

Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content

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ABSTRACT

At the German Antarctic research station (70°S, 8°W), long-term observations of the chemical and radio-chemical composition of atmospheric particulate matter were started in spring 1983. Based on the analysis of high-volume aerosol filters sampled continuously for nearly 5 years, concentration records of the following aerosol components are presented here: (a) major ions (sea-salt, sulfate, nitrate); (b) cosmogenic ^7Be and terrigenous ^{210}Pb ; (c) trace elements (crustal Mn, heavy metal Pb). All species mentioned, with the exception of stable and radioactive Pb, show annual cycles. The maximum occurs in austral summer for ^7Be , sulfate, and crustal Mn. For sea-salt, however, the maximum is found in local autumn, and for nitrate in local spring. In local summer, the enhanced ^7Be to ^{210}Pb ratio is attributed to intenser large scale vertical mixing. The pattern of total sulfate seems to be controlled by the nss-sulfate production from marine organo-sulfur species during local summer, whereas in polar night, nss-sulfate shows very low or even negative concentration. Crustal aerosol (indicated by Mn) shows a mean summer contribution of 16 ng/SCM which exceeds the mean winter level by more than a factor of two. Based on a mean wash-out ratio of $0.27 \cdot 10^6$ observed for ^{210}Pb bearing aerosol particles, a Pb snow concentration of 3.0 pg/g is deduced from the mean air concentration of 11 pg/SCM.

1. Introduction

Antarctica is supposed to be the region of earth's surface which is least of all influenced by continental sources of primary and secondary aerosols. Due to the permanent snow cover, there is no ground-level aerosol production in central Antarctica, apart from small areas of exposed rock and from local research activities. Exclusively controlled by the cycle of naturally derived aerosol-species, the chemical composition and the physical parameters of the Antarctic aerosol can provide basic information on the major natural source, the clean-air transformation processes and the prevailing long-range transport pattern of the aerosol components in question (Shaw, 1979).

Part of this information is found to be conserved in the Antarctic ice cap providing a glacio-chemical record (De Angelis et al., 1984).

Decoding this paleo-climatic record, however, needs precise knowledge of the actual behavior of the Antarctic background aerosol.

The most comprehensive information on atmospheric aerosols in Antarctica, provided by numerous programs carried out at the Amundsen-Scott base, is available for the geographic South-Pole: condensation nucleus and nephelometer readings (Bodhaine, 1983), trace elements (Cunningham and Zoller, 1981; Maenhaut et al., 1979a).

The data by Cunningham and Zoller (1981) show a seasonal pattern of crustal, marine and sulfate aerosol concentration, with a maximum for the crustal and sulfate species and with a minimum for the marine component during local summer.

No data, however, on the chemistry of bulk aerosol samples collected all year over are available for sites other than the South Pole. South Pole

data, being representative for central Antarctica, therefore cannot be compared to corresponding data from coastal sites. The latter region is expected to be influenced more directly by the surrounding ocean, by the seasonal cycle of sea-ice cover, and by the prevailing unstable weather conditions, producing a higher precipitation rate and a more complex aerosol record.

Up to now, information on aerosol chemistry from other Antarctic sites is drawn mostly from analyses of deposited snow. Analyzing the ionic composition of firn and ice-core samples, Legrand and Delmas (1984) succeeded in establishing a detailed picture of the ion budget in recent and ancient precipitation from various Antarctic regions. That work made it evident that the dominant component of present-day snow impurities in central Antarctica is associated with gas-derived, strong mineral acids (H_2SO_4 , HNO_3 , HCl) (Delmas et al., 1982). Up to now, most snow concentration measurements of minor trace elements in Antarctica such as heavy metals have been subjected to serious contamination problems already discussed by Boutron and Patterson (1983). Snow-derived data therefore do not provide a routine base in studying the trace element composition of the Antarctic aerosol.

For studying the present day aerosol chemistry in Antarctica, firn sampling, if compared with direct aerosol sampling, suffers from two specific problems: (a) due to the small precipitation rate only a poor time resolution is achieved (b) to deduce from snow data reliable air concentrations, much more information than presently available on the air to snow transfer of particulate and reactive gases is needed.

To reduce the deficiency of Antarctic clean air studies, a long term program for the collection of aerosol and trace gas samples in a *coastal* region (Georg von Neumayer station, hereafter referred to as GvN) was initiated and realized by the Heidelberg University, Institute of Environmental Physics (see maps of Fig. 1) (Augstein, 1984).

This paper intends to give a survey of the results drawn from chemical and radiochemical analysis of the high-volume aerosol samples collected since 1983 at the GvN station. The data will mainly be discussed with respect to the time pattern of the aerosol components in question. These are the

ionic species (sulfate, nitrate, and sea salt), which control the mass of the total aerosol sampled. In addition, data on crustal manganese and on common lead (being a good candidate for verification of an anthropogenic impact on Antarctic aerosol chemistry) are reported, characterizing the clean air character of the site. The natural radioisotopes beryllium-7 and lead-210, being measured along with the chemical aerosol parameters, are presented, illustrating the potential of these submicron aerosol markers in refining the chemical data interpretation.

