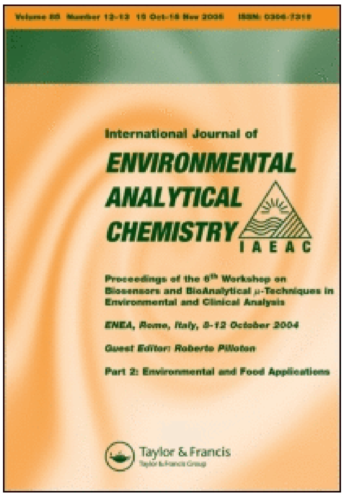

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R. Udisti[a]
[a] Department of Public Health and Environmental Analytical Chemistry, University of Florence, Florence, Italy

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MULTIPARAMETRIC APPROACH FOR CHEMICAL DATING OF SNOW LAYERS FROM ANTARCTICA

R. UDISTI

Department of Public Health and Environmental Analytical Chemistry, University of Florence, 9 Via Gino Capponi, I-50121 Florence, Italy

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A dating method for successive snow layers is proposed which is based on a combination of concentration profiles of three chemical parameters measured for each sample: H_2O_2, MSA, and $nssSO_4^{2-}$. In the studied area (Northern Victoria Land, Antarctica), these substances demonstrate a clear seasonal character with summer maxima and winter minima which together can constitute an univocal annual indicator. The proposed method involves searching for maximum values and normalizing the concentration/depth profile of each substance; a smoothed sum of the contribution for each component, for each depth value, gives a resulting profile which is better adapted to objective interpretation of the seasonal trends.

This method is applied to the dating of snow and firn samples coming from two snowpits and one shallow firn core at three different stations, which are found at different altitudes and distances from the sea, within approximately 200 Km from the Italian base at Terra Nova Bay.

The variations in concentration of the three substances with depth were examined and the relative trends were evaluated as a function of the geographic position of the sampling stations.

KEY WORDS: Snow layer dating, seasonal trends, multiparametric dating method, annual indicators, snow analysis, antarctica.

INTRODUCTION

The recognition of successive annual snow layers is an important instrument for the relative dating of snow, firn, or ice samples taken from snowpits or firn/ice cores. By counting successive annual layers, with reference to the surface or to a known temporal event found in a particular annual layer, it is possible to determine the absolute date for each snow layer sampled. This dating, and even more so the seasonal setting of the analysed sample, is useful in many areas of study, including:

* the study of seasonal trends of various components;

* the identification of principal and secondary sources of the components;

* the identification and study of transport mechanisms;

* the interpretation of existing correlations between the various components;

* the characterization of a station from the perspective of average annual accumulation;

* the importance of altitude, distance from the sea and geographic position on snow fall accumulation.

Generally, relative dating of successive snow layers is carried out following the seasonal trend of only one parameter, such as H_2O_2, NO_3^-, Na^+, Cl^-, Cl^-/Na^+, $\delta^{18}O$, non sea salt sulphate ($nssSO_4^{2-}$), methanesulphonic acid (MSA), electrical conductivity (ECM), stratigraphy or by "visual" comparison of concentration profiles with the depth for more than one parameter[1-19]. These methods, however, can be difficult to interpret objectively. Therefore, a method to obtain a dating hypothesis based on less subjective criteria seems to be very useful.

In the present work a simple multiparametric method of dating is proposed which is based on a linear combination of concentration of H_2O_2, MSA and $nssSO_4^{2-}$, measured for the same sample of snow or firn, after a process of normalization and smoothing carried out on concentration profiles with the depth for each of the three components.

EXPERIMENTAL

Instrumentation

The determination of H_2O_2 is carried out using a method of Flow Injection Analysis with a spectrofluorimetric detector (Shimadzu RF 551). This method is based on the formation of a fluorescent dimer for the reaction of p-hydroxy-phenyl-acetic acid with H_2O_2 in the presence of peroxidase[20,21].

The determination of MSA and of the ionic species necessary for the determination of the concentration of $nssSO_4^{2-}$ (total SO_4^{2-}, Na^+ or Cl^-) is carried out by ionic chromatography using a Dionex 4000i Ion Chromatograph with anionic or cationic conductivity suppressor and Dionex AI-450 intergration software.

Further details regarding methods used, manipulation of samples, contamination problems, and analytical results obtained are described in our previously published works[22-25] and other work in preparation[26]. Table 1 shows a synthesis of the determination methods and the principal operative variables.

Reagents

In ion chromatographic measurements, for the preparation of eluents, regenerants and all standard solutions, ultrapure water (> 18 mΩ) was used, obtained from a Millipore MilliQ apparatus and continuously recycled in an Elga UHQ apparatus. The water produced was then bidistilled further, using a solution of $KMnO_4$ in the first phase of distillation to destroy trace residues of H_2O_2, and then used for the H_2O_2 determination[26]. Stock standard solutions (1000 mg/l) were obtained from Merck Suprapur, when available, or Merck, Fluka or Sigma Reagent Grade reagents.

Sampling

The proposed method was applied to samples taken from two snowpits of approximately 2 m excavated during the Italian Antarctic Expedition of 1990/91 and from a shallow firn core, approximately 7.5 m deep, obtained during the Italian Antarctic Expedition of 1992/93. The Italian Antarctic Expeditions were a part of the Antarctic National Research Program (PNRA). The three sampling stations, located in Northern Victoria Land (Antarctica) and within a range of 200 Km from the Italian base at Terra Nova Bay,

Table 1 Methods for concentration determination of the compounds utilised as seasonal indicators.

H_2O_2

Reagents: 3.9 10^{-2} M p-hydroxy-phenyl-acetic acid
0.13 M NH_3
8.4 10^{-4} M EDTA
375 Peroxidase units/100 ml
Carrier: H_2O Milli-Q bidistilled on $KMnO_4$ and filtered on 0.45 μm.

MSA

Separator Column: Dionex AS5A-5 μm (guard column: Dionex AG5A)
Eluent: 1 ml/min 1.8–30 mM $Na_2B_4O_7$
Conductivity suppressor: Dionex AMMS-1
Regenerant: 7.0 ml/min 1.25 10^{-2} M H_2SO_4

nss-SO_4^{2-}

SO_4^{2-} and Cl^-
Separator Column: Dionex AS4A (guard column: Dionex AG4A)
Eluent: 2 ml/min 1.2 10^{-3} M $NaHCO_3$ + 1.3 10^{-3} M Na_2CO_3
Conductivity suppressor: Dionex AMMS-1
Regenerant: 3.0 ml/min 1.25 10^{-2} M H_2SO_4

Na^+

Separator Column: Dionex CS 10 (guard column: Dionex CG10)
Eluent: 1 ml/min 2 10^{-2} M HCl + 5 10^{-4} M Diaminopropionic acid (DAP)
Conductivity suppressor: Dionex CMMS-2
Regenerant: 2.0 ml/min 5 10^{-2} M Tetrabutyl-ammonium hydroxide (TBAOH)

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differ in altitude and distance from the sea. This difference is useful for the evaluation of average annual accumulations in the studied area and the understanding of phenomena related to the origin and transport of substances present in the atmospheric aerosol, which make up a part of the snow composition[4,10,25,27–36]. The geographic position and characteristic of the sampling stations are reported in Figure 1 and Table 2.

Snowpit samples (47 samples from Station 19, 58 samples from Station 27) were collected by inserting pre-cleaned polyethylene vials (35 × 100 mm) into the vertical snow walls after having removed about 10 cm of snow from the exposed surface. Anti-contamination procedures were followed during sampling, storage (at –20°C), and manipulation of the samples.

Results relative to the analysis of a series of smaller vials (16 × 100 mm) taken in parallel columns from the same snowpits have been previously published. The results of the respective concentration trends, as a function of the depth, are in excellent agreement. This is evidenced by the comparison of Figures 2 and 3 of the present work with Figures 1, 2, 7 and 8 of Piccardi *et al.*[25]. This fact is of particular importance with regards to the concentration of $nssSO_4^{2-}$, the determination which carries the greatest risk of experimental error[37]. The findings seem even more significant considering the fact that in the previous series, due to a shortage of sample volume, it was not possible to determine the cations; as a consequence the previously obtained values for $nssSO_4^{2-}$ were determined as a function of Cl^- content. Noting that the relative trends for the two series of vials for each station are superimposable, we can deduce that for stations of this typology and in this area the use of Na^+ or Cl^- as indicators of the sea salt contribution is fundamentally the same. This holds true particularly for stations situated at low elevations and near the sea[27].

