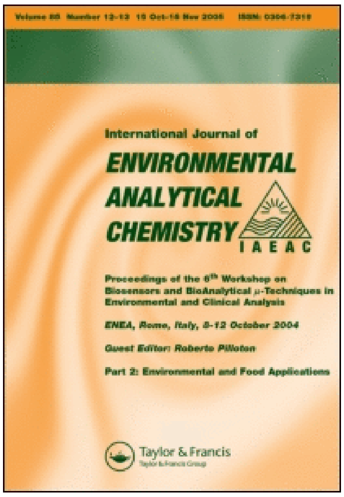

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SEASONAL TRENDS AND CHEMICAL COMPOSITION OF SNOW AT TERRA NOVA BAY (ANTARCTICA)

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Snow samples from two snow-pits, located at different altitudes and distances from the sea, were analyzed to establish the H_2O_2, NO_3^-, Cl^-, SO_4^{2-}, nss SO_4^{2-} and MSA concentrations.

The mean annual accumulation rates were calculated from the layer dating based on the H_2O_2 depth profile.

The seasonal trends of the examined components' time series are discussed. The results obtained for the two stations are compared and found to be coherent. MSA appears to be the most promising seasonal tracer for the Terra Nova Bay region which is characterized by a strong marine contribution.

KEY WORDS: Seasonal trend, snow analysis, Antarctica, snow accumulation rate, snow-pit samples.

INTRODUCTION

The analysis of principal and trace components of snow and ice from Antarctica is important in understanding the global transport phenomena, the biochemical and geochemical cycles and in assessing the background concentration values of various components. Theoretical considerations by Junge[1], experimentally supported by the results of Lambert *et al.*[2] and Pourchet *et al.*[3], suggest the existence of a good correlation between snow and atmospheric composition. The snow regularly deposited on the ice surface provides an archive of the chemical composition of the local atmosphere over many thousands of years[4].

During the last three expeditions (1987–1990) of the Italian Antarctic National Research Project (PNRA), surface and fresh snow samples were collected in various stations at different altitudes and distances from the sea, in an area of about 150 Km in the vicinity of the Italian base of Terra Nova Bay (lat.: 74° 41′ 42″ South: 164° 07′ 23″ East).

The principal (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} and H^+) and trace (F^-, CH_3COO^-, $HCOO^-$, $CH_3SO_3^-$) components of these samples were determined to examine their spatial distribution and to evaluate the contribution of the different natural sources to the composition of the snow precipitation[5–7]. The marine aerosol was generally found to be dominant (mainly for Cl^-, Na^+, SO_4^{2-}, Mg^{2+}), but its contribution diminishes in the stations further away from the sea or at higher elevation sites. A net crustal and atmospheric contribution can be pointed out in this case or in the case of the stations with particular orogenic profiles.

The samples analyzed so far in this laboratory were relative to summer depositions only, therefore they cannot be considered sufficiently representative for a survey of the regional aerosol composition. Furthermore, the data of the snow annual accumulation rates for the Terra Nova Bay region were missing. Since the concentration of some atmospheric components follows a seasonal pattern, snow and ice layers can be dated based on their concentration depth profiles.

The H_2O_2 profile is especially useful for this purpose [8, 9], but a seasonal signal is also exhibited by MSA and nss sulphates [10, 11] and by nitrates[12].

In order to study the composition of successive events of atmospheric precipitations, snow-pit samples were collected in two stations differing in their elevation and distance from the sea: the Terra Nova Bay area will thus be characterized based on precipitation composition and quantity; in addition the chemical history of precipitation during recent years can be reconstructed.

EXPERIMENTAL

Instrumentation

Ion Chromatography The analyses were performed with a Dionex mod. 4000i Ion Chromatograph interfaced with a MS-DOS PC. The separations were achieved with ion-exchange columns: Dionex AS4A ($NaHCO_3$ 1.2 mM + Na_2CO_3 1.3 mM eluent) for inorganic ions and Dionex AS5A 5 µm ($Na_2B_4O_7$ 3.3 mM eluent) for organic ions[13]. Detection was achieved with a Dionex CDM-1 detector following background conductivity suppression (Dionex AMMS-1 anion micromembrane suppressor). The analytical responses were recorded and processed with the Dionex AI-450 chromatographic software.

Flow Injection Analysis The H_2O_2 content in the samples was determined by the FIA method with spectrofluorimetric detection. The FIA system includes a 4 channel peristaltic ISMATEC MS-Reglo pump, a 4-way Rehodyne 5020 Teflon injection valve and a Shimadzu RF-551 spectrofluorimetric detector with a 12 µl volume cell.

Data were recorded with a HP 3396A integrator. Fluorescence was obtained by means of the reaction between 3.9 10^{-2} M p-hydroxy-phenyl-acetic acid and 375 peroxidase units/100 ml in 0.13 M ammonia solution ($\lambda_{ex} = 323$ nm; $\lambda_{em} = 408$ nm).

Reagents

The water used for blanks and standard solutions was purified through a Millipore Milli-Q system (Resistivity > 18MΩ) and continuously recycled in an ELGA-UHQ apparatus (ion chromatography) or distilled on MnO_4^- (Spectrofluorimetric determination).

Table 1 Snowpit sampling stations—1990–91 campaign.

19 SN IV—	Styx Glacier (Plateau), Lat. 73° 51.9′ S Long. 163° 41.5′ E height 1700 m above the sea level—about 50 Km in a straight line from the sea.
27 SN IV—	Mc Carthy Ridge, Lat. 74° 32′ 57″ S Long. 162° 56′ 29″ E height 700 m above the sea level—about 40 Km in a straight line from the sea.

Diluted standard solutions were prepared, right before the analysis, from 1 g/l stock solutions.

All of the reagents used were Suprapur or reagent grade (Merck, Fluka and Sigma).

SAMPLING AND ANALYSIS

During the 1990/91 Italian Antarctic expedition, 226 samples were collected in two 2.2 m-deep snow-pits, at two stations varying in height and distance from the sea within a radius of approximately 50 Km from Terra Nova Bay—Victoria Land. The stations' geographic parameters are reported in Table 1. The progressively numbered samples were collected by inserting pre-cleaned polyethylene vials (16 × 100 mm) into the vertical walls of the snow-pit, after having removed 10 cm of snow from the exposed surface with pre-cleaned polyethylene scoops. While working, the operators wore full clean room garb (over the down-clothing), polyethylene (over silk) gloves and particle masks. All samples were stored at −20 °C after collection.