2. Experimental

2.1. Collection site and sampling procedure

The aerosol is sampled in a specially designed over-snow laboratory located 1500 m south to the main facilities of the GvN station. A survey of the entire air chemistry program carried out routinely in this satellite station and of its technical realization has already been given by Wagenbach et al. (1983). The GvN Station is situated on the Ekström ice-shelf ($70^\circ 37'\text{S}$, $8^\circ 22'\text{W}$) only 6.5 km from the ice-edge, facing the open sea during austral summer (see map in Fig. 1). The local glacio-meteorological regime relevant to the air chemistry studies is characterized by a relatively high net snow accumulation of 75 cm per year (equivalent to about $35 \text{ g cm}^{-2} \text{ yr}^{-1}$) (Reinwarth et al., 1982), by surface winds consistently blowing out of easterly directions at an annual mean wind speed of about 9 m/s (Schug, 1985), and by frequent occurrence of heavy snowdrift.

Via a ventilated stack (air intake 7 m above snow surface), aerosol is collected on double Whatman 541 cellulose filters (diameter 24 cm) at a flow rate of $150 \text{ m}^3/\text{hour}$. To minimize filter contamination by the main station, sampling is automatically interrupted if the preset levels of local condensation nucleus concentration, wind direction, and wind speed appears to be out of range. Further reduction of the general contamination risk is achieved in separating the air chemistry laboratory from the main station by 1500 m. The electrical power supply is provided by two under-snow cables. The total air sample volume starts with about $50,000 \text{ m}^3$ (equivalent to

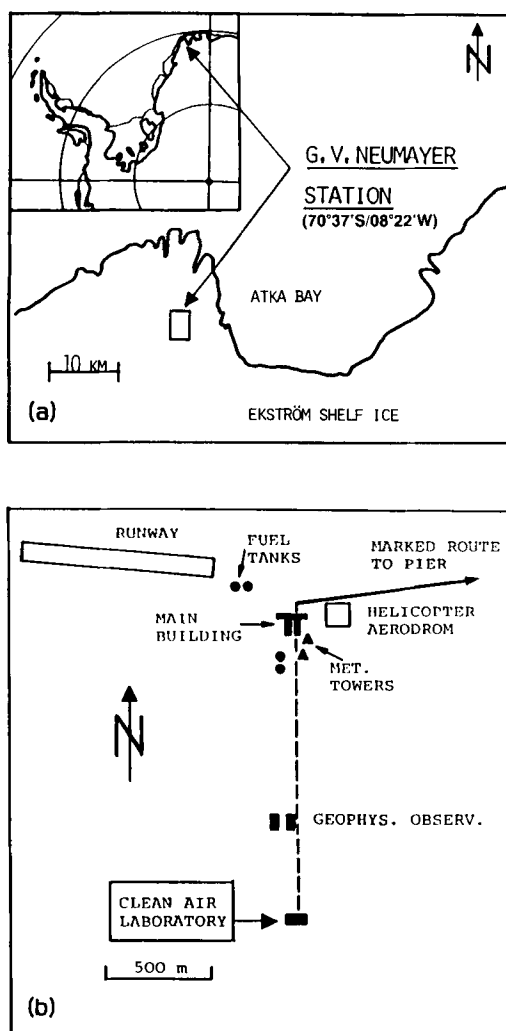


Fig. 1. (a) Map of a part of the Ekström Ice-shelf area, showing the position of the Georg von Neumayer station (GvN). (b) Location of the (GvN) clean-air observatory related to the technical facilities of the main base.

a 2–3 weeks sampling period) at the beginning of the overwintering season in late summer, and is chosen to decrease steadily to only about $10,000 \text{ m}^3$ for the following summer. This reduction in time resolution for the older filters of a sampling campaign is chosen to compensate for the considerable radioactive decay of the rather short-lived ($T_{1/2} = 53$ days) beryllium-7.

2.2. Measuring techniques

Prior to use, filters and polyethylene bags for shipment were rigorously cleaned by subsequent steps of soaking in isopropylene alcohol and in diluted solution of HNO_3 and HF (Merck reagent grade and suprapure). Final rinsing with $18 \text{ M}\Omega$ deionized water was applied to the acid-cleaned material until no significant increase of the electrolytical conductivity could be observed in the rinsewater. The total cleaning procedure typically takes about two weeks.

Immediately after return to the Heidelberg laboratory, the first and second filters of each sample set were folded separately in a clean-bench and assayed for the ^7Be activity by using a large HPGe p-type coaxial detector. The ^{210}Pb -activity was calculated from the α activity of its ^{210}Po -decay product. Filter aliquots were extracted in hot HCl and HNO_3 , previously spiked with ^{208}Po and ^{10}Be . The polonium isotopes were spontaneously deposited from a diluted HCl solution to a silver disk and counted on a surface barrier detector. The remaining solution was preserved for ^{10}Be measurements by AMS. In addition, direct γ spectroscopy of the 46 keV line of ^{210}Pb was performed on the filters collected after March 1985 by means of a planar n-type HPGe-detector (same counting geometry as for the ^7Be spectroscopy). The time delay between sample collection and counting (total range from one year to about two months) caused the following counting errors of the short-lived ^7Be activity: 10–30% for filters collected during austral autumn, 5–10% and 1.5% for mid-winter and summer samples, respectively. Counting errors of the ^{210}Pb measurements typically are in the range of 5–10%.

Whenever possible, the collection efficiency of the cellulose filters (being representative for submicron aerosol particles) has been deduced from the ^{210}Pb and ^7Be activity found on the first and the second filter. Apart from some filters wet with snow particles, the filter efficiencies calculated in this way appear to be relatively constant ($84 \pm 5\%$), no significant difference between the collection efficiency of ^{210}Pb and ^7Be bearing aerosol particles was observed.