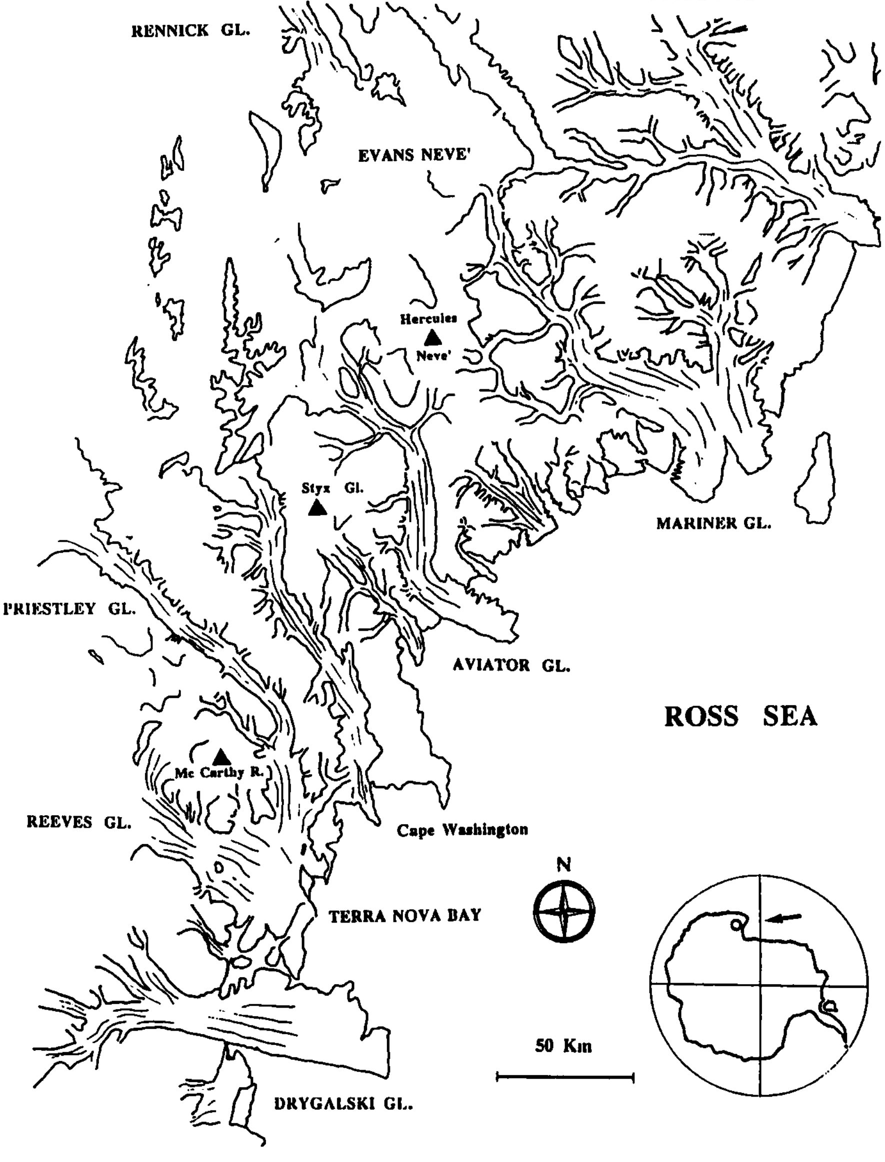

Figure 1 Sampling map of stations sampled during Italian Antarctic Expeditions 1990/91 (Mc Carty Ridge and Styx Glacier) and 1992/93 (Hercules Nevé).

Table 2 Sampling stations.

Station Code	*Station Name*	*Lat. Sud*	*Long. Est*	*Height m a.s.l.*	*Km from coast line*
27 SN IV/B	Mc Carthy Ridge	74°32'57"	162°56'29"	700	40
19 SN IV/B	Styx Glacier Plateau	73°51'54"	163°41'30"	1700	50
36 FC VIII	Hercules Neve'	73°07'34"	164°58'12"	2990	90

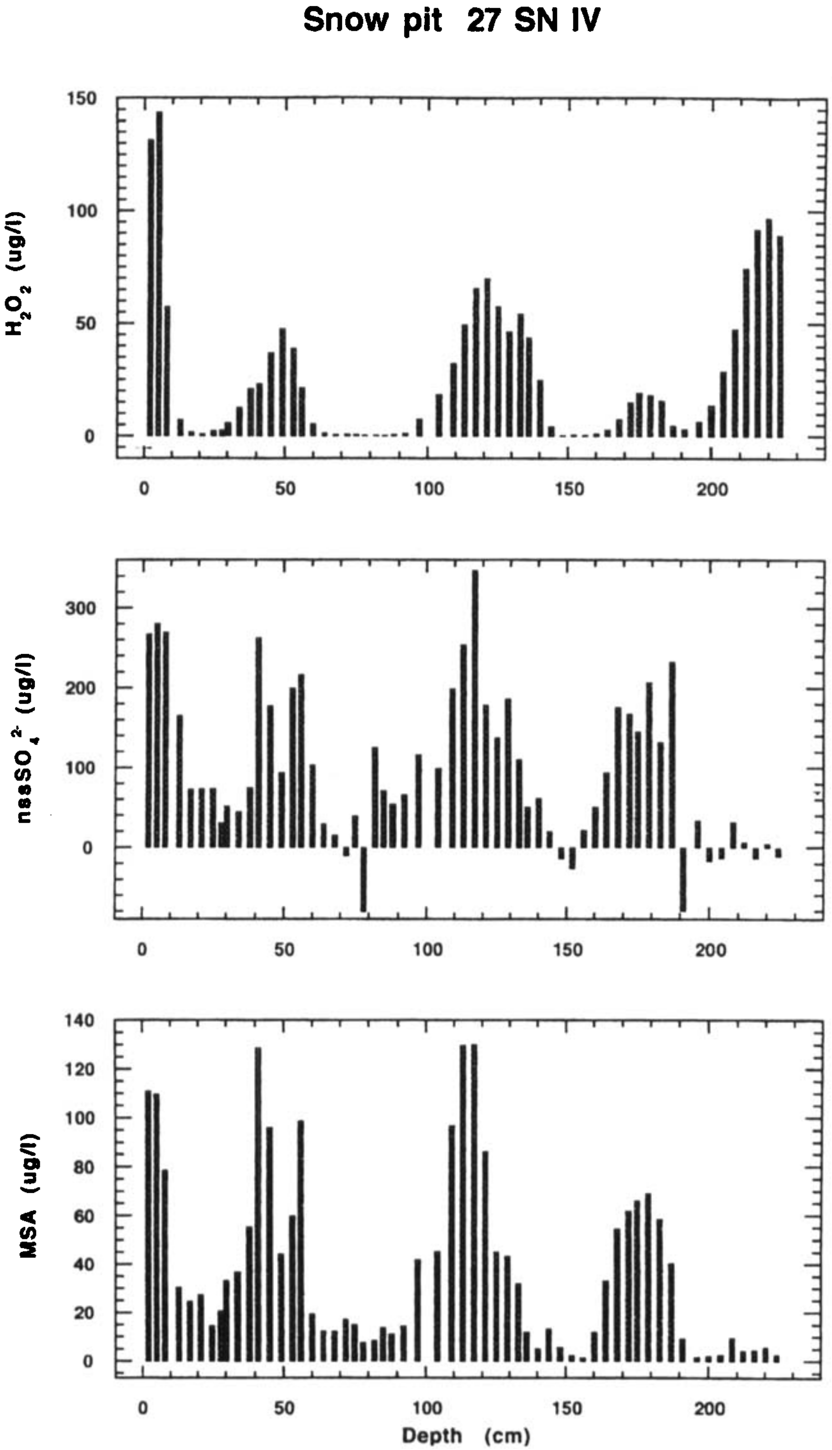

Figure 2 Station 27—Original concentration profiles for H_2O_2, $nssSO_4^{2-}$ and MSA.