The samples were melted, still closed in polyethylene bags, at room temperature in the laboratory. The vials were opened under a laminar flow hood class 100 and the just melted liquid was drown up with an all-polyethylene syringe by an operator equipped with polyethylene gloves and a particle mask. The samples were filtered on a 0.45 μm Teflon membrane filter prior to analysis.

RESULTS AND DISCUSSION

The odd-numbered samples were analyzed for H_2O_2 determination. The hydrogen peroxide analysis should be carried out soon after melting as H_2O_2 can undergo decomposition in solution. The even-numbered samples were analyzed by ion chromatography to determine the principal and trace anions. The resolution was 3 cm of snow sampled for all the vials. The apparent density of the snow layer was roughly evaluated weighing all of the vials with a homogeneous snow filling, with and without the sample.

H_2O_2

H_2O_2 is produced in the gas phase by the reaction of two O_2H radicals: the O_2H radicals arise from the photolysis of O_3 followed by a series of reactions involving OH radicals.

H_2O_2 is also produced in the liquid phase, i.e. in cloud droplets, by dissolved OH and O_2H radicals [14].

The H_2O_2 present in the atmosphere is scavenged and transferred to the ground by the frozen deposition, where it is preserved for a long time. This component can be used as a

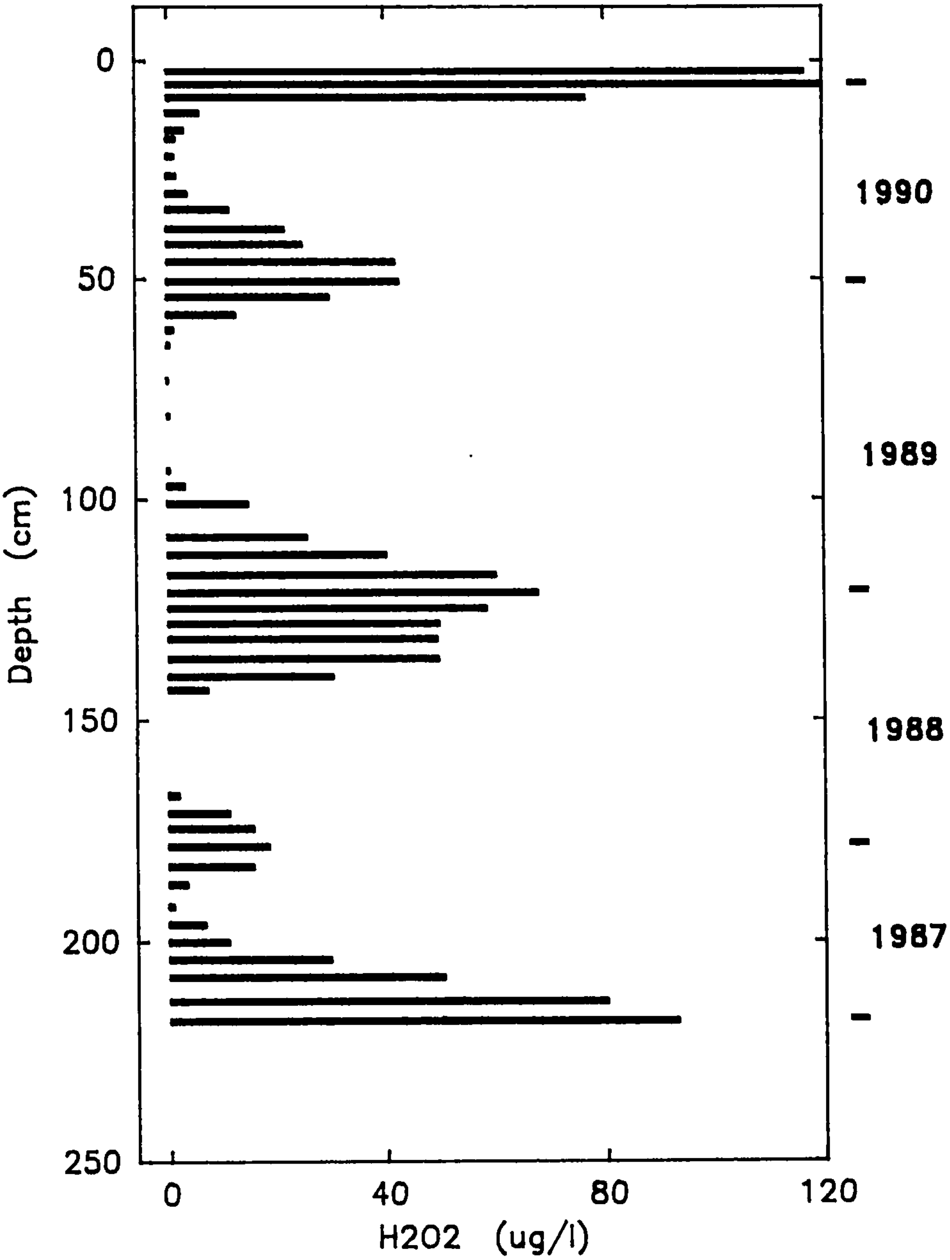


Figure 1 Hydrogen peroxide concentration profile in snowpit samples from Station 27.

tracer to date the annual snow layers because it is mainly produced during the light summer months, giving rise to a seasonal signal that can be retrieved due to its chemical stability. The seasonal cycle has also been reported for rain samples [15]. The concentration range reported by Sigg and Neftel[9] for Antarctic ice cores is 10 μg/Kg in the winter and 100–150 μg/Kg in the summer. Higher maximum values were found in Greenland melted snow layers [8,9].

When compared to the $\delta^{18}O$ time series used to date the layers, the H_2O_2 maxima were found to be synchronous to the $\delta^{18}O$ ones.

Figure 1 shows the plot of the concentrations of H_2O_2 vs. depth for the Station 27 samples: the maxima indicate the summer layers. As the snow was collected during the 1990–91 summer, 4 annual layers were estimated on the basis of the maxima in the depth profile, as reported in the same figure.