About $1/6$ of the total filter area was used to analyze sodium, chloride, nitrate, and sulfate by suppressed ion chromatography. The filter segments were extracted in small vials filled with

deionized water, the vials were placed in an ultrasonic bath for about 40 min. The subsequent ion chromatographical procedure, individually depending on the relative amount of sea-salt, was adjusted from the electrolytical conductivity of the solution. By means of a series of duplicate analyses (in which two segments were randomly cut from the filter and analyzed in parallel) the analytical precision was estimated to be approximately 5% for all ions examined in the 1983 samples and about 2% for the filters collected later. Note that during the 1983 overwintering period no *double* Whatman filters had been used for aerosol sampling. For none of the ions studied was a relevant blank contribution arising from the filter matrix or the sample manipulations observed. To prove this, blank filters, subjected to the same field procedure and placed in the filter holder for about one day, were analyzed. For the 1983–85 sampling period the average blank of these filters was found to be $< 5 \mu\text{g}$, $< 70 \mu\text{g}$, $< 40 \mu\text{g}$, and $(6.7 \pm 2.6) \mu\text{g}$ for Na, Cl, NO_3 , and SO_4 , respectively. Since the typical air volumes sampled are in the range of $15\text{--}30,000 \text{ m}^3$, there is no relevant contribution to the overall uncertainty of the ion analysis by the variability of the individual blanks. For nitrate this may sound surprising because all filters had been previously cleaned in diluted nitric acid; adequate removal of this nitrate component was additionally confirmed by analyzing a series of the second filters of each double filter pack.

A detailed description of the Pb and Mn measuring techniques used in this study is given by Görlach (1988). In brief, filter segments corresponding to approximately 4000 m^3 were leached in 3 n and hot 0.14n HNO_3 . The resulting solution was analyzed for Pb and Mn by flameless atomic absorption spectroscopy (Perkin Elmer 5000, HGA 500), using pyrolytically coated graphite tubes and a pyrographitic L'vov platform. Since sea-salt concentrations were found to be up to 1.2% in the filter extracts, part of the samples were analyzed by the standard addition method. Filter blanks contributed 5–10% of Pb ($24 \pm 7 \text{ ng}$ per total blank filter) and $< 3\%$ of Mn ($3.5 \pm 2 \text{ ng}$ per total blank filter) to the measured metal concentrations. The handling and the analysis of two aliquots out of 15 filters resulted in an approximate reproducibility of 15% for Pb and 10% for Mn.

3. Results and discussion

3.1. Radioisotopes

In Fig. 2 the temporal records of the long-lived radon decay product ^{210}Pb and of the cosmic ray produced ^7Be are shown for the period February 1983 to February 1987. Both nuclides may be regarded as a kind of secondary aerosol since their atmospheric precursors are known to be the terrigenous noble gas radon-222 (in the case of ^{210}Pb) and O_2 or N_2 in the case of ^7Be . Immediately after production, both nuclides become attached to aerosol particles, and, as a result of further coagulation processes, their atmospheric activity is found to be concentrated on aerosol particles in the submicron size range (Sanak et al., 1981). Therefore ^{210}Pb may be used here as a marker for secondary submicron aerosol, originating from a ground-level continental source, and

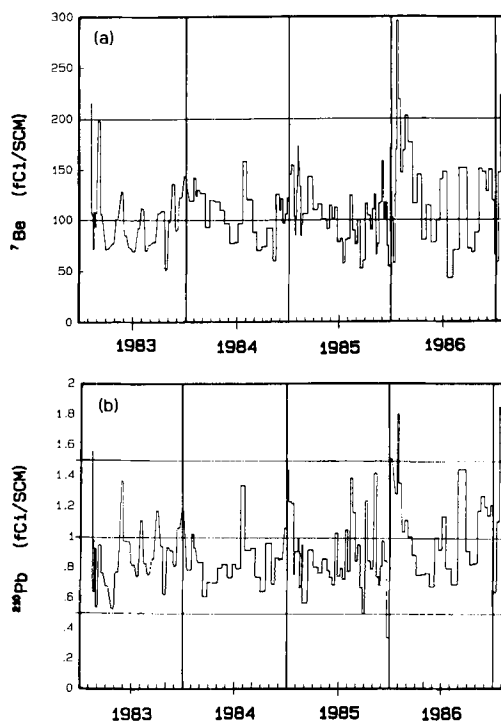


Fig. 2. Record of ^7Be -activity (a) and ^{210}Pb -activity (b) in bulk aerosol samples collected from February 1983 to February 1987 at the GvN base, Antarctica. Counting errors of ^7Be exceed 20% level during March and April 1983 only.

^7Be as a marker for submicron aerosol, originating from the higher troposphere or lower stratosphere.

The relatively large short-time variation found in the ^{210}Pb and ^7Be records is frequently parallel for both nuclides. This episodic variation may be attributed mainly to changes of vertical mixing intensity in the local boundary layer and (or) to local precipitation and cloud scavenging processes. The long-term pattern of the record shows no clear annual cycle in ^{210}Pb concentration, whereas ^7Be exhibits a weak seasonal cycle with a slightly enhanced concentration level during the local summer months. As discussed by various authors (Dutkiewicz and Husain, 1985; Viezee and Singh, 1980), intrusion of stratospheric air may be responsible for the ^7Be cycle. The pattern of the ^7Be annual cycle found at the GvN station has been reported before from the South Pole (Maenhaut et al., 1979b) and from coastal Terre Adélie (Sanak et al., 1985) where, however, a significantly higher ^7Be level could be observed.