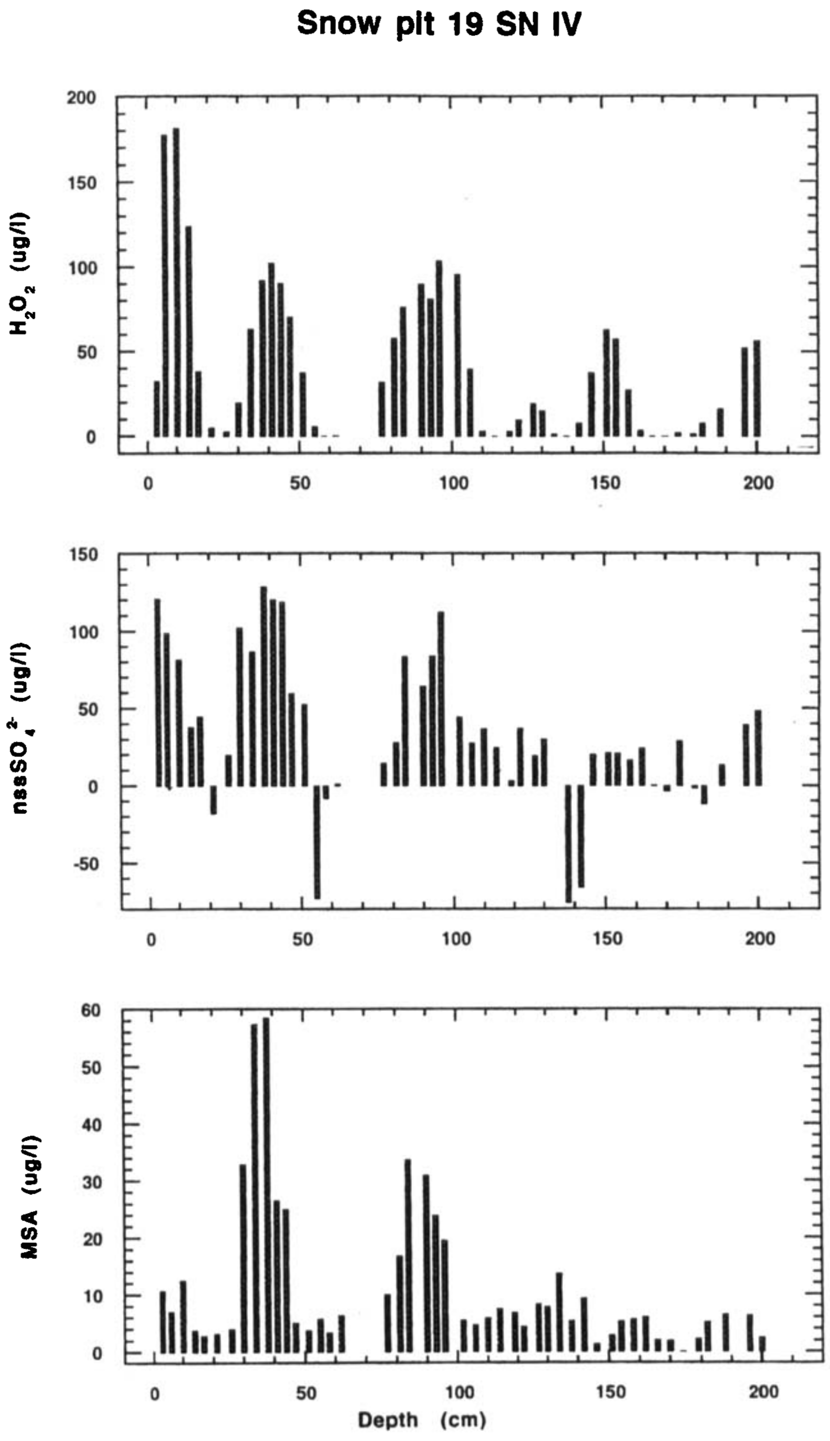

Figure 3 Station 19—Original concentration profiles for H_2O_2, $nssSO_4^{2-}$ and MSA.

The firn core from Station 36 (Hercules Neve') was transported frozen (at –20°C) to Italy in 50–70 cm long pieces in two sealed polyethylene sacks. Working in a cold chamber and under a laminar flow hood, each piece of firn core was cleaned removing approximately 1 cm of the exterior and then divided into sub-samples (total of 234) each about 3 cm long. The sub-samples were kept in pre-cleaned polyethylene containers and placed in double polyethylene sacks. The samples were thawed immediately prior to taking measurements under a class 100 laminar flow hood. Control blanks were tested periodically for the sampling and analysis procedures and for the cleanliness of the containers, which showed contamination values below the detection limit or at least two orders lower than the concentration values determined in the samples.

DISCUSSION

The contemporary consideration of more than one parameter with the aim of dating can present some limits:

1. The choice of parameters to be considered.
   It seems appropriate to choose those chemical substances which present clear and unequivocal seasonal concentration variations, due either to seasonality at the source or in the transport mechanisms. The choice of parameters is also tied to the typology of the sampling station, with particular attention to aerosol of marine origin (primary and secondary) and, therefore, to the station's geographic position.
2. The non-contemporaneousness of concentration maxima relative to the various components in the annual temporal series.
3. The lack, or difficult interpretation, of some concentration maxima for one or more of the observed components.
4. The presence of annual maxima relatively lower than other nearby annual maxima, or in any case belonging to the same temporal series, for a given component.

With regards to the first point, given the goal of obtaining an evaluation of the dating exclusively by chemical means, dating techniques based on the $\delta^{18}O$ isotopic ratio, ECM and stratigraphy have not been included.

Based on points 1 and 2, neither the concentration profile of the Na^+ or Cl^- ions nor the Cl^-/Na^+ ratio have been taken into consideration for dating. In fact the Na^+ ion does not appear to be a reliable seasonal indicator in our study area due to the strong sea influence. As previously mentioned[25,27], the study area is characterized by a relatively high number of precipitation events such as salt storms with notably high values of Cl^- and Na^+, which are found at the same ratio in sea water. These precipitation events, more frequently a winter occurrence, are not so rare in summer, or at least, in the seasons of transition, which are characterized by considerable variability in the peri-Antarctic atmospheric circulation.

Neither nitrate concentration seems to be useful for dating in studied area because the seasonal signal is less distinct with increasing depth[25].

On the basis, therefore, of previous analyses of snow from snowpit samples in the Northern Victoria Land, the following substances have been selected as parameters indicating seasonality:

* H_2O_2

* $nssSO_4^{2-}$

* MSA

Examining the seasonal trends of the concentrations of these compounds in the snow or firn samples, also in the case of these parameters, problems due to seasonal maxima which do not perfectly correspond persist. In fact, H_2O_2 presents concentration maxima as a function of the period of maximum solar radiation (late-spring, early-summer), while the other two substances are tied to the development of marine life, particularly to that of algal bloom (late-summer). The dephasing among the parameters will be, therefore, elevated as much as the number and extent of snow deposition occurring in the critical period between the respective maxima (early- to mid-summer). Moreover, this dephasing will depend, considerably, on the sample resolution and, therefore, both on the extent of the annual deposition which characterizes the station and on the sampling technique.

These limitations are, however, unavoidable and can be considered acceptable if they cause a widening of the annual peaks which is not too exalted. If the widening is excessive it can impede the complete distinction between summer maxima and winter minima.

Some fundamental observations regarding the three parameters selected for the dating of collected snow samples should be examined.

H_2O_2

H_2O_2 is principally produced from radical reactions originating from photolysis of O_3[38]. Since this is a photochemical process, maximum concentration of H_2O_2 in the atmosphere is reached during the period of maximum solar radiation, which coincides, in the studied area, with late-spring to early-summer. The H_2O_2 which is contained in snow remains stable for long periods of time[17,39,40]. In areas where the accumulation of snow is undisturbed, not burdened by the possibility of diffusion layers caused by superficial fusion of summertime snow (sufficiently low summer temperatures), the seasonal variation of the H_2O_2 content is one of the most reliable chemical methods for sequential dating of successive snow layers. Numerous Authors[3,8,9,11–13,16,17] have used this parameter for dating snow samples coming from snowpits, firn cores and ice cores of moderate depth. Positive comparisons with the dating method based on isotopic $\delta^{18}O$ ratio variations have permitted the use of this parameter as a reliable seasonal indicator[11].

The determination of H_2O_2 in snow is carried out on the sample as soon as it is thawed because this compound is not stable in aqueous solution, above all not at very low concentration (a few µg/l).

Table 3 reports the obtained values for linearity, reproducibility, and detection limits.

The Figure 4 shows box plots relative to the distribution of H_2O_2 concentration for the three different stations. One can note the progressive increase of median concentration

Table 3 Analytical parameters for spectrofluorimetric (H_2O_2) and ion chromatographic determinations.

	Linearity range µg/l	*Sensitivity nS µg^{-1} l*	*St. deviation (5 means.)*	*Detection limit ng/l*
H_2O_2	0– 200	–	5%	10
Na^+	0–3000	70.5	2%	155
Cl^-	0–1500	32.5	3%	175
SO_4^{2-}	0–1000	8.2	3%	220
MSA	0– 250	13.1	3%	225

The loops used were 1000 µl for anions and cations and 200 µl for H_2O_2. The standard deviation was calculated for standard solution with concentration about 50 times higher than the detection limit.