Station 19 data, with the same resolution of the layer sampled (3 cm), show a similar seasonal periodicity (Figure 2). For this station we observed six summer maxima in the H_2O_2 concentration profile relative to five annual layers. The presence of an extra annual layer in this station snow-pit when compared to the snow-pit of the same depth sampled at Station 27, indicates that the annual snow precipitation at this site is less abundant in agreement with the differences in elevation and distance from the sea between the two sampling sites.

The comparison between the summer peak values measured for the two stations shows that the Station 19 maxima are about 20% higher than the corresponding values for Station 27. As the measures' reproducibility is about 3 % this difference can be regarded as significant. Figure 3 shows the annual accumulation rates, expressed in cm of snow, for both stations: a coherent accumulation trend results for the two stations, with abundant (1989) and scarce (1987) precipitation periods. The mean annual accumulation rates for the sampled years, expressed as $g\ cm^{-2}\ yr^{-1}$, are also reported in the same figure.

The apparent snow density was calculated solely from the weight of the completely filled vials.

Very homogeneous values, all distributed around an average of 0.48 g/ml, were obtained for Station 27, along the depth profile.

The average accumulation rate for this station was calculated as $27\ g\ cm^{-2}\ yr^{-1}$, using the multi-year mean density value.

The samples relative to Station 19, on the other hand, show a slight tendency to increase with depth, varying from 0.2 to 0.6 g/ml.

A mean annual density value was preferred in this case, and the average annual accumulation rate resulted $16\ g\ cm^{-2}\ yr^{-1}$.

The apparent density values are in agreement with the ones reported for the same area by Meneghel and Smiraglia [16].

NO_3^-

The NO_3^- present in the atmosphere, and subsequently determined in the precipitation, has multiple sources: anthropogenic input, lightning, NO_2 oxidation, cosmic rays, biomass burning, long range transport, denitrification of the lower stratosphere [12,17,18]. In the Northern emisphere the principal emissions are of anthropogenic origin, with maximum values in the industrialized continental regions and minimum values over the oceans[19]. The primary sources of NO_3^- in Antarctica are not clearly assessed: Herron[20] excludes a relevant anthropogenic contribution. Legrand and Delmas[21] found no correlation between volcanic input and NO_3^-. Herron[20], Delmas[22] and Neubauer and Heumann[23] exclude the marine aerosol as the main NO_3^- source. Determinations of the isotopic ratio $^{15}N/^{14}N$ suggest a non-biogenic origin[24].

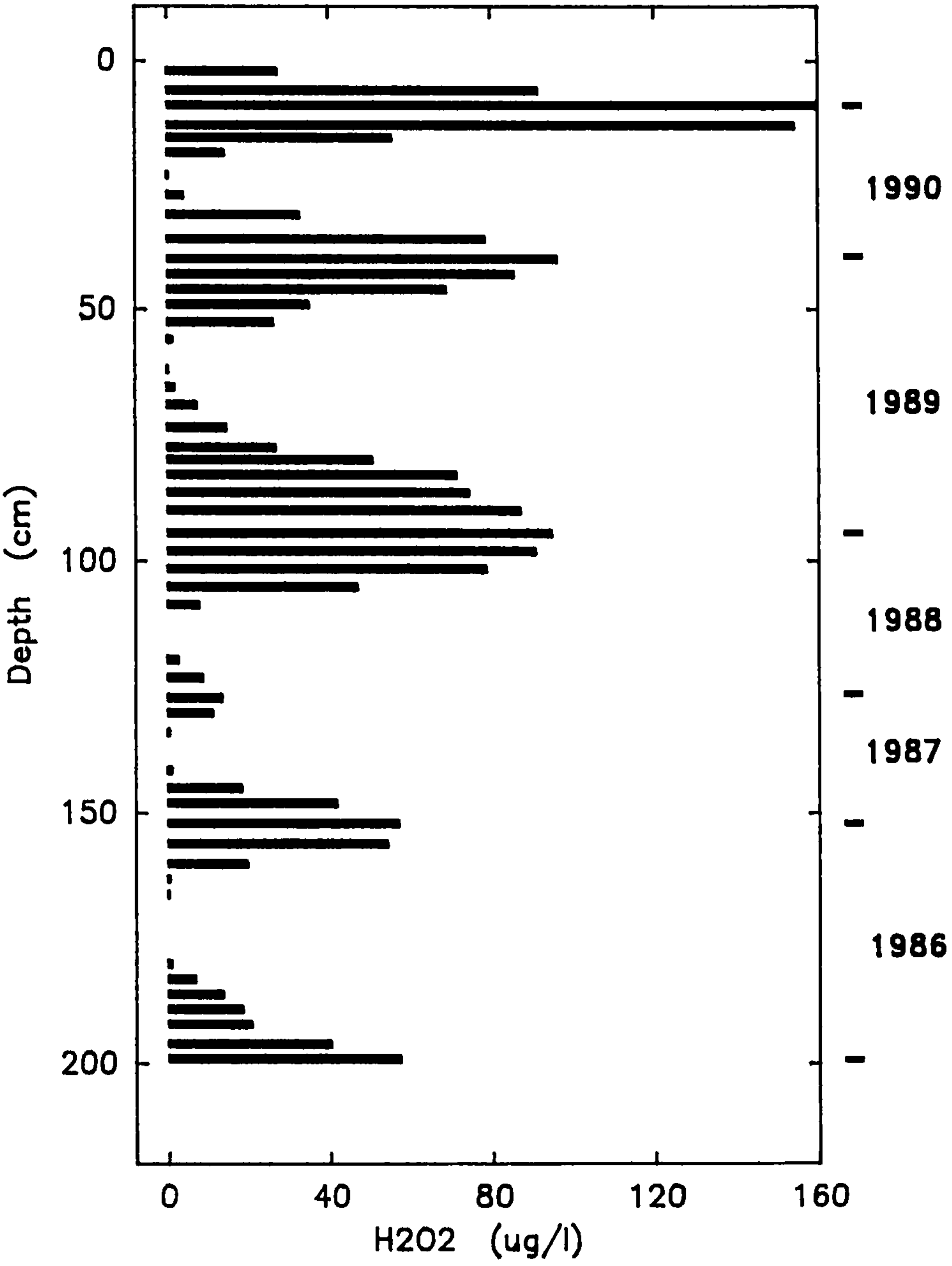
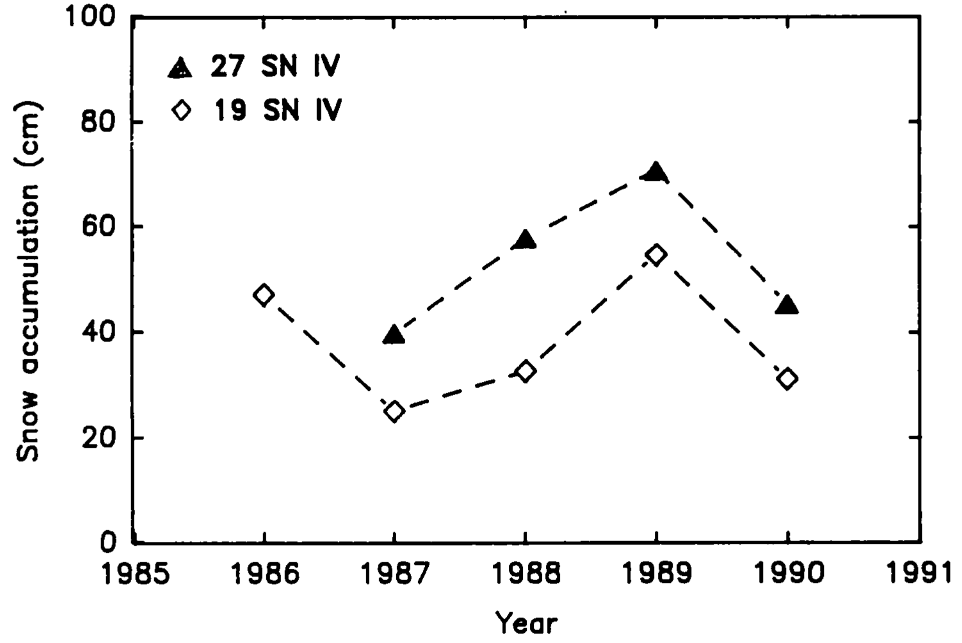