A more striking picture of the frequency of "stratospheric air" extrusions is obtained if the $^7\text{Be}/^{210}\text{Pb}$ activity ratio is plotted. By this procedure short-term variations are suppressed. Fig. 3 shows that the ^7Be to ^{210}Pb ratio in ground-level air follows a pronounced annual cycle with a broad maximum between December and May. Note that, due to the increasing aerosol residence time with height, the ^{210}Pb -concentration in the upper Antarctic troposphere is expected to be significantly larger in comparison with ground-level air. A quite similar but much more pronounced annual cycle is shown by the ^{10}Be to ^7Be ratio measured in the 1983–85 GvN-filters (to

be presented in a forthcoming paper). These results and the $^7\text{Be}/^{210}\text{Pb}$ ratios give evidence to the assumption that, apart from episodic events, downward-mixing of stratospheric air mass tracers to the GvN station will be more likely between early local summer and late autumn than during other seasons; a maximum influence of probably stratospheric air is observed during January and February.

From the weighted mean (with respect to the large range in the air volume sampled) of 1983–86 ^{210}Pb in air concentration of 0.84 fCi/SCM and the grand average of ^{210}Pb in snow (surface snow sampled on a monthly base and newly fallen snow) of 0.23 fCi/g the mean wash-out ratio, probably most representative for non reactive submicron aerosol particles, is estimated to be approximately $0.27 \cdot 10^6$. For the sake of simplicity, it is proposed here to interpret this wash-out ratio in the sense of a dimensionless total aerosol deposition velocity which is normalized to the local net snow accumulation rate expressed in water equivalent. Later on, this wash-out ratio will be used to deduce from the observed atmospheric lead concentration the mean common lead concentration in recent snow deposited in the vicinity of the GvN station.

3.2. Major ions

The time pattern of sea-salt, sulfate, and nitrate measured in the high-volume filters from March 1983 to December 1985 is presented in Fig. 4(a–d).

3.2.1. Sea-salt. Sea-salt concentrations are either calculated from Na (assuming that all Na observed originates from sea-salt production) or from Cl if no Na data have been available so far. The air-borne sea-salt particles, which are produced by wind-induced bubble bursting at the ocean surface, are obviously the only relevant primary aerosol of local origin. At the GvN site the aerosol mass concentration is dominated by this marine aerosol component which in turn is strongly influenced by the local wind parameters and the actual extent of sea-ice cover. Therefore the sea-salt results reported here are considered to be representative only on a regional scale. The main features of the long-term pattern of atmospheric sea salt at the GvN are summarized below.

(a) The grand average concentration (weighted mean) of $1.2 \mu\text{g}/\text{SCM}$ exceeds mean South Pole concentration (Cunningham and Zoller, 1981) by a factor of 16, approximately, but is lower by a factor

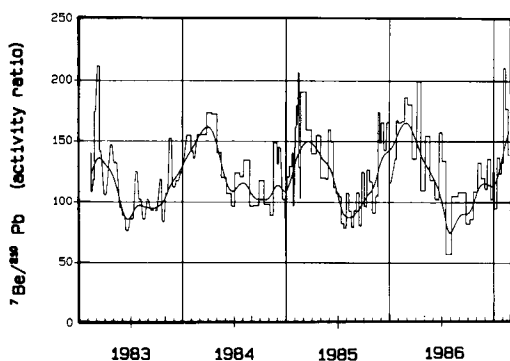


Fig. 3. Ratio of ^7Be to ^{210}Pb activity from Fig. 2.