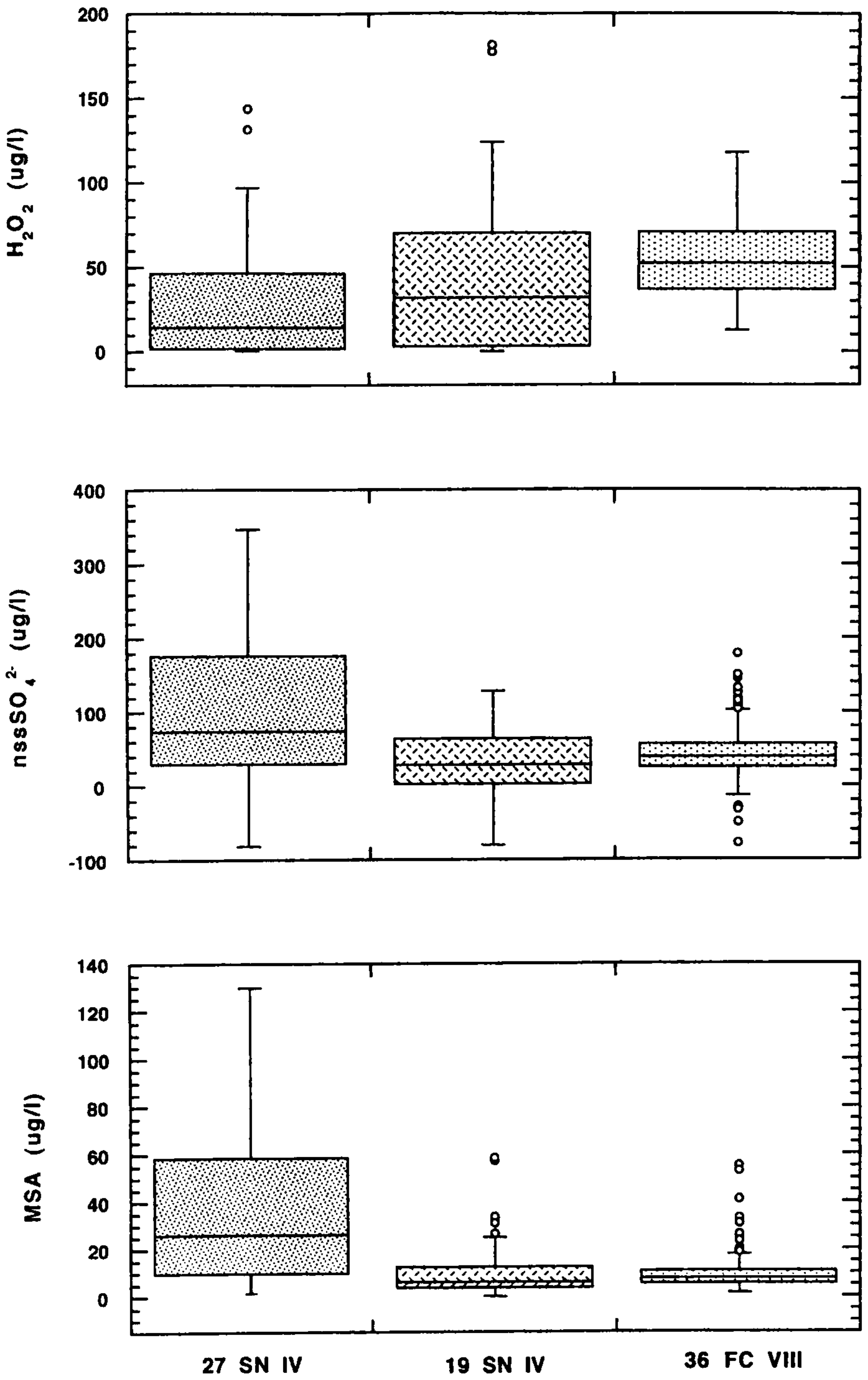

Figure 4 Box plots indicating the concentration distributions of the considered compounds in the three stations.

(line in the box) with altitude. The range encompassing 50% of the samples (box) appears to be sufficiently ample to be able to give a significant seasonal variation between high summer and low winter values. For the highest station (36 FC VIII) the twenty-fifth percentile line (bottom line in the box) is shifted toward values which are clearly higher than the other two stations. This implies the presence of relatively higher winter minima.

$nssSO_4^{2-}$

The term $nssSO_4^{2-}$ refers to the contribution of sulphates not coming from sea spray to the total sulphate concentration. For each sample considered, the $nssSO_4^{2-}$ concentration is calculated using the following formula:

$$[nssSO_4^{2-}] = [SO_4^{2-}]_{tot} - [SO_4^{2-}]_{sw}$$

where: $[SO_4^{2-}]_{sw} = [X]_s * ([SO_4^{2-}]/[X])_{sw}$

and $[SO_4^{2-}]_{sw}$ is the sample concentration of sulphate from sea spray, $[X]_s$ is the concentration of the indicator element for sea contribution (Na^+ or Cl^-) in the sample, and $([SO_4^{2-}]/[X])_{sw}$ is the ratio between sulphates and Na^+ or Cl^- present in sea water. Therefore, for the $nssSO_4^{2-}$ concentration calculation, all sodium or chlorides found in the sample are considered to be of marine origin.

In Antarctica, the principal contribution to $nssSO_4^{2-}$, at least during summer, comes from the oxidation of biogenic dimethylsulphide (DMS)[8,41–48] with respect to other postulated sources such as volcanic origin, crustal origin, and long range transport effect[19,42,46,49–53]. Due to this fact, the $nssSO_4^{2-}$ concentration presents maxima in the period of phytoplanktonic bloom and in the immediately following period. For the studied area this period is during the months of January-February (full-late-summer).

The clear seasonality of the $nssSO_4^{2-}$ concentration has been evidenced both by measurements taken from snow in snowpits, ice and firn cores[6,7,18,25,29,34,54] as well as in aerosol measurements[55–59]. The presence, therefore, of summer maxima in the concentration profiles of this component can be utilised for dating purposes.

The level of $nssSO_4^{2-}$ concentration depends largely, in the studied area, on the geographic position and in particular on the distance from the sea and the altitude. Figure 4 shows the distribution of this component for the three different stations examined (box plot). One can note the distinct reduction of the median concentration and the maximum values with altitude passing from 700 m a.s.l. at Station 27 to 1700 m a.s.l. at Station 19. The levels then remain relatively constant for Station 36 (2990 m a.s.l.). In addition, with increasing altitude there is a narrowing of the range which encompasses 50% of the data. This is in accordance with the fact that the principal source is from the sea, even if the distribution can be considered atmospheric, given that the oxidation of DMS into SO_2 takes place in the atmosphere.

The small range between summer maxima and winter minima, however, does not compromise its use as a seasonal indicator, even at higher altitudes.

From an analytical point of view, the measurement of $nssSO_4^{2-}$ concentration depends therefore on the linear combination of two analytical measurements: determination of Na^+ or Cl^- concentration and determination of total SO_4^{2-} concentration in each sample. The determinations are carried out using ionic chromatography. Table 3 reports the most significant analytical characteristics. Since these measurements are obtained by the difference between two experimental data, there is greater possibility of error, compared with those for the determination of MSA and H_2O_2[37,60,61], for the determination of $nssSO_4^{2-}$ concentration. Naturally, to the analytical error the contribution (not easily quantifiable) due to the initial hypothesis must be added: the ratio $([SO_4^{2-}]/[X])_{sw}$ which is known and constant, the concentration of Na^+ and Cl^- in the sample which is attributable only to marine contribution, the absence of selective fractionation phenomena.

For Station 19 and 27 the $nssSO_4^{2-}$ concentration was established by taking the concentration of Na^+ as references for marine origin. For Station 36, measurements for the determination of the cation concentration are still in progress, and therefore the $nssSO_4^{2-}$ concentration values have been taken from the concentration of Cl^-.

MSA

Methanesulphonic acid derives only from oxidative processes of DMS of phytoplanktonic origin (same reference as $nssSO_4^{2-}$; see above). This compound, hence, comes from the same origin and precursor as the most important summer contributor of $nssSO_4^{2-}$, but with the difference that the origin of MSA is univocal and can, therefore, be utilised as a reliable indicator of biological marine activity[23,25,28,29,44,45,62,63]. The seasonal trend of this compound is the same as for the $nssSO_4^{2-}$ (assuming similar atmospheric transport mechanisms) with concentration maxima present in late-summer. Also for this substance a strong seasonality is evidenced both from measurements of the snow cover (snowpit and firn core)[6,34] and from aerosol[55-59,64], and this seasonality has made it possible to use MSA for dating successive snow layers[25,29]. There is, however, a difficulty for use of this parameter as a seasonal indicator. Low concentrations are found, also during summer, in areas far from the sea and at high elevations. This can be noted, in fact, from the distribution of this component for the three stations (Figure 4); the box plots relative to MSA show a distinct lowering of both the median value and, above all, of the summer maxima with increased elevation. In particular, for Station 36, 90% of the samples had a MSA content between 1 and 20 μg/l. Therefore, particularly sensitive methodologies are necessary which are able to detect such low concentrations without turning to pre-concentration techniques, which are normally affected by contamination problems. Table 3 shows the analytical performance of the method used. Notwithstanding the small range of concentration values of MSA for Station 36, the difference between summer and winter concentrations is sufficiently clear to render the concentration vs. depth profile of this component useful for dating.