Figure 2 Hydrogen peroxide concentration profile in snowpit samples from Station 19.

Therefore the principal sources of nitrogen in Antarctica seem to be due to long-range transport of HNO_3, stratosphere-troposphere transfer and physical phenomena like lightning and aurora.

Ehhalt and Drummond [19] state that HNO_3, derived from the NO_x produced in the atmosphere, is the most abundant nitrogen species present in the troposphere due to its relatively long life. HNO_3 is removed in 2–6 days mainly by wet deposition. Legrand and Delmas[25], on the basis of ionic balances calculated for snow samples collected in the interior and in the coastal areas of Antarctica, deduces that the NO_3^- ion derives solely from HNO_3.

The difficultly in interpreting the NO_3^- seasonal trend is related to the difficulty of assessing a single primary source. Various authors report a clear seasonal signal, with winter minima and summer maxima, for samples collected both in Antarctica and in Greenland[12, 20, 25, 26, 27]. Others find an ambiguous seasonal signal[23, 28].



Mean values

	Density g/ml	Accumulation g/cm2 Yr
27 SN IV	0.48	27
19 SN IV	0.33 – 0.50	16

Figure 3 Annual snow accumulation profiles for Stations 27 and 19. Mean values of density and accumulation rates for the two stations.

The plot of the Station 27 nitrate concentration vs. depth is shown in Figure 4. When comparing this vertical profile with that of H_2O_2, well defined summer maxima are evident for the last three years, while the signal corresponding to the 1987–88 summer is not significantly higher than the average winter value. The NO_3^- maxima are slightly out of