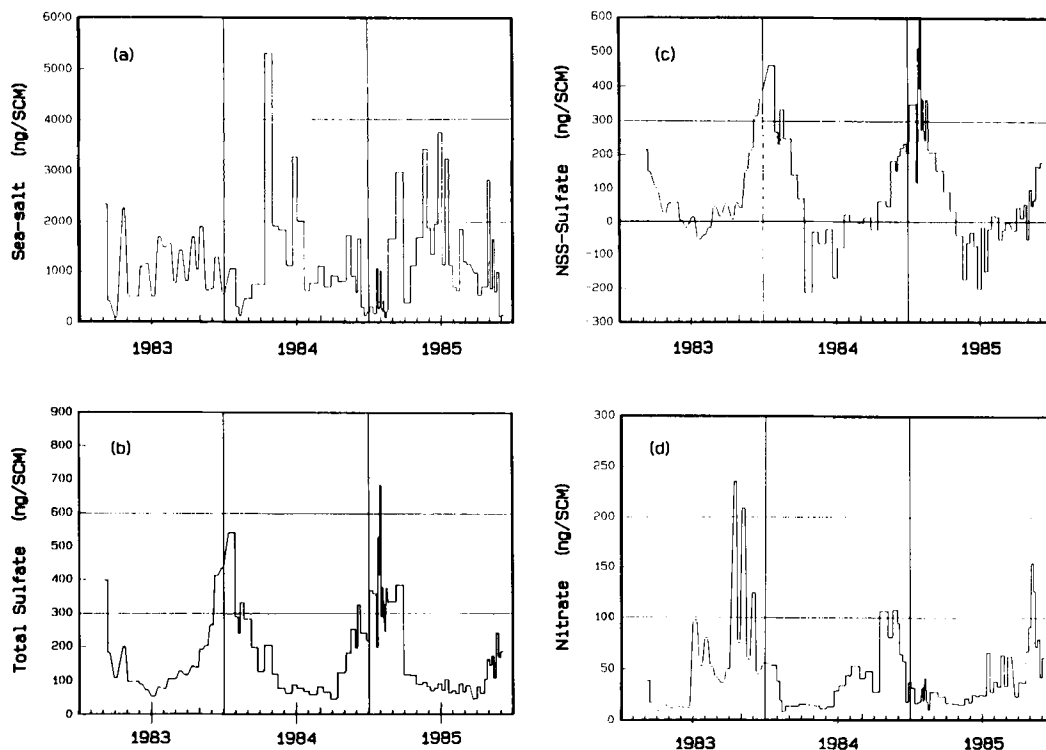


Fig. 4. Major ions concentration in GvN aerosol samples (a): sea-salt, (b): total sulfate, (c): non-sea-salt sulfate and (d): nitrate.

of about 20 in comparison with the open ocean concentrations estimated by Erickson et al. (1986) for this latitude.

(b) At the GvN site maximum concentrations occur during austral autumn (due to frequent sampling interruptions in 1983, this peak was missing in the high volume filters, but was clearly identified in the continuously sampled filters of a ^{222}Rn -monitor run in parallel). It is assumed that the generally enhanced storm activity coinciding with a relatively low sea-ice extent during this period are responsible for the autumn sea-salt peak.

During the spring maximum of sea-ice cover no clear sea-salt minimum is observed; it is still under discussion whether the persistence of large polynias or a very effective long-range transport of sea-salt particles from lower latitudes is the reason for this observation (note that at the South Pole station, the annual sea-salt maximum occurs between winter and spring) (Cunningham and

Zoller, 1981; Bodhaine et al., 1986). An example of the sea-salt and $\delta^{18}\text{O}$ isotope records analyzed in shallow ice-cores in close vicinity to the GvN station is shown in Fig. 5. This data confirms the previous finding that the maximum sea-salt input occurs during local autumn. It can be deduced from congruent aerosol and surface-snow samples, that the extremely high mean snow concentrations (if compared with the mean air level) are mainly due to episodes of large sea-salt dry deposition fluxes and to the advection of drifting snow heavily loaded with sea-salt particles.

3.2.2. Sulfate. The total sulfate (marine plus non-marine) record is characterized by a prominent seasonal cycle showing a maximum sulfate level in the period of November to March (weighted mean of two annual peaks 278 ± 93 ng/SCM) and a broad minimum during polar night (April to October: weighted mean of three annual minimums 82 ± 31 ng/SCM). During the latter period the concentration of non-sea-salt

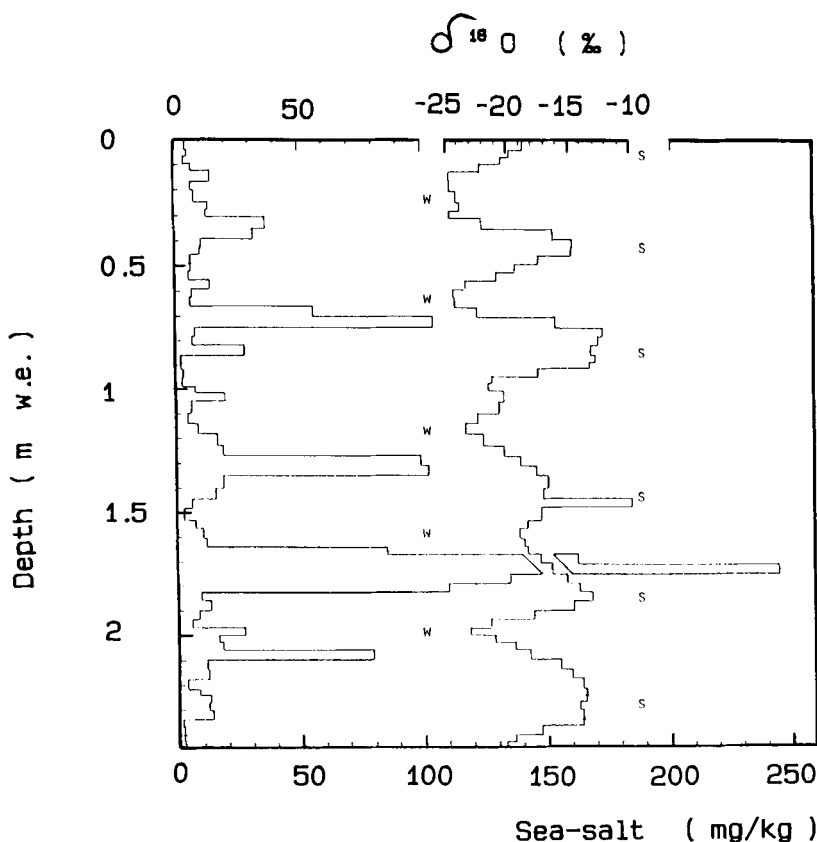


Fig. 5. Seasonal variation of sea-salt concentration in a shallow firn-core gathered in summer 1982/83 near the clean-air observatory at the GvN station. Depth below snow surface is given in meters of water equivalent (m w.e.). As can be seen from the tentative isotopic $\delta^{18}\text{O}$ stratigraphy, the extremely strong sea-salt deposition events predominantly occur during local autumn; (s): summer precipitation; (w): winter precipitation.

sulfate (nss-sulfate) results in negative values lasting for a significant fraction of time. This finding seems to be a common phenomenon in polar marine areas. Similar observations have been reported from various marine sites in higher latitudes (Aristarain et al., 1982; Gjessing, 1984; Salzman et al., 1986). A satisfying explanation for this phenomenon, however, is not given. The GvN data show that experimental artefacts such as systematic analytical errors or a size fractionation during aerosol sampling cannot be responsible for the large negative values observed. It is therefore proposed that, due to the low air temperatures, a significant sulfate-fractionation during sea-salt aerosol production might occur, leading to a lower sulfate to sodium ratio in airborne sea-salt par-

ticles compared to the bulk sea-water ratio. The experimental results (wind tunnel studies with freezing sea-water) on this subject will be discussed in a separate paper.