Dating

Figure 2 reports data relative to the temporal distribution of H_2O_2, $nssSO_4^{2-}$ and MSA concentrations for snowpit 27 SN IV, and likewise for snowpit 19 SN IV in Figure 3. A decisive seasonal behaviour appears evident for all the concentration profiles. One can note the presence of summer peaks which are relatively low in some years and peaks which are very high for others. For example, at a depth of approximately 125 cm for snowpit 19 and 175 cm for snowpit 27, the concentration of H_2O_2 presents a small peak with particularly low values. This peak seems to be, with good probability, a summer maxima since the same situations is found in an analogous way for the two snowpits which were sampled contemporaneously (the fourth peak starting from the surface; presumed date: summer 1987/88).

As for the concentration profiles of the other two components, similar behaviour can be observed but some summer peaks are more pronounced and clearly confirm the H_2O_2 trend, while others are much more ambiguous.

To be able to compare summer maximum peaks on a mathematical basis, even if they do not perfectly coincide on a temporal level, all annual peaks for each series relative to the various components must be "normalized". This term is used to mean the construction of a concentration profile in which peaks, which are with good probability maximum summer indicators, are assigned the same numerical importance independent of their absolute value.

The curve for the concentration profile can, therefore, be expressed as a series of ratios between each concentration value and the nearest maximum within a defined interval in the neighbourhood of that value. Therefore, the maximum value of each peak, if it is sufficiently isolated from the other picks, will take on the numerical value = 1. Thus, all the peaks will assume the same numerical importance, independent of the effective value of the concentration reached for that year for that parameter.

The equation used is the following:

$$\text{n.v.} = \frac{\text{a.v.}}{\max\,(\text{a.v.} \pm q)} \qquad \text{where} \qquad \begin{array}{l} \text{n.v.} = \text{normalized value} \\ \text{a.v.} = \text{analytical value} \end{array}$$

Where max (a.v. ± q) represents the maximum value of concentration found in the interval of amplitude 2 q + 1 (q data before, the chosen value, and q data after) with respect to the analytical value considered. The search for maxima becomes, therefore, a mobile search procedure. This procedure could be defined as normalization by mobile maximum in a defined interval.

Obviously, particular care is given to the choice of interval in the neighbourhood of each experimental value in the search for maxima. In fact, there is risk of considering as summer peaks oscillations of relatively low winter values by using an interval which is too small; in practice each higher value in its small neighbourhood could be recognised as a summer peak and could assume the value = 1. Instead, by using interval values which are too large there is the risk of not recognising, as summer peaks, small peaks which are positioned between two annual peaks presenting much higher maximum values. The ideal situation could be that which permits full recognition of all certainly summer peaks independent of their maximum value. Hence it is clear that the ideal system would involve a prior knowledge of summer peaks, while this knowledge is actually the objective. A compromise could be to set the interval of search for maxima equal to the number of samples between the most distant peaks which can certainly be attributed to the summer period. Thus, the resulting error is almost exclusively conservative in that there is risk of not giving value = 1 to small peaks found between higher peaks. This occurs, however, only in particularly unfavorable situations.

Once a normalized profile is obtained, it is possible to recognize the annual trends more clearly and, by iterative process, to be able to choose a smaller interval. This makes it possible to better highlight peaks found near other higher peaks, which appear to have a fairly clear connotation of summer maximum. On the other hand, it is quite improbable that an unfavorable situation for the recognition of a small peak would exist contemporaneously for all three components in the same year. By summarizing the normalized values of all three components point by point it is possible to obtain a new temporal profile in relation to depth. This parameter sum presents high values (maximum value = 3) for depth where normalized peaks are present for all three examined substances; instead, very low values are relative to snow layers for which there is no peak value. Intermediate peaks are described for layers in which at least two sufficiently high normalized peaks overlap.

Due to the considerable dispersion of the original data and the imperfect contemporaneousness of the annual maxima for the three components, peaks which are somewhat widened and articulated have been obtained making some smoothing necessary. Figures 5 and 6 show normalized profiles for the three parameters and their smoothed (order 3) sums for the two snowpits.

In the case of the two snowpits, the good interpretability of the H_2O_2 concentration profiles permits the selection of a relatively small interval, considerably inferior to the number of samples between the two most distant summer maxima (18 points, Station 27, Figure 5). This interval was established as 11 points; each concentration value was divided by the maximum concentration value measured for the five samples before and the five after the examined sample. The choice of such a limited interval permits easy recognition of the small peaks for H_2O_2 positioned at a depth of approximately 180 cm for snowpit 27 (Figure 2) and approximately 130 cm for snowpit 19 (Figure 3). It can be noted how the normalized concentration profiles better evidence the summer maxima making it easier to base the annual accumulation calculation on them. The sum profiles obtained do not seem to demonstrate ambiguity of interpretation for either station: the annual peaks have been numbered progressively and an absolute dating has been superimposed for the two snow pits (Figures 5 and 6). The numbering of the summer peaks has been based on the normalized sum profile and some peaks can therefore do not appear in the temporal series of the individual compounds (for istance, peak n. 5 for MSA ad $nssSO_4^{2-}$ in the station 27—Figure 5).

It is interesting to note how the profiles of the original data are not well-defined (for example, layers deeper than 100 cm for MSA and $nssSO_4^{2-}$ for Station 19, Figure 3) but are clearer after normalization (peaks, 4, 5, and 6—Figure 6).

The normalized profile of $nssSO_4^{2-}$ for Station 27 (Figure 5) offers a good example of how trends of difficult interpretation, relative to only one of the normalized profiles, are toned down in the summed profile. In fact the presence of three maxima near each other at a depth of 70–140 cm makes peak n. 3 difficult to interpretate for $nssSO_4^{2-}$; since the other two compounds are quite evident at the same depth, that peak becomes clear and not ambiguous in the normalized sum profile.

The annual and average annual accumulation values obtained are in complete agreement with previous reports on annual accumulation for the same snowpits for the series of samples taken in parallel columns[25,30]. The previous annual snow accumulation values were based simply on a visual comparison of the original concentration profile, paying particular attention to the H_2O_2 profile which appears to be the most reliable for the two snow pits.

For Hercules Heve' firn core (samples 36 FC VIII) instead, simple visual observation of the concentration profiles for the three parameters does not permit good discernment of the summer peaks though the H_2O_2 concentration still seems to be the most reliable for most of the depth scale (Figure 7). As already evidenced by the box plot of H_2O_2 for this Station (Figure 4), elevated concentration values even in winter are often observed particularly in the last part of the firn core. This section appears, instead, to be better explained by the temporal progression of the other two parameters which have unclear profiles at other depths (for istance, between 200 and 350 cm). However it is evident that a reliable dating based on clear and univocal seasonal signals is not possible from just a visual analysis of the concentration profiles of each component. The normalization of the concentration peaks for each component (given the very different concentration values