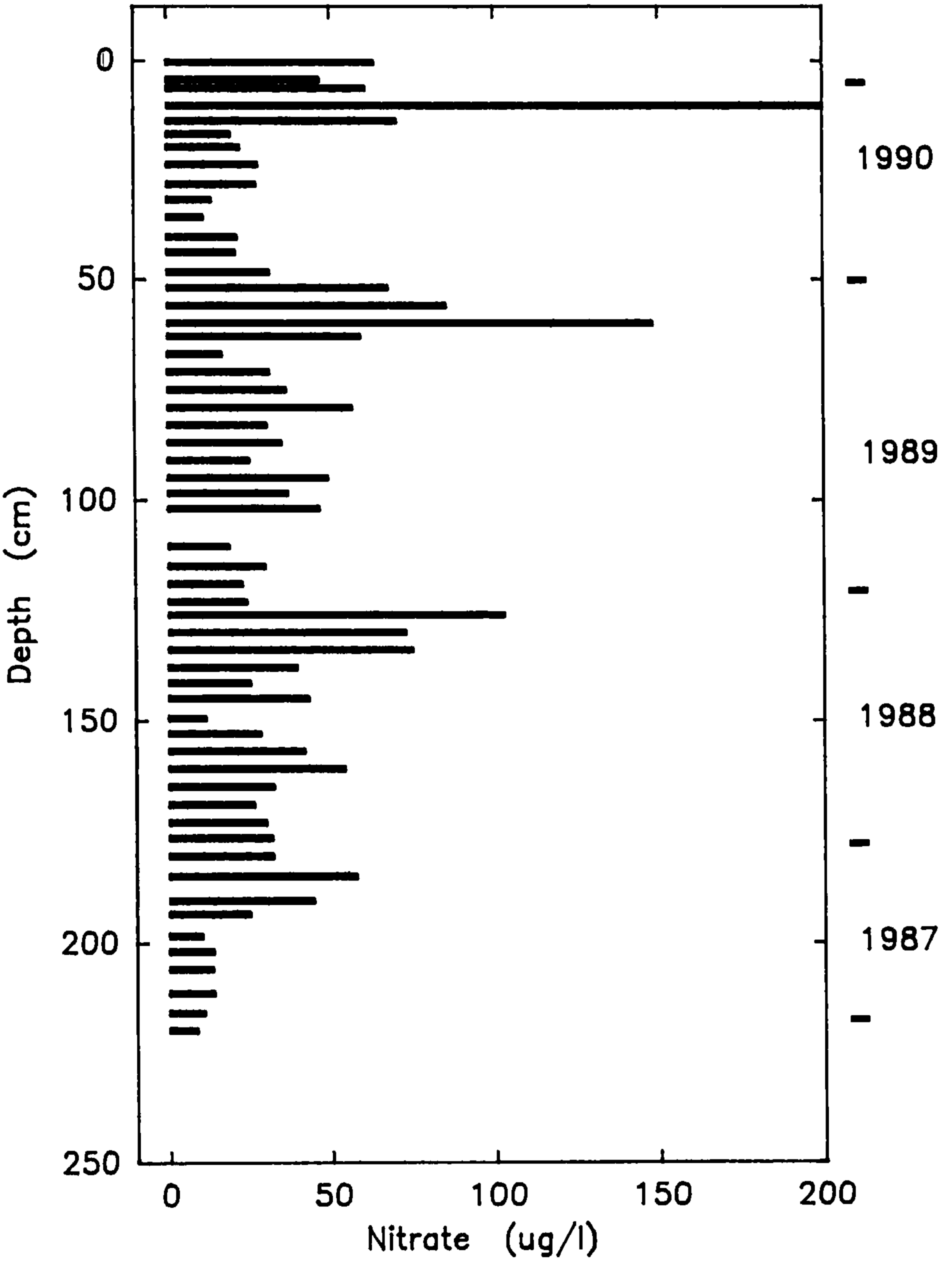


Figure 4 Nitrate concentration profile in snowpit samples from Station 27.

phase and precede the H_2O_2 summer peaks. The lack of coherence can be explained by considering that one of the possible causes of the seasonal nitrate content variation is the denitrification of polar stratospheric clouds (PSCs) in the spring season[12]. Photochemical oxidation of NO_x producing HNO_3[25] or long-range atmospheric circulation phenomena may be another explanation of the observed behavior[23, 25].

An analogous clear seasonal trend for the last three years was found for the Station 19, but the signal is less distinct with increasing depth. Spring values much higher than the average for the last three years were also found by Mayewski and Legrand[12] in snow-pit samples collected near the South Pole. Neubauer and Heumann[26] reported values relative to fresh snow and one year old snow: he suggested that the NO_3^- content in the snow is time dependent due to post-depositional effects. The trend observed for more recent years can thus be explained by re-emission into the atmosphere.

Cl^-

In Antarctica the sources of chlorides are essentially the marine spray and volcanic emissions of HCl, with a major contribution from the sea[4, 20]. The marine origin is supported by a Cl/Na ratio close to the one exhibited by these two components in sea-water (1.8 by weight). Deviations from this value may be a consequence of exchange reactions in the atmospheric aerosol between NaCl and H_2SO_4 producing Na_2SO_4 and gaseous HCl which follow different distribution pathways. This reaction is more likely to occur in the summer, when higher concentration of biologically related H_2SO_4 are available [4, 27]. While the areas in the interior of the continent are more influenced by the secondary aerosol (HCl), the main contribution to the Cl^- in the coastal zones is the primary aerosol (marine spray)[4].

This is clearly verified by the composition of the surface snow samples collected in various stations near Terranova Bay during the 1987/88[5] and 1988/89[6] field seasons which exhibit Na^+ based enrichment factors of Cl^- close to 1, even for stations relatively remote from the sea (Priestly nevé, 160 Km).

With regard to the surface snow samples, an inverse correlation was found between the marine aerosol contribution and the station geographical position, in terms of distance from the sea and altitude, in agreement with data reported in various literature [20, 21, 29]

Figure 5 shows the Cl^- concentration depth profile for Station 27: a definite seasonal trend is absent but, instead, singular events of strong marine spray depositions can be evidenced. These events occur mainly during the winter months, specially in 1987 and 1989, where Cl^- concentration of 5–10 mg/l were found.

The Cl^- series for the Station 19 is analogous to that for Station 27, but the average concentration levels are lower. A more definite seasonal trend is evident for the Station 19 profile showing winter maxima.

High marine spray winter depositions at Terra Nova Bay are justified by the presence of an annually recurring polimnya in the western Ross Sea which markedly influences sea-ice dynamics in that region[30]. The presence of ice free sea water in the winter, due both to the screening effect of the Drygalski Ice Tongue and to the strong catabatic winds, may explain the input of significant quantities of marine spray associated with easterly winds. The average Cl^- concentration values for the Stations 19 and 27 are 670 µg/l and 1250 µg/l respectively. These data, even when considering their high dispersion due to the numerous winter events, are in agreement with the conclusion that the parameter controlling the sea-salt transport is elevation rather than distance from the sea[21].