The summer maximum in the sulfate record, however, is not substantially affected by the problems in differentiating between total and nss-sulfate.

Based on the actual knowledge about the sulfur cycle in the remote marine troposphere (Andreae, 1986), it is assumed that the observed annual cycle of atmospheric sulfate concentration predominantly reflects the corresponding cycle of the emission and the subsequent photochemical oxidation of marine organosulfur species (mainly DMS and probably to a lesser extent the long-lived

COS). In fact, the in situ production of these sulfur species in the polar ocean surface water (related to the actual biological activity) as well as their subsequent chemical transformation in the atmosphere (related to the availability of OH-radicals) will be strongly influenced by the extreme summer-winter contrast in the supply of solar radiation. Due to the relatively short tropospheric aerosol residence time, the long-range transport from the surrounding continents, although known to operate most effectively during austral summer (see chapter on crustal material), does not essentially contribute to the summer nss-sulfate maximum at the GvN site. Furthermore, the substantial differences in the records of sulfate concentration and $^{7}\text{Be}/^{210}\text{Pb}$ -ratio make it very unlikely that the stratospheric/tropospheric exchange is responsible for the seasonal variation of the atmospheric sulfate concentration shown in Fig. 4.

3.2.3. Nitrate. In contrast with the annual cycle of total and nss-sulfate, the nitrate concentration shows a seasonal variation with an enhanced concentration between late winter and early summer, the significance of the apparent bimodal nitrate variation during this period still remains open. According to Delmas et al. (1982), the Antarctic nitrate is predominantly attributed to nitric acid; therefore the nitrate data reported here are represented by particulate nitrate and an unknown fraction of gas-phase HNO_3 and should be regarded as a lower limit of the total atmospheric nitrate present. Due to the build-up of relatively high sea-salt loadings (up to $500 \mu\text{g}/\text{cm}^2$) on the filter surface, it seems plausible that a substantial fraction of the gaseous HNO_3 has been collected by the high-volume filters (ratios of total nitrate found on the second and first filters vary from 0.015 to 0.3, mean 0.09 ± 0.07).

Annual variations showing a nitrate peak in snow layers of the summer half year are observed by Legrand and Delmas (1984) at South Pole, and by Zeller et al. (1986) and by Herron (personal communication, 1980) on the Ross Ice Shelf. Considering the poor time resolution, these findings will not significantly contrast with the GvN pattern of atmospheric nitrate concentration.

There is a controversy about the ultimate origin of the nitrate observed in Antarctic snow; among other sources, N-fixation by lightning in the mid-

Table 1. *Volume-weighted mean nitrate concentration (particulate and partly vapor phase nitrate) during different seasons at the GvN station*

Year	Period	Nitrate (ng/SCM) weighted mean	Weighted standard deviation
1983	Feb–June	15	9.3
	July–January	73	90
1984	Feb–June	15	6.6
	July–January	48	26
1985	Feb–June	19	5.1
	July–December*	46	28

* Until early December only.

latitudinal upper troposphere (Legrand and Delmas, 1986) and, alternatively, the stratospheric source being modulated by the solar activity are proposed to be dominant (Zeller et al., 1986).

At present, no explanation for the quite regular behavior of the GvN nitrate data can be given. The weighted mean nitrate concentration for different time intervals is presented in Table 1. Compared with the $^{7}\text{Be}/^{210}\text{Pb}$ -record which is assumed to indicate the subsidence of stratospheric air masses, the nitrate record gives no evidence to the supposition that in Antarctica the stratospheric nitrate (NO_x) source controls the time variation of the ground-level nitrate.

3.3. Trace elements

The knowledge of the minor components of Antarctic aerosol is still very incomplete, particularly for heavy metals and volatile species. From the data set of the trace elements obtained at the GvN station so far, Mn is here representatively reported for crustal aerosol (from a well-known source) and Pb for species frequently referred to as anomalously enriched trace elements (of mainly unknown origin).

The time series of Mn and Pb for the 1983–84 collection period are shown in Fig. 6. A pronounced annual cycle is observed for the crustal Mn, and a more than twofold higher mean value of crustal aerosol can be deduced for the summer half-year. Since the source region of this primary aerosol is definitely on the surrounding continents, it is assumed that the observed difference is due to a change in the efficiency of meridional long-range transport. A quite similar