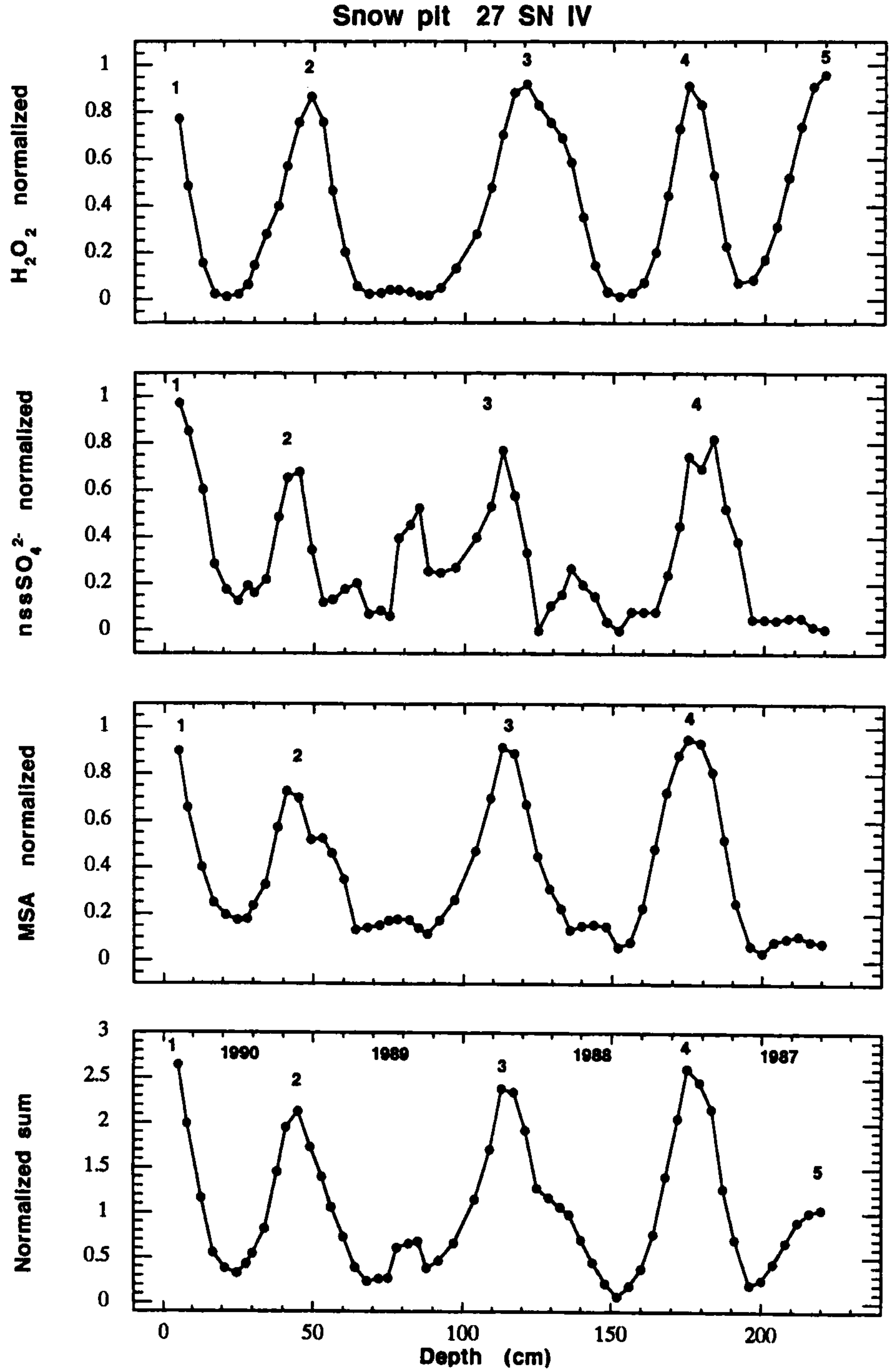

Figure 5 Station 27—Normalized profiles for H_2O_2, $nssSO_4^{2-}$ and MSA concentrations and their sum. The individuation of annual summer peaks is performed on the basis of the normalized sum profile (see text).

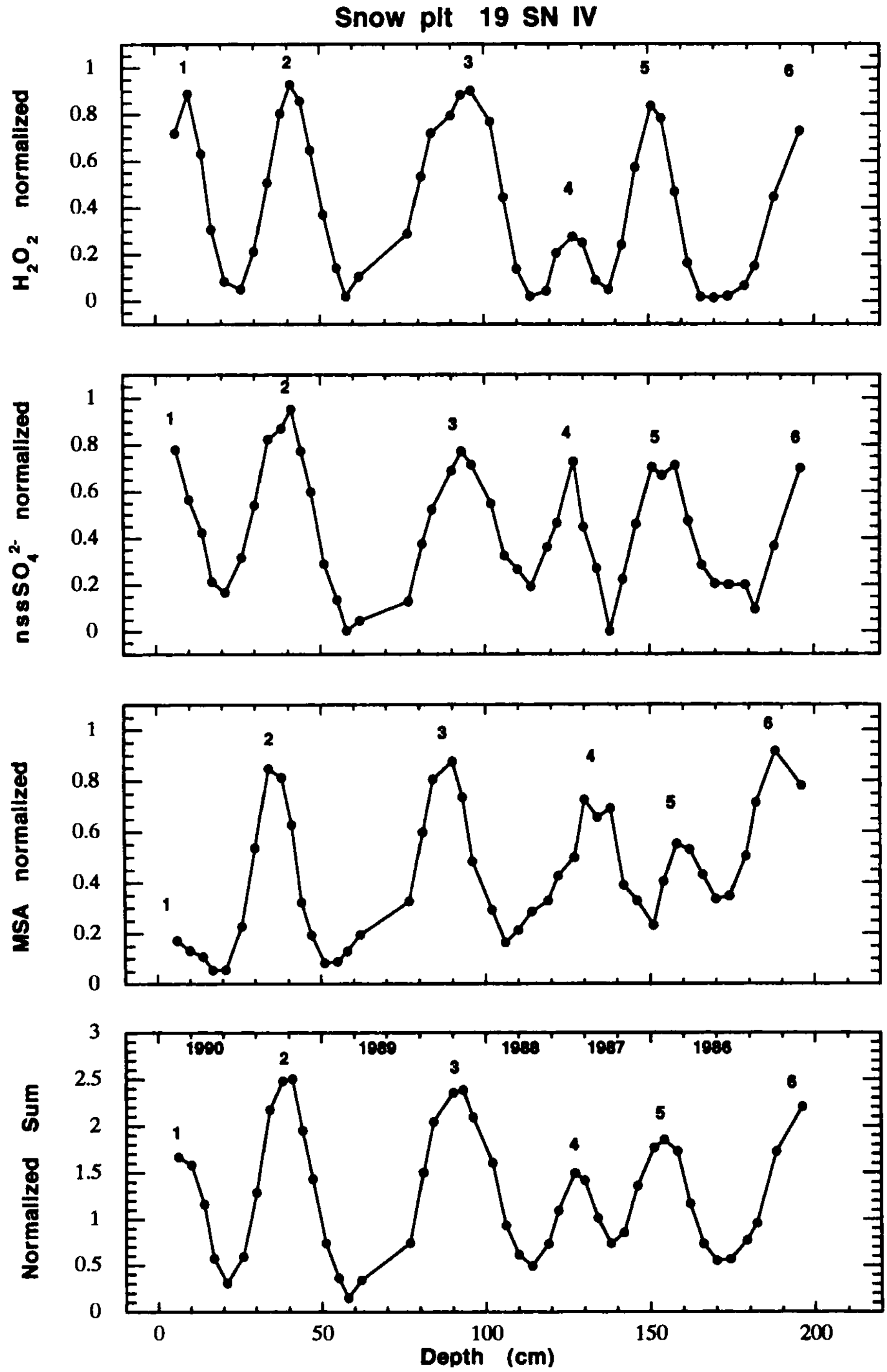

Figure 6 Station 19—Normalized profiles for H_2O_2, $nssSO_4^{2-}$ and MSA concentrations and their sum. The individuation of annual summer peaks is performed on the basis of the normalized sum profile (see text).

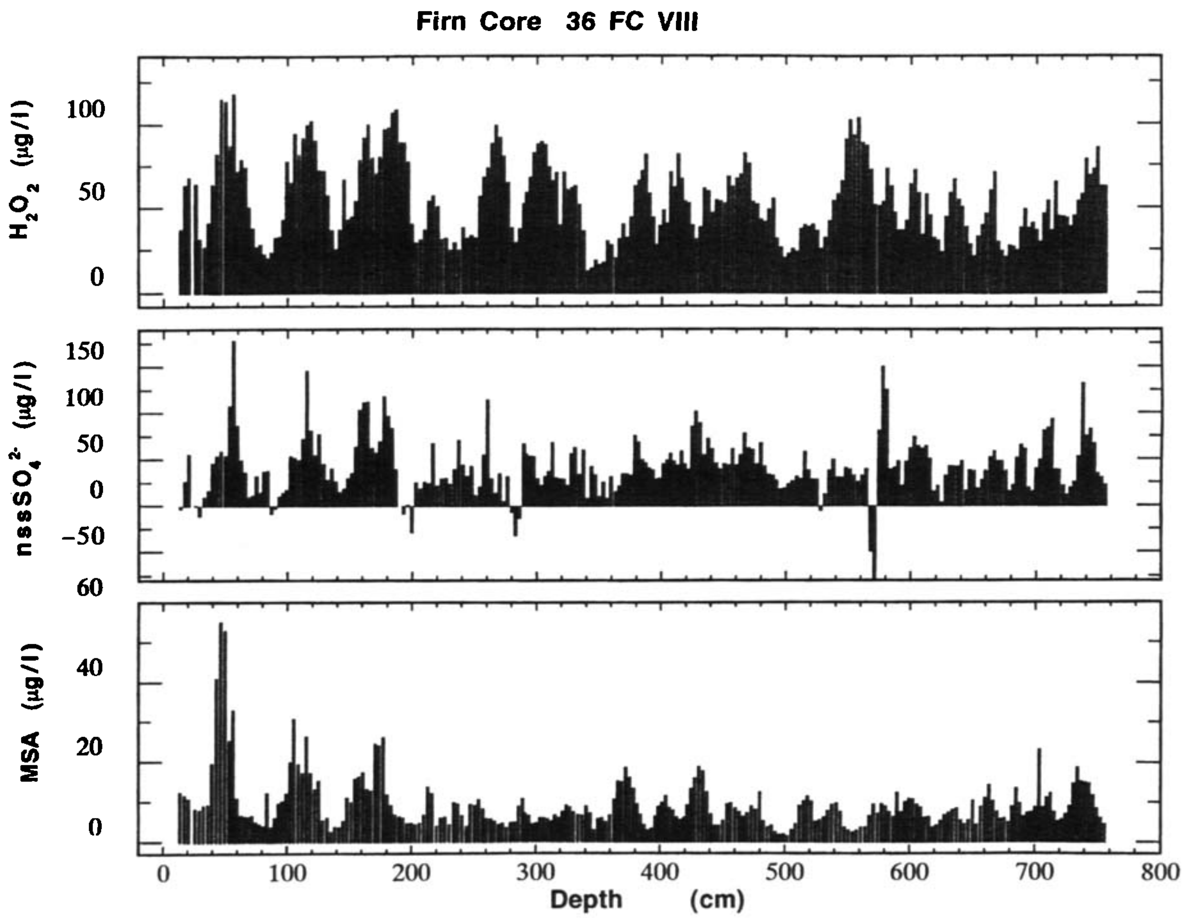

Figure 7 Station 36—Original concentration profiles for H_2O_2, $nssSO_4^{2-}$ and MSA.