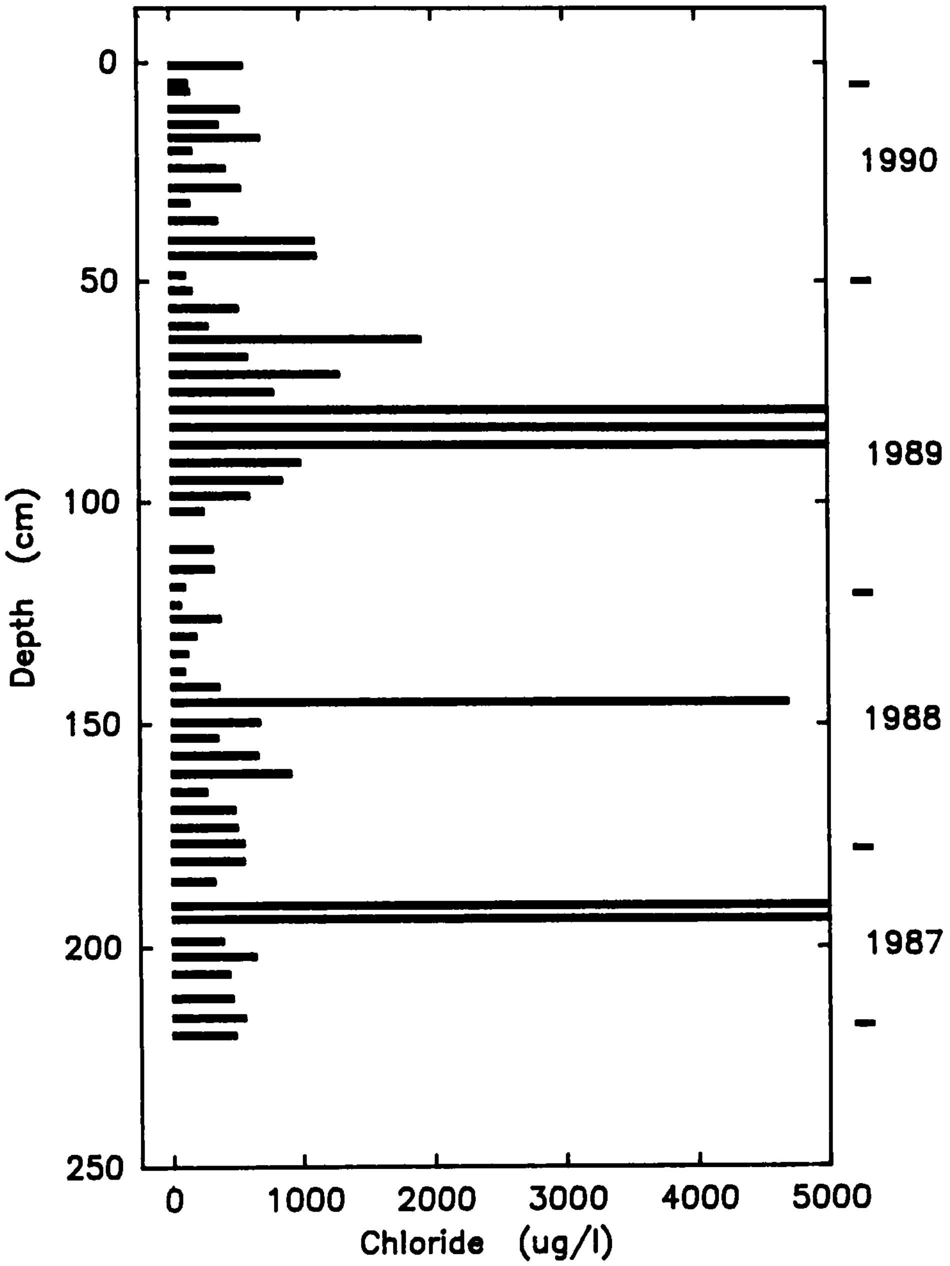


Figure 5 Chloride concentration profile in snowpit samples from Station 27.

SO_4^{2-} and nss SO_4^{2-}

The total SO_4^{2-} depth profile for Station 27 is shown in Figure 6

Its trend is similar to that of the chlorides, justifying the assumption that in coastal zones the main contribution to the sulphate content comes from marine aerosol. In Antarctica, no

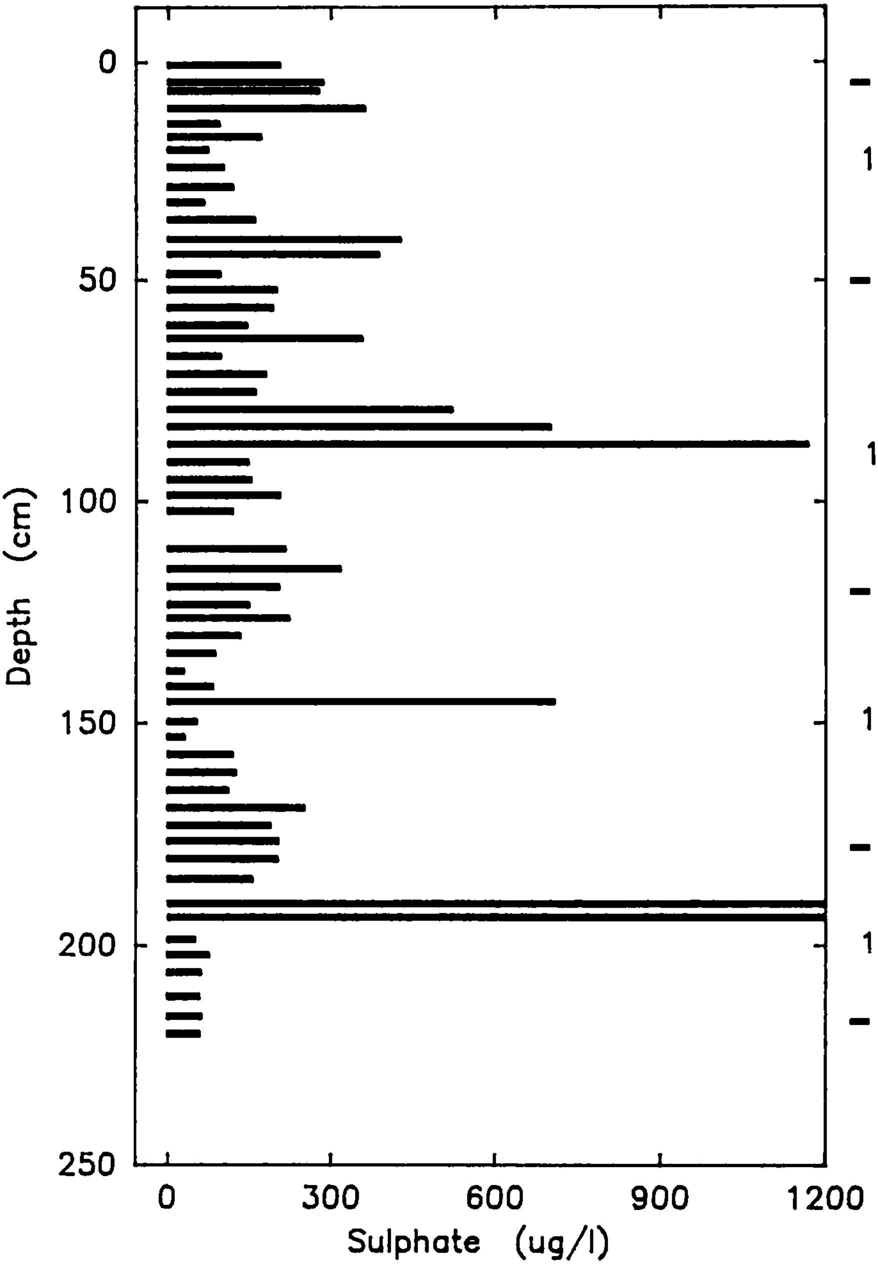


Figure 6 Total sulphate concentration profile in snowpit samples at Station 27.

anthropogenically-related increase in the sulphates was found, as opposed to the situation in Greenland[20]. The same considerations already developed for the chlorides can be made for the sulphates as well: concentration maxima found in winter layers, especially for 1987, and lower average values for Station 19 (130 μg/l) compared to those of Station 27 (256 μg/l).