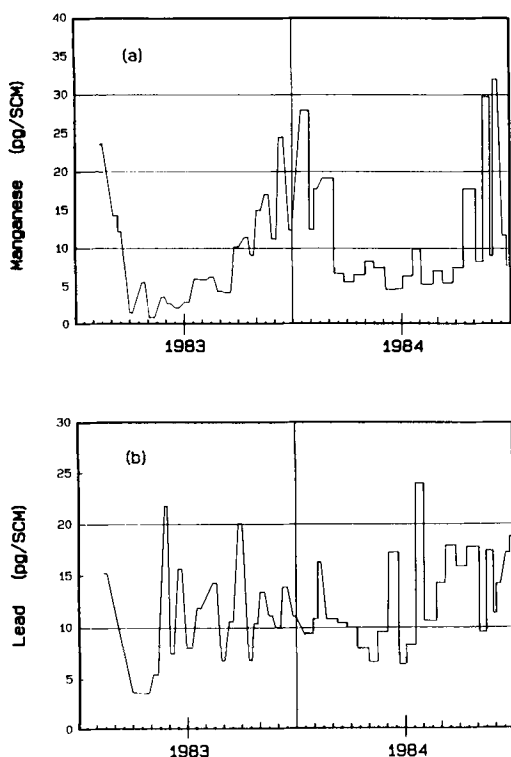


Fig. 6. Trace element concentration in GvN aerosol samples (a): manganese and (b): common lead.

annual cycle of crustal aerosols had been observed at the South Pole station by Cunningham and Zoller (1981), with a mean Mn-concentration of 14 pg/SCM (GvN 13 pg/SCM) in the summer season, and 6.7 pg/SCM (GvN 5.4 pg/SCM) in the winter season.

Therefore, a rather uniform distribution of the mineral aerosol component may be expected in the upper troposphere over Antarctica, leading to a widespread seasonal signal of insoluble micro-particles in the snow and ice layers. In fact, the micro-particle method used for dating the Antarctic ice-cores had essentially been based on these findings (Mosley-Thompson and Thompson, 1982).

Like the radioactive ^{210}Pb , stable Pb does not follow the seasonal cycle of crustal aerosol. Since three samples had to be excluded from the Pb data-set owing to their suspiciously large deviation from the otherwise good correlation with ^{210}Pb ($r = 0.64$), Pb contamination (occurring

most likely during the rather long collection periods) cannot be completely ruled out. Thus the annual cycle of Pb, if any exists, might probably be obscured by the local Pb-contamination. However, the (weighted geometric) mean Pb-concentration of 11 pg/SCM (weighted geometric standard deviation 1.5) observed at the GvN site does not seriously contrast with the upper limit of 8.5 pg/SCM observed by Dick and Peel (1985) at the Antarctic Peninsula during the rather short collection period in local summer. Finally, by using the mean wash-out ratio deduced from the ^{210}Pb in air and snow (see previous chapter) of $0.27 \cdot 10^{-6}$, a mean snow concentration of common lead of 3 pg/g is estimated from the observed mean air concentration. According to Boutron and Patterson (1987) as well as to Wolff and Peel (1985), the most reliable Pb concentration value for the recent Antarctic surface snow is now found to be in the range of 2–13 pg/g which agrees surprisingly well with the mean concentration estimated for the GvN site.

4. Summary and conclusions

Chemical and radio-chemical investigations of bulk-aerosol samples collected during 1983–86 from the ground-level atmosphere at a coastal Antarctic site provide for the first time some insight into the temporal behavior of various aerosol components quite different in origin and in importance to the chemistry of the remote south-polar atmosphere. The most relevant findings are listed below:

(a) enhanced mixing with upper troposphere or lower stratosphere during early summer and late autumn, indicated by an elevated ^7Be to ^{210}Pb ratio;

(b) maximum sea-salt production during local autumn presumably due to strong storm activities and relatively low sea-ice extent (atmospheric sea-salt concentration not relevantly reduced, however, by the maximum of sea-ice cover in spring);

(c) pronounced maximum in total and nss-sulfate during local summer, most likely related to production and photochemical transformation of reduced marine organosulfur species;

(d) evidence for a lower sulfate to sodium

(chloride) ratio in air-born sea-salt particles (if compared with bulk sea-water ratio), leading to a significantly negative nss-sulfate concentration during polar night;

(e) regular seasonal cycle of the nitrate concentration (particulate and partly vapor-phase HNO_3) showing enhanced concentration in the second half of the year and a pronounced spring peak;

(f) seasonal variation of meridional long range transport from the surrounding continents as indicated by a significantly higher mineral dust concentration during austral summer;

(g) a (probably upper) Pb level of about 10 pg/SCM associated with lowest values in the range of 4–7 pg/SCM being consistent with the Pb level in surface snow observed by other authors in different Antarctic snow fields.

The GvN air chemistry station provides high resolution records of the Antarctic aerosol chemistry. These records are particularly useful since they may be representative for the region intermediate between the meteorological regimes of the central Antarctic plateau and the South Polar ocean. Much more detailed information will be achieved, if the data presented here are combined with records available of radon-222, conden-

sation nuclei (University of Mainz), local meteorology, and surface snow chemistry.