that the summer peaks have in every temporal series) and the evaluation of the temporal trend of their sum seems, therefore, inevitable to obtain an acceptable resolution of the summer peaks. Another difficulty is presented by double peaks which can at times be considered distinct or effectively relative to only one year, since they do not appear double in all three observed parameters.

Due to the relatively elevated dispersion of the original concentration data, in the case of the Hercules Neve' samples, a light smoothing (order 3) of the data before calculating the normalized values was preferred, so as to obtain curves which were more easily interpretable. In Figure 8 the results of the three normalizations and the representative sum for the temporal trends for the normalized parameters are reported. Here an interval of 21 values was chosen for the search for maxima. This interval is prudently more ample compared to that for the two snowpits due to the increased difficulty in interpreting the seasonal trends for each component. The supposed summer indicator peaks have also been numbered progressively on the basis of the normalized profile sum. Different peaks that might belong to the same year have been indicated with the same number (e.g. 4 and 4').

By examining the result it is possible to highlight summer maxima which are generally well-defined. The fact that they are relative to three different parameters and obtained with different methodologies reinforces the probability of their existence as true summer peaks.

The normalized profiles of $nssSO_4^{2-}$ and MSA are well-defined even at depths of 200–350 cm where original profile concentrations cannot be reliably evaluated. Even though the presence of multiple peaks makes not clear the profile interpretation in this range of depth, the normalized profiles of the two substances are very similar to each other, especially the two groups of peaks numbered 5, 5' 6 and 7, 7', 8. In general, the normalized temporal series for $nssSO_4^{2-}$ and MSA are quite similar for the entire depth range. The normalized H_2O_2 values are instead different from the other two components but it is precisely this difference in the data series which confirms or eliminates some poorly resolved peaks as annual indicators.

An excellent agreement between the three normalized profiles is noted for peaks 1, 2, 3, 4, 4' 6, 9, 11, 13, 17 and 20. Relatively small or poorly defined peaks in the H_2O_2 profile are fully confirmed by the other two profiles (peaks 8, 10, 12) or vice versa (peaks 9', 14, 15, 16). Peaks 18 and 19 do not appear in the H_2O_2 profile but they are very distinct and reliable in the MSA and $nssSO_4^{2-}$ profiles. Peaks 5 and 7 which are single for H_2O_2 and double for MSA and $nssSO_4^{2-}$ cannot be clearly or certainly interpreted.

By analyzing the sum profile it is possible to almost certainly identify 20 annual peaks plus 4 others that can be attributed to distinct years or to the same year (peaks 4', 5' 7' and 9'). In conclusion, it is possible to individuate 22 ± 2 summer peaks, with a 10% margin of uncertainty for the entire firn core. This margin is acceptable for the purpose of estimating single annual and average annual accumulations for this firn core.

The resulting water equivalent annual average deposition of about 160 Kg/m^2 Yr is in good agreement with that reported by Allen III (1985)[2] for a near area (182 Kg/m^2 Yr—core E10, Rennick Glacier area).

Integration of the available data with those still being obtained from the approximately 10 m firn cores, taken at various stations during the last Antarctic campaign (1993/94), can result in a valid discussion about the reliability of dating methods and a qualitative and quantitative characterization of snowfall in Northern Victoria Land.

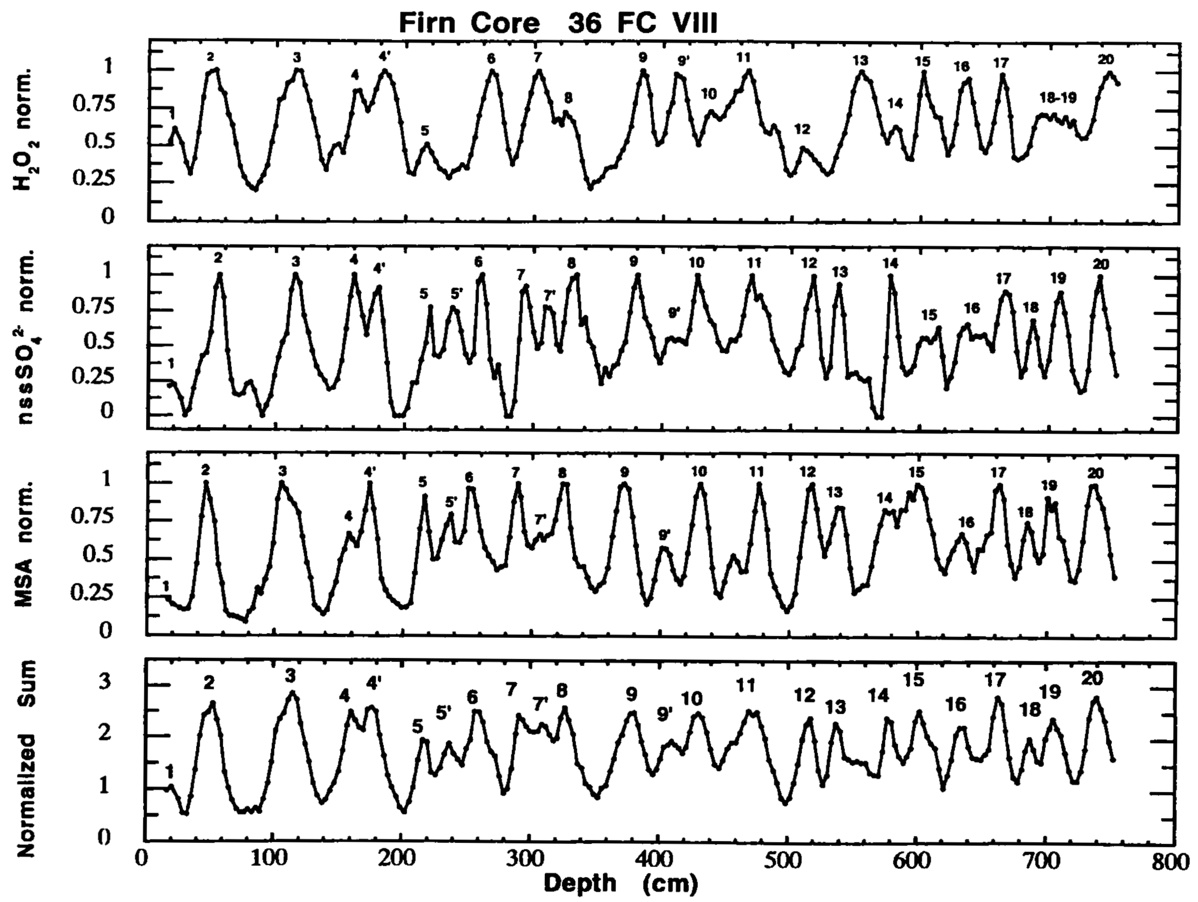

Figure 8 Station 36—Normalized profiles for H_2O_2, $nssSO_4^{2-}$ and MSA concentrations and their sum. The individuation of annual summer peaks is performed on the basis of the normalized sum profile (see text).

CONCLUSIONS

It is possible to obtain a more reliable estimation of annual snow layers using a sum of three normalized profiles of seasonal indicators, rather than observing original concentration trends.

The sum of normalized values gives maximum values which are sufficiently defined and reliable with greater sampling frequency and less temporal dephasing of the measured parameters.

The mobile search for defined interval maxima and normalization of concentration values appears easily applicable and seems to give satisfactory results, provided that an optimal interval is selected using iterative processes.

The obtained results are in agreement with the trend of average accumulations for Northern Victoria Land as a function of altitude and distance from the sea.