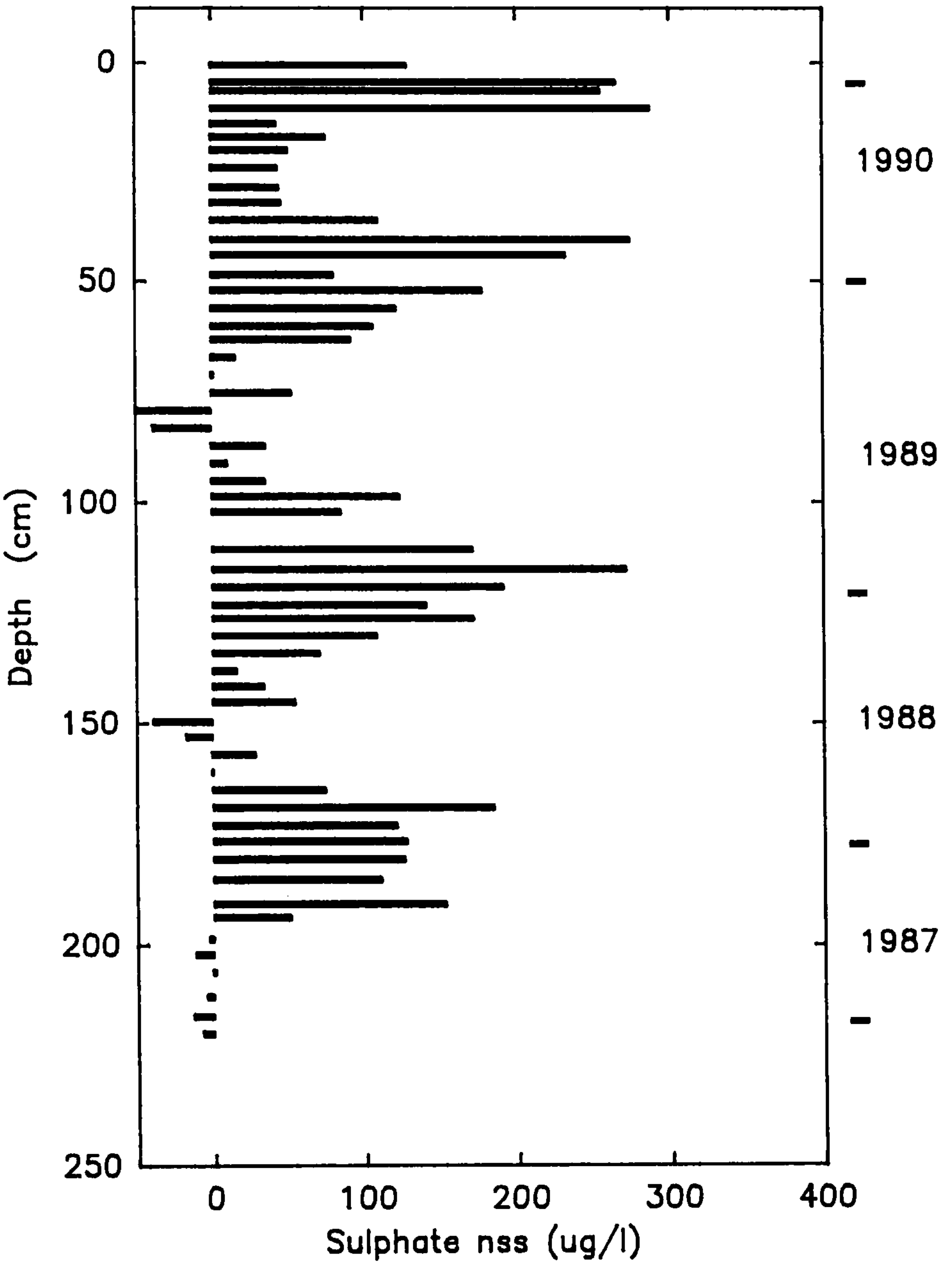


Figure 7 Sulphate non-sea salt concentration (calculated from Cl^- content) profile in snowpit samples from Station 27.

Legrand and Delmas[27] conclude that the secondary aerosol is the main source of sulphates, present as H_2SO_4 of volcanic or bio-marine origin, in the interior of the continent. The contribution of non-marine spray origin sulphates, nss SO_4^{2-}, can be evaluated subtracting the sea-salt sulphate calculated from the Cl^- or Na^+ content of the sample.

The concentration profile of nss SO_4^{2-}, based on the Cl^- content, for Station 27 is shown in Figure 7. A clear seasonal signal, synchronous with the H_2O_2, with summer maxima and winter minima, is evident.

The same summer maxima are exhibited by Station 19 nss SO_4^{2-}, except for 1987, where the nss SO_4^{2-} maxima appear in the winter.

The nss SO_4^{2-} for the coastal zones is closely related to the dimethylsulfide (DMS) cycle, because the DMS photochemical oxidation is the main source of this sulphate. DMS is produced by the metabolic processes of phytoplancton blooms of different species present in the sea[11, 31, 32].

Some negative values appear in the nss SO_4^{2-} depth profile, almost exclusively in the winter months, when their concentration is minimal. Negative values have been reported by different authors for stations with a dominant marine contribution.

As already reported for the total sulphates, the average nss SO_4^{2-} concentration values for Station 19 (36 µ/l) are significantly lower than for Station 27 (82 µ/l).

MSA

The DMS produced by the phytoplancton is also oxidized to methane sulfonic acid (MSA): MSA has normally been found in the Antarctic snow[7, 33–36].