5. Acknowledgements

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REFERENCES

- Andreae, M. O. 1986. The ocean as a source of atmospheric sulfur compounds. In *The role of air-sea exchange in geochemical cycling* (ed. P. Buat-Menard). Dordrecht/Holland: D. Reidel, NATO ASI series C, 185, 331–361.
- Aristarain, A. J., Delmas, R. J. and Briat, M. 1982. Snow chemistry on James Ross Island (Antarctic Peninsula). *J. Geophys. Res.* 87, 11004–11012.
- Augstein, E. 1984. The observatory of the Georg von Neumayer station. *Report on Polar Research*. Bremerhaven, special issue no. 5.
- Bodhaine, B. A. 1983. Aerosol measurements at four background sites. *J. Geophys. Res.* 88, 10753–10768.
- Bodhaine, B. A., Deluisi, J. J., Harris, J. M., Houmère, P. and Bauman, S. 1986. Aerosol measurements at the South Pole. *Tellus* 38B, 223–235.
- Boutron, C. and Patterson, C. C. 1983. The occurrence of lead in Antarctic recent snow, first deposited over the last two centuries and prehistoric ice. *Geochim. Cosmochim. Acta* 47, 1355–1368.
- Boutron, C. and Patterson, C. C. 1987. Relative levels of natural and anthropogenic lead in recent Antarctic snow. *J. Geophys. Res.* 92, 8454–8464.
- Cunningham, W. L. and Zoller, W. H. 1981. The chemical composition of remote area aerosols. *J. Aerosol Sci.* 4, 367–384.
- De Angelis, M., Legrand, M., Petit, J. R., Borkow, N. I., Korotkevich, Y. S. and Kotlyakov, V. M. 1984. Soluble and insoluble impurities along the 950 m deep Vostok ice core (Antarctica), climatic implications. *J. Atmos. Chem.* 1, 215–239.
- Delmas, R. J., Barnola, J. M. and Legrand, M. 1982. Gas-derived aerosol in central Antarctic snow and ice: the case of sulphuric and nitric acids. *Ann. Glaciol.* 3, 71–76.
- Dick, A. L. and Peel, D. A. 1985. Trace elements in Antarctic air and snowfall. *Ann. Glaciol.* 7, 12–19.
- Dutkiewicz, V. A. and Husain, L. 1985. Stratospheric and tropospheric components of ^7Be in surface air. *J. Geophys. Res.* 90, 5783–5788.
- Erickson, D. J., Merrill, J. T. and Duce, R. A. 1986. Seasonal estimates of global atmospheric sea-salt distributions. *J. Geophys. Res.* 91, 1067–1072.
- Gjessing, Y. 1984. Marine and non-marine contribution to the chemical composition of snow at the Riiser Larsen ice shelf in Antarctica. *Atmos. Environ.* 18, 825–830.

- Görlach, U. 1988. The seasonal variation of atmospheric lead, zinc and manganese in coastal Antarctica (in German). PhD thesis, University of Heidelberg, FRG.
- Legrand, M. R. and Delmas, R. J. 1984. The ionic balance of Antarctic snow: a 10 year detailed record. *Atmos. Environ.* 18, 1867–1874.
- Legrand, M. and Delmas, R. J. 1986. Relative contribution of tropospheric and stratospheric sources to nitrate in Antarctic snow. *Tellus* 38B, 236–249.
- Maenhaut, W., Zoller, W. H., Duce, R. A. and Hoffmann, G. L. 1979a. Concentration and size distribution of particulate trace elements in the South Pole atmosphere. *J. Geophys. Res.* 84, 2421–2431.
- Maenhaut, W., Zoller, W. H. and Coles, D. G. 1979b. Radionuclides in the South Pole atmosphere. *J. Geophys. Res.* 84, 3131–3138.
- Mosley-Thompson, E. and Thompson, L. G. 1982. Microparticle analysis of the Ross ice shelf Q-13 core and preliminary results from the J-9 core. *Ann. Glaciol.* 3, 211–215.
- Reinwarth, O., Rauert, W. G., Stichler, W. and Moser, H. 1982. Preliminary investigations on accumulation at the Filchner/Ronne ice-shelve and Atka bay. *Ann. Glaciol.* 3, 274–278.
- Salzman, E. S., Savoi, D. L., Prespero, J. M. and Zirka, R. G. 1986. Methanesulfonic acid and non-sea-salt sulfate in Pacific air: Regional and seasonal variations. *J. Atmos. Chem.* 4, 227–240.
- Sanak, K. J., Gaudry, A. and Lambert, G. 1981. Size distribution of ^{210}Pb aerosols over oceans. *Geophys. Res. Lett.* 8, 1067–1069.
- Sanak, J., Lambert, G. and Ardouin, B. 1985. Measurement of stratosphere to troposphere exchange in Antarctica by using short-lived cosmonuclides. *Tellus* 37B, 109–115.
- Schug, J. 1985. The Georg von Neumayer Antarctic Research station. *J. Meteorology UK.* 10, 96.
- Shaw, G. E. 1979. Considerations on the origin and properties of the Antarctic aerosol. *Rev. Geophys. Space Phys.* 17, 1983–1998.
- Vieze, W. and Singh, H. B. 1980. The distribution of beryllium-7 in the troposphere: Implications on stratospheric/tropospheric air exchange. *Geophys. Res. Lett.* 7, 805–808.
- Wagenbach, D., Junghans, H. G. and Volpp, H. J. 1983. Langzeitmessung atmosphärischer Spurenstoffe an Luft- und Firnproben im Bereich der Georg von Neumayer Station. *Reports on Polar Research*, No 13. Alfred-Wegener-Institut für Polarforschung, Bremerhaven, 36–44.
- Wolff, E. W. and Peel, D. A. 1985. Closer to true value for heavy metal concentrations in recent Antarctic snow by improved contamination control. *Ann. Glaciol.* 7, 61–65.
- Zeller, E. J., Dreschoff, G. A. M. and Laird, C. M. 1986. Nitrate flux on the Ross ice shelf, Antarctica and its relation to solar cosmic rays. *Geophys. Res. Lett.* 13, 1264–1267.