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References

1. M. De Angelis and M. Legrand, *J. Geophys. Res.*, **99–D1**, 1157–1172 (1994).
2. B. Allen III, P. A. Mayewski, W. B. Lyons and M. J. Spencer, *Ann. Glaciol.*, **7**, 1–6 (1985).
3. S. Whitlow, P. A. Mayewsky and J. E. Dibb, *Atmos. Environ.*, **26A**, 2045–2054.
4. P. A. Mayewsky, *Ann. Glaciol.*, **14**, 186–190 (1990).
5. P. A. Mayewsky and M. R. Legrand, *Nature*, **346**, 258–260 (1990).
6. C. C. Langway Jr, K. Osada, H. B. Clausen, C. U. Hammer, H. Shoji and A. Mitani, *Tellus*, **46B**, 40–51 (1994).
7. E. Mosley-Thompson, J. Dai, L. G. Thompson, P. M. Grootes, J. K. Arbogast and J. F. Paskievitch, *J. Glaciol.*, **37**, 11–22 (1991).
8. R. J. Delmas, *Sci. Total Environ.*, **143**, 17–30 (1994).
9. V. I. Morgan, I. D. Goodwin, D. M. Etheridge and C. W. Wookey, *Nature*, **354**, 58–60 (1991).
10. E. Isaksson and W. Karlen, *J. Glaciol.*, **40**, 399–409 (1994).
11. A. Sigg and A. Neftel, *Ann. Glaciol.*, **10**, 157–162 (1988).
12. A. Sigg, T. Steffelbach and A. Neftel, *J. Atmos. Chem.*, **14**, 223–232 (1992).
13. A. Sigg, K. Fuhrer, M. Anklin, T. Staffelbach and D. Zurmuhle, *Environ. Sci. Technol.*, **28**, 204–209 (1994).
14. J. Neubauer and K. G. Heumann, *Fresenius Z. Anal. Chem.*, **331**, 170–173 (1988).
15. J. Neubauer and K. G. Heumann, *Atmos. Environ.*, **22**, 537–545 (1988).
16. A. Neftel, P. Jacob and D. Klockow, *Tellus*, **38D**, 262–270 (1986).
17. A. Neftel, in: *NATO ASI Series, Vol.* G28—*Seasonal Snowpacks*, (T. D. Davies *et al.* eds., Heidelberg, 1991), pp. 385–415.
18. J. P. Ivey, D. M. Davies, V. Morgan and G. P. Ayers, *Tellus*, **38B**, 375–379 (1986).
19. M. R. Legrand and R. J. Delmas, *Atmos. Environ.*, **18**, 1867–1874 (1984).
20. H. Hwang and P. K. Dasgupta, *Anal. Chim. Acta*, **170**, 347–352 (1985).
21. A. L. Lazrus, G. L. Kok, S. N. Gitlin and J. A. Lind, *Anal. Chem.*, **57**, 917–922 (1985).
22. G. Piccardi , R. Udisti and E. Barbolani, *Annali di Chimica (Rome)*, **79**, 701–712 (1989).
23. R. Udisti, E. Barbolani and G. Piccardi, *Annali di Chimica (Rome)*, **81**, 325–341 (1991).
24. R. Udisti, S. Bellandi and G. Piccardi, *Fresenius J. Anal. Chem.*, **349**, 289–293 (1994).
25. G. Piccardi, R. Udisti and F. Casella, *Intern. J. Environ. Anal. Chem.*, **55**, 219–234 (1994).
26. R. Udisti, E. Barbolani and G. Piccardi *in progress.*
27. G. Piccardi, F. Casella and R. Udisti, *Intern. J. Environ. and Chem.*, **63**, (1996).
28. G. Piccardi, R. Udisti, S. Bellandi and E. Barbolani, in: *CNR—PNRA—Proceedings Environmental Impact in Antarctica*—Rome, 1990, pp. 55–62.

29. R. Udisti, F. Casella and G. Piccardi, in: "*Dimethylsulphide: Oceans, Atmosphere and Climate*", (G. Restelli and G. Angeletti Eds., 1993,ECSC, EEC, EAEC, Brussels and Luxembourg, Printed in Netherlands) pp. 153–162.
30. G. Piccardi, E. Barbolani, S. Bellandi, F. Casella and R. Udisti, *Terra Antartica, Antarctic Earth Science Newsletter*, **1**, 134–137 (1994).
31. Y. Gjessing, *Atmos. Environ.*, **18**, 825–830 (1984).
32. Y. Gjessing, *Atmos. Environ.*, **23**, 155–160 (1989).
33. P. A. Mayewsky, M. J. Spencer, W. B. Lyons and M. S. Twickler, *Atmos. Environ.*, **21**, 863–869 (1987).
34. R. Mulvaney, G. F. J. Coulson and H. F. J. Corr, *Tellus*, **45B**, 179–187 (1993).
35. P. Pettre, J. F. Pinglot, M. Pourchet and L. Reynaud, *J. Glaciol.*, **32**, 486–500 (1986).
36. M. Legrand and R. Delmas, *Ann. Glaciol.*, **7**, 20–25 (1985).
37. M. E. Hawley, J. N. Galloway and W. C. Keene, *Water, Air and Soil Poll.*, **42**, 87–102 (1988).
38. H. Sakugawa, I. R. Kaplan, W. Tsai and Y. Cohen, *Environ. Sci. Technol.*, **24**, 1452–1462 (1990).
39. A. Neftel and K. Fuhrer, in: *NATO ASI Series. Vol.* **17**—*The Tropospheric Chemistry of Ozone in the Polar Regions*. (H. Niki and K. H. Beker eds., Heidelberg, 1993) pp. 219–233.
40. K. Fuhrer, A. Neftel, M. Anklin and V. Maggi, *Atmos. Environ.*, **27A**, 1873–1880 (1993).
41. M. O. Andreae and H. Raemdonck, *Science*, **221**, 744–747 (1983).
42. G. E. Shaw, *Rev. Geophis.*, **26**, 89–112 (1988).
43. B. C. Nguyen, N. Mihalopoulos, J. P. Putaud, A. Gaudry, L. Gallet, W. C. Keene and J. N. Galloway, *J. Atmos. Chem.*, **15**, 39–53 (1992).
44. M. Legrand, C. Feniet-Saigne, E. S. Saltzman, C. Germain, N. I. Barkov and V. N. Petrov, *Nature*, **350**, 144–146 (1991).
45. M. Legrand and C. Saigne, *Atmos. Environ.*, **22**, 1011–1017 (1988).
46. M. R. Legrand, R. J. Delmas and R. J. Charlson. *Nature*, **334**, 418–420 (1988).
47. E. S. Saltzman, in: NATO A.R.W.—Ice core studies of global biogeochemical cycles—Annecy (F) 1993.
48. D. L. Savoie and J. M. Prospero, *Nature*, **339**, 685–687 (1989).
49. R. J. Delmas, *Nature*, **299**, 677–678 (1982).
50. R. J. Delmas, M. Legrand, A. J. Aristarain and F. Zanolini, *J. Geophys. Res.*, **90–D7**, 12901–12920 (1985).
51. R. J. Delmas, in: *NATO ASI Series. Vol.* **G6**—*Chemistry of Multiphase Atmospheric Systems* (W. Jaeschke ed., Heidelberg, 1986), pp. 249–266.
52. M. R. Legrand and R. J. Delmas, *Nature*, **327**, 671–676 (1987).
53. M. H. Herron, *J. Geophys. Res.*, **87–C4**, 3052–3060 (1982).
54. D. Wagenbach, U. Gorlach, K. Moser and K. O. Munnich, *Tellus*, **40B**, 426–436 (1988).
55. J. M. Prospero, D. L. Savoie, E. S. Saltzman and R. Larsen, *Nature*, **350**, 221–223 (1991).
56. G. P. Ayers, J. P. Ivey and R. W. Gillet, *Nature*, **349**, 404–406 (1991).
57. T. S. Bates, J. A. Calhoun and P. K. Quinn, *J. Geophys. Res.*, **97–D9**, 9859–9865 (1992).
58. E. S. Saltzman, D. L. Savoie, J. M. Prospero and R. G. Zika, *J. Atmos. Chem.*, **4**, 227–240 (1986).
59. D. L. Savoie, J. M. Prospero, R. J. Larsen and E. S. Saltzman, *J. Atmos. Chem.*, **14**, 181–204 (1992).
60. W. C. Keene, A. A. P. Pszenny, J. N. Galloway and M. E. Hawley, *J. Geophys. Res.*, **91-D6**, 6647–6658 (1986).
61. F. Maupetit and R. J. Delmas, *J. Atmos, Chem.*, **14**, 31–42 (1992).
62. C. Saigne and M. Legrand, *Nature*, **330**, 240–242 (1987).
63. C. Saigne, S. Kirchner and M. Legrand, *Anal. Chim. Acta*, **203**, 11–21 (1987).
64. G. P. Ayers and J. L. Gras, *Nature*, **353**, 834–835 (1991).