The MSA depth profile for Station 27 is reported in Figure 8.

Its signal is coherent with that of nss SO_4^{2-}: the correlation coefficient between MSA and nss SO_4^{2-} is $r = 0.84$, which suggests that both components have the same origin and similar transport mechanisms. The MSA summer maxima exactly match that of H_2O_2.

For the Station 19, an analogous correlation between MSA and nss SO_4^{2-} results, while the signal vs H_2O_2 is ambiguous for 1987.

The MSA signal as a seasonal tracer appears very promising as long as the MSA-based annual layer dating matches exactly the one based on the H_2O_2 record. For the examined region, MSA-based dating can completely substitute nss SO_4^{2-} dating. Using either MSA or nss SO_4^{2-} leads to the same conclusions as regards dating: the advantage of using MSA as a seasonal tracer is that it is measured rather than calculated, as is nss SO_4^{2-}, and thus its determination is more reliable.

CONCLUSIONS

The study of time series data for the two stations examined confirms that the marine component is dominant in snow precipitations at Terra Nova Bay. The interesting result is that the long-range transport components (H_2O_2, HNO_3) exhibit higher concentrations in the station at a higher elevation, while the components mainly related to the marine source (Cl^-,

SO_4^{2-} from sea-salt, MSA and nss SO_4^{2-} of biogenic marine origin) show higher concentrations at the less elevated site (Station 27).

Almost all of the examined components exhibit a seasonal cycle: H_2O_2, NO_3^-, nss SO_4^{2-} and MSA, in particular, can be used to identify the annual deposition layers. H_2O_2 may seem

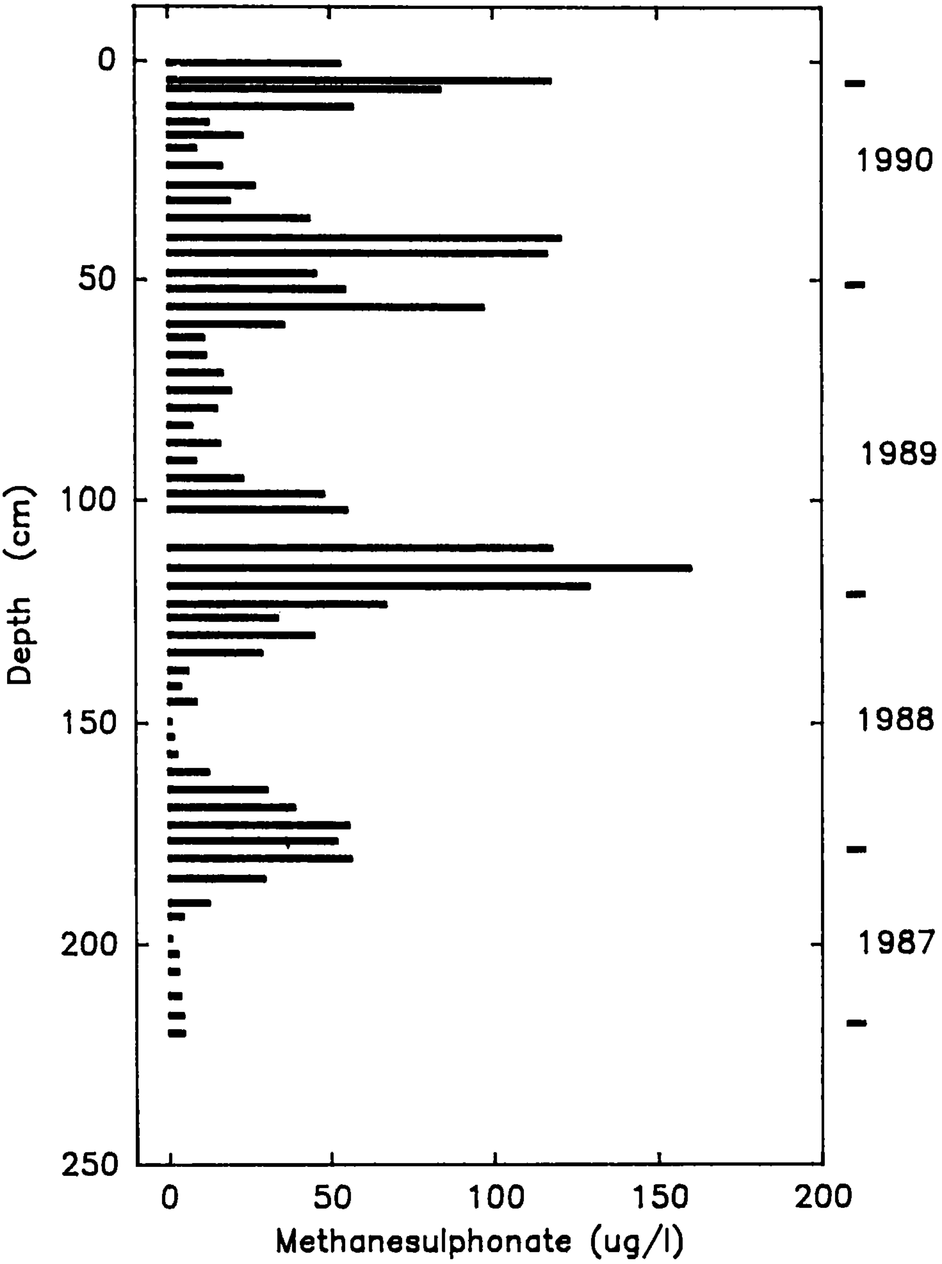


Figure 8 Methanesulphonate concentration profile in snowpit samples from Station 27.

to be the best choice because its signal is not dependent on the age of the snow, at least for limited sampled depths. Unfortunately, the H_2O_2 determination is subject to contamination and post melting decomposition problems. The NO_3^- signal is more easily determined, but the range of its seasonal variation decreases with depth. For the examined region, MSA seems to be optimal as a seasonal tracer because its measurements is not highly subject to contaminations and is highly reproducible even at µg/l or sub µg/l levels. Moreover, it is a direct measurement, as opposed to nss SO_4^{2-}, and it is not subject to interpretational errors as it derives from a well studied unique source.

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