and continental sources of non-sea-salt over the Pacific Ocean. *Nature*, **339**(6227), 685–687.
- Shaw, G. E. 1988. Antarctic aerosols: a review. *Rev. Geophys.*, **26**(1), 89–112.
- Tuncel, G., N. K. Aras and W. H. Zoller. 1989. Temporal variations and sources of elements in the South Pole atmosphere. I. Nonenriched and moderately enriched elements. *J. Geophys. Res.*, **94**(D10), 13,025–13,038.
- Udisti, R. 1996. Multiparametric approach for chemical dating of snow layers from Antarctica. *Int. J. Environ. Anal. Chem.*, **63**, 225–244.
- Udisti, R., E. Barbolani and G. Piccardi. 1991. Determination of some organic and inorganic substances present at ppb level in Antarctic snow and ice by ion chromatography. *Ann. Chim.*, **81**(7–8), 325–341.
- Udisti, R., F. Casella and G. Piccardi. 1993. The role of methanesulphonic acid in snow samples from Terra Nova Bay (Antarctica). In Restelli, G. and G. Angeletti, eds. *Dimethylsulphide: oceans, atmosphere and climate (1992)*. Dordrecht, etc., Kluwer Academic Publishers, 153–162. (Air Pollution Research Report 43)
- Udisti, R., S. Bellandi and G. Piccardi. 1994. Analysis of snow from Antarctica: a critical approach to ion-chromatographic methods. *Fresenius' J. Anal. Chem.*, **349**(4), 289–293.
- Udisti, R., R. Traversi, S. Becagli and G. Piccardi. 1998. Spatial distribution and seasonal pattern of biogenic sulphur compounds in snow from northern Victoria Land, Antarctica. *Ann. Glaciol.*, **27**, 535–542.
- Wagenbach, D. 1996. Coastal Antarctica: atmospheric chemical composition and atmospheric transport. In Wolff, E.W. and R.C. Bales, eds. *Chemical exchange between the atmosphere and polar snow*. Berlin, etc., Springer-Verlag, 173–199. (NATO ASI Series I: Global Environmental Change 